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

Response to Anonymous Referee #1

1) Comments from referee
The manuscript “Temperature-dependence of the relationship between pCO2 and dissolved organic carbon in lakes” by Pinho et al. analyzes pCO2, DOC, and temperature data from 166 tropical and subtropical Brazilian lakes, concluding that in these systems, ambient pCO2 concentrations are frequently temperature dependent, not DOC dependent as concluded by Sobek et al. (2005). The paper does a good job highlighting the temperate lake bias in freshwater carbon cycling literature, and clearly demonstrates that low latitude lakes with warm annual temperatures may be functioning and processing carbon very differently than what is commonly reported. I think that this is a very important point, and that it should, as the authors propose, receive more attention in the literature. That said, I am not sure that the findings in this paper make a strong enough case to negate the findings of Sobek et al. (2005), as Pinho et al. lack the DOC gradient in the much larger Sobek dataset. The findings do, however, compliment this previous study by highlighting the variability of surface water pCO2 concentrations within tropical and subtropical biomes, and their deviation from trends seen across larger latitudinal gradients. This does not lessen the importance of this manuscript, but may require some generalizations to be tempered. Specific comments are below.

1) Author’s response:
First, we would like to thank the referee #1 for the very constructive comments, confirming the current paucity of data of the p\textsubscript{CO2} - DOC relationship in low-latitude lakes, a research topic that could reveal potentially important unknown processes of C cycling at warmer tropical regions.

Also, we fully recognize the importance of the general positive relationship between p\textsubscript{CO2} and DOC described by Sobek et al (2005), and better clarify this issue in the manuscript (see comments and action to address the Reviewer # 1’s comment 3).

2) Comments from referee
Overall, the scientific methods and assumptions are clearly outlined. Field, analytical, and statistical methods are clear, appropriate, and easily reproducible. Among the strengths of this paper are its clarity and brevity. The authors demonstrate that they are familiar with related work on DOC-pCO2 relationships, and explain well how their results compliment previous findings. Some references may need updating as the most recent reference is from 2013, but this is a minor point.

2) Author’s response:
We agree and added more recent references as Raymond et al. 2013, Hanson et al. 2015, Abril et al. 2015.
2) Author’s changes in manuscript

We included the following sentences.

“Hence, relationship between $pCO_2$ and DOC reported in comparative analyses based on data sets dominated by temperate and high-latitude lakes may not be extrapolated for all kinds of lakes, mainly because of the tropical warm lakes are generally underrepresented in global caught [Raymond et al., 2013].”

“One of priority for comparative study 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].”

“Aware of the difficulties in determining the $pCO_2$ in lakes with high contribution of organic compounds [Wang et al., 2013] and also the possible overestimation due to the method of TA and pH rather than direct measurements of $pCO_2$ [Abril et al., 2015], we tested the relationship of $pCO_2$ and DOC considering the raw data and after correcting the contribution of organic acids on TA and subsequent $pCO_2$ data, using the fitted linear regression for the medians and averages values of the relative difference between calculated and measured $pCO_2$ with ranked pH and DOC values, according the data disposable of Abril et al., [2015] (Figure 3 and 4, more detail in support material).”

3) Comments from referee

Primary criticisms of this work are first, that the results may be slightly overstated. While the authors’ findings do diverge from the generally accepted positive relationship between $pCO_2$ and DOC across latitudes and biomes, overlaying these data onto the larger Sobek dataset does not negate the entire relationship, particularly when lower DOC and higher latitude ecosystems are considered.

3) Author’s response:

In the larger dataset already published in the literature, Sobek et al. [2005] analyzed 4902 lakes globally distributed (CO$_2$ data), but only one warm tropical lake with $pCO_2$ and DOC data. Therefore, we do not intend to deny the positive relationship between $pCO_2$ and DOC consistently reported by Sobek et al. [2005] using a dataset dominated by high latitude lake waters. Our aim was in turn to complement it by adding new data and insights from warm-low latitude tropical lakes.

In order to clarify this point, we added the following sentences:

3) Author’s changes in manuscript.

