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Interactive comment on "Technical Note: Large overestimation of pCO₂ calculated from pH and alkalinity in acidic, organic-rich freshwaters" *by* G. Abril et al.

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C.W. Hunt (Referee) chunt@unh.edu Received and published: 18 August 2014 Review of Abril et al. "Technical Note: Large overestimation of pCO2 calculated from pH and alkalinity in acidic, organic-rich freshwaters."

Comment 1 - "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 CO2 fluxes. The featured dataset of concurrent ph/TA/pCO2 measurements represents a valuable first step in examining potential errors in large-scale pCO2 flux estimates based on TA

and pH measurements, and the 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 pCO2 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 CO2 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 pCO2 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."

Reply 1 – We thank C.W. Hunt for his very positive overall evaluation of our MS. Indeed, one crucial question raised by the three referees can be summarized as: "Is it possible to correct the bias in calculated pCO2 data?". In fact, we tested several methods to derive empirical relationships that could be used to correct the pCO2 calculated from pH and TA. Unfortunately, we found no reliable consistent quantitative relationships to allow correcting for the bias in pCO2 when values are derived from pH, DOC, and TA.

The first approach consisted in calculating organic alkalinity from pH and DOC using the models of Driscoll et al (1989) –which assumes a single apparent pK value for organic acids- and the model of Hruska et al. (2003) – a triprotic model which assumes three apparent pK values-. These two organic acid models applied to our data led to very similar organic alkalinity values (See attached figure 1A). The organic alkalinity was then subtracted from the TA and the pCO2 was re-calculated from the measured pH and the TA value corrected from organic acids. pCO2 values corrected that way were, however, still very different from those measured in the field (See figure 1B), being sometimes higher and sometimes lower than the measured values.

The second approach consisted in subtracting from the measured TA, the alkalinity calculated with the CO2sys program using as input parameters the measured pH and pCO2, in order to derive a non-carbonate alkalinity (NCA). Besides the fact that NCA derived that way was often negative (probably due to large sensitivity of calculation

from the pCO2/pH pairing), it was neither (or weakly) correlated with DOC, nor with pH (See Figure 2). Consequently, we could not derive any empirical relationship useful to correct for the bias in pCO2 calculation.

Change 1 – In the revised version of our MS, we include a description of these attempts to correct calculated pCO2 from the available parameter (pH, TA, DOC and measured pCO2).

Comment 2 - "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.

Reply 2 – All our TA measurements were made on filtered samples. We agree with the referee that filtering is crucial in freshwaters. However, we made no comparison between filtered and unfiltered samples, so we cannot improve any understanding on this aspect. However, we expect that in white water rivers, with high TSM values, there could be an effect of dissolution of CaCO3 particles during titration that should affect the TA values. If we refer to definition of total alkalinity of Dickson (1981) it refers to the total sum of bases in one kilogram of sample for a pH > 4.5. Hence, TA should by definition relate solely to solutes and exclude particles.

Dickson, AG. 1981. An exact definition of total alkalinity and a procedure for the estimation of alkalinity and total inorganic carbon from titration data. Deep-Sea Research Part a-Oceanographic Research Papers. 28:609-623.

Change 2 – In the absence of comparative data, we avoided a long discussion on TA titration on unfiltered samples. Nevertheless, we mentioned in the revised MS that TA measurements should be done on filtered samples, otherwise some additional bias would appear in turbid samples.

Comment 3 – "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 pCO2 overestimation, but I urge the authors to explore the interactions between pCO2 over- estimation and pH and DOC further. I point this out because although the pairing of TA and pH to estimate pCO2 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 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 pCO2 values. I wonder if such a correction factor could yield 'good enough' corrected calculated pCO2 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."

Reply 3 – Refer also to reply 1. We fully agree it would be useful to provide such empirical correction factor. The referee refers to a method he used to estimate non carbonate alkalinity (NCA), based on the comparison of measured TA with that calculated from pH and DIC. Our dataset concerns pCO2, pH, TA, Temperature and DOC only. So we could calculate TA from the pH/pCO2 pairing, which is relatively uncertain in comparison with calculation from the pH/DIC pairing, owing to the strong correlation between these two parameters (pCO2 and pH, see also comment 5). As can be seen

in Figure B, we found no correlation between NCA (or the proportion of NCA in TA) and pH or DOC.

