

1 Temperature-dependence of the relationship between $p\text{CO}_2$ and dissolved organic carbon in
2 lakes

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21

22 Abstract

23 **The relationship between the partial pressure of carbon dioxide ($p\text{CO}_2$) and dissolved**
24 **organic carbon (DOC) concentration in Brazilian lakes, encompassing 194 lakes across a**
25 **wide latitudinal range in the tropics, was tested. Unlike the positive relationship reported**
26 **for lake waters, which was largely based on temperate lakes, we found no significant**
27 **relationship for low-latitude lakes ($< 33^\circ$), despite very broad ranges in both $p\text{CO}_2$ and**
28 **DOC levels. These results suggest substantial differences in the carbon cycling of low**
29 **latitude lakes, which must be considered when up scaling limnetic carbon cycling to global**

30 **scales.**

31

32 1.Introduction

33 Lakes cover less than 2% of the continent's surface [Downing et al., 2006; McDonald,
34 2012] but play a significant role in the global carbon (C) cycle [Cole et al., 1994; 2007; Tranvik
35 et al., 2009], contributing significantly to C burial and emissions to the atmosphere [Cole et al.,
36 2007; Downing et al., 2008 and Tranvik et al., 2009]. Dissolved organic carbon (DOC)
37 represents a major C pool in lakes, with both autochthonous and allochthonous contributions
38 [Duarte and Prairie, 2005; Cole et al., 2007; Prairie 2008; Tranvik et al., 2009], supporting
39 heterotrophy [Sobek et al., 2007] and affecting key biological and physico-chemical processes
40 involved in C cycling [Steinberg et al., 2006]. Large inputs of terrestrial organic C and its
41 subsequent mineralization have been suggested to be a major driver of CO₂ supersaturation
42 commonly encountered in lakes [Duarte and Prairie, 2005; Cole et al., 2007; Prairie 2008;
43 Marotta et al., 2009].

44 The mechanistic connection between DOC and heterotrophic CO₂ production is believed to
45 underpin the significant positive relationship between *p*CO₂ and DOC reported in comparative
46 analyses [Houle, 1995; Sobek et al., 2005; Larsen et al., 2012]. However, recent analyses have
47 revealed that the relationship between *p*CO₂ and DOC in lake waters is regionally variable and
48 not universal [Lapierre and del Giorgio, 2012]. Hence, the relationship between *p*CO₂ and DOC
49 reported in comparative analyses based on datasets dominated by temperate and high-latitude
50 lakes (> 33°) may not be extrapolated for all types of lakes, mainly because the tropical low
51 latitude lakes (< 33°) are generally underrepresented in global datasets [Raymond et al., 2013].

52 One priority of comparative studies is the latitudinal variance, where lake temperature, ice
53 cover and mixing regime will differ and these climatically driven processes, in turn, should
54 strongly influence OC cycling [Hanson et al., 2015]. At low latitudes, warm conditions over the
55 whole year may increase the metabolic rates involved in the C cycling in terrestrial [Ometto et
56 al., 2005] and aquatic [Marotta et al., 2009; 2010] ecosystems on an annual basis compared to
57 the high latitude lakes. High temperatures affect heterotrophic activity and the associated
58 mineralization rates of organic matter in soils [Davidson et al., 2006], waters [López-Urrutia et
59 al., 2007; Wohlers et al., 2008; Regaudie-de-Gioux and Duarte 2012] and aquatic sediments
60 [Wadham et al., 2012; Gudas et al., 2010, Marotta et al., 2014]. Enhanced heterotrophic activity

61 in warm ecosystems would support high aquatic CO₂ production and subsidize high CO₂ evasion
62 from global lake water to the atmosphere.

