

## ***Interactive comment on “Technical Note: Large overestimation of $p\text{CO}_2$ calculated from pH and alkalinity in acidic, organic-rich freshwaters” by G. Abril et al.***

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Review of Abril et al. "Technical Note: Large overestimation of  $p\text{CO}_2$  calculated from pH and alkalinity in acidic, organic-rich freshwaters."

### GENERAL COMMENTS

I read this manuscript with great interest, as it addresses a topic my colleagues and I have been considering for quite a while, with large implications for the current understanding of freshwater air-water  $\text{CO}_2$  fluxes. The featured dataset of concurrent pH/TA/ $p\text{CO}_2$  measurements represents a valuable first step in examining potential errors in large-scale  $p\text{CO}_2$  flux estimates based on TA and pH measurements, and the

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decision to structure the manuscript as a technical note seems sound. However, the data also present an opportunity to explore possible ways to refine or even correct estimates of  $p\text{CO}_2$  from the TA/pH pairing. While such refinements or corrections would most likely be variable and site-dependent, they offer a chance to substantially improve current regional or global  $\text{CO}_2$  flux estimates.

The scientific quality of this paper is high. The authors employed well-documented methods for field and laboratory measurements, and a reasonable approach to derive  $p\text{CO}_2$  from TA/pH. Except for some suggestions to improve language usage listed in under Technical Corrections, the authors do a fine job presenting their data and findings.

### SPECIFIC COMMENTS

P11708 L22: Some discussion of the effect of filtering TA samples would be helpful. The one study I am aware of which discusses the filtration effect on freshwater alkalinity is Williams et al. (2009), who did not observe a significant difference between filtered and unfiltered alkalinities. However, that study examined low-DOC waters, which may differ from the waters in this study. Technically you measured dissolved alkalinity (DA), not total alkalinity (TA). They are probably functionally equivalent, but it is a point worth mentioning. Chanson and Millero (2007) discuss the filtration question with regard to open-ocean samples, and found no difference between filtered and unfiltered alkalinity. However, the particulate loads in your sampled rivers are probably much larger than open ocean waters.

P11710 L14-28 This section provides some very valuable insights, and I especially appreciate the ranking of sites in Table 2 by pH and TA to illustrate the trends in  $p\text{CO}_2$  overestimation, but I urge the authors to explore the interactions between  $p\text{CO}_2$  overestimation and pH and DOC further. I point this out because although the pairing of TA and pH to estimate  $p\text{CO}_2$  is problematic, as well illustrated in this work, it is also potentially extremely valuable, as there is a wealth of TA and pH data worldwide stretching

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back many decades. In our Hunt et al. (2011) paper we observed a relatively robust linear relationship between pH and the percentage of TA comprised of NCA, especially at pH<7. Subsequent unpublished data has shown the same trend, albeit with a somewhat different slope of the linear regression. It seems that the authors could attempt a similar regression, which may offer a simple pH-based correction factor, either gross or site-specific, which could be applied to the calculated pCO<sub>2</sub> values. I wonder if such a correction factor could yield 'good enough' corrected calculated pCO<sub>2</sub> to make the use of TA and pH on broad regional or global scales possible. Additionally, we have seen promise in power relationships between DOC concentration and non-carbonate alkalinity concentration, which could potentially also be used to derive a correction factor for use with the TA-pH pairing. Further, it seems that the authors have all the data to test a multivariate regression of pCO<sub>2</sub> overestimation against a combination of DOC and pH, which may be even more robust. Any insights the authors could provide to improve the use of TA and pH to calculate pCO<sub>2</sub> would be of great value.

P11711 L18-23: This is interesting! There is evidence in the coastal ocean literature as well that pairing pCO<sub>2</sub> and pH to derive TA and DIC produces problematic results (Cullison Gray et al. 2011). The authors of this coastal paper also conclude that the pH-pCO<sub>2</sub> pairing are particularly sensitive to measurement error, but did not address how precise pH and pCO<sub>2</sub> measurements would need to be in order to accurately retrieve DIC and TA. Mention of this topic is useful in the current manuscript, but perhaps deserves further exploration. It is clear that this manuscript focuses on the derivation of pCO<sub>2</sub> from pH and TA, but the authors have all the data needed to perform a very nice sensitivity analysis on the pH-pCO<sub>2</sub> pairing. While this may deviate from the central question of the manuscript, I would be very interested in the results of such an analysis.

#### TECHNICAL CORRECTIONS

General: Would it make sense to present alkalinity in  $\mu\text{mol L}^{-1}$  instead of  $\text{mmol L}^{-1}$ ?

