

Interactive comment on “Contribution of non-carbonate anions to river alkalinity and overestimation of $p\text{CO}_2$ ” by C. W. Hunt et al.

Anonymous Referee #2

Received and published: 15 July 2011

1. Does the paper address relevant scientific questions within the scope of BG?

The MS analysis the relevance of non-carbonate alkalinity (NC-ALK) for PCO_2 -estimations of aquatic systems. Knowledge about the proportion of NC-ALK is relevant, because total-alkalinity measurements are traditionally used to calculate the PCO_2 of aquatic systems. The presented research question is thus within the scope of BG and the presented data add to the many data gaps existing.

2. Does the paper present novel concepts, ideas, tools, or data?

The manuscript presents new data from watersheds in New Hampshire, USA. Applied tools and concepts are according with the standard textbooks in the field. Interesting is the comparison of calculated PCO_2 data using either Alkalinity and pH or DIC and pH.

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However, the presentation and discussion should be improved. See below.

3. Are substantial conclusions reached?

In case the presented numbers/values of the contribution of NC-ALK to the PCO₂ hold, the data set provides new data for the analysed setting (dilute river water in temperate climate; rock type?, land cover?). This setting is important, because not many data with the combination of the parameters ALK-DIC-pH for temperate rivers have been published. The identified conclusions are not new and the methodology should be reviewed, or, improved. See for below. For example a more critical discussion and comparison with previous studies, as suggested below, would be good.

4. Are the scientific methods and assumptions valid and clearly outlined?

I have not looked deeply into the equations behind the CO₂SYS-tool. However, I am surprised that the authors use old K-values and not the revised ones by Millero, published recently. The K-values applied are trained, to my knowledge, to fit best marine settings and/or settings along the salinity gradient in the land-ocean transition zone.

I suggest, the authors comment to this problem and argue, why they have chosen not more new constants or constants developed for freshwater settings. The waters they analysed are rather dilute.

In addition, the authors could use PHREEQC as additional tool to evaluate their results. This software is used often for freshwater settings. Using PHREEQC, the authors could apply constants for the DOC, and thus test if their conclusions are valid.

I am missing DOC-data for the same samples analysed, which would support their conclusions.

Question: Are there data on the quality of the DOC, in the analysed rivers? This could help to discuss the results. At least the influence of the quality of DOC should be discussed in the text, in addition with potential sources of DOC causing the shown PCO₂ overestimation. Or, are there other chemical species contributing to the shown

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bias? The authors should add one sentence, specifically as they introduce a number of candidates, which may not be important, in the introduction equation (1).

Measurement of the DIC: The authors use the Dickson standard, which is to my knowledge, a sea-water standard. Alkalinity of this standard is much higher than of the waters analysed here. I was wondering if the authors could add some justification-sentence for explanation. The authors claim that the precision of the measurement is 0.1%. From lab-experience: This is exactly the value traditionally provided to the readership; however often this precision is not reached. I am wondering, because on page 5163, line 11, the authors explain the accuracy of the system is 3 to 4 $\mu\text{eq/l}$. Is this not a larger value of uncertainty/accuracy? And if taking into account the dilute water characteristic of the sampled river: The precision/accuracy should be different from 0.1% ?

Question: If you are interested in the TALK and contributing anions, why don't you do both, titrate with and without filtered samples? Alkalinity could in some cases be different. May be you could add a sentence to this problem.

Question: Page 5164; Why should there be a LINEAR correlation between pH and TALK. Considering the fundamental equations of the carbonate system: Can you justify why? What is the cause?

5. Are the results sufficient to support the interpretations and conclusions?

See Point 4. Not all data mentioned in the text are shown, but should.

In Table 1 all data should be provided, therefore that the reader can compare with the figures 2 and 3. The authors should consider, if they add a comparison with past work about the contribution of NC-ALK to tot-ALK, e.g. comparing with data from the Amazon, coastal zones, etc.

The large overestimation they find, is partly because the waters are dilute and this is not representative for all rivers. E.g. a river with a higher TDS-concentration, specifically

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if training a carbonate rock catchment, would show different results, with respect to calculated PCO₂-overestimation.

This leads to the question: How representative are the data in comparison to other regions. The MS would benefit if this would be described. The abstract reads a bit as if the authors believe their results are universal (PCO₂-overestimation in river water). I suggest a different wording.

6. Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)?

See above.

7. Do the authors give proper credit to related work and clearly indicate their own new/original contribution?

Introduction, first sentence: There is more, older work to reference, which show the statements. C.f. Degens et al., 1991 (SCOPE book), or SCOPE 13, Carbon in the rock cycle, or work referencing to this work. Or, compare for with the work work of W.Ludwig, 1996 and related.

Relevant work about the contribution of NC-ALK to TOT-ALK (and PCO₂) is missing.

8. Does the title clearly reflect the contents of the paper?

Yes

9. Does the abstract provide a concise and complete summary?

The authors may consider to name some of their calculations in the abstract.

10. Is the overall presentation well structured and clear?

Yes

11. Is the language fluent and precise?

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Yes

12. Are mathematical formulae, symbols, abbreviations, and units correctly defined and used?

OK

13. Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated?

See comments above: The authors should think, if they would not improve their presentation of results based on new calculations, including a different set of constants, or using in addition PHREEQC or another advanced tool for comparison.

14. Are the number and quality of references appropriate?

The chosen references are not too much, and it seems that the authors studied not in deep detail the literature about the contribution of NC-ALK to tot-ALK, and the relevance for the calculation of the PCO₂. I suggest that they refer to work referencing to the classic text book by Drever about the Geochemistry of Natural Waters or use a database to gain easily more relevant literature.

They might add some comparison with past work presenting data of similar or different settings. This would round up the discussion part.

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8, C2027–C2031, 2011

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