

Interactive comment on
**“Temperature-dependence of the relationship
between $p\text{CO}_2$ and dissolved organic carbon in
lakes” by L. Pinho et al.**

G. Abril

g.abril@epoc.u-bordeaux1.fr

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I would like to draw attention of Pinho and coll. to the occurrence of a large bias in $p\text{CO}_2$ calculation in freshwaters that can potentially alter their conclusions. In their paper, Pinho et al. (2015) present a dataset of $p\text{CO}_2$ calculated from pH and TA in Brazilian lakes and compare it to a larger dataset (Sobek et al. 2005), which contains a mixture of calculated and measured $p\text{CO}_2$. In a recent study (Abril et al. 2015) we reported large discrepancies between calculated $p\text{CO}_2$ (pH & TA) and measured $p\text{CO}_2$, particularly in acidic and poorly buffered waters. Our findings may impact the conclusion Pinho et al., as some of their absolute values of calculated $p\text{CO}_2$ in Brazil-

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ian 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 ($\text{pH} < 6$, $\text{TA} < 0.5\text{mM}$), it is probable that part of their calculated pCO_2 data are also highly impacted by the same bias (Fig.1b). Pinho et al. mention in their MS a correction of calculated pCO_2 for organic acids based on the study of Wang et al. (2013) in the Congo River. This correction led to pCO_2 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. In the Amazon river and floodplain lakes, we found a weak correlation between the difference in calculated and measured pCO_2 and the DOC concentration (Fig1.c). In addition, the bias is due to the cumulative effect of organic alkalinity and to a lower buffering capacity of the carbonate system at low pH (an exponentially increasing sensibility of calculated pCO_2 to the presence of organic alkalinity). In our study, we also attempted to correct TA for organic alkalinity using the models of Driscoll et al. (1989), and Hruska et al. (2003) that compute organic alkalinity from pH and DOC. In addition to the fact that in some samples modelled organic alkalinity were higher than measured TA, the pCO_2 recalculated from the measured pH and the TA corrected from organic alkalinity were still very different from those measured in the field. Unfortunately, no robust procedure is available yet to correct for the bias, pH/TA being the less reliable pair of parameters for quantifying pCO_2 in acidic waters. I fully agree with Pinho and Coll. on the importance of characterizing pCO_2 variations in inland waters and particularly across latitudinal gradients. However, it is questionable to what extent the bias in calculated pCO_2 may affect the comparison between the Brazilian pCO_2 dataset (calculated) with the global dataset (mixed measured and calculated). More generally, it would be prudent to perform a detailed quality check before continuing using calculated pCO_2 in global databases.

References

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Legend of fig 1 Comparison of measured pCO₂ and calculated pCO₂ (from pH and TA) in Amazon rivers and floodplain lakes (Data from Abril et al. 2015, *Biogeosciences*). (a) calculated versus measured pCO₂ ; (b) pCO₂ overestimation (calculated pCO₂ minus measured pCO₂) as a function of pH ; pCO₂ overestimation as a function of DOC.

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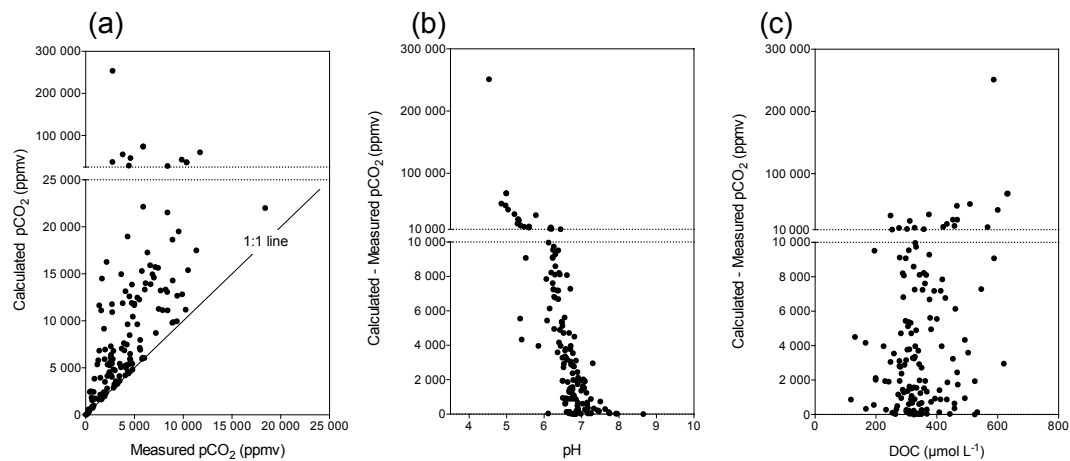


Fig. 1. see legend at the end of the comment

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