Temperature-dependence of the relationship between $p\mathrm{CO_2}$ and dissolved organic carbon in lakes

L. Pinho[1,2,3], C. M. Duarte[2,4], H. Marotta[5,6], A. Enrich-Prast[1,7]

1. Postgraduate Program in Ecology, Department of Ecology, Institute of Biology, Federal University of Rio de Janeiro, Rio de Janeiro. Av. Carlos Chagas Filho, 373 Cidade Universitária (Ilha do Fundão), P. O. Box 68020, Rio de Janeiro, RJ, Brazil.

2. Global Change Department, IMEDEA (CSIC-UIB), Mediterranean Institute for Advanced Studies. C. Miquel Marquès, 21, 07190, Esporles, I. Baleares, Spain.

3. Department of Chemical Oceanography, Rio de Janeiro State University, Rua São Francisco Xavier, 524 – Rio de Janeiro - RJ - CEP 20550-900, Pavilhão João Lyra Filho, 4º andar, sala 4008 Bloco E.

4. King Abdullah University of Science and Technology (KAUST), Red Sea Research Center (RSRC), Thuwal, 23955-6900, Saudi Arabia

5. Research Center on Biomass and Water Management (NAB/UFF), Sedimentary Environmental Processes Laboratory (LAPSA/UFF), International Laboratory of Global Change (LINCGlobal), Federal Fluminense University. Av. Litorânea s/n, Campus Praia Vermelha, 24210 340, Niterói, RJ, Brazil.

6. Postgraduate Program in Geography, Postgraduate Program in Geosciences (Geochemistry), Federal Fluminense University, 24220-900, Niterói, RJ, Brazil.

7. Department of Environmental Changes, Linköping University, 581 83, Linköping, Sweden.

Corresponding author: luana.pinho@uerj.br

Abstract

The relationship between the partial pressure of carbon dioxide ($p\mathrm{CO_2}$) 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 low-latitude lakes (< 33°), despite very broad ranges in both $p\mathrm{CO_2}$ and DOC levels. These results suggest substantial differences in the carbon cycling of low latitude lakes, which must be considered when up scaling 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 [Duarte and Prairie, 2005; Cole et al., 2007; Prairie 2008; Tranvik et al., 2009], supporting heterotrophy [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 [Duarte and Prairie, 2005; Cole et al., 2007; Prairie 2008; Marotta et al., 2009].

The mechanistic connection between DOC and heterotrophic CO_2 production is believed to underpin the significant positive relationship between pCO_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 pCO_2 and DOC in lake waters is regionally variable and not universal [Lapiere and del Giorgio, 2012]. Hence, the relationship between pCO_2 and DOC reported in comparative analyses based on datasets dominated by temperate and high-latitude lakes (> 33^o) may not be extrapolated for all types of lakes, mainly because the tropical low latitude lakes (< 33^o) are generally underrepresented in global datasets [Raymond et al., 2013].

One priority of comparative studies is the latitudinal variance, where lake temperature, ice cover and mixing regime will differ and these climatically driven processes, in turn, should strongly influence OC cycling [Hanson et al., 2015]. At low latitudes, warm conditions over the whole year may increase the metabolic rates involved in the C cycling in terrestrial [Ometto et al., 2005] and aquatic [Marotta et al., 2009; 2010] ecosystems on an annual basis compared to the high latitude lakes. 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]. Enhanced heterotrophic activity in warm ecosystems would support high aquatic CO_2 production and subside high CO_2 evasion from global lake water to the atmosphere.

The largest previous comparative analysis already published in the literature for global lake waters [Sobek et al., 2005] reported a significant positive relationship between DOC and pCO_2 and a non-significant variation of pCO_2 among lakes with changing temperature. However, both analyses were characterized by a paucity of low latitude data. A strong positive relationship between temperature and pCO_2 was observed when subtropical and tropical ecosystems were included in the dataset [Marotta et al., 2009], likely caused by the potential increase in metabolic rates under warmer conditions [Brown et al., 2004: López-Urrutia et al., 2006]. Hence, the relationship between lake pCO_2 and DOC could also be temperature-dependent and, therefore, may differ between temperate and tropical lakes. The extensive low latitude territory of Brazil, which has a high density of lakes and ponds [Downing et al., 2006], is appropriate to examine general patterns in the tropics [e.g., Marotta et al., 2009, Kosten et al., 2010]. Here, we test the applicability of the relationship between pCO_2 and DOC using inputs derived from a high latitude dataset [Sobek et al., 2005] with added tropical and subtropical data of low latitude lakes from Brazil.