63 The largest previous comparative analysis already published in the literature for global lake
64 waters [Sobek et al., 2005] reported a significant positive relationship between DOC and *p*CO₂
65 and a non-significant variation of *p*CO₂ among lakes with changing temperature. However, both
66 analyses were characterized by a paucity of low latitude data. A strong positive relationship
67 between temperature and *p*CO₂ was observed when subtropical and tropical ecosystems were
68 included in the dataset [Marotta et al., 2009], likely caused by the potential increase in metabolic
69 rates under warmer conditions [Brown et al., 2004; López-Urrutia et al., 2006]. Hence, the
70 relationship between lake *p*CO₂ and DOC could also be temperature-dependent and, therefore,
71 may differ between temperate and tropical lakes. The extensive low latitude territory of Brazil,
72 which has a high density of lakes and ponds [Downing et al., 2006], is appropriate to examine
73 general patterns in the tropics [e.g., Marotta et al., 2009, Kosten et al., 2010]. Here, we test the
74 applicability of the relationship between *p*CO₂ and DOC using inputs derived from a high
75 latitude dataset [Sobek et al., 2005] with added tropical and subtropical data of low latitude lakes
76 from Brazil.

77

78 2.Methods

79 2.1.Study area and Lakes

80 Brazil extends from 5° 16' 20" North to 33° 44' 42" South, showing an area of
81 approximately 8,547,000 km², constituting half of South America and encompasses a high
82 diversity of low-latitude landscapes [Ab`Saber, 2003] that are predominantly located within
83 tropical latitudes. We conducted a survey of pH, alkalinity and DOC between 2003 and 2011 in
84 surface waters of 166 permanent lakes from 0 to 33° of south latitude across Brazil (Figure 1),
85 yielding a total of 225 water samples. The lakes were sampled in representative biomes of Brazil:
86 (1) the Amazonia Forest (Amazonia Biome, n = 65), (2) the Pantanal Floodplain (Pantanal
87 Biome, n = 29) and (3) the Tropical (< 24° of latitude) and (4) Subtropical (> 24° and < 33° of
88 south latitude) Coasts, both in the Atlantic Forest Biome (n = 35 and n = 37 lakes, respectively;
89 Figure 1). These biomes follow the classification of the Brazilian Institute of Geography and
90 Statistics for biomes (IBGE 2004,
91 ftp://geoftp.ibge.gov.br/mapas_tematicos/mapas_murais/biomas.pdf). Our dataset encompasses a

92 broad inter-lake heterogeneity (n=166) for pH, alkalinity and DOC simultaneously sampled
93 among Brazilian biomes and along the latitudinal gradient, independent of the year's season.

94 The Amazonian Forest biome is formed by the most extensive hydrographic network on the
95 globe: the Amazon River basin, which occupies a total area of approximately 6.11 million km²
96 from its headwaters in the Peruvian Andes to its mouth in the Atlantic Ocean (ANA –
97 www.ana.gov.br). The Amazon Forest is the Brazilian biome with the highest mean annual
98 precipitation (approximately 2200 mm) and has warm mean air temperatures, approximately
99 25°C, high cloud coverage and high humidity with low fluctuations over the whole year
100 [Chambers, 1999]. We sampled a wide variety of lakes, characteristic of different areas of the
101 Amazonian Forest, encompassing “clear” (low DOC and suspended solids), “white” (low DOC
102 and high suspended solids) and “dark” (high DOC and low suspended solids) lakes.

103 The Pantanal Floodplain is the world's largest tropical freshwater wetland, extending
104 across an area of approximately 150,000 km² between 16° and 20° S and 58° and 55° W [Por,
105 1995]. The annual average temperature and precipitation are approximately 22°C and 1,000 mm,
106 respectively [Mariot et al., 2007], with a strong seasonality and subsequent variation in the
107 flooded area [Junk and Nunes da Cunha, 2005]. The high-water period occurs during the rainy
108 summer (usually from September to December), and low waters typically occur during the dry
109 winter (from March to July) [Hamilton, 2002].

