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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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Anonymous Referee #2 Comments to the manuscript by Abril et al. bg-2014-341, Technical note: “Large over- estimation of $p\text{CO}_2$ calculated from pH and alkalinity in acidic, organic-rich freshwaters”. Comment 1 – Overview : The study presents a technical note where directly determined $p\text{CO}_2$ (equilibrator or headspace techniques) and indirectly calculated $p\text{CO}_2$ (from total alkalinity, pH and temperature) were compared across a wide range of freshwater systems. The authors found a large deviation between the two methods where the indirect determination generally overestimate the $p\text{CO}_2$. They further found that this overestimation was highest in low carbonate alka-

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linity, low pH and high DOC waters (> 100% in the 25% most organic-rich and acidic samples). They explain the large deviation by the influence of organic acids on the total alkalinity determination but also that the lower buffering capacity of the carbonate system at low pH increases the sensitivity of the calculated pCO₂. The main message of the study is consequently that large scale studies of pCO₂ should not solely use indirect determination, this is especially true for low pH and organic-rich waters. Based on this the authors further suggest that recent large scale studies on CO₂ emissions from inland waters might have overestimated the flux due to being based on potentially biased data. The manuscript focus on an important methodological topic that is very suitable for publication in Biogeosciences I believe. The amount of published papers dealing with inland freshwater CO₂ emissions at various scales is rapidly increasing. Many of these are based on such indirect methods without or with little validation of the results. In the race of getting these global/regional estimates and due to the lack of directly determined pCO₂, general chemistry data bases are often used but without considering the limitations of the data nor the methods used. Although the knowledge about weaknesses in the indirect determination of pCO₂ is not totally new, there is a need for bringing the discussion to light, something that I think this manuscript really does.

Reply 1 – We thank the referee for his/her very positive overall evaluation of our MS.

Comment 2 – General comments: With this background the manuscript is an important contribution to the research field. The authors present an impressive data set covering a wide geochemical and geographical range. Even not directly important for the comparison I especially appreciate the African contribution since this part of the world often is underrepresented in related studies. The manuscript is well written, includes solid data derived from standard and clear methodology and should be publishable after rather minor clarifications/additions. However, I find it a bit strange that the authors do not present ways to compensate for the influence of organic acids on the total alkalinity determination. This would be of great interest and use for future pCO₂ estimates

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based on standard water chemistry data. Methods to do that are there in the literature (see detailed comments below) and with the great data set that the authors present this would really lift the story and the overall impact.

Reply 2 – 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 poorly) 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 2 – 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

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pCO₂).

Comment 3 – Detailed comments: Ln 5 p.11702. Replace “Nowadays” with “Still” for example. Ln 15-17 p. 11703. I suggest to rephrase this sentence. In non-carbonate and organic- rich soils I would say that DOC commonly exceeds the DIC. Of course it is tricky to write about general global patterns. But I suggest to formulate it differently. Reply / Change 3 – Modified in the revised MS, as suggested

Comment 4 – Ln 24-27 p.11703. It is not totally clear to me what variability the authors refer to when they mention that pCO₂ can vary more than 4 orders of magnitude. Spatially, temporally or maybe spatiotemporally? Could be clarified. Reply / Change 4. In the revised MS, we specify that this refers to spatiotemporal variations.

Comment 5 – Ln 28 p. 11703. Again replace “Nowadays” with something more suitable Ln 3 p. 11704. Should be “carbonic acid” not “carbon acid” Ln 16 p. 11705. Include “pCO₂” before “values” Reply / Change 5 – Modified in the revised MS, as suggested

Comment 6 – Ln 23- p. 11706-11707. The whole section about the pH determination sounds a bit vague (see below) and since pH is such a critical parameter in the calculations I think it needs to be improved. “Water temperature and pH were measured in the field with different probes depending on the origin of the dataset”. To measure pH is not easy, this is especially true for waters with low-ionic strength. In such waters specific electrodes are needed in order to receive a stable and accurate pH reading. It is not easy to judge how well this is considered or if it is a potential problem in the included systems from the existing pH description in the manuscript. From my own experience I often find field based pH meters more unreliable (even if well-calibrated) than lab based ones, however bringing the water to lab is associated with other uncertainty as the authors also mention.