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 km^2, constituting half of South America and encompasses a high diversity of low-latitude landscapes [Ab`Saber, 2003] that are predominantly located within tropical latitudes. We conducted a survey of pH, alkalinity and DOC between 2003 and 2011 in surface waters of 166 permanent lakes from 0 to 33° of south latitude across Brazil (Figure 1), yielding a total of 225 water samples. The lakes were sampled in representative biomes of Brazil: (1) the Amazonia Forest (Amazonia Biome, n = 65), (2) the Pantanal Floodplain (Pantanal Biome, n = 29) and (3) the Tropical (< 24^o of latitude) and (4) Subtropical (> 24^o and < 33^o of south latitude) Coasts, both in the Atlantic Forest Biome (n = 35 and n = 37 lakes, respectively; Figure 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.pdf). Our dataset encompasses a broad inter-lake heterogeneity (n=166) for pH, alkalinity and DOC simultaneously sampled among Brazilian biomes and along the latitudinal gradient, independent of the year's season.

The Amazonian Forest biome is formed by the most extensive hydrographic network on the globe: the Amazon River basin, which occupies a total area of approximately 6.11 million km² from its headwaters in the Peruvian Andes to its mouth in the Atlantic Ocean (ANA – www.ana.gov.br). The Amazon Forest is the Brazilian biome with the highest mean annual precipitation (approximately 2200 mm) and has warm mean air temperatures, approximately 25°C, high cloud coverage and high 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 approximately 150,000 km^2 between 16° and 20° S and 58° and 55° W [Por, 1995]. The annual average temperature and precipitation are approximately 22°C and 1,000 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 occur 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 the subtropics to tropics and a narrow longitudinal section between 55° and 56° W, and occupies 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 [$< 24^o$ of latitude; Chellappa et al., 2009] and from 17 and 20°C at the subtropical coast [$> 24^o$ of latitude; Waechter, 1998]. The mean annual precipitation reaches 1,164 mm [Henriques et al., 1986] and 1,700 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

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

pH, salinity and temperature were measured *in situ*. pH was determined using a pH meter (Digimed – DM2) with reference standards certified by Mettler Toledo (4.00 ± 0.01 and 7.00 ± 0.01 units) before each sampling hour. Temperature and salinity were measured using a Thermosalinometer (Mettler Toledo - SevenGo SG3) coupled to a probe in Lab 737 previously calibrated with 0.01 M KCl. Surface lake water was collected for total alkalinity and DOC analyses, taking care to avoid bubbles at approximately 0.5 m of depth using a 1 L Van Dorn bottle. Total alkalinity (TA) was determined in the field by the Gran´s titration method with 0.0125 M HCl immediately after sampling [Stumm and Morgan, 1996]. Water samples for DOC were pre-filtered (0.7 µm, Whatman GF/F) and preserved by acidification with 85% H_3PO_4 to reach a 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, quality control was checked with calibration curve made with potassium hydrogen phthalate before each sample battery analisys. $p\mathrm{CO}_2$ 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].

In order to address the potential contribution of DOC to TA, which is especially important in DOC-enriched acid freshwaters, we used the data set from Abril et al., [2015] to correct $p\mathrm{CO}_2$ values calculated from pH and TA after the corrections for temperature, altitude and ionic strength [Cole et al., 1994]. Full details on fitted regression equations to correct $p\mathrm{CO_2}$ in function of the DOC and pH are described in the supplementary information section. (Figure S3).

2.3. Statistical Analyses

The variables $p\mathrm{CO_2}$ and DOC did not meet the assumptions of parametric tests even after logarithmic transformations [Zar, 1996] as the data were not normally distributed (Kolmogorov-Smirnov, $p < 0.05$) and the 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, $p < 0.05$). The linear regression equations were fitted to compare our results with those of previous studies from Sobek et al., [2005]. 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) than in Pantanal and Amazonian lakes (29.5° C, 27.7 – 31.4 and 29.4° C, 27.6 – 31.0, respectively; Dunn’s test, $p < 0.05$, Figure 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) than in the tropical coast (13.4 mg C L^{-1}, 6.1 – 32.8; Figure 2b; Dunn’s test, $p < 0.05$). Most lakes (approximately 83% of raw data) showed surface waters supersaturated in $\mathrm{CO_2}$ relative to the atmospheric equilibrium ($p\mathrm{CO_2}$ in atmospheric equilibrium is 400.83 μatm, 2015 annual mean; data available in www.esrl.noaa.gov/gmd/ccgg/trends), with much higher $p\mathrm{CO_2}$ values in Amazonian lakes (7,956 μatm, 3,033 – 11,346) than in subtropical coastal lakes (900 μatm, 391.3 – 3,212; Figure 2c; Dunn’s test, $p < 0.05$).