110 The Atlantic Forest biome extends along a broad latitudinal belt, between 5° and 30° S
111 from the subtropics to tropics and a narrow longitudinal section between 55° and 56° W, and
112 occupies an area of 1.11 million km² along the Brazilian coast (IBGE-www.ibge.gov.br). This
113 biome is characterized by numerous shallow coastal lakes receiving high inputs of refractory
114 organic matter [Farjalla et al., 2009] derived from the typical open xerophytic vegetation on
115 sandy soils, where water retention is low [Scarano, 2002]. The mean air temperatures vary from
116 27°C in winter to 30°C in summer at the tropical coast [$< 24^\circ$ of latitude; Chellappa et al., 2009]
117 and from 17 and 20°C at the subtropical coast [$> 24^\circ$ of latitude; Waechter, 1998]. The mean
118 annual precipitation reaches 1,164 mm [Henriques et al., 1986] and 1,700 mm [Waechter, 1998]
119 in the tropical and subtropical Brazilian coast, respectively. This biome is also characterized by
120 strong seasonality, with rainy summers and dry winters [Chellappa et al., 2009].

121

122 2.2 Sampling Design and Analytical Methods

123 Our sampling design encompassed the most representative Brazilian biomes from tropical
124 and subtropical coastal areas to tropical and subtropical forests (Amazon and Atlantic Forest)
125 and inland wetlands (Pantanal), with the intra-lake heterogeneity and seasonal fluctuations
126 randomly assessed and further integrated by means of each ecosystem. To analyze the
127 relationship between $p\text{CO}_2$ and DOC in tropical lake waters, we joined data on 194 lakes ($< 33^\circ$
128 of latitude) with both variables sampled at the same time, including 166 data samples from our
129 own survey and 28 from the literature compilation (Table S1). The values reported here
130 represented, gathered in an opportunistic manner, represent daily averages ($N= 4$ or 5 samples)
131 for a given year's season or/and one sampling time over different seasons, which were also both
132 integrated by means of each lake. To test the global importance of the relationship between $p\text{CO}_2$
133 and DOC, we added our low latitude data (225) to the Sobek et al. [2005] dataset (4902 lakes) as
134 this dataset had a paucity of tropical ecosystem data (148 tropical lakes, but only one with $p\text{CO}_2$
135 and DOC sampled at the same time).

136 pH, salinity and temperature were measured *in situ*. pH was determined using a pH meter
137 (Digimed – DM2) with reference standards certified by Mettler Toledo (4.00 ± 0.01 and $7.00 \pm$
138 0.01 units) before each sampling hour. Temperature and salinity were measured using a
139 Thermosalinometer (Mettler Toledo - SevenGo SG3) coupled to a probe in Lab 737 previously
140 calibrated with 0.01 M KCl. Surface lake water was collected for total alkalinity and DOC
141 analyses, taking care to avoid bubbles at approximately 0.5 m of depth using a 1 L Van Dorn
142 bottle. Total alkalinity (TA) was determined in the field by the Gran's titration method with
143 0.0125 M HCl immediately after sampling [Stumm and Morgan, 1996]. Water samples for DOC
144 were pre-filtered ($0.7 \mu\text{m}$, Whatman GF/F) and preserved by acidification with 85% H_3PO_4 to
145 reach a $\text{pH} < 2.0$ in sealed glass vials [Spyres et al., 2000]. In the lab, DOC was determined by
146 high-temperature catalytic oxidation using a TOC-5000 Shimadzu Analyzer, quality control was
147 checked with calibration curve made with potassium hydrogen phthalate before each sample
148 battery analysis. $p\text{CO}_2$ concentrations in surface waters were calculated from pH and alkalinity
149 following Weiss [1974], after corrections for temperature, altitude and ionic strength according
150 to Cole et al. [1994].

