

## ***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 #1**

Received and published: 28 June 2011

The authors measure pH, DIC and alkalinity using a gran titration for a number of rivers. They find that estimates of alkalinity using the titration are generally higher than alkalinity calculated from pH and DIC. That is: they find that the carbonate system does not close with their three measurements. They conclude that the difference is due to organic acids contributing to alkalinity in their titrations. The manuscript is certainly intriguing and compelling. It would have greatly benefited from  $\text{CO}_2$  measurements. My biggest problem with this paper is the amount of organic acids needed to make up the difference. Two estimates (citation below) argue that  $\sim 10\%$  of organic acids contribute to alkalinity titrations and thus you would need very high concentrations of organic acids to make up the differences showed here. Here the authors have to invoke 50% of organic acids contributing to alkalinity. This leaves me a bit nervous that there could be a bias somewhere in the measurements, possibly in the pH measure-

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ment. The measured alkalinity and pH are never provided though, making it difficult to determine. So in summary I think that a  $100\text{--}300\mu\text{eq L}^{-1}$  contribution to alkalinity from organic acids seems a bit implausible and the authors need to widen their discussion of their reported discrepancy.

Using unfiltered samples might impact study. Particulate material can have non carbonate alkalinity (Kim et al. L&O 2006 51:331-338). This is probably minor.

The authors should incorporate Lozovik et al. (J. Analyt. Chem. 2005 vol 60:1000-1004). Lozovik concluded that on average only 10% of humic acids will be measured in a titration. The Cai paper cited here also has  $\sim 10\%$  of the humics measured as org-alkalinity in the Altamaha and Savannah river. This paper for the freshwater end-member reported org-Alk concentrations of  $\sim 20\text{--}40\mu\text{M}$ . Thus the values reported here ( $100\text{--}300\mu\text{eq/L}$ ) are much higher than what can seemingly be justified by organic acids. What could all this NC-Alk be coming from?

The gran titration isn't the only method used to estimate alkalinity. Most historic data was to a single end point often around 4.5. Are you aware of any critical review of how using these different methodologies might impact these findings?

Page 5163 line 14. How long was the pH probe allowed to acclimate with the sample before pH was measured? I still wonder what type of bias could be introduced with a very small error in pH measurement (0.1 units). The Cai paper cited here noted a bias of 0.05-0.15 between two different probes. Could the authors run through a more thorough evaluation of the bias? Seeing how it might impact both the alkalinity and DIC measurement?

Page 5165 line 6. How do you estimate the reproducibility of the pH measurement at 0.05?

Page 5166 line 10. How are you predicting the amount of total organic acids in your samples? Again: 50% of humic acids being titrated does not seem to be justified by

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the literature.

Add measured Talk, pH and DIC to Table 1.

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Interactive comment on Biogeosciences Discuss., 8, 5159, 2011.

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