The text now reads:

“Despite limitations in the method of measuring the $pCO_2$, our work is important because it adds to the literature a data set about DOC and $pCO_2$ of tropical lakes so far not included in the global calculations until now. Therefore, our results
suggest potentially important latitudinal differences from depositional aquatic environments, whose causes still need to be better addressed to improve accuracy of global C cycle models.”

4) Comments from referee
Second, I would suggest more attention be given to effects of productivity in these lakes. The authors deemphasize temperature effects on increased productivity, but it is well known that many phytoplankton prefer warmer temperatures (particularly bloom-forming Cyanobacteria, e.g., Paerl and Huisman, 2008).

4) Author’s response:
We agree that tropical conditions (not only temperature but also solar incidence) could control productivity and subsequent releases of DOC produced from CO₂ fixation by aquatic organisms, constraining the positive DOC- pCO₂ relationship in lake waters at low latitudes.

4) Author’s changes in manuscript.
The text now reads:

“Tropical conditions based on higher annual temperatures and solar incidence typically increases the aquatic primary productivity activity [Paerl and Huisman 2008] that releases into waters the DOC produced by the CO₂ uptake of algae and submerged plants [Staehr and Sand Jansen 2007], that can withstand a negative variation in the pCO₂ with an increase in the DOC concentration.”

5) Comments from referee
Finally, the discussion section would benefit from some speculation on how these findings might be important in the context of warming and climate change in higher latitude lake ecosystems. This would give better context for the broad impact of the main findings of the paper.

5) Author’s response:
We agree and follow this suggestion

5) Author’s changes in manuscript.
The text now reads:

“Therefore, our results suggest potentially important latitudinal differences from depositional aquatic environments, whose causes still need to be better addressed to improve accuracy of global C cycle models.”

6) Comments from referee
p. 2790, line 15 & p. 2796, lines 20-23. Emphasis is placed on high temperatures enhancing heterotrophy, not productivity. Nutrient availability is mentioned, but a brief mention or discussion of productivity would also be useful. Related to this, the manuscript would benefit from a table of general limnological/ water quality characteristics of the study lakes (e.g., Chl a, TN, TP). These could be summarized by biome for brevity if these data are available.
6) Author’s response:
Unfortunately, we do not have data of nutrients and Chl-a for most lakes included in the dataset. However, we agree with the relevance of DOC exudation from primary producers, adding a brief discussion on this topic in the manuscript (see our response and action for Reviewer #1’s comment 4).

7) Comments from referee
p. 2790, line 19-20. Further clarification is needed as to how tropical and subtropical lakes reported in Sobek et al. (2005, n=310) are qualitatively different than those presented here (n=166). It may not be appropriate to describe this paper as having a “paucity” of low latitude data, as it contained more low latitude lakes than this study.

7) Author’s response:
We had mentioned the warm (>20 oC) tropical lakes that were included in the positive DOC-pCO2 relationship reported in Sobek et al (2005), totaling only one lake (Lake Tupé, Amazon). Even in temperate lakes, the highest temperature found in Sobek’s paper was less than 22 degrees.

7) Author’s changes in manuscript.
We added a new graphic in the support material that shows the pCO2 across the temperature bins for all data and Sobeks data.

“Analyzing both data set in temperature bins, the lakes studied in Sobek et al., 2005 ranged between 0 and 24 degrees, while tropical lakes ranged from 6 and 37 degree. However, the variation was pCO2 was about 3 times greater for tropical lakes.”

8) Comments from referee
Figure 3: It is unclear how the strong relationship reported was generated from the data and line shown. These data would be better fit by a curvilinear relationship than a linear one, which is an interesting result in itself.

8) Author’s response:
We agree and removed this figure on the manuscript.

9) Comments from referee
Figure 4: This plot is slightly misleading. At a glance, it appears that the authors have reanalyzed the full Sobek dataset including data from this study, resulting in an overall non-significant trend. Upon closer inspection, it seems that the non-significant trend line is only fit to data from this study. If the authors can acquire access to the Sobek dataset and reanalyze it with their own contributions, it would make a much stronger case (but this understandably may not be realistic).