151 In order to address the potential contribution of DOC to TA, which is especially
152 important in DOC-enriched acid freshwaters, we used the data set from Abril et al., [2015] to
153 correct $p\text{CO}_2$ values calculated from pH and TA after the corrections for temperature, altitude

154 and ionic strength [Cole et al., 1994]. Full details on fitted regression equations to correct $p\text{CO}_2$
155 in function of the DOC and pH are described in the supplementary information section. (Figure
156 S3).

157 2.3. Statistical Analyses

158 The variables $p\text{CO}_2$ and DOC did not meet the assumptions of parametric tests even after
159 logarithmic transformations [Zar, 1996] as the data were not normally distributed (Kolmogorov-
160 Smirnov, $p < 0.05$) and the variances were heterogeneous (Bartlett, $p > 0.05$). Therefore, we used
161 medians and non-parametric tests to compare these variables among biomes (Kruskall-Wallis
162 followed by Dunn's multiple comparison post hoc test, $p < 0.05$). The linear regression equations
163 were fitted to compare our results with those of previous studies from Sobek et al., [2005].
164 Statistical analyses were performed using the software Graphpad Prism version 4.0 for
165 Macintosh (GraphPad Software, San Diego, CA).

166 3. Results

167 The lake waters surveyed were warm across all biomes (median 25-75% interquartile
168 range = 27.5°C , $25.2 - 30.1$) but colder in subtropical coastal lakes (23.4°C , $20.0 - 26.2$) than in
169 Pantanal and Amazonian lakes (29.5°C , $27.7 - 31.4$ and 29.4°C , $27.6 - 31.0$, respectively;
170 Dunn's test, $p < 0.05$, Figure 2a). DOC concentrations were consistently high (6.3 mg C L^{-1} , 4.3
171 $- 11.9$) for all Brazilian biomes but significant lower in the Amazonian Forest (3.8 mg C L^{-1} , 2.7
172 $- 5.8$) than in the tropical coast (13.4 mg C L^{-1} , $6.1 - 32.8$; Figure 2b; Dunn's test, $p < 0.05$).
173 Most lakes (approximately 83% of raw data) showed surface waters supersaturated in CO_2
174 relative to the atmospheric equilibrium ($p\text{CO}_2$ in atmospheric equilibrium is $400.83\text{ }\mu\text{atm}$, 2015
175 annual mean; data available in www.esrl.noaa.gov/gmd/ccgg/trends), with much higher $p\text{CO}_2$
176 values in Amazonian lakes ($7,956\text{ }\mu\text{atm}$, $3,033 - 11,346$) than in subtropical coastal lakes (900
177 μatm , $391.3 - 3,212$; Figure 2c; Dunn's test, $p < 0.05$).

178 The $p\text{CO}_2$ in the surface waters of Brazilian lakes was independent of DOC
179 concentrations (Linear regression for raw data, $p > 0.05$, Figure 3). The same absence of positive
180 significance pattern was found comparing at corrected data. Negative (Linear regression, $p <$
181 0.05 , $R^2 = 0.03$, $n = 194$, $p\text{CO}_2 = -98.76 (\pm 39.92) \times \text{DOC} + 6529 (\pm 641.1)$) or non significant
182 (Linear regression, $p > 0.05$) DOC- $p\text{CO}_2$ relationship for tropical lakes ($N = 194$, DOC and pH
183 corrected, respectively (figure S3a and c) contrasting with a significant positive relationship for

184 those at other latitudes ($N = 4,433$) (Linear regression, $p < 0.05$, $R^2 = 0.20$, $p\text{CO}_2 = 64.43 (\pm 2.04)$
185 $\times \text{DOC} + 625.1 (\pm 20.87)$ and $R^2 = 0.12$, $p\text{CO}_2 = 45.70 (\pm 1.84) \times \text{DOC} + 623.7 (\pm 18.83)$) for
186 DOC corrected data and pH corrected data, respectively (Figure S3b and d, full details on
187 corrections in the supplementary information). The range of $p\text{CO}_2$ for a similar DOC range in
188 Brazilian lakes was larger than that reported by Sobek et al., [2005] for the dataset dominated by
189 high-latitude cold lakes, despite the number of lakes in their dataset being much larger (more
190 details in supplementary information section, figure S3).

