Riverine CO_2 and dissolved inorganic carbon fluxes: Organic carbon titration effects and estimate uncertainties

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1. Background

Current estimates suggest that global rivers release CO_2 on the order of 1.0 – 1.8 Pg C yr^{-1} and at the same time export ~0.4 Pg C to the ocean in the form of dissolved inorganic carbon (DIC):

$$DIC = [CO_2^*] + [HCO_3^-] + [CO_3^{2-}] \quad (1)$$

Where CO_2^* is the sum of dissolved CO_2 and carbonic acid. Riverine CO_2 and DIC fluxes are important carbon fluxes that have global and regional significance. However, the current estimates may bear large uncertainties due to two issues:

Issue One: The riverine CO_2 flux was mostly estimated from partial pressure of CO_2 (pCO_2) in water, which was primarily calculated from measured pH and titration alkalinity (TA), which is defined as:

$$TA = \underbrace{[HCO_3^-] + 2\times[CO_3^{2-}]}_{\text{Carbonate Alkalinity (CAlk)}} + \underbrace{[OrgAlk]}_{\text{Organic Alkalinity}} + [\text{other Alk}] + [OH^-] - [H^+] \quad (2)$$

However, due to existence of undefined non-carbonate alkalinity (nCAlk), particularly organic acids (OrgAlk) in dissolved organic carbon (DOC), pH-TA calculated pCO_2 and thus **the CO_2 flux may be significantly over-estimated**. **OrgAlk may have an 'titration effect' to the riverine CO_2 system**.

Issue Two: Riverine DIC fluxes was estimated from TA, assuming that bicarbonate ion (HCO_3^-) is the dominate carbonate species in TA and DIC so that TA ≈ DIC. However, as pH decreases, CO_2^* (Eq. 1) becomes increasingly important in DIC, and **the assumption of TA ≈ DIC becomes an issue**. Issue one and Issue two may interact as well.

Through a few case studies and theoretical calculation, this work **aims to assess the significance and impacts of the nCAlk and CO_2^* issues on riverine pCO_2 and DIC flux estimates**.

2. Congo River: High DOC, low DIC

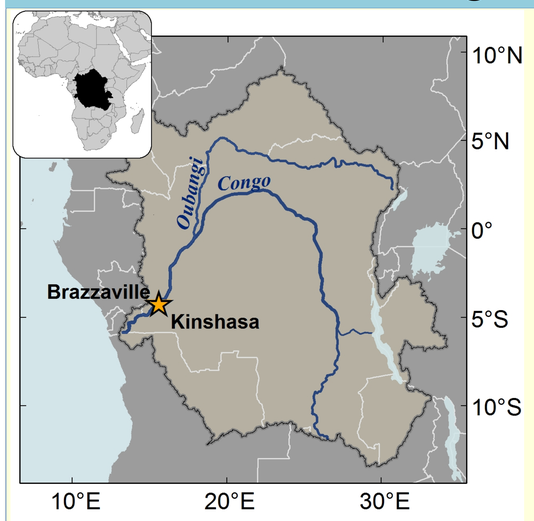

Fig. 1. Congo River basin with a monthly time-series sampling station (star).