9) Author’s response:
We agree with this comment and we changed the figure for a new one where we show each correlation separately

9) Author’s changes in manuscript.
We included a new figure

Figure 3. The relationship between $pCO_2$ values and DOC concentrations for surface lake waters at (a) warm low latitudes from our compilation, and (b) cold high latitudes from the data set of Sobek et al. (2005). Each circle represents integrated values for each lake (see details in the Methods section). The solid line represents the fitted linear regression equation for cold lakes ($pCO_2$ [µatm] = 2.67 + 0.414 log DOC [mg C L$^{-1}$]; $R^2 = 0.26; p < 0.05, n = 4554$). A non-significant linear regression was observed for warm low-latitude lakes ($p>0.05, n = 194$).

10) Comments from referee
Figures 5 and 6: Not necessary and can be removed.

10) Author’s response:
We agree and removed Figure 5 and 6

11) Comments from referee
Overall the manuscript is very clear, concise, and well written. A few grammatical errors described below need attention.
p. 2793, line 15: Multiple grammatical errors (tense, sentence construction, word spacing); generally unclear. p.2794, line 16: Clarify what is meant by “Most pCO2 lakes...”;

11) Author’s response:
We are glad that s/he finds our manuscript well written and followed these corrections.

“Most lakes (approximately 83% of raw data) showed surface waters supersaturated in CO$_2$ relative to atmospheric equilibrium”
12) Comments from referee

12) Author’s response:
We deleted these sentences.

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

Response to Anonymous Referee #2

1) Comments from referee
“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.”

1) Author’s response:
We thank the referee #2 for very constructive concerns, and we are glad that s/he finds our data from low latitude lakes new and highly needed.

2) Comments from referee
“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 5a).”

2) Author’s response:
Our results clearly support that the previously reported positive relationship between DOC and $pCO_2$ for cold high-latitude lakes ($<24^\circ$ C) was not confirmed for warm lakes at low latitudes ($>24^\circ$ C). Considering the raw data or even using corrected data incorporating the contribution of organic acids on the TA with respect to pH or DOC concentrations we confirmed the absence of any positive relationship between DOC and $pCO_2$ in surface warm low latitude lake waters. This shows that the pattern is strong and is not only influenced by possible errors in the method. Some corrections can decrease more than an order of magnitude the value of $pCO_2$ and the positive relationship does not appear, indicating that the lack of correlation is not just an overestimation problem. We added new figures in
a support material to illustrate all corrections developed.

We decided to remove the previous correction according the article by Wang et al. 2013 and made further corrections considering the DOC values in Abril et al. 2015 to have the same standard of correctness regarding the classes of pH and DOC.

2) Author’s changes in manuscript:

The original text:
Page 2793, Line 15: “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:
“Aware of the difficulties in determining the pCO₂ in lakes with high contribution of organic compounds [Wang et al., 2013] and also the possible overestimation due to the method of TA and pH rather than direct measurements of pCO₂ [Abril et al., 2015], we tested the relationship of pCO₂ and DOC considering the raw data and after correcting the contribution of organic acids on TA and subsequent pCO₂ data, using the fitted linear regression for the medians and averages values of the relative difference between calculated and measured pCO₂ with ranked pH and DOC values, according the data disposable of Abril et al., [2015] (Figure 3 and 4, more detail in support material).”

3) Comments from referee
“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. This study has several shortcomings which the authors would need to address (see specific comments for more detail):

Calculated values of pCO₂ are biased and absolute values of calculated pCO₂ in Brazilian lakes may be significantly and systematically overestimated.

3) Author’s response:
We agree and address this issue using the fitted linear regression for corrections of pCO₂ associated with pH changes in lake waters following the very recent paper of Abril et al. (2015).

3) Author’s changes in manuscript:
See author’s changes to address the Reviewer’s comment 2.

4) Comments from referee
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?

4) Author’s response:
All corrections employed to reduce bias in the pH-TA method supported same conclusions: the positive significant relationship between DOC and pCO2 previously reported for high-latitude lake waters was not confirmed in our low-latitude dataset. For full details, see our response and changes to address the Reviewer’s comment 2 and 3.

5) Comments from referee
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.

5) Author’s response:
We pulled Figure 5 to avoid misunderstood about different bins classes and focus only on the difference in behavior between the relationship of DOC and pCO2.