The $p\mathrm{CO_2}$ in the surface waters of Brazilian lakes was independent of DOC concentrations (Linear regression for raw data, $p > 0.05$, Figure 3). The same absence of positive significance pattern was found comparing at corrected data. Negative (Linear regression, $p < 0.05$, $R^2 = 0.03$, $n = 194$, $p\mathrm{CO_2} = -98.76\ (\pm 39.92) \times \mathrm{DOC} + 6529\ (\pm 641.1)$ or non significant (Linear regression, $p > 0.05$) DOC-$p\mathrm{CO_2}$ relationship for tropical lakes ($N = 194$, DOC and pH corrected, respectively (figure S3a and c) contrasting with a significant positive relationship for those at other latitudes (N = 4,433) (Linear regression, $p < 0.05$, $R^2 = 0.20$, $pCO_2 = 64.43\ (\pm 2.04)$ x DOC + 625.1 (± 20.87) and $R^2 = 0.12$, $pCO_2 = 45.70\ (\pm 1.84)$ x DOC + 623.7 (± 18.83)) for DOC corrected data and pH corrected data, respectively (Figure S3b and d, full details on corrections in the supplementary information). The range of pCO_2 for a similar DOC range in Brazilian lakes was larger than that reported by Sobek et al., [2005] for the dataset dominated by high-latitude cold lakes, despite the number of lakes in their dataset being much larger (more details in supplementary information section, figure S3).

4.Discussion

The Brazilian lakes sampled here were characterized by a prevalence of CO_2 supersaturation, consistent with general trends previously reported for global lakes [e.g., Raymond et al, 2013; Cole et al., 1994; 2007] including those at tropical latitudes [Marotta et al., 2009]. The very high pCO_2 levels observed here, with a median of 900 and 8,300 µatm for subtropical and Amazon lake waters, respectively, are consistent with those reported previously for the Amazon River and tributaries (2,000-12,000 µatm; Richey et al., [2002]), Amazon floodplain lakes (3,000 - 4,898 µatm; Rudorff et al., [2012]), Pantanal lakes and wetlands (2,732-10,620 µatm; Hamilton et al., [1995]), and coastal lakes (768 - 9,866 µatm; Kosten et al., [2010]; 361-20,037 µatm; Marotta et al., [2010]) and for global values for tropical lakes (1,255-35,278 µatm; Marotta et al., [2009]), reservoirs (1,840 µatm; Aufdenkampe et al., [2011]) and wetlands (3,080-6,170 µatm; Aufdenkampe et al., [2011]).

The non-significant or weakly negative relationship (Figure S3) between DOC and pCO_2 reported here for warm low-latitude lakes contrasted with significant positive relationships derived from previous datasets dominated by high-latitude 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]. The results presented show that warm low-latitude lakes range widely in pCO_2, reaching very high and low values, but tend to have comparatively more uniform DOC concentrations (Figure 3). More intense metabolic processes that uptake and release CO_2 in lake waters, respectively autotrophy and heterotrophy, could determine an enhanced variability in lake pCO_2 with decreasing latitude [Marotta et al., 2009].

In this way, the inclusion of warm tropical data in our study revealed novel increases in the variability of the DOC-pCO_2 relationship in lakes over the latitudinal gradient. One explanation for this pattern is that even similar DOC concentrations, representing the total pool of DOC, may show different mixtures between origins from aquatic primary producers and terrestrial sources [Kritzberg et al., 2006]. The autochthonous DOC (i.e. produced in the lake) is related to the net CO_2 uptake [Staehr and Sand Jansen 2007], while the allochthonous DOC (i.e. produced in the catchment) is resource to the net CO_2 release in lake waters [Sobek et al., 2007]. The increased DOC release from aquatic primary producers into waters under tropical conditions, especially warmer annual conditions and higher solar incidence, can offset any positive relationship between $p\mathrm{CO}_2$ and the terrestrial DOC that subsides the net aquatic heterotrophy [Marotta et al., 2010; 2012]. This contributes to explain non-significant relationships reported here (Figure 3), suggesting a temperature dependence of the DOC-$p\mathrm{CO}_2$ relationship in global lakes

In conclusion, the finding that $p\mathrm{CO}_2$ does not increase with DOC concentration in Brazilian tropical lakes rejects the hypothesis that DOC serves as a universal predictor for $p\mathrm{CO}_2$ in lake waters [Larsen et al., 2012]. Even discounting a possible artifact of the method that could be causing an overestimation in the values of $p\mathrm{CO}_2$ or considering the contribution of organic acids on the alkalinity, the pattern of no relationship between DOC and $p\mathrm{CO}_2$ in the Tropical lakes was strongly confirmed (Figure S3). Therefore, our results contributing to fill the tropical gap suggest potentially important latitudinal differences for depositional aquatic environments, whose causes still need to be better addressed to improve accuracy of global C cycle models.