Reply 6 – We totally agree that it is not easy to judge how well pH is measured in general. If this is true for our own dataset, it may be even more critical for pH data obtained by environmental agencies. Comments by the referee were based on his/her

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own experience, as in fact, no quantitative study that compares pH-meters, electrodes, field and lab measurements, storage impact, etc. . . , are available in the literature. In the discussion of the first version of our MS we wrote “Thus, one factor of variability throughout the dataset as well as in literature data is the accuracy of pH measurements – despite the care taken (e.g, calibrations with NBS buffers for each day of measurements), we cannot rule out that drift or malfunction of pH electrodes contribute to the observed variability, constituting an additional disadvantage compared to direct pCO₂ measurements with very stable gas analysers”.

Change 6 – in the revised MS, we stress more the difficulties of pH measuring, also in the method section of the paper, following the suggestions of the reviewer.

Comment 7 – Ln 6 p. 11707. I suggest to move the date to after “Rivers” Ln 16 p. 11707. What kind of IR gas analyser? Ln 21 p. 11708. Add “determination” after GC. Reply/change 7 Modified in the revised MS as suggested.

Comment 8 – A general concern in the method section is the lack of info about the basic chemistry of the carbonate system. Below pH 5.4-5.6 there should in theory be no carbonate alkalinity. These limits (or similar) are also often used in studies where pCO₂ is calculated from alkalinity Reply 8 – Alkalinity is operationally defined (in our case the GRAN function between pH 4 and 3, but also in the case of end-point titrations used in environmental agencies, titration can still be performed at pH of less than 5 (the pK of HCO₃⁻/CO₂ being around 4.5). In addition, as stated in our submitted MS, we used to aerate our sample before titration in order to remove a fraction of dissolved CO₂ before HCO₃⁻ titration. This aeration increases the pH at the start of the titration and improves the quality (repeatability) of the alkalinity titration, even at pH around 5. Typical TA values in these cases are generally below 100 μmol L⁻¹. Change 8 – We provide more details on our TA protocol and mention these pH limits as suggested by the reviewer.

Comment 9 – Ln 2-4 p. 11710. The sentence that starts with “Our dataset. . .” Do not

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belong in the results as I see it. This is a reflection that is suitable for the discussion.
Reply / Change 9 – Sentence has been moved to discussion.

Comment 10 – Ln 1- p. 11711-. Here comes my main concern directly in the discussion. The influence of organic acids on the total alkalinity is not a new finding and there are ways to quantify and eventually compensate for the influence. In earlier acidification related research, for example Hruska et al. (2003) determined the organic acid concentration just by using pH and DOC as input parameters. This could then be removed from the total alkalinity (similar to the NCA derived from titration) in order to get a more reliable calculated pCO₂. This procedure has also been used in earlier studies (see Humborg et al. 2010; Wallin et al. 2014). In addition, Wallin et al. (2014) presented a similar comparison as conducted in this manuscript where alkalinity based pCO₂ and pCO₂ derived from DIC measurements were compared. Despite considering the organic acids the comparison still showed rather large deviation in the low alkaline waters (highlighting the sensitivity of the carbonate system at low pH). Of course there might be problematic to use such a universal organic acid model over the wide range of included systems as in this study. But to not even mention this opening in the paper feels strange. I think this manuscript really quantify the problems but also has the potential to suggest solutions. I definitely agree though that an increased use of methods focusing on CO₂ determination are needed in the future with standardized protocol to follow. Reply/changes 10 – see also reply 2 and the additional figure A As in Wallin et al. 2014, we have used the tri-protic model for organic acids of Hruska et al. (2003) in order to estimate the alkalinity of organic acids. We subtracted this organic alkalinity to our measured TA and we re-calculated the pCO₂ from the pH and the corrected alkalinity. Water pCO₂ corrected that way were not better correlated to the measured pCO₂. To the contrary, some highly negative pCO₂ values appeared in the corrected dataset (Figure 1). In our revised MS, we describe these calculations in more details.