Change 3 – In table 2, we added a ranking of our dataset by DOC concentration. This ranking confirmed the general interpretation on the role of DOC on pCO2 overestimation.

Comment 4 – "Further, it seems that the authors have all the data to test a multivariate regression of pCO2 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 pCO2 would be of great value."

Reply 4 – A multivariable regression against DOC and pH is inappropriate as these two variables are not independent, since DOC contributes to acidity and is thus correlated with pH. Indeed, any insight to improve the use of TA and pH to calculated would be of great value. However, we found no evidence for the feasibility of a generally valid approach to correct for the bias, and until further studies provide more insights, our conclusion remains that pH/TA pairing should be abandoned in acidic waters.

Change 4 – No change related to this specific comment (multivariable analysis)

Comment 5 – P11711 L18-23: This is interesting! There is evidence in the coastal ocean literature as well that pairing pCO2 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- pCO2 pairing are particularly sensitive to measurement error, but did not address how precise pH and pCO2 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 pCO2 from pH and TA, but the authors have all the data needed to perform a very nice sensitivity analysis on the pH-pCO2 pairing. While this may deviate from the central question of the manuscript, I would be very interested in the results of such an analysis.

Reply 5 – Indeed, this deviates from the central question of the MS. Nevertheless, we stress in our MS the difficulty to calculate TA from the pH/pCO2 pairing, as these variables are generally well correlated.

Change 5 – we cite Cullison Gray et al. (2011) in our revised MS to strengthen our argumentation.

TECHNICAL CORRECTIONS Comment 6 - General: Would it make sense to present alkalinity in μmol L-1 instead of mmol L-1? Reply/Change 6 – We now use μmol L-1 throughout the manuscript.

Comment 7 – General: I suggest defining shorthand terms: perhaps pCO2calc (calculated pCO2) and pCO2obs (measured pCO2). Reply 7 – If these expressions are correct, we find it easier, more confortable, and clearer to repeat "calculated pCO2" and "measured pCO2" throughout the ms.

Comment 8 – 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' Change 8 – Modified in the revised MS, as suggested

Comment 9 – P11703 L29 and throughout: Change 'water' to 'aquatic' Reply 9 – "water pCO2" is widely used by opposition to air pCO2, and may have a different meaning from "aquatic pCO2"

Comment 10 – P11704 L1-2: Some citations here comparing usage of direct and indirect pCO2 observations may be needed Reply 10 – it is difficult to provide a reference list, as it will never be exhaustive or quantitative (how many papers using calculated versus measured ? how many measured versus calculated pCO2 data in each paper ?, etc. . .). We have chosen two significant references at the global scale (Cole et al 1994, Raymond et al. 2013).

Comment 11 – P11704 L3: change to 'carbonic acid (which are a function of temperature) P11704 L16: change to 'adapted to the variability of pCO2 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' Reply/ Change 11 – modified in the revised MS as suggested

Comment 12 – P11704 L26: Is 7% agreement excellent? This level might be better described as a 'good' agreement. I suspect pairing TA with a pCO2 +/- 7%, or even +/- 5%, would yield extremely variable calculated pH DIC values, for example. Reply/ Change 12 – changed to "good agreement"

Comment 13 – 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 pCO2 calculation. . .' P11705 L7: change to 'organic acid anions' P11705 L15: 'exponentially' is a really quantitative term. Consider substituting 'dramatically' Reply/ Change 13 – modified in the revised MS as suggested

Comment 14 – P11706 L4-12: A map of sampling locations, perhaps with unique markers corresponding to the various publications referenced, would be very helpful Reply 14 – A world map showing the 12 sampling sites is provided in the revised MS

Comment 15 – 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 pCO2 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 pCO2calc occurred in the most. . .' P11710 L14 Should this refer to Fig 3b, instead of Fig. 2b? P11711 L3: the phrase 'calculated pCO2 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' Reply / change 15 – modified in the revised MS as suggested.