6) Comments from referee
The effect of spatial autocorrelation in the dataset is not discussed.

6) Author’s response:
Our aim was not to assess the intra-lake heterogeneity, and we integrated spatial data in averages for each ecosystem to minimize the effects of autocorrelation.

6) Author’s changes:
For full details, see our response and changes to address the Reviewer’s comment 7.

7) Comments from referee
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.”

7) Author’s response:
We clarified in the manuscript that our aim was not to assess seasonal fluctuations,
but to integrate them by means per lake, which was, in turn, randomly compiled with or without seasonal data. In this way, we highlight that the present dataset represents the first efforts to fill the knowledge gap in the DOC- pCO$_2$ relationship for those warm lake waters, showing potentially more intense carbon sink and source on an annual basis in relation to those cold at high latitudes. To address this issue, we have also added more tropical data from the literature (Barreto et al., 2005; Petrucio et al., 2006; Pagioro et al.; 1999; Ulloa et al., 2004; Romeiro 2005; Rocha 2003; Costa 2000; Rodrigues 2007; Pereira 2000; Esteves et al., 2010).

7) Author’s changes in manuscript:

The original text:
Page 2792, Line 24: “We sampled 166 lakes collecting 4 to 5 samples over 24 h at each lake. The values reported here represents daily averages for pCO$_2$ 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).”

The text now reads:
“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. 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 also both integrated by means of each lake.”

8) Comments from referee

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 pCO$_2$ and DOC (?), but line 7-8 states: "Closer examination showed that the strength of pCO$_2$ 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?"

8) Author’s response:
We agree and clarify these sentences in the manuscript.

8) Author’s changes in manuscript:
The original text:
Page 2789, Line 2: “The relationship between the partial pressure of carbon dioxide (pCO$_2$) 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 pCO$_2$ and DOC. Closer examination showed that the strength of pCO$_2$ 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.”

New abstract: “The relationship between the partial pressure of carbon dioxide ($p\text{CO}_2$) 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 $p\text{CO}_2$ and DOC. These results suggest substantial differences in carbon cycling in warm lakes, which must be considered when upscaling limnetic carbon cycling to global scales.”

9) Comments from referee
P 2793, line 12-19: First the $p\text{CO}_2$ 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 $p\text{CO}_2$, 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?

9) Author’s response:
The method we use to calculate $p\text{CO}_2$ was Weiss 1974 with corrections for temperature, altitude and ionic strength, as Cole et al 1994 (Both methods coupled in the same calculation).

We decided to take the correction by Wang et al. 2013 method to avoid further doubts and redid the calculations with new equations from the same paper of Abril et al. 2015.

Our approach was to use independent corrections to make the conclusions more robust. We highlight that all corrections employed in the manuscript did not confirm that positive relationship between $p\text{CO}_2$ and DOC previously reported for cold lake waters at high latitudes for tropical lakes. For full details, see our response and changes to address the Reviewer’s 2 comment 2 and 3.

10) Comments from referee
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 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.

10) Author’s response:
We have used the corrections available in Abril et al. (2015) to minimize this bias, confirming the non-significant positive relationship between pCO2 and DOC for warm lake waters at low latitudes. For full details, see our response and changes to address the Reviewer's comment 2 and 3.

11) Comments from referee
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?

11) Author’s response:
We have used only one mean for each lake (comment 7), we changed figures 3, 4, 5 and 6.

12) Comments from referee
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 µatm). It would be informative to know how the value for atmospheric equilibrium was reached. 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.

12) Author’s response:
The range of medians was between 900 and 8300 µatm, but for raw data for each lake we had a 17% under saturated lakes. We agree and clarify this issue in the manuscript.

12) Author’s changes in manuscript:
The original text:
Page 2794, Line 16: “Most pCO2 lakes (approximately 83 %) showed surface waters supersaturated in CO2 relative to atmospheric equilibrium (390 µatm),...”

The text now reads:
Most pCO2 lakes (approximately 83% of raw data) showed surface waters supersaturated in CO2 relative to atmospheric equilibrium (pCO2 in atmospheric equilibrium of 390 µ atm, according Tans and Keeling 2014; data available in www.esrl.noaa.gov/gmd/ccgg/trends/global.html#global),...”
The original text:
Page 2795, Line 22: “The very high pCO₂ values observed here (900–8300 µatm) are consistent with those reported earlier for the Amazon River and tributaries...”