Comment 11 – Ln 26-28 p. 11714. An evaluation of a pCO₂ method based on calcula-

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tion from direct DIC determination was recently published this year (Åberg and Wallin, 2014). In this study the method was also compared to a direct headspace technique with good result. Reply/change 11 – we mention and refer to the results of the paper of Åberg and Wallin, 2014 in the revised MS, as suggested. However, we continue recommending in our MS field direct pCO₂ determination, as this is very precise, cheap and easy, and it does depends on the quality of pH measurements.

Comment 12 – References : Hruska, J., S. Köhler, H. Laudon, and K. Bishop (2003), Is a universal model of organic acidity possible: Comparison of the acid/base properties of dissolved organic carbon in the boreal and temperate zones, *Environ. Sci. Technol.*, 37(9), 1726-1730, doi:10.1021/es0201552 Humborg, C., C. M. Mörth, M. Sundbom, H. Borg, T. Blenckner, R. Giesler, and V. Ittekkot (2010), CO₂ supersaturation along the aquatic conduit in Swedish watersheds as constrained by terrestrial respiration, aquatic respiration and weathering, *Glob. Change Biol.*, 16(7), 1966-1978, doi:10.1111/j.1365-2486.2009.02092.x Wallin, M. B., S. Löfgren, M. Erlandsson, and K. Bishop (2014), Representative regional sampling of carbon dioxide and methane concentrations in hemiboreal headwater streams reveal underestimates in less systematic approaches, *Glob. Biogeochem. Cycles*, 28(4), 465-479, doi:10.1002/2013gb004715 Åberg, J., and M. B. Wallin (2014), Evaluating a fast headspace method for measuring DIC and subsequent calculation of pCO₂ in freshwater systems, *Inland Wat.*, 4(2), 157-166, doi:10.5268/IW-4.2.694

Reply/change 12 We cited Wallin et al (2014), in the submitted MS We added Hruska et al (2003), and Åberg, and Wallin (2014), and Humborg et al (2010) in the revised MS

additional figure Captions

Figure 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 al. (2003) – which assumes three apparent

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pK values-. These two organic acid models applied to our data led to very similar organic alkalinity values (A). B: this calculated organic alkalinity was then subtracted from the measured TA. Then the pCO₂ was re-calculated from the measured pH and the TA corrected from organic acids. pCO₂ values corrected that way were still very different from those measured in the field (B), although being sometime higher and sometimes lower than the measured values.

Figure 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 either in concentration (A,C) or as percentage of TA (B,D) was often negative and was neither (or weakly when expressed as % of TA) correlated with DOC, nor with pH. No quantitative empirical relationship could be deduced from these plots.