191

192 4. Discussion

193 The Brazilian lakes sampled here were characterized by a prevalence of CO_2
194 supersaturation, consistent with general trends previously reported for global lakes [e.g.,
195 Raymond et al, 2013; Cole et al., 1994; 2007] including those at tropical latitudes [Marotta et al.,
196 2009]. The very high $p\text{CO}_2$ levels observed here, with a median of 900 and 8,300 μatm for
197 subtropical and Amazon lake waters, respectively, are consistent with those reported previously
198 for the Amazon River and tributaries (2,000-12,000 μatm ; Richey et al., [2002]), Amazon
199 floodplain lakes (3,000 - 4,898 μatm ; Rudorff et al., [2012]), Pantanal lakes and wetlands (2,732-
200 10,620 μatm ; Hamilton et al., [1995]), and coastal lakes (768 - 9,866 μatm ; Kosten et al., [2010];
201 361-20,037 μatm ; Marotta et al., [2010]) and for global values for tropical lakes (1,255-35,278
202 μatm ; Marotta et al., [2009]), reservoirs (1,840 μatm ; Aufdenkampe et al., [2011]) and wetlands
203 (3,080-6,170 μatm ; Aufdenkampe et al., [2011]).

204 The non-significant or weakly negative relationship (Figure S3) between DOC and $p\text{CO}_2$
205 reported here for warm low-latitude lakes contrasted with significant positive relationships
206 derived from previous datasets dominated by high-latitude lakes [Houle, 1995; Prairie et al.,
207 2002; Jonsson et al., 2003; Sobek et al., 2005; Roehm et al., 2009; Lapierre and del Giorgio,
208 2012; Larsen et al., 2012]. The results presented show that warm low-latitude lakes range widely
209 in $p\text{CO}_2$, reaching very high and low values, but tend to have comparatively more uniform DOC
210 concentrations (Figure 3). More intense metabolic processes that uptake and release CO_2 in lake
211 waters, respectively autotrophy and heterotrophy, could determine an enhanced variability in lake
212 $p\text{CO}_2$ with decreasing latitude [Marotta et al., 2009].

213 In this way, the inclusion of warm tropical data in our study revealed novel increases in
214 the variability of the DOC- $p\text{CO}_2$ relationship in lakes over the latitudinal gradient. One

215 explanation for this pattern is that even similar DOC concentrations, representing the total pool
216 of DOC, may show different mixtures between origins from aquatic primary producers and
217 terrestrial sources [Kritzberg et al., 2006]. The autochthonous DOC (i.e. produced in the lake) is
218 related to the net CO₂ uptake [Staehr and Sand Jansen 2007], while the allochthonous DOC (i.e.
219 produced in the catchment) is resource to the net CO₂ release in lake waters [Sobek et al., 2007].
220 The increased DOC release from aquatic primary producers into waters under tropical
221 conditions, especially warmer annual conditions and higher solar incidence, can offset any
222 positive relationship between *p*CO₂ and the terrestrial DOC that subsidizes the net aquatic
223 heterotrophy [Marotta et al., 2010; 2012]. This contributes to explain non-significant
224 relationships reported here (Figure 3), suggesting a temperature dependence of the DOC-*p*CO₂
225 relationship in global lakes

226 In conclusion, the finding that *p*CO₂ does not increase with DOC concentration in
227 Brazilian tropical lakes rejects the hypothesis that DOC serves as a universal predictor for *p*CO₂
228 in lake waters [Larsen et al., 2012]. Even discounting a possible artifact of the method that could
229 be causing an overestimation in the values of *p*CO₂ or considering the contribution of organic
230 acids on the alkalinity, the pattern of no relationship between DOC and *p*CO₂ in the Tropical
231 lakes was strongly confirmed (Figure S3). Therefore, our results contributing to fill the tropical
232 gap suggest potentially important latitudinal differences for depositional aquatic environments,
233 whose causes still need to be better addressed to improve accuracy of global C cycle models.

