

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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Received and published: 24 October 2014

Anonymous Referee #3 Received and published: 27 August 2014 Comment 1 – I believe this is a well written and well structured manuscript on a topic of current and relevant interest to a wide community. The subject of methodological bias in calculated $p\text{CO}_2$ values is extremely important as more and more people are beginning to utilise large datasets to estimate GHG contributions from inland water systems. Whilst the concept of overestimation is not new, particularly in relation to DOC rich systems, this study presents a very nice dataset with which to test the hypotheses and explore links to other water characteristics. My comments below, which are few, are aimed primarily

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at improving what I believe is a very good manuscript in its current format. Reply 1 – We thank the referee for his/her very positive overall evaluation of our MS.

Comment 2 – Introduction: whilst I realise there are practical limitations to the use of high temporal resolution sensors for in-situ CO_2 monitoring and therefore the number of studies are so far limited, it may be worth highlighting submerged NDIR sensors as an alternative direct method to measure $p\text{CO}_2$. Reply/change 2. We mention this membrane technique in our revised MS and cite the paper “Direct and continuous measurement of dissolved carbon dioxide in freshwater aquatic systems” method and applications by Johnson et al. (2010) in *ECOHYDROLOGY*.

Comment 3 – Methods: I am generally happy with the methods section, I felt it was well written and sufficiently detailed using standard and reliable methods. Results section 3.2: I think more could be made of the correlations that are described but not statistically modelled. Correlation statistics are not shown despite significant correlations being described. Reply/change 3 – correlation statistics (p values of linear regressions) are now provided in the revised MS, as suggested.

Comment 4 – General Comment: Could simple empirical modelling be used to attempt a correction for the bias? Whilst this may not work across all systems it would be very interesting to try. The authors have shown an important overestimation in studies which utilise large datasets of water quality to indirectly calculate $p\text{CO}_2$ and subsequent evasion, they have not however attempted to produce a solution. If an additional calculation step, e.g. including a DOC correlation value, would allow better $p\text{CO}_2$ estimates from the available data that would be extremely useful and significantly improve the science. This may not be possible but I would like to see evidence it had been attempted.

Reply 4 - Indeed, one crucial question raised by the three referees can be summarized as: “Is it possible to correct the bias in calculated $p\text{CO}_2$ data?”. In fact, we tested several methods to derive empirical relationships that could be used to correct the $p\text{CO}_2$

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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 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 4 – 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).

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 pK values-. These two organic acid models applied to our data led to very similar

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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.

Interactive comment on Biogeosciences Discuss., 11, 11701, 2014.

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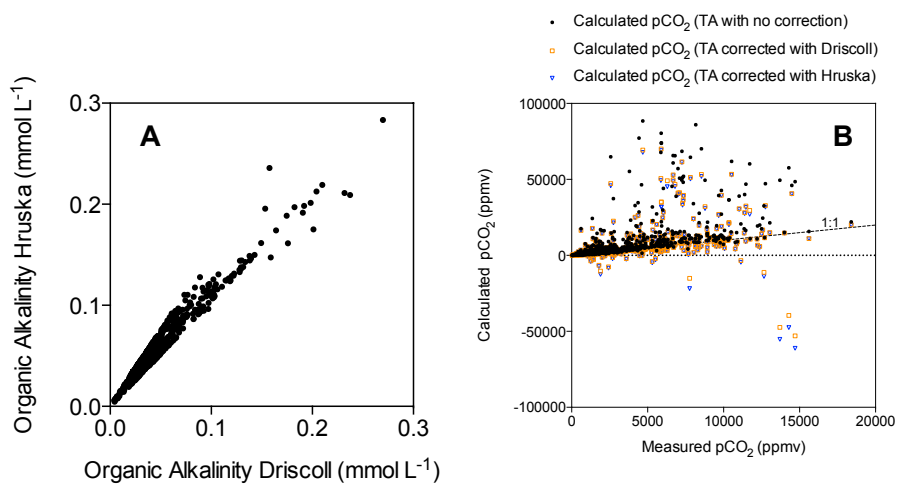


Fig. 1. see caption in response text

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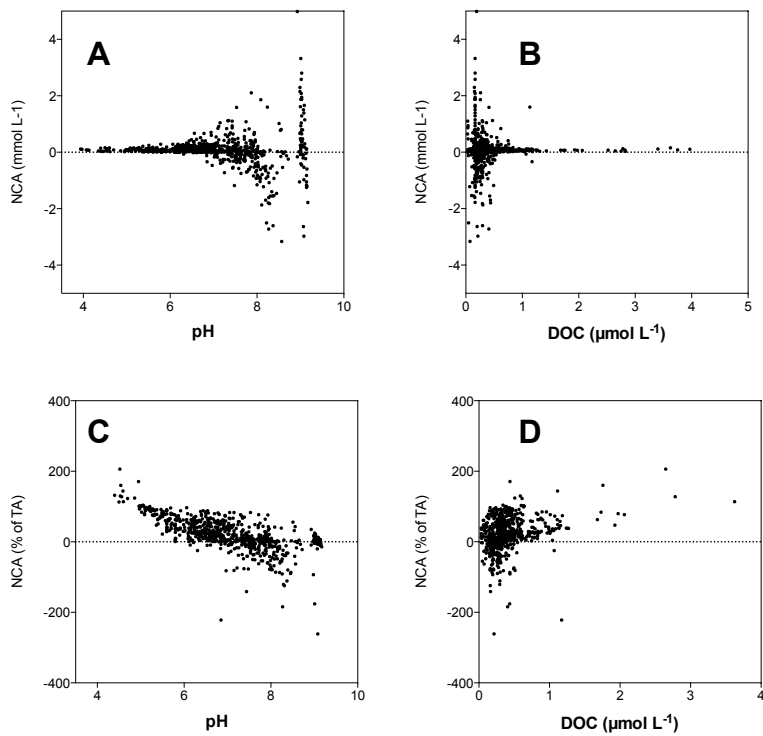


Fig. 2. see caption in response text

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