Biogeosciences Discuss., 12, C978–C982, 2015
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Biogeosciences
Discussions
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Interactive comment on "Temperature-dependence of the relationship between pCO_2 and dissolved organic carbon in lakes" *by* L. Pinho et al.

Anonymous Referee #2

Received and published: 1 April 2015

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 litterature is biased towards data sets from boreal/temperate lakes. This paper presents new, and highly needed, data from low latitude lakes.

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).

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): 1) Calculated values of pCO2 are biased and absolute values of calculated pCO2 in Brazilian lakes may be significantly and systematically overestimated. 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? 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. 4) The effect of spatial autocorrelation in the dataset is not discussed. 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.

SPECIFIC COMMENTS 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 expeted to ask – "So, if there were no relationships, how can a closer examination show that the relationships decline with temperature?"

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) were performed – and this last correction lead 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?

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."

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?

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. 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.

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)."

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?

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

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.

Figure 6 The relevance of figure 6 is not clear.

TECHNICAL CORRECTIONS 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" P 2794, line 16: "Most pCO2 lakes...". It is unclear

what is meant with "pCO2 lakes". P 2795, line 1: "... in Brazilian dates...". Should "dates" be "lakes"? P 2795, line 9: "maybe" or "may be"? P 2785, line 23: "The very high pCO2...". It is unclear if "very high" is compared to expectations, other studies or something else.

Interactive comment on Biogeosciences Discuss., 12, 2787, 2015.