

Interactive comment on “Temperature-dependence of the relationship between pCO₂ and dissolved organic carbon in lakes” by L. Pinho et al.

L. Pinho et al.

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Response to Anonymous Referee #2

Referee #2 GENERAL COMMENTS

“The topic of the paper is very relevant, as it address the general lack of data from sub-/tropical lakes studies on dissolved organic carbon (DOC) and CO₂ concentration in lakes (pCO₂). The data pool on DOC and pCO₂ available from published literature is biased towards data sets from boreal/temperate lakes. This paper presents new, and highly needed, data from low latitude lakes.”

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Response: We thank the referee #2 for very constructive concerns, and we are glad that he finds our data new, and highly needed, from low latitude lakes.

Referee #2 “The primary conclusion is that for tropical and subtropical Brazilian lakes the relationship between DOC and pCO₂ is non-significant or weak negative. This conclusion is not very clear from the presented study. A linear regression analysis of the data grouped in 3 degree bins showed significant and positive slopes for all lakes with temperature < 24 degree C. Moreover, all negative slopes were non-significant (Figure 5 a).”

Response: The main result of this manuscript is the well-known positive relationship between DOC and pCO₂ was not found for lakes at warm low latitudes. In this way, additional analyses incorporating the contribution of organic acids in changes of alkalinity from Wang et al. 2013 also confirmed the absence of positive relationship between DOC and pCO₂, revealing even a weakly negative DOC-pCO₂ relationship.

Our results support that the DOC- pCO₂ relationship could be significant for cold high-latitude lakes (<24° C) and not for those at warm low latitudes (>24° C).

The original text: “Additional statistical analyses were doing assuming corrections of [HA]=[DOC] = 8.33 in the alkalinity to correct the calculated pCO₂ for the contribution of organic acids, after Wang et al. (2013). This correction lead, a change of non-significant relationship between pCO₂ and DOC for a negative significant relationship (slope= -16.8 ± 52.5; p < 0.05).”

The text now reads: “Additional statistical analyses were doing assuming corrections of [HA]=[DOC] = 8.33 in the alkalinity to correct the calculated pCO₂ for the contribution of organic acids, after Wang et al. (2013). This correction also confirmed the absence of positive relationship between pCO₂ and DOC, revealing even weakly negative relation (slope= -16.8 ± 52.5; p < 0.05).”

Referee #2 “There is no established un-biased protocol for calculating pCO₂ from

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pH/TA, and in my opinion the method used in this study, unfortunately, casts serious doubt on the conclusions. This study has several shortcomings which the authors would need to address (see specific comments for more detail):

Referee #2 1) Calculated values of pCO₂ are biased and absolute values of calculated pCO₂ in Brazilian lakes may be significantly and systematically overestimated. Response: In order to address criticisms on pCO₂ values from pH/TA method, we corrected all pCO₂ values following the fitted regression equation for median pH and % of measured pCO₂ data available in table 2 from Abril et al. (2015): Log pCO₂ correction (%) = - 0.9638 *pH + 7.755; R² = 0.9752, p < 0.005). After these corrections, both tropical and non-tropical lakes showed same trends observed before (significantly positive for cold high-latitude waters and non-significant for those at warm low-latitudes).

Referee #2 2) The study operates with two datasets with different corrections applied to the calculated pCO₂ values. The conclusion (significant or non-significant relationships) depends on the type of correction used. Which of the dataset do the authors have most confidence in – and why?

Response: Corrections to reduce bias in the pH-alkalinity method were performed and supported same conclusions: the positive relationship between DOC and pCO₂ could be significant only at cold high latitudes.

Referee #2 3) A linear regression analysis of the data grouped in 3 degree bins showed significant and positive slopes for all lakes with temperature < 24 degree C. Moreover, all negative slopes were non-significant (Figure 5 a) - but the conclusion of the dataset as a whole, is that the slope is negative and significant.

Response: This figure 5a consistently supports that only colder lake waters could show a significant positive relationship between DOC and pCO₂, and the slope could significantly decrease with increasing temperature.

Referee #2 4) The effect of spatial autocorrelation in the dataset is not discussed.

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Response: We integrated spatial and temporal data in averages for each lake to avoid effects of autocorrelation. Also, our aim was not to assess the intra-lake heterogeneity.

Referee #2 5) The effect of sampling scheme (dry/wet season) on the range of pCO₂ is not discussed. Are there any systematic differences in pCO₂ from dry season samples compared to wet season samples? The abstract could be clarified, see specific comments. The overall presentation is well structured and clear." Response: Our aim was not to assess seasonal fluctuations, integrating randomly lakes with or without seasonal data. Also, we highlight the dataset pointed out in this manuscript represents first efforts to fill the gap on DOC- pCO₂ relationship in tropical lake waters. Now we include more ~1/6 of literature data.

The original text: "The relationship between the partial pressure of carbon dioxide (pCO₂) 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 pCO₂ and DOC. Closer examination showed that the strength of pCO₂ 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."

