**Biogeosciences
Discussions**

Interactive comment on "Contribution of non-carbonate anions to river alkalinity and overestimation of pCO$_2$" *by* C. W. Hunt et al.

Anonymous Referee #3

The manuscript "Contribution of non-carbonate anions to river alkalinity and overestimation of pCO2" is a well written description of what appears to be a valuable study. However, I feel that a number of major and minor points should be addressed before the paper can be considered for publication in BG. The significance of inland waters and their CO2 efflux for the global C cycle has been highlighted during the last decade. However, the amount of data that those global estimates are based on is often limited. In addition, there are a number of methodologies used in the literature for determining pCO2 and those methods are often poorly evaluated or compared with each other. In this context I particularly like the method investigating focus of the study since it critically evaluates a widely used method for determining pCO2 indirectly from total alkalinity. The authors show that the contribution of organic acids to total alkalinity (T-Alk) can cause an overestimation of pCO2 when determined indirectly from T-alk.

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General comments

Since the paper evaluates a method I miss a better method description of the DIC sampling and analysis in the manuscript. At least suitable references describing the methodology (which is not familiar to me) should be added to the method section, but I recommend that the method is described in detail. How were the samples taken? Any headspace created? How were the samples transferred to the analyzer? By open systems? Any source of degassing when transferring such a small volume (0.5 ml) can potentially affect the determined DIC concentration. This is especially true at lower pH why I also miss a better presentation of pH.

The paper really suffers from not having direct or semi direct measurements of pCO2 by gastight headspace techniques (Cole et al.1994 already cited; Hesslein et al. 1991; Wallin et al. 2010) or similar. I realize that this is not possible to do for the actual samples presented in this paper. But it would be good to get a sense on how the methods correspond to a direct measurement.

I am not familiar with the river systems of the study but the high levels of NC-Alk measured, which if I understand it right, in some cases contribute up to 101%(?) of the T-Alk (according to Table 1) makes me a bit suspicious. In general organic acids are concluded to represent 10-15 % of the T-Alk according to the literature. I suggest that the authors describe the area a bit better in the method section but also discuss the high levels of organic acids determined and try to explain it in comparison to existing literature. To present DOC concentrations (and if possible character of the DOC) would also help the reader to understand the system and the results.

I was surprised that the authors used carbonate dissociation constants derived from what I understand seawater systems. I don't know if using other constants derived from freshwater systems (for example Gelbrecht et al. 1998) would change the results, but I suggest that the most suitable constants should be used and that the authors motivate why specific constant were chosen. In addition, I am not familiar with the CO2SYS

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program and therefore miss some of the constant options in the reference list. I find it hard to understand what the authors have done when varying the different constant options and not present the references.

Detailed comments

Page 5162 Ln 15 – remove "of" Table 1. T-alk, DIC, pH, DOC Figure 2. I miss the indications of the scale on the y-axis

References

Gelbrecht, J., Fait, M., Dittrich, M. & Steinberg, C. 1998. Use of GC and equilibrium calculations of CO2 saturation index to indicate whether freshwater bodies in north-eastern Germany are net sources or sinks for atmospheric CO2. Fresenius Journal of Analytical Chemistry, 361, 47-53,

Hesslein, R. H., Rudd, J. W. M., Kelly, C., Ramlal, P. & Hallard, K. A. 1991. Carbon-dioxide pressure in surface waters of Canadian lakes, New York, Amer Soc Civil Engineers.

Wallin, M., Buffam, I., Öquist, M., Laudon, H. & Bishop, K. 2010. Temporal and spatial variability of dissolved inorganic carbon in a boreal stream network: Concentrations and downstream fluxes. Journal of Geophysical Research-Biogeosciences, 115, doi:10.1029/2009jg001100.

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