Authors Contribution

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

Acknowledgments

This research is a contribution to projects from Brazilian research agencies (FAPERJ, CAPES and CNPq). L. P. was supported by PhD scholarships from CAPES (period in Brazil) and FAPERJ (period in Spain). A. E-P. received postdoctoral and other CAPES and CNPq fellowships during studies at Linkoping University. H.M. was supported by a research fellowship from FAPERJ (Programa Jovem Cientista do Nosso Estado), and a research grant from CNPq

References

Abril, G., Bouillon, S., Darchambeau, F., Teodoru, C., Marwick, T., Tamooh, F., Ochieng Omengo, F., Geeraert, N., Deirmendjian, L., Polsenaere, P., and Borges, A.: Large overestimation of $p\mathrm{CO}_2$ calculated from pH and alkalinity in acidic, organic-rich freshwaters. Biogeoscience, 12, 67-78, 2015.

Ab`Saber, A.: Os Domínios de Natureza no Brasil: Potencialidades paisagísticas, Ateliê editorial Brazil, 2003.

Aufdenkampe, A., Mayorga, E., Raymond, P., Melack, J. and Doney, S.: Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere, Front. Ecol. Environ., 9, 1, 53-60, 2011.

Brow, J.,Gillooly, J., Allen, A., Savage, V., West, G.: Toward a metabolic theory of ecology, Ecology, 85 (7), 1771-1789, 2004.

Chambers, J., Higuchi, N., Schimel, J., Ferreira, L. and Melack, J.: Decomposition and carbon cycling of dead trees in tropical forests of the central Amazon, Oecologia, 122, 380-388, 1999.

Chellappa, N., Câmara, F. and Rocha, O.: Phytoplankton community: indicator of water quality in the Armando Ribeiro Gonçalves Reservoir and Pataxó Channel, Rio Grande do Norte, Brazil, Braz. J. Biol., 69, 241-251, 2009.

Cole, J. J., Caraco, N. F., Kling, G. W. and Kratz, T. K.: Carbon-Dioxide Supersaturation in the Surface Waters of Lakes, Science, 265, 1568-1570, 1994.

Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G., Duarte, C. M., Kortelainen, P., Downing, J. A., Middelburg, J. J. and Melack, J.: Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget, Ecosystems, 10, 171-184, 2007.

Davidson, E. and Janssens, I.: Temperature sensitivity of soil carbon decomposition and feedbacks to climate change, Nature, 440, doi:10.1038/nature04514, 2006.

Downing, J.A., Praire, Y.T., Cole, J.J., Duarte, C.M., Tranvik, L.J., Stiegl, R.G., McDowell, W.H., Kortelainen, P., Caraco, N.F., Melack, J.M. and Middleburg, J.: The global abundance and size distribution of lakes, ponds, and impoundments, Limnol. Oceanogr., 51, 2388-2397, 2006.

Downing, J. A., Cole, J. J., Middelburg, J. J., Striegl, R. G. and Duarte, C. M.: Sediment organic carbon burial in agriculturally eutrophic impoundments over the last century, Glob. Biogeochem. Cy., 22, GB1018, doi:10.1029/2006GB002854, 2008.

Duarte, C. M. and Prairie, Y. T.: Prevalence of heterotrophy and atmospheric CO_2 emissions from aquatic ecosystems, Ecosystems, 8, 862-870, 2005.

Farjalla, V. F., Amado, A. M., Suhett, A. L., and Meirelles-Pereira, F.: DOC removal paradigms in highly humic aquatic ecosystems, Environm. Sci. and Pol. Res. 16, 531-538, 2009.

Gudasz, C., Bastviken, D., Steger, K., Premke, K. and Sobek, S.: Temperature-controlled organic carbon mineralization in lake sediments, Nature, *466*, 478- 481, 2010.

Hamilton, S. K., Sippel, S.J. and Melack, J.M.: Oxygen depletion and carbon dioxide and methane production in waters of the Pantanal wetland of Brazil. Biogeochem. 30, 115-141, 1995.

Hamilton, S. K., Sippel S. J. and Melack, J. M.: Comparison of inundation patterns among major South American floodplains, Journ. of Geophysic. Res., 107, D20, 8038, doi:10.1029/2000JD000306, 2002.

Hanson, P., Pace, M., Carpenter, C., Cole, J. and Stanley, E.: Integrating Landscape Carbon Cycling: Research Needs for Resolving Organic Carbon Budgets of Lakes, Ecosystems, DOI: 10.1007/s10021-014-9826-9, 2015.

Henriques, R.P.B., Araújo, D.S.D. and Hay, J.D.: Descrição e classificação dos tipos de vegetação da restinga de Carapebús, Rio de Janeiro. Rev. Bras. Bot. 9: 173 – 189, 1986.

Houle, D., Carigan, R., Lachance, M. and DuPont, J.: Dissolved organic carbon and sulfur in southwestern Québec lakes: Relationships with catchment and lake properties, Limnol. Oceanogr., 40, 710-710, 1995.

Jonsson, A, Karlsson, J. and Jansson, M.: Sources of carbon dioxide supersaturation in clearwater and humic lakes in Northern Sweden, Ecosystems, 6, 224-235, 2003.

