Review on Müller et al. (2018, BGD): Alkalinity and nitrate concentrations in calcareous watersheds: Are they linked, and is there an upper limit to alkalinity?

Müller et al. find a covariation of alkalinity with nitrate concentration ([NO$_3^-$]) in ‘aquifers in calcareous watersheds in Switzerland’. For [NO$_3^-$] up to 0.25 mmol L$^{-1}$ alkalinity increases linearly with nitrate, for higher concentrations is levels off never exceeding 8 mmol L$^{-1}$. The authors try to explain these variations and the existence of a maximum alkalinity concentration (at 8 mmol L$^{-1}$) by various processes.

In a paper where alkalinity is a central concept (and the first word in the title) I would expect a definition or at least a reference to the definition (I suggest citing Dickson, 1981, who gave the most precise definition) and a description or reference how alkalinity (better total alkalinity, TA) was measured or estimated (for example, Dickson et al., 2007).

Based on the TA definition by Dickson (1981) and the electro-neutrality of aquatic solutions, Wolf-Gladrow et al. (2007) derived a different way to express TA in seawater, namely:

$$
\begin{align*}
[\text{Na}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}] + [\text{K}^+] + 2[\text{Sr}^{2+}] + ... \\
- [\text{Cl}^-] - [\text{Br}^-] - [\text{NO}_3^-] - ... \\
- \text{TPo}_4 + \text{TNH}_3 - 2\text{TSO}_4 - \text{THF} - \text{THNO}_2 \\
= \text{TA}^{(ec)}
\end{align*}
$$

(1)

where TPo$_4 = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}],$ TNH$_3 = [\text{NH}_3] + [\text{NH}_4^+],$ TSO$_4 = [\text{SO}_4^{2-}] + [\text{HSO}_4^-],$ THF $= [\text{F}^-] + [\text{HF}],$ and THNO$_2 = [\text{NO}_2^-] + [\text{HNO}_2]$ are total phosphate, ammonia, sulphate, fluoride, and nitrite, respectively.

In the current context (freshwater with Ca$^{2+},$ Mg$^{2+},$ and NO$_3^-$) this expression can be simplified to

$$
\text{TA}^{(ec)} \approx 2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] - [\text{NO}_3^-]
$$

(2)
(the other terms are probably small or roughly cancel each other). This expression for TA shows that addition of nitrate would decrease TA. The observed increase of TA with increasing nitrate is, therefore, not a direct effect of nitrate addition (concentration too small and wrong sign in the TA expression), but is rather a proxy for other processes, namely CaCO₃ dissolution (enhanced weathering) caused by agriculture. Although TA varies almost linearly with nitrate concentration for nitrate concentrations up to 0.25 mmol L⁻¹, the relation become nonlinear (levels off, saturates) for higher concentrations. This also speaks against a direct impact of nitrate, but suggests that nitrate could be a proxy for other processes.

p. 3 L2-3: “If a titrated alkalinity was not reported, we approximated it as the reported molar concentration of HCO₃⁻.” It is not clear which values are based on proper titration and which on HCO₃⁻ concentration. Also missing: description of measurement procedures for alkalinity, HCO₃⁻, and [Ca²⁺] + [Mg²⁺] (p. 4 L8: ‘Ranging from 0.51 to 0.72, the molar ([Ca]+[Mg]) : [HCO₃⁻] ratio ...’)

p. 5 The use of Redfield ratios (C:N = 106:16 mol mol⁻¹) for land plants is unrealistic and has already been criticized by Reviewer # 1.

The impact on alkalinity by adding various nitrogen compounds (nitrate, ammonia, urea) and by conversion processes needs more attention (see Wolf-Gladrow et al. 2007 for some hints).

The authors have compiled a lot of data that are somewhat hidden in various archives. It would be great if these data could be made publicly/more easily available at, for example, the Carbon Dioxide Information Analysis Center, https://cdiac.ess-dive.lbl.gov.

Minor points:

p. 2 L9-12: “Therefore, in calcareous soils, in-soil production of CO₂ (e.g., due to root respiration and heterotrophic mineralization of organic matter) ... result in an increased alkalinity concentration. In contrast, in the absence of carbonate minerals, alkalinity is expected to decrease in proportion to the amount ... in-soil CO₂ production (Perrin et al., 2008).” This can be misleading or is wrong. Addition of CO₂ does not change total alkalinity. However, addition of CO₂ will decrease pH and may lead to dissolution of CaCO₃ resulting in the increase of total alkalinity.
I suggest changing ‘$10^{-3.5}$ to $10^{-3.4}$ atm’ to ‘316 to 398 $\mu$atm’ (or after ‘rounding’: 300 to 400 $\mu$atm).

... in the absence of acids other than $\text{H}_2\text{CO}_3$, an alkalinity concentration of 1.42 mmol L$^{-1}$ and a pH of 8.24 would be expected in water draining a hypothetically N-free (and thus sterile) calcareous soil, assuming a groundwater temperature of 8$^\circ$C.” Which assumptions have been made? (I guess $\Omega_{\text{calcite}} = 1$, equilibrium of CO$_2$ partial pressures, alkalinity $\approx [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] \approx \text{Ca}$) Can you give a reference? Which equilibrium constants did you use?

We calculated the CO$_2$ saturation index of water as $\Omega_{\text{CO}_2} = \text{CO}_2(\text{aq})/\text{CO}_2(\text{atm})$, where CO$_2$(aq) is the partial pressure of CO$_2$ in the water (in atm) and CO$_2$(atm) is the partial pressure of CO$_2$ in the atmosphere ...

I suggest to use the notation pCO$_2$ for partial pressures.

As pCO$_2$ increases and as pH concurrently decreases, the extent to which $\text{H}_2\text{CO}_3$ dissociates into $\text{HCO}_3^-$ and $\text{CO}_3^{2-}$ decreases (because increasingly greater percentages of the DIC remain as $\text{H}_2\text{CO}_3$ as the $\text{H}^+$ concentration increases).

This could be quantified and illustrated by a Bjerrum plot.

Supplement:

S-4: “p” is the probability value of the slope or intercept being equal to 0 (i.e., $p < 0.05$ indicates significant difference from zero)

No! $p$ is the probability to obtain an estimate $\hat{\beta}$ or more extreme values for the slope, $\beta$, under the null hypothesis $H_0$ : ‘slope $\beta$ is zero’. The null hypothesis is rejected if $p < \alpha$ where $\alpha$ is the level of significance (commonly chosen as $\alpha = 0.05$). Same for the intercept.
References

[1] Dickson, A.G. An exact definition of total alkalinity and a procedure for the estimation of alkalinity and total inorganic carbon from titration data. Deep Sea Research Part A. Oceanographic Research Papers, 28(6):609–623, 1981.

[2] Dickson, A.G., C.L. Sabine, and J.R. Christian. Guide to best practices for ocean CO$_2$ measurements. North Pacific Marine Science Organization, 2007.

[3] Wolf-Gladrow, D.A., R.E. Zeebe, C. Klaas, A. Körtzinger, and A.G. Dickson. Total alkalinity: The explicit conservative expression and its application to biogeochemical processes. Marine Chemistry, 106(1):287–300, 2007.