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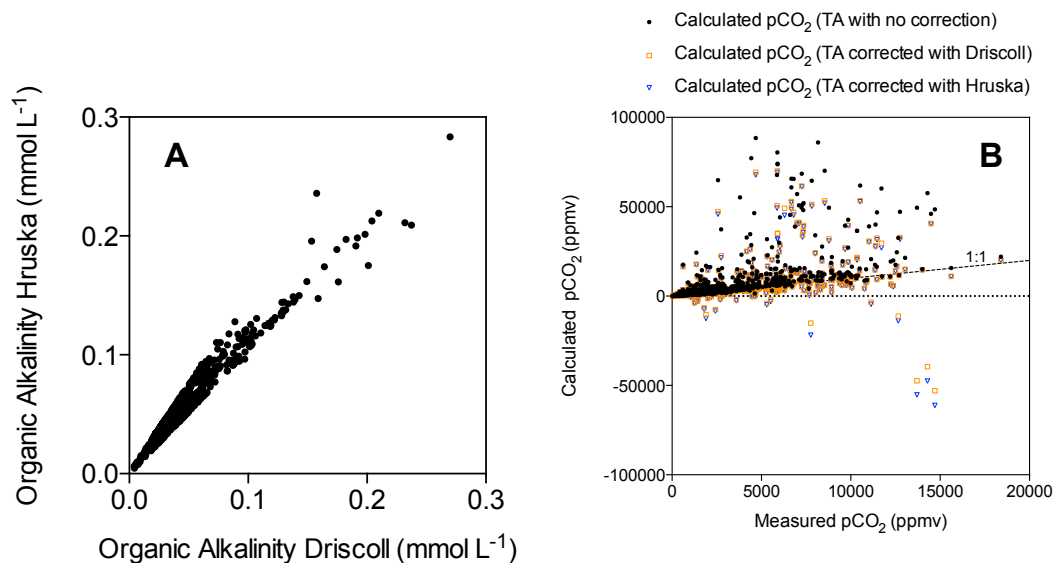


Fig. 1. A: comparison organic alkalinity calculated from pH and DOC using the models of Driscoll et al (1989) –which assumes a single apparent pK value for organic acids- and the triprotic model of Hruska et

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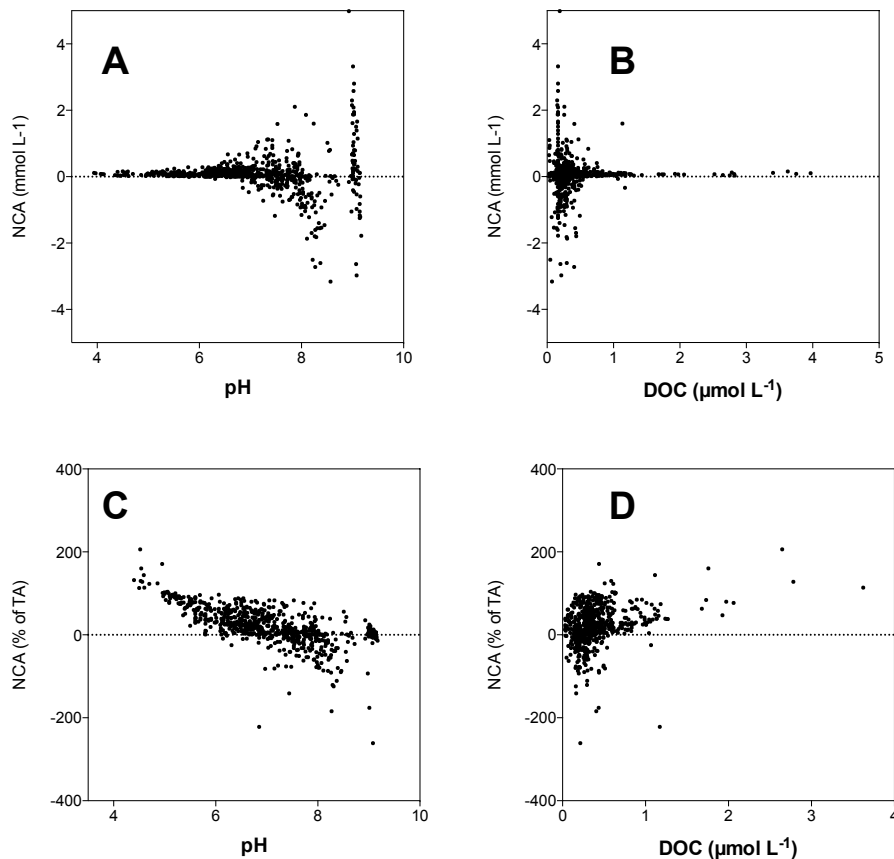


Fig. 2. Non carbonate alkalinity (NCA), as the difference between the alkalinity calculated with the CO2sys program using pH and pCO₂ as input parameters, and the measured TA. NCA derived that way, expressed