Junk, W. J. and Nunes de Cunha, C.: Pantanal: a large South American wetland at a crossroads, Ecol. Eng., 24, 391- 401, 2005.

Kritzberg, E., Cole, J., Pace, M. and Granéli, W.: Bacterial growth on allochthonous carbon in humic and nutrient-enriched lakes: Results from whole-lake 13C addition experiments, Ecosystems, 9, 489-499, 2006.

Kosten, S., Roland, F., Da Motta Marques, D., Van Nes, E., Mazzeo, N., Sternberg, L., Scheffer, M. and Cole, J.: Climate-dependent CO_2 emissions from lakes, Glob. Biogeochem.Cy., 24, doi:10.1029/2009GB003618, 2010.

Lapierre, J. F. and del Giorgio, P. A.: Geographical and environmental drivers of regional differences in the lake $p\mathrm{CO}_2$ versus DOC relationship across northern landscapes, Biogeosciences., 117, G03015, doi: 10.1029/2012JG001945, 2012.

Larsen, S., Andersen, T. and Hessen, D.: The $p\text{CO}_2$ in boreal lakes: Organic carbon as a universal predictor?, Glob. Biogeochem. Cy., 25, GB2012, doi:10.1029/2010GB003864, 2012.

López-Urrutia, Á. and Morán, X. A. G.: Resource limitation of bacterial production distorts the temperature dependence of oceanic carbon cycling, Ecology, 88, 817–822, 2007.

Mariot, M., Dudal, Y., Furian, S., Sakamoto, A., Valles, V., Valls, V., Fort, M. and Barbiero, L.: Dissolved organic matter fluorescence as a water-flow tracer in the tropical wetland of Pantanal of Nhecolândia, Brazil, Sci. Total Environm., 388, 184-193, 2007.

Marotta, H., Duarte, C. M., Sobek, S. and Enrich-Prast, A.: Large CO_2 disequilibria in tropical lakes, Glob. Biogeochem. Cy., 23, doi:10.1029/2008GB003434, 2009.

Marotta, H., Duarte, C. M., Pinho, L. and Enrich-Prast, A.: Rainfall leads to increased $p\text{CO}_2$ in Brazilian coastal lakes, Biogeosciences, 7, 1607-1614, 2010.

Marotta, H., Duarte, C.M., Guimarães-Souza, B. and Enrich-Prast, A.: 2012 Synergistic control of CO2 emissions by fish and nutrientes), Oecologia, 168, 3, 839-847, 2012.

Marotta, H., Pinho, L. Gudasz, C., Bastviken, D., Tranvik, L. and Enrich-Prast, A.: Greenhouse gas production in low-latitude lake sediments responds strongly to warming, Nat. Clim. Change, 4, 467-470, 2014.

McDonald, C., Rover, J., Stets, E. and Striegl, R.: The regional abundance and size distribution of lakes and reservoirs in the United States and implications for estimates of global lake extent, Limnol. Oceanogr., 57, 597-606, 2012.

Ometto, J. P. H. B., Nobre, A., Rocha, H., Artaxo, P. and Martinelli, L.: Amazonia and the modern carbon cycle: lessons learned, Oecologia, 143, 483-500, 2005.

Prairie, Y.: The summer metabolic balance in the epilimnion of southeastern Quebec lakes, Limnol. and Oceanogr., 47, 1, 316-321, 2002.

Prairie, Y. T.: Carbocentric limnology: looking back, looking forward, Canadian Journal of Fisheries and Aquatic Sci., 65(3), 543-548, 2008.

Raymond, P., Hartmann, J., Lauerwald, R., Sobek, S., McDonald, C., Hoover, M., Butman, D., Striegl, R., Mayorga, E., Humborg, C., Kortelainen, P., Durr, H., Meybeck, M., Ciais, P. and Guth, P.: Global carbon dioxide emissions from inland waters. Nature, 503, 355- 359, 2013.

Regaudie-de-Gioux A and Duarte C.M.: Temperature dependence of planktonic metabolism in the ocean, Glob. Biogeochem. Cycles, 26, GB1015, 2012.

Richey, J. E., Melack, J. M., Aufdenkampe, A. K., Ballester, V. M., and Hess, L. L.: Outgassing from Amazonian rivers and wetlands as a large tropical source of atmospheric CO_2, Nature, 416(6881), 617–620, 2002.

Roehm, C., Prairie, Y. T. and del Giorgio, P.: The *p*CO_2 dynamics in lakes in the boreal region of northern Québec, Canada, Global Biogeochem. Cy., 23, GB3013, doi:10.1029/2008GB00329, 2009.

Rudorff, C. M., Melack, J. M.; MacIntyre, S.; Barbosa, C. C. F.; and Novo, E. M. L. M.: Seasonal and spatial variability of CO_2 emission from a large floodplain lake in the lower Amazon, J. Geophys. Res., 117, G01002, doi: 10.1029/2011JG001699, 2012.