The text now reads: "The relationship between the partial pressure of carbon dioxide (pCO₂) and dissolved organic carbon (DOC) concentration in Brazilian lakes, encompassing 194 lakes 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 warm low-latitude lakes, despite very broad ranges in both pCO₂ and DOC. The linear regression of pCO₂ vs. Temperature bins 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."

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The original text: "We sampled 166 lakes collecting 4 to 5 samples over 24 h at each lake. The values reported here represents daily averages for pCO₂ 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)."

The text now reads: "We joined 194 lakes, including 166 from our own survey and 28 from the published literature. The values reported here represented, on an opportunistic manner, daily averages (N= 4 or 5 samples) for a given year season or/and one sampling time over different seasons, which were both integrated in averages for each lake. The intra-lake heterogeneity was randomly assessed among ecosystems. The sampling design encompassed the most representative brazilian biomes."

Referee #2 SPECIFIC COMMENTS

Referee #2 P 2789: The abstract is somewhat confusing. line 5-6 states "...,we found no significant relationship for tropical and subtropical Brazilian lakes, ..." – I take that the authors mean that they did not find any relationships between pCO₂ and DOC (?), but line 7-8 states: "Closer examination showed that the strength of pCO₂ vs. DOC relationships declines with increasing water temperature,...". A reader, who has not read the whole paper could be expected to ask – "So, if there were no relationships, how can a closer examination show that the relationships decline with temperature?"

Response: The original text: "The relationship between the partial pressure of carbon dioxide (pCO₂) 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 pCO₂ and DOC. Closer examination showed that the strength of pCO₂ vs. DOC relationships declines with increasing water temperature, suggesting substantial differences in carbon cycling in

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warm lakes, which must be considered when upscaling limnetic carbon cycling to global scales."

The text now reads: "The relationship between the partial pressure of carbon dioxide (pCO₂) and dissolved organic carbon (DOC) concentration in Brazilian lakes, encompassing 194 lakes 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 warm low-latitude lakes, despite very broad ranges in both pCO₂ and DOC. The linear regression of pCO₂ vs. temperature 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."

Referee #2 P 2793, line 12-19: First the pCO₂ is calculated according to Weiss (1974) and corrected according to Cole (1994). The resulting data are used in the initial analysis. Then another correction according to Wang (2013) was performed – and this last correction leads to a significant relationship. Since this study address pCO₂, the correct determination of this variable is crucial. Which of the calculated PCO₂ data sets do the authors believe is correct - the pre-Wang or the post-Wang correction? It cannot be both – so why use both?

Response: The method used to calculate of pCO₂ was according Cole et al. [1994], that represent the Weiss (1974) method with corrections for temperature, altitude, and ionic strength following Cole et al. [1994]. The correction according Wang (2013) was performed only to check if the influence of humic acid could be disguising a positive correlation, but this didn't happen.

Referee #2 There is no established un-biased protocol for calculating pCO₂ from pH/TA, and in my opinion the method used in this study, unfortunately, casts serious doubt on the conclusions. G. Abril has also addressed this issue in a comment: "In a recent study (Abril et al. 2015) we reported large discrepancies between calculated

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pCO₂ (pH & TA) and measured pCO₂, particularly in acidic and poorly buffered waters. Our findings may impact the conclusion Pinho et al., as some of their absolute values of calculated pCO₂ in Brazilian lakes may be significantly overestimated: for instance in the Amazon River and floodplain lakes (which were also sampled here) we found an average overestimation of 200%, reaching 500% in acidic "black waters" (Fig1a). If Pinho et al.'s dataset includes such physicochemical conditions typical of tropical waters (pH<6, TA<0.5mM), it is probable that part of their calculated pCO₂ data are also highly impacted by the same bias (Fig.1b). Pinho et al. mention in their MS a correction of calculated pCO₂ for organic acids based on the study of Wang et al. (2013) in the Congo River. This correction leaded to pCO₂ inconsistent with DOC (negatively correlated). Indeed, it is likely that the fraction of DOC that contributes to TA is highly variable and site specific, and thus cannot be derived from a single generic equation."

Response: The same previous response can explain the action to reduce this problem. In order to address criticisms on pCO₂ values from pH/TA method, we corrected all pCO₂ values following the fitted regression equation for median pH and % of measured pCO₂ data available in table 2 from Abril et al. (2015): Log pCO₂ correction (%) = -0.9638 *pH + 7.755; R² = 0.9752, p < 0.005). After these corrections, both tropical and non-tropical lakes showed same trends observed before (significantly positive for cold high-latitude waters and non-significant for those at warm low-latitudes).

Referee #2 P 2793, line 28 The description of the significant negative relationship between DOC and pCO₂ lacks information of the degree of freedom. Is this the linear regression for log-transformed data mentioned later (P 2793, line28)? If so, how did the authors address the influence of spatial auto-correlation in the dataset? Response: In the new approach we recalculated only one data for each lake (as explained before) and used only the raw data to develop the linear regression between DOC x pCO₂ relationship. Referee #2 P 2794, line 16-20 It is a minor issue, but it is stated, that 83 % of lakes were supersaturated in lakes relative to atmospheric equilibrium (390 uatm). It would be informative to know how the value for atmospheric equilibrium was reached.