234

235 Authors Contribution

236 All authors contributed to the study design, data interpretation and preparation or
237 refinement of the manuscript. L. P. and H. M. performed the sampling and sample analyses.

238

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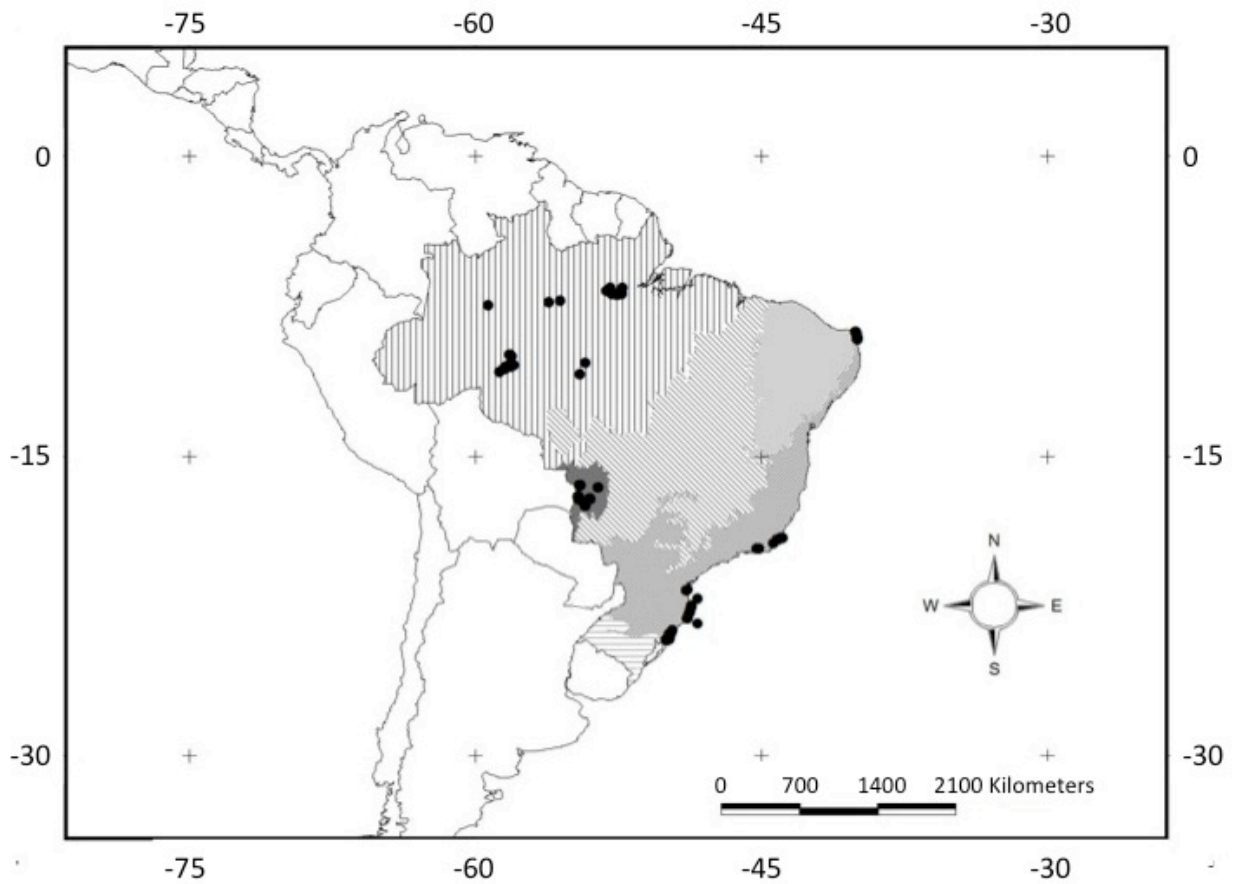
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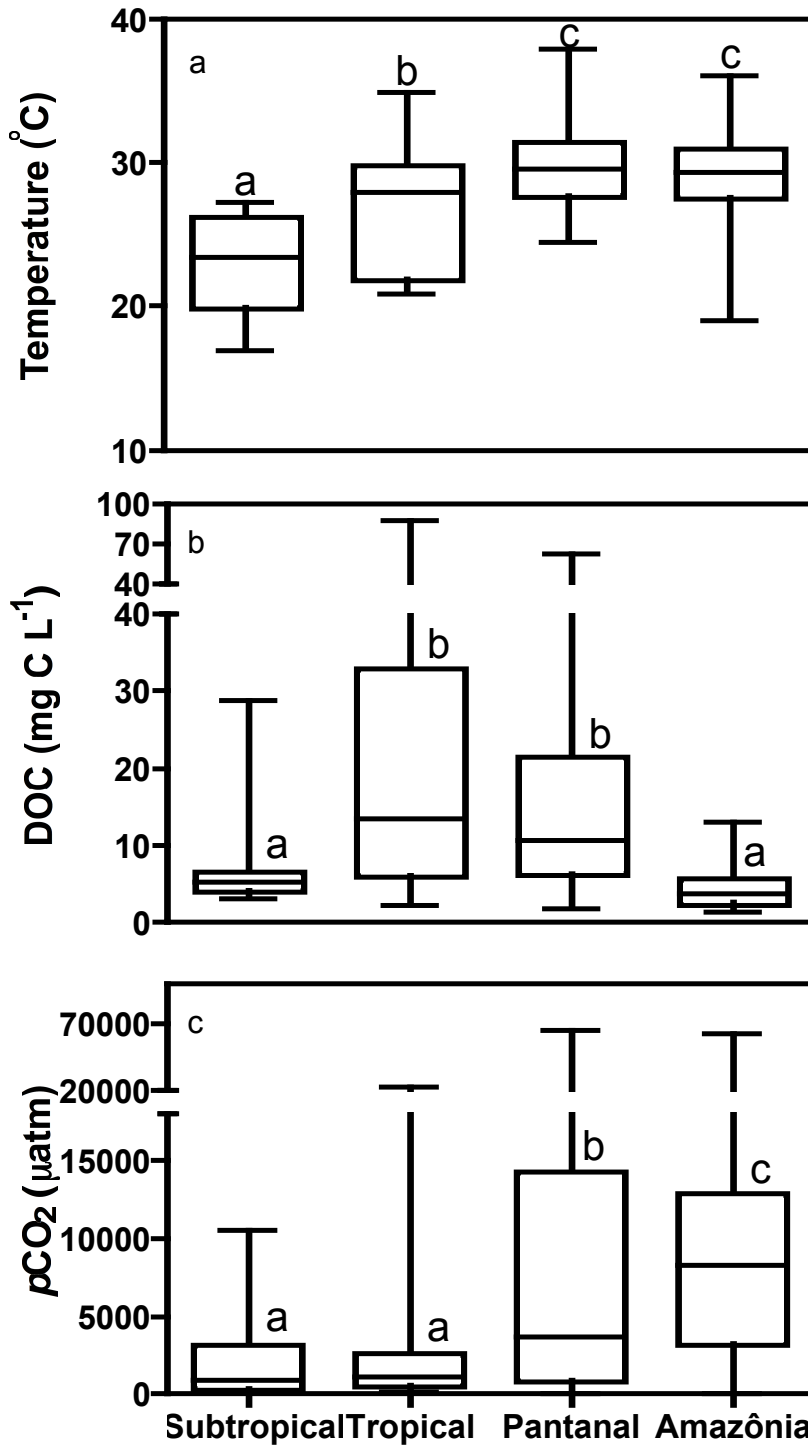
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395 Figures and subtitles



