Riverine CO2 and dissolved inorganic carbon fluxes: Organic carbon titration effects and estimate uncertainties

1. Background

Current estimates suggest that global rivers release CO2 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):

\[ \text{DIC} = [\text{CO}_2^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \]  

Where CO2* is the sum of dissolved CO2 and carbonic acid. Riverine CO2 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 CO2 flux was mostly estimated from partial pressure of CO2 (pCO2) in water, which was primarily calculated from measured pH and titration alkalinity (TA), which is defined as:

\[ \text{TA} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OrgAlk}] + [\text{alk}^-] - [\text{H}^+] \]

However, due to existence of undefined non-carbonate alkalinity (nCAlk), particularly organic acids (OrgAlk) in dissolved organic carbon (DOC), pH-TA calculated pCO2 and thus the CO2 flux may be significantly over-estimated. OrgAlk may have an ‘titration effect’ to the riverine CO2 system.

**Issue Two**: Riverine DIC fluxes was estimated from TA, assuming that bicarbonate ion (HCO3⁻) is the dominate carbonate species in TA and DIC so that TA ≈ DIC. However, as pH decreases, CO2* (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 CO2* issues on riverine pCO2 and DIC flux estimates.

3. Fraser River: Medium DOC, Medium DIC

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

Carbonate Alkalinity Organic Alkalinity

(CAlk) (OrgAlk)

Over-estimate of DIC% as a function of pH in the Congo, Fraser, and Mackenzie rivers. The over-estimate is calculated by the difference between pH-DIC calculated CAlk. HA₃ was calculated from DOC concentration (Wang et al. 2013).

4. Uncertainties and Potential Global Issues

**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 CO2*, pCO2 and nCAlk% in TA

**Potential errors in riverine CO2 and DIC flux estimates**

- nCAlk, including OrgAlk, can cause over-estimate of pCO2 using pH and TA data; The overestimate 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.

**Acknowledgements**

Funding for this project was provided by the WHOI Arctic Research Initiative and Coastal Ocean Institute (to Z.A. Wang, WHOI), and the National Science Foundation ETBC program, the Global Rivers Project (NSF 0851101; to B. Peucker-Ehrenbrink, WHOI).

**Reference**