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Was it calculated, or sampled? Furthermore, 83% of the lakes were supersaturated, but the described ranges of PCO₂ do not encompass any PCO₂ values below 390 uatm. On P 2795, line 23 the range of pCO₂ for this study is stated (900-8300 uatm) – the entire range is above saturation level. The text could clarify which lakes were sub-saturated.

Response: The equilibrium with atmosphere was according Tans and Keeling 2014 (NOAA data available in www.esrl.noaa.gov/gmd/ccgg/trends/global.html#global). The values of pCO₂ showed in the line 23, p2795 represent the lower median (subtropical) and higher median (Amazonia) and not the absolute values founded.

The original text: "The very high pCO₂ values observed here (900–8300 μ atm) are consistent with those reported earlier for the Amazon River and tributaries..."

The text now reads: "The very high medians of pCO₂ observed here (900–8300 μ atm – subtropical and Amazonia, respectively) are consistent with those reported earlier for the Amazon River and tributaries..."

Referee #2 P 2795, line 10 The reference to figure 4 seems out of context, as the figure does not show how pCO₂ or DOC increase with temperature. "... and the lack or weak negative relationship in Brazil lakes suggest that the relationship maybe (sic) temperature dependent, at pCO₂ increased with temperature in Brazilian lakes but DOC did not (Fig.4)."

Response: We apologize by de mistake The original text: "The contrast between the positive relationship between pCO₂ and DOC concentration in the, largely temperate, data set of Sobek al. (2005) and the lack or weak negative relationship in Brazil lakes suggest that the relationship maybe temperature dependent, as pCO₂ increased with temperature in Brazilian lakes but DOC did not (Fig. 4)."

The text now reads: "The contrast between the positive relationship between pCO₂ and DOC concentration in the, largely temperate, data set of Sobek al. (2005) and the

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lack or weak negative relationship in Brazil lakes suggest that the relationship maybe temperature dependent, as pCO₂ increased with temperature in Brazilian lakes but DOC did not (Fig. 2a and 2c)."

Referee #2 Figure 2, pane C The whiskers for the 10% percentile seem to extend to a value below zero. Did the calculation of pCO₂ result in negative values – or is the graphic ambiguous? Response: A new graph was created breaking the y-axis below.

Referee #2 Figure 3 The text should clarify what the line in pane b represent. The info on linear regression should include degree of freedom.

Response: The original text: Figure 3. The linear relationship between the mean (\pm SE) of Brazilian lakes: (a) DOC (mg C L-1) and (b) pCO₂ (μ atm) 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 log pCO₂ was significant ($R^2 = 0.83$, $F = 19.87$; $p < 0.05$). The text now reads: Figure 3. The linear relationship between the mean (\pm SE) of Brazilian lakes: (a) DOC (mg C L-1) and (b) pCO₂ (μ atm) 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 log pCO₂ was significant ($R^2 = 0.83$, $F = 19.87$; $p < 0.05$, solid line represent the fitted equation). Referee #2 Figure 4 The dashed line represents linear regression for all Brazilian data points. It should be clarified whether the data points are from corrected values or not.

Response: This is now clarified in the text.

"The linear regression of raw data between pCO₂ (after corrections of Abril et al. 2015) and DOC in surface waters of warm low-latitude lakes was not significant ($p > 0.05$) while cold high-latitude lakes maintained the positive significant relationship ($pCO_2=45,7+-1,8 \times DOC + 623,7 +- 16,8$, $R^2= 0,12$, $p < 0,0001$)"

Figure 6 The relevance of figure 6 is not clear. Response: The figure 6 was removed.

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Referee #2 TECHNICAL CORRECTIONS

Referee #2 P 2793, line27-28 "... linear regression equation were fitted for log-transformed to compare..." – I suggest that the word "data" or "values" is inserted after "log-transformed"

Response: This sentence was removed.

Referee #2 P 2794, line 16: "Most pCO₂ lakes...". It is unclear Figure 2, pane C The whiskers for the 10% percentile seem to extend to a value below zero. Did the calculation of pCO₂ result in negative values – or is the graphic ambiguous?

Response: A new graph was created breaking the y-axis below.

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Response: The original text: Figure 3. The linear relationship between the mean (\pm SE) of Brazilian lakes: (a) DOC (mg C L-1) and (b) pCO₂ (μ atm) 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 log pCO₂ was significant ($R^2 = 0.83$, $F = 19.87$; $p < 0.05$). The text now reads: Figure 3. The linear relationship between the mean (\pm SE) of Brazilian lakes: (a) DOC (mg C L-1) and (b) pCO₂ (μ atm) 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 log pCO₂ was significant ($R^2 = 0.83$, $F = 19.87$; $p < 0.05$, solid line represent the fitted equation). Referee #2 Figure 4 The dashed line represents linear regression for all Brazilian data points. It should be clarified whether the data points are from corrected values or not.

Response: This graph was changed.

Referee #2 Figure 6 The relevance of figure 6 is not clear. Response: The figure 6 was removed.

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