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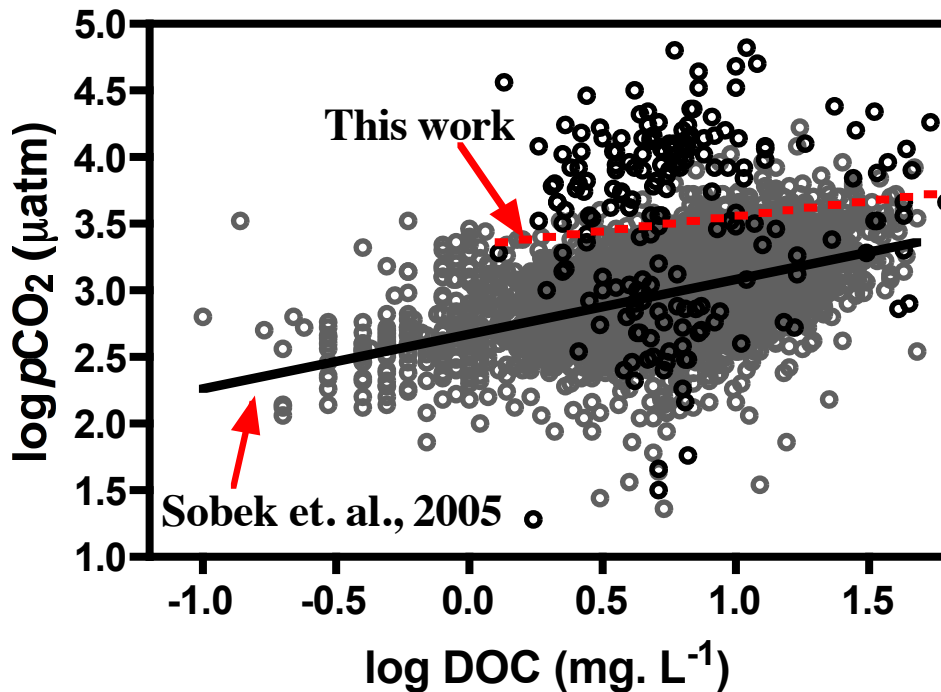
397 Figure 1. Geographic location of Brazilian lakes sampled in different biomes (IBGE 2004,
 398 available in ftp://geoftp.ibge.gov.br/mapas_tematicos/mapas_murais/biomas.pdf): Amazonia
 399 Forest (vertical lines), Pantanal Floodplain (dark gray), and Atlantic Forest (gray; Tropical and
 400 Subtropical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



401

402 Figure 2. Values of (A) temperature (°C), (B) DOC concentrations (mg C L⁻¹) and (C) pCO₂
 403 concentration (µatm) of Brazilian lakes sampled from different biomes, as defined by (SUBT)
 404 Subtropical Coastal lakes (n = 37), (TROP) Tropical coastal lake (n = 63), (PANT) Pantanal

405 Floodplain (n = 58) and (AMAZ) Amazonia Forest (n = 67). The line depicts the median. The
406 boxes show the quartiles, and the whiskers mark the 10th and 90th percentiles. Different
407 lowercase letters near the boxplot indicate significant statistic differences between the groups
408 (Kruskall-Wallis followed by Dunn`s multiple comparison post hoc test, p < 0.05).



409

410 Figure 3. Comparisons of *p*CO₂ against DOC concentrations for lakes from this study (black
411 circles) and from Sobek et al. [2005] (gray circles). Each point in the plot represents one
412 measurement. The dashed line represents the linear regression for all Brazilian data points (not
413 significant; p > 0.05), and the solid line represents the linear regression from Sobek et al. [2005]
414 (p < 0.05, R² = 0.26, log *p*CO₂ (μatm) = 2.67 + 0.414 log DOC (mg C L⁻¹)).

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