Scarano, F.: Structure, function and floristic relationships of plant communities in stressful habitats marginal to the Brazilian Atlantic rainforest, Annals of botan., 90, 4, 517-524., 2002.

Stumm, W. and Morgan, J. J.: Aquatic chemistry: chemical equilibria and rates in natural waters, vol 3. Wiley, New York, 1996.

Sobek, S., Tranvik, L. J. and Cole, J. J.: Temperature independence of carbon dioxide supersaturation in global lakes, Global Biogeochem. Cy., 19, GB2003, doi:10.1029/2004GB002264, 2005.

Sobek, S., Tranvik, L. J. and Cole, J. J.:, Patterns and regulation of dissolved organic carbon: An analysis of 7,500 widely distributed lakes, 2007.

Spyres, G., Nimmo, M., Worsfold, P., Achterberg, E., Miller, A.: Determination of dissolved organic carbon in seawater using high temperature catalytic oxidation techniques, Trends in Analytic Chem., 19, 8, 498-506, 2000.

Staehr, P. and Sand-Jansen, K.: Temporal dynamics and regulation of lake metabolism, Limnol. and Oceangr. 52 (1), 108-110, 2007.

Steinberg, C. E. W., Kamara, S., Prokhotskaya, V., Manusadzianas, L., Karasyova, T., Timofeyev, M., Jie, Z. Paul, A., Meinelt, T., Farjalla, V., Matsuo, A., Burnison, B. and Menzel, R.: Humic substances in the environment with an emphasis on freshwater systems, Environm. Sci. Pollut. Res. Int., 15, 15-16, 2006.

Tranvik, L.J., Downing, J.A., Cotner, J.B., Loiselle, S.A., Striegl, R.G., Ballatore, T.J., Dillon, P., Finlay, K., Fortino, K., Knoll, L.B., Kortelainen, P.L., Kutser, T., Larsen, S., Laurion, I., Leech, D.M., McCallister, S.L., McKnight, D.M., Melack, J.M., Overholt, E., Porter, J.A., Prairie, Y., Renwick, W.H., Roland, F., Sherman, B.S., Schindler, D.W., Sobek, S., Tremblay, A., Vanni, M.J., Verschoor, A.M., von Wachenfeldt, E. and Weyhenmeyer, G.A.: Lakes and reservoirs as regulators of carbon cycling and climate. Limnol. Oceanogr., 54, 2298-2314, 2009.

Wadham, J., Arndt, S., Tulaczyk, S., Stibal, M., M. Tranter, M., Telling, J., Lis, G., Lawson, E., Ridgwell, A., Dubnick, A., Sharp, M., Anesio, A. and Butler, C.: Potential methane reservoirs beneath Antarctica, Potential methane reservoirs beneath Antarctica, Nature, 488, 633-637, 2012.

Waechter, J. L.: Epiphyticorchids in eastern subtropical South America. Proc. 15th World Orchid Conference. Naturalia Publications, pp. 332-341, 1998.

Weiss, R. F.: Carbon Dioxide in water and seawater: The solubility of non-ideal gas, Mar. Chem., 2, 203-215, 1974.

Wohlers, J., Engel, A., Zollner, E., Breithaupt, P., Jurgens, K., Hoppe, H., Sommer, U. and Riebesell, U.: Changes in biogenic carbon flow in response to sea surface warming. PNAS, 106,17, 7067-7072, 2008.

Zar, J. H.: Biostatistical analysis, 3 ed., Prentice Hall., New Jersey, 1996.