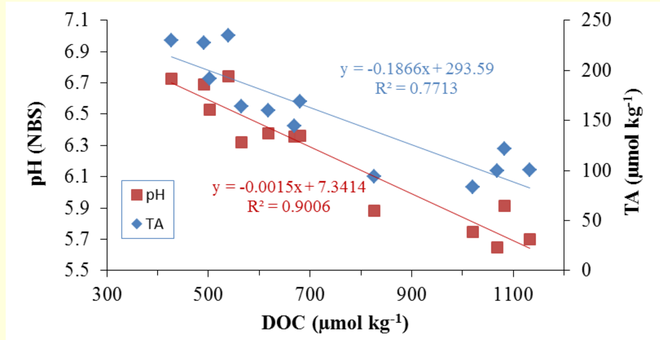

Fig. 2. pH(NBS) – DOC and TA – DOC relationships over 12 months in 2010-2011

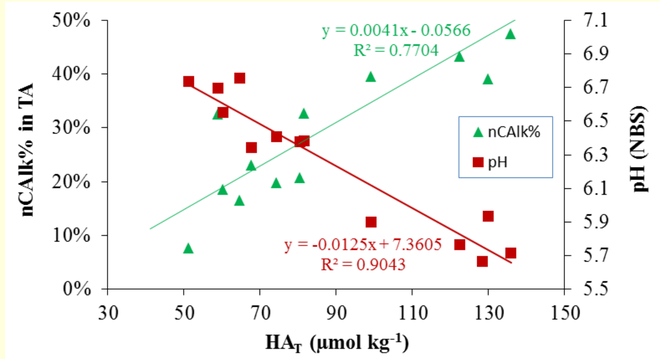

Fig. 3. nCAlk% in TA and pH (NBS) as a function of total organic acid concentration (HA_T). nCAlk was calculated by the difference between TA and pH-DIC calculated Calk. HA_T was calculated from DOC concentration (Wang et al. 2013).

Contribution of OrgAlk and organic carbon 'titration' effect

- ✓ **A strong negative linear correlation between DOC and pH/TA (intercept values → background values)**
- ✓ **40 – 50% of organic acid (25 – 56 μmol kg^{-1}) contribute 11 – 61% of TA**
- ✓ **Organic acid lowers water pH and increases CO_2^*, pCO_2 and nCAlk% in TA**

3. Fraser River: Medium DOC, Medium DIC

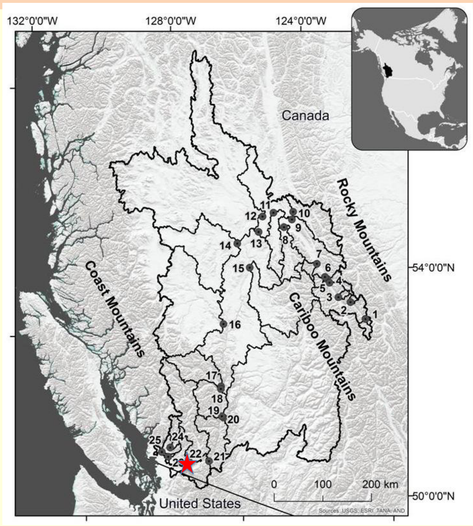

Fig. 4. Fraser River basin with a time-series (monthly) sampling station (star).

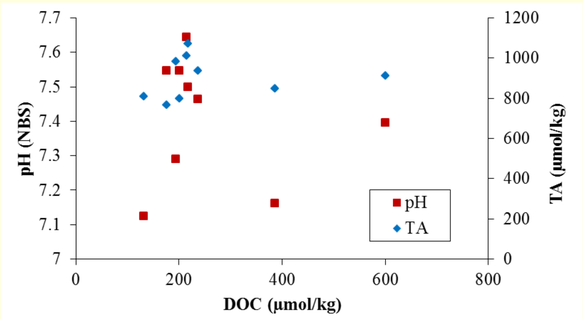

Fig. 5. pH(NBS) – DOC and TA – DOC relationships in 2011-2012

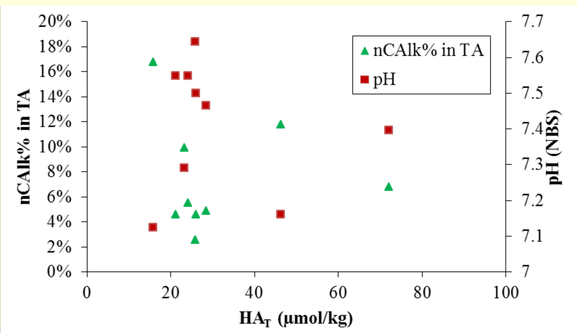

Fig. 6. Non-carbonate alkalinity percentage in TA (nCAlk%) and pH (NBS) as a function of total organic acid concentration (HA_T).

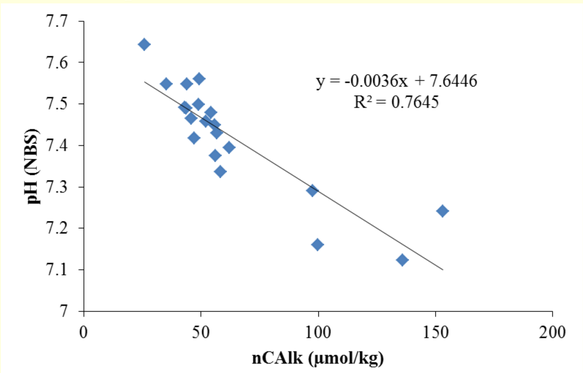

Fig. 7. pH vs. Non-carbonate alkalinity (nCAlk) in 2011-2012.