Comment 16 – 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 assumptions 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. Reply / change 16 – We changed the sentence "in addition, the contribution of inorganic species other than carbonate was negligible and most of the NCA could be attributed to organic acid anions" to "in addition, the contribution of inorganic species other than carbonate was assumed negligible and most of the NCA was attributed to organic acid anions".

Comment 17 – 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' Reply / change 17 – modified in the revised MS as suggested.

Comment 18 – 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. Reply / change 18 We cite the Cullison Gray paper in order to strengthen the sensitivity to analytical errors in TA calculated from pH and pCO2.

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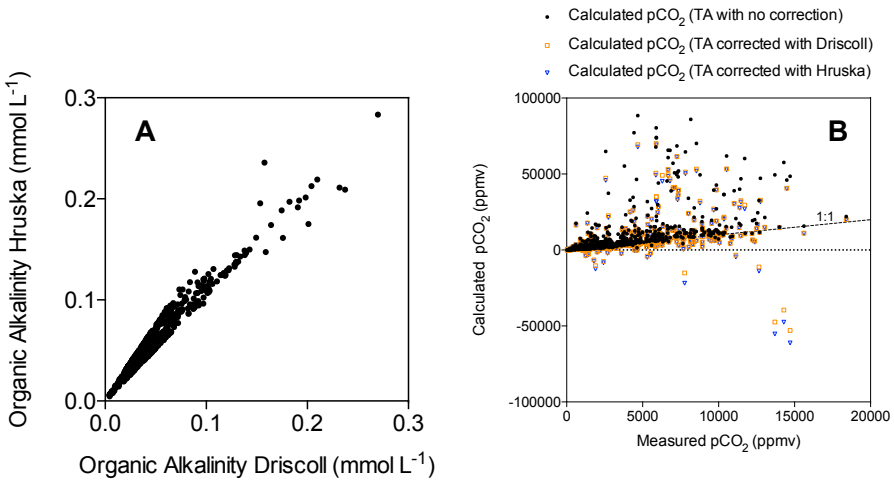

Fig. 1. A: comparison organic alkalinity calculated from pH and DOC using the models of Driscoll et al (1989) –which assumes a single apparent pK value for organic acids- and the triprotic model of Hruska et

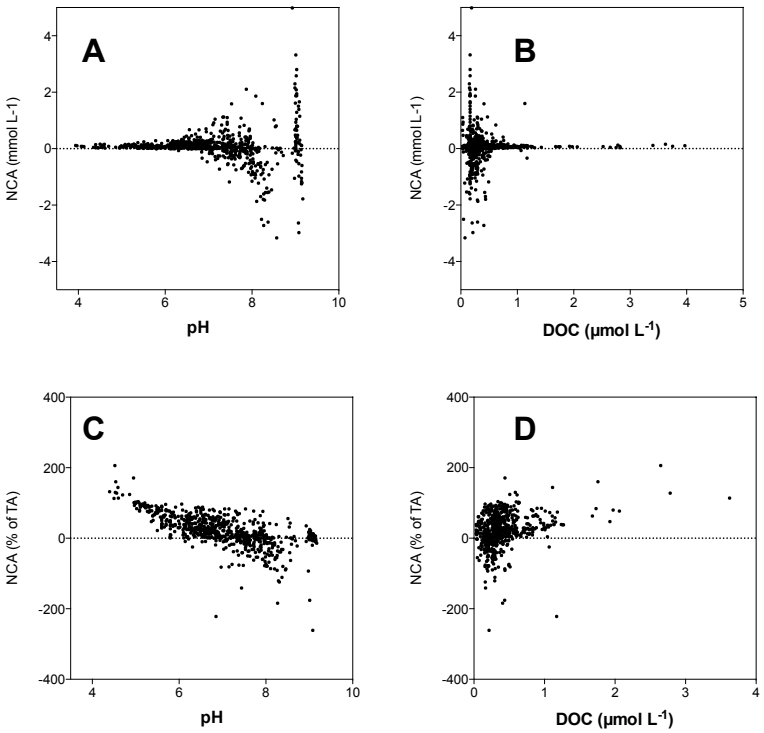

Fig. 2. Non carbonate alkalinity (NCA), as the difference between the alkalinity calculated with the CO2sys program using pH and pCO2 as input parameters, and the measured TA. NCA derived that way, expressed