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General: I suggest defining shorthand terms: perhaps pCO<sub>2</sub>calc (calculated pCO<sub>2</sub>) and pCO<sub>2</sub>obs (measured pCO<sub>2</sub>).

P11702 L5: I would recommend avoiding 'Nowadays'. For this line perhaps substitute 'Currently'

P11702 L6: add comma: 'freshwaters, and...'

P11702 L20-23: awkward sentence

P11703 L28: I would recommend avoiding 'Nowadays'. For this line perhaps substitute 'Presently'

P11703 L29 and throughout: Change 'water' to 'aquatic'

P11704 L1-2: Some citations here comparing usage of direct and indirect pCO<sub>2</sub> observations may be needed

P11704 L3: change to 'carbonic acid (which are a function of temperature)'

P11704 L16: change to 'adapted to the variability of pCO<sub>2</sub> found in freshwaters.'

P11704 L17: change 'and' to 'to'

P11704 L18: change 'First works consisted in' to 'Earlier examples provided a'

P11704 L22: change to 'showed a variability of +/-500'

P11704 L26: Is 7% agreement excellent? This level might be better described as a 'good' agreement. I suspect pairing TA with a pCO<sub>2</sub> +/- 7%, or even +/- 5%, would yield extremely variable calculated pH DIC values, for example.

P11704 L27: change to 'or underestimated, but'

P11704 L27-29: In this case, I don't think 'we' refers to all the authors of this manuscript. Consider rewriting this sentence to avoid the 'we' pronoun: 'Concurrent measurements of...performed in 2003 in acidic, humic-rich...showed that pCO<sub>2</sub>

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calculation. . .'

P11705 L7: change to 'organic acid anions'

P11705 L15: 'exponentially' is a really quantitative term. Consider substituting 'dramatically'

P11706 L4-12: A map of sampling locations, perhaps with unique markers corresponding to the various publications referenced, would be very helpful

P11708 L12-13: awkward sentence

P11708 L16: Separate into two sentences, suggest changing to 'In addition to the IR analysers generally used in this work, in the Sinnamary River pCO<sub>2</sub> was also. . .'

P11708 L29: change to 'capped'

P11709 L1: change to 'Shimadzu'

P11709 L17-18: awkward sentence

P11709 L24-25: awkward sentence

P11710 L7: change to 'more than 10%'

P11710 L12: change to 'The largest overestimation of pCO<sub>2</sub>calc occurred in the most. . .'

P11710 L14 Should this refer to Fig 3b, instead of Fig. 2b?

P11711 L3: the phrase 'calculated pCO<sub>2</sub> overestimation' is awkward

P11711 L6: the rivers in Hunt et al. 2011 were located in New Hampshire, Massachusetts, and Maine (USA) and New Brunswick (Canada). Perhaps just say 'New England (USA) and New Brunswick (CA) rivers'

P11711 L9-10: In our Hunt et al. 2011 paper we made some important assumptions about non-carbonate inorganic contributions to alkalinity, but did not test these assump-

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tions experimentally. We did not have concurrent nutrient measurements, so our N, P and Si values were taken from other work in the Oyster River. For other rivers described in that paper we did not have any N,P or Si data to examine their effects upon alkalinity. From the pKa values of nitrate, phosphate and silicate it is probably safe to assume that they do not contribute to alkalinity at the observed river pH. We also assumed that aluminum species did not contribute, which may or not be true.

P11711 L16-18 Awkward sentence, suggest 'evidencing the predominant role of organic acids in DIC speciation and pH in such acidic systems. Because we did not directly measure DIC. . .'

P11712 L3 Suggest change 'far from' to 'not only'

P11712 L23 Suggest changing 'above' to 'requiring'

P11714 L1 'World' does not need to be capitalized P11714 L6 Suggest removing 'ones'.

P11714 L5-10 This is a very long sentence. Suggest separating into two or three shorter sentences.

P117714 L25 Suggest removing 'as such'

## REFERENCES

Chanson, M. and F.J. Millero. 2007. Effect of filtration on the total alkalinity of open-ocean seawater. *Limnol. and Oceanogr.: Methods* 5: 292-295.

Cullison Gray, S.E., DeGranpre, M.E., Moore, T.S., Martz, T.R., Friedrich, G.E. and K.S. Johnson. 2011. Applications of in situ pH measurements for inorganic carbon calculations. *Marine Chemistry* 125: 82-90.

Williams, A.J., Andersen, C.B. and G.P. Lewis. 2009. Evaluating the effects of sample processing treatments on alkalinity measurements. *Journal of Hydrology* 377: 455-464.

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