Contribution of nCAlk and organic carbon 'titration' effect

- ✓ **The organic carbon titration effect is less apparent in the Fraser than in the Congo, likely due to much higher water buffering capacity in Fraser**
- ✓ **Over 97% of organic acid (15 – 70 μmol kg^{-1}) contribute 2 – 8% of TA**
- ✓ **nCAlk still appears to lower water pH and increases CO_2^* and pCO_2.**

4. Uncertainties and Potential Global Issues

Over-estimate of pCO_2

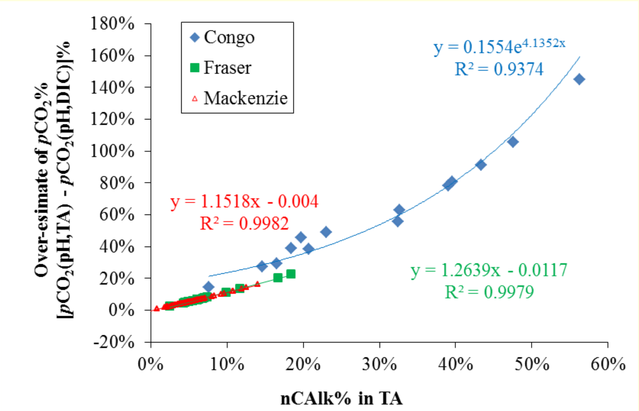

Fig. 8. Over-estimate of pCO_2% as a function of nCAlk% in TA in the Congo, Fraser, and Mackenzie rivers. The over-estimate is calculated by the difference between pH-TA and pH-DIC calculated pCO_2. nCAlk was calculated by the difference between measured TA and pH-DIC calculated CAlk.

Under-estimate of DIC

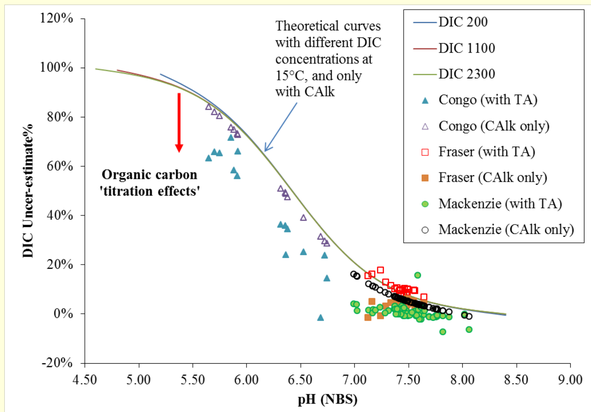

Fig. 9. Under-estimate of DIC% as a function of pH in the Congo Fraser, and Mackenzie rivers and by theoretical calculations. The under-estimate is calculated by the difference between measured DIC and TA or CAlk. Congo (with TA) means measured TA was used to calculate under-estimate; Congo (CAlk only) means only carbonate alkalinity was used for calculation.

Potential errors in riverine CO_2 and DIC flux estimates

- ✓ **nCAlk, including OrgAlk, can cause over-estimate of pCO_2 using pH and TA data; The over-estimate is 0-20% in the Fraser and Mackenzie, two relatively well-buffered rivers; 20-140% for the Congo, a less buffered river.**
- ✓ **Using TA to approximate DIC can cause under-estimate of DIC by 20-70% in the Congo. This is less a problem for well buffered rivers (Fraser and Mackenzie). The organic carbon titration effect can reduce such an error.**
- ✓ **The estimate errors become significant (>20%) when nCAlk% > 20% in TA and pH < 6.5.**

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Reference

Wang, Z. A., D. J. Bienvenu, P. J. Mann, K. A. Hoering, J. R. Poulsen, R. G. M. Spencer, and R. M. Holmes. 2013. Geophys. Res. Lett. 40: 511-516.

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