Figures and subtitles

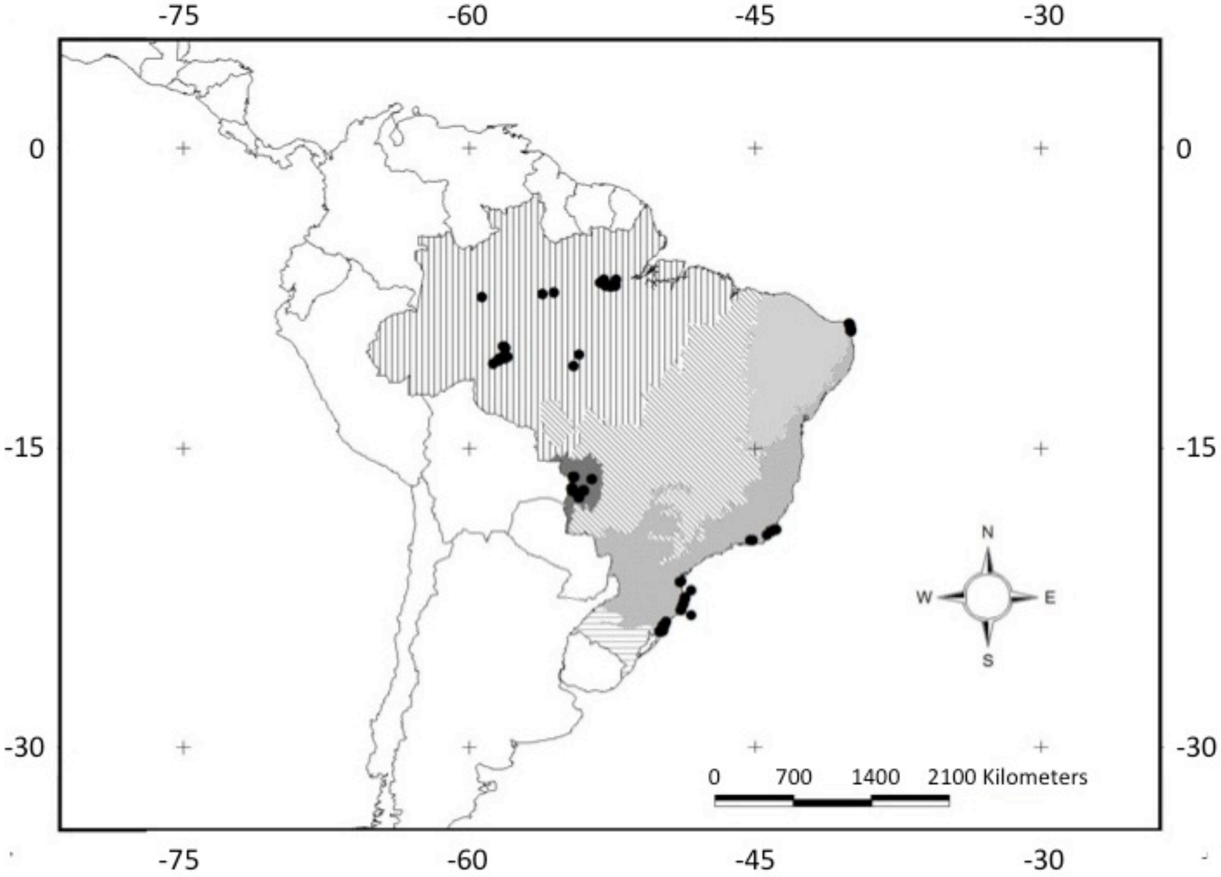

Figure 1. Geographic location of Brazilian lakes sampled in different biomes (IBGE 2004, available in ftp://geoftp.ibge.gov.br/mapas_tematicos/mapas_murais/biomas.pdf): Amazonia Forest (vertical lines), Pantanal Floodplain (dark gray), and Atlantic Forest (gray; Tropical and Subtropical costal lakes).

