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

Anonymous Referee #2

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Comments to the manuscript by Abril et al. bg-2014-341, Technical note: "Large over-estimation of pCO2 calculated from pH and alkalinity in acidic, organic-rich freshwaters".

Overview:

The study presents a technical note where directly determined pCO2 (equilibrator or headspace techniques) and indirectly calculated pCO2 (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 pCO2. They further found that this overestimation was highest

in low carbonate alkalinity, 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.

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 author's 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 based on standard water chemistry

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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.

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.

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.

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"

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.

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.

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

Ln 2-4 p. 11710. The sentence that starts with "Our dataset...." Do not belong in the results as I see it. This is a reflection that is suitable for the discussion.

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.

Ln 26-28 p. 11714. An evaluation of a pCO2 method based on calculation 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.

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

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