The text now reads:
“The very high pCO₂ observed here, in median 900 and 8300 µatm for subtropical and Amazon lake waters respectively) are consistent with those reported earlier for the Amazon River and tributaries...”

13) Comments from referee
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)."

13) Author’s response:
We agree and deleted this sentence.

14) Comments from referee
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?

14) Author’s response:
All pCO₂ values were above zero, and a new broken Y-axis graph was made to avoid any graphic ambiguous.
15) Comments from referee
Figure 3 The text should clarify what the line in pane b represent. The info on linear regression should include degree of freedom.

15) Author’s response:
We deleted the figure 3 and include 2 new figures.

Figure 3. The relationship between $p$CO$_2$ values and DOC concentrations for surface lake waters at (a) warm low latitudes from our compilation, and (b) cold high latitudes from the data set of Sobek et al. (2005). Each circle represents integrated values for each lake (see details in the Methods section). The solid line represents the fitted linear regression equation for cold lakes ($p$CO$_2$ [µatm] = 2.67 + 0.414 log DOC [mg C L$^{-1}$]; $R^2 = 0.26$; $p < 0.05$, n = 4554). A non-significant linear regression was observed for warm low-latitude lakes ($p>0.05$, n = 194).
Figure 4: The relationship between $pCO_2$ values and DOC concentrations for surface lake waters after correcting the contribution of organic acids on TA and subsequent $pCO_2$ data, compiled as described in Figure 3 and using corrections from the fitted linear regression for the median values of the relative difference between calculated and measured $pCO_2$ with pH (see methods for details; data for corrections available in Abril et al., 2015). The solid line represents the fitted linear regression equation for cold high-latitude lake waters ($pCO_2 = 45.70 \pm 1.84 \times DOC + 623.7 \pm 18.83$, $R^2 = 0.12$, $p < 0.0001$, $n=4433$). A non-significant linear regression was observed for warm low-latitude lakes ($p>0.05$, $n = 194$).

16) Comments from referee
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.

16) Author’s response:
We agree and changed the figures (comment 15)

17) Comments from referee
Figure 6 The relevance of figure 6 is not clear.

17) Author’s response:
We agree and removed figure 6.

18) Comments from referee
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"

18) Author’s response:
This sentence was removed.
19) Comments from referee
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?

19) Author’s response:
All pCO2 values were above zero, and new broken Y-axis graphs were made to avoid any graphic ambiguous. See in comment 14.

20) Comments from referee
Figure 3 The text should clarify what the line in pane b represent. The info on linear regression should include degree of freedom.

20) Author’s response:
We agree and changed the figures (comment 15)

21) Comments from referee
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.

21) Author’s response:
We agree and changed the figures (comment 15)

22) Comments from referee
Figure 6 The relevance of figure 6 is not clear.

22) Author’s response:
The figure 6 was removed.
The contrast between the positive relationship between \( pCO_2 \) 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 \( pCO_2 \) increased with temperature in Brazilian lakes but DOC did not (Figure 4). 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 (Figure 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 (\( p < 0.05 \); Figure 6).

Figure 3. The linear relationship between the mean (±SE) of Brazilian lakes: (a) DOC (mg C L\(^{-1}\)) and (b) \( pCO_2 \) (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 \(p\text{CO}_2\) was significant (\(y = 357.1 \pm 80.11x + -5649 \pm 2005; R^2 = 0.83, F = 19.87; p < 0.05\)).
Figure 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 \( p\text{CO}_2 \) and DOC concentrations for each bin interval (n varying from 7 and 1540). The solid lines represent both fitted regression equation encompassing all bins. Linear Slope \( (y) = -0.04 \pm 0.01x + 0.91 \pm 0.28 \) temperature 3° bin; \( R^2 = 0.46 \); \( F = 8.45; p < 0.05 \), and linear \( R^2 \) \( (y) = -0.01 + 0.48 \pm 0.07 \) temperature 3° bin; \( R^2 = 0.69 \); \( F = 21.9; p < 0.05 \).

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