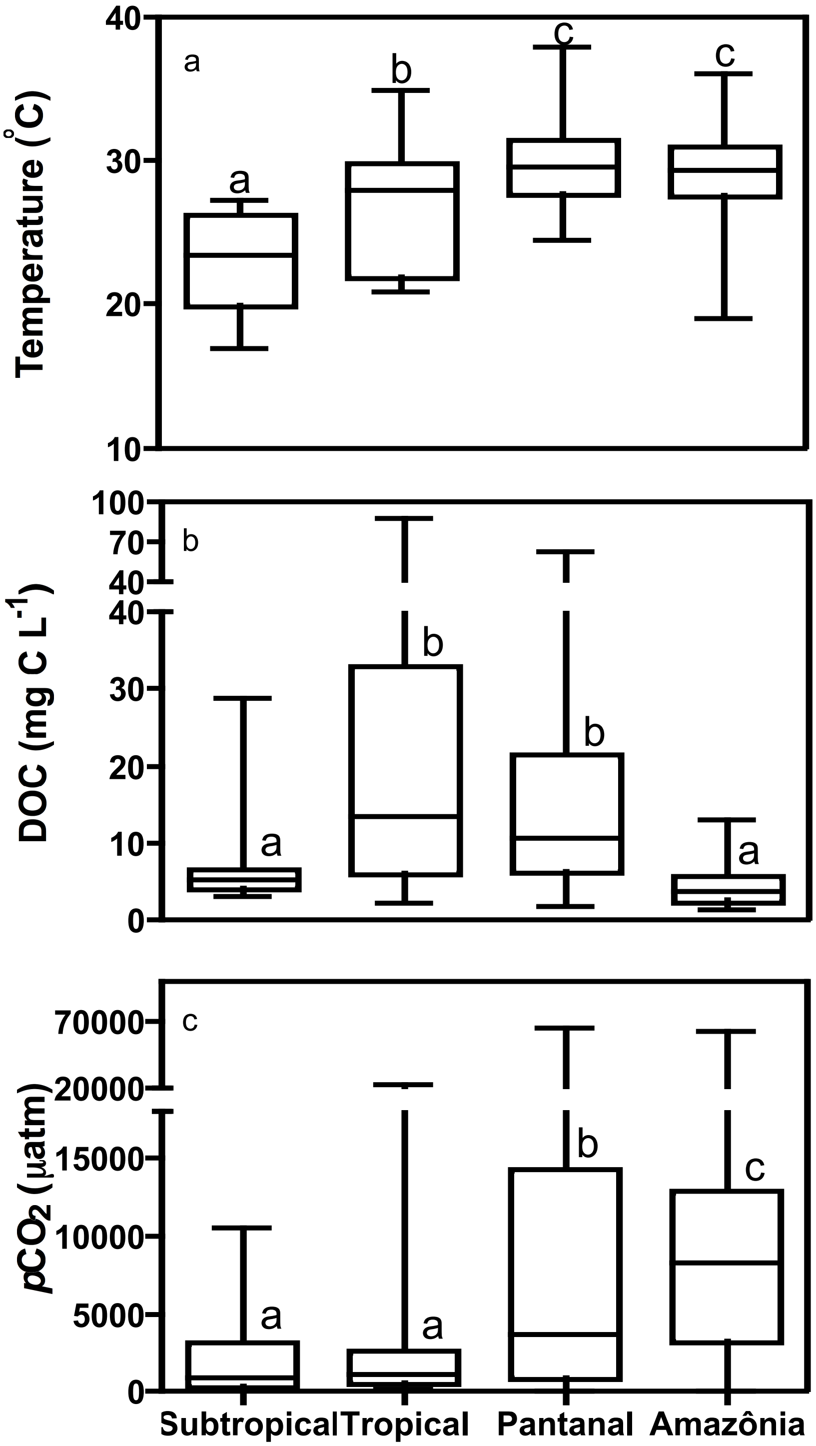

Figure 2. Values of (A) temperature (ºC), (B) DOC concentrations (mg C L^{-1}) and (C) pCO$_2$ concentration (µatm) of Brazilian lakes sampled from different biomes, as defined by (SUBT) Subtropical Coastal lakes (n = 37), (TROP) Tropical coastal lake (n = 63), (PANT) Pantanal

Floodplain (n = 58) and (AMAZ) Amazonia Forest (n = 67). The line depicts the median. The boxes show the quartiles, and the whiskers mark the 10th and 90th 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, $p < 0.05$).

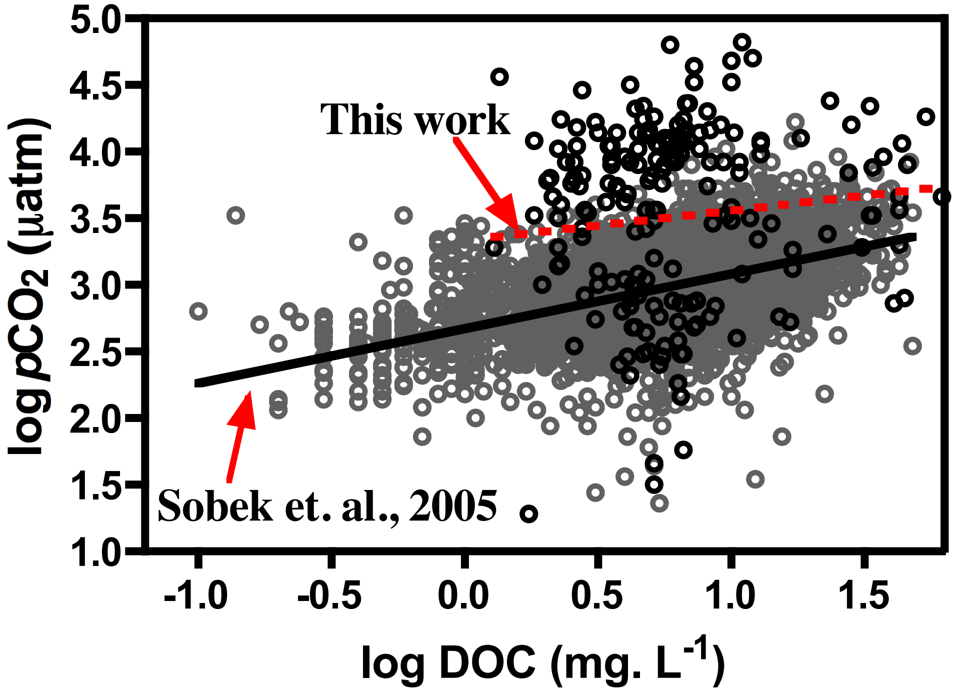

Figure 3. Comparisons of pCO_2 against DOC concentrations for lakes from this study (black circles) and from Sobek et al. [2005] (gray circles). Each point in the plot represents one measurement. The dashed line represents the linear regression for all Brazilian data points (not significant; $p > 0.05$), and the solid line represents the linear regression from Sobek et al. [2005] ($p < 0.05$, $R^2 = 0.26$, log pCO_2 (µatm) = 2.67 + 0.414 log DOC (mg C L^{-1})).