

Interactive comment on “Alkalinity and nitrate concentrations in calcareous watersheds: Are they linked, and is there an upper limit to alkalinity?” by Beat Müller et al.

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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 ($[\text{NO}_3^-]$) in 'aquifers in calcareous watersheds in Switzerland'. For $[\text{NO}_3^-]$ 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

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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).

RESPONSE: Because our manuscript deals with groundwater (not seawater) with alkalinity values exceeding 1 mmol L⁻¹ (p. 3, line 2), we refer to Stumm and Morgan (1996) and define alkalinity as described in eq. 1 (line 35): Alkalinity [mmol L⁻¹] = [HCO₃⁻] + 2[CO₃²⁻] + [OH⁻] – [H⁺] (1).

We are aware of the alternative definition, which Stumm and Morgan discuss as well. However, due to the dissolution of calcite in these calcareous Swiss watersheds, alkalinity is always much higher than other acid anions. Thus, we do not see an advantage to using the alternative definition of alkalinity, and it would not change our general line of thought. Because these systems are well-buffered with respect to pH (pH 7 to 8.3, see Figure 1d in the manuscript), the concentrations of OH⁻ and H⁺ are always negligible in comparison to HCO₃⁻ concentrations; and at pH 8.3, [CO₃²⁻] contributes only 2% to the alkalinity. Therefore, Alkalinity [mmol L⁻¹] ≈ [HCO₃⁻]. (2) In cases in which all alkalinity originated from the dissolution of carbonates, equivalent concentrations of alkalinity and the sum of Ca²⁺ and Mg²⁺ must be equal: Alkalinity [mmol L⁻¹] = [HCO₃⁻] = 2([Ca²⁺] + [Mg²⁺]). (3) This relationship is very helpful because the ratio ([Ca²⁺] + [Mg²⁺])/[HCO₃⁻] (4) indicates whether alkalinity originates solely from the dissolution of carbonates by CO₂ (=0.5). If part of the alkalinity originates from proton-(Ca/Mg)-carbonate interactions, the ratio exceeds 0.5. —————

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: [Na⁺] + 2[Mg²⁺] + 2[Ca²⁺] + [K⁺] + 2[Sr²⁺] + ... – [Cl⁻] – [Br⁻] – [NO₃⁻] – ... – TPO₄ + TNH₃ – 2TSO₄ – THF – THNO₂ = TA(ec) (1) where TPO₄ = [H₃PO₄] + [H₂PO₄⁻] + [HPO₄²⁻] + [PO₄³⁻], TNH₃ = [NH₃] + [NH₄⁺], TSO₄ = [SO₄²⁻] + [HSO₄⁻], THF = [F⁻] + [HF], and THNO₂ = [NO₂] + [HNO₂] are total phosphate, ammonia, sulphate, fluoride, and nitrite, respectively. In the current context (freshwater with Ca²⁺,

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Mg²⁺, and NO₃⁻) this expression can be simplified to $TA(ec) \approx 2 [Ca^{2+}] + 2 [Mg^{2+}] - [NO_3^-]$ (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.

RESPONSE: We agree with the reviewer's perception of the subject. None of the concentrations of the accompanying base cations (except for Ca and Mg) or acid anions was high enough to bias alkalinity. In the manuscript, we hypothesized that the covariation of alkalinity and nitrate is a result of (i) mineralization of organic (nitrogen) fertilizer, (ii) exchange of OH⁻ or H⁺ ions from plant roots during the uptake of NO₃⁻ or NH₄⁺, respectively, and (iii) CO₂ release (and subsequent dissolution of soil carbonates) due to fertilizer-stimulated plant growth. Thus, we do not need believe additional discussion is needed. _____

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 ...')

RESPONSE: The Swiss Federal Office for the Environment (responsible for the NAQUA dataset) informed us that their term "HCO₃⁻" was used instead of "alkalinity", but the parameter was determined by endpoint titration to pH 4.2, which is commonly used to measure alkalinity in groundwaters. Therefore, our remark (p. 3, line 2-3) that we replaced missing 'alkalinity' by "HCO₃⁻" concentration is unnecessary. We will

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delete this sentence in the revised version. _____

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.

RESPONSE: We are currently searching for more appropriate of C:N ratios for crop plants. In the revised manuscript, we will discuss the effect of this ratio on alkalinity formation. _____

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).

RESPONSE: We agree that it is essential for the subject of soil acidification that conversion processes of the various nitrogen compounds applied to the soil are considered. Therefore, we placed Table 1 in the supplemental information detailing 24 pertinent chemical-transformation reactions that can be expected to generate alkalinity or acidity in soils. We refer to those reactions at many places in the manuscript, e.g. p.1, line 27-28; p.2, line 23; p.3, line 4; p.4, lines 24-26, etc. Due to the diversity of processes affecting the acid-base chemistry of fertilized soils and plant growth and in an effort to not clutter the main text, we prefer to separate this subject from the main manuscript and place it in the supplemental file. _____

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>.

RESPONSE: Data sources are listed in Table 1. In addition, we will deposit the data in a FAIR-aligned data repository. _____

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,

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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.

RESPONSE: We agree with the reviewer. However, if CO₂ in an aqueous solution reacts with CaCO₃, HCO₃⁻ ions are formed, thus, increasing alkalinity. We will clarify this in the revised manuscript as follows: “Therefore, in calcareous soils, in-soil production of CO₂ (e.g., due to root respiration and heterotrophic mineralization of organic matter) and/or generation of protons by nitrification result in an increased alkalinity concentration due to the additional dissolution of carbonates.” The subsequent sentence will be omitted. _____

p.2 L38-39: I suggest changing '10^{-3.5} to 10^{-3.4} atm' to '316 to 398 μatm' (or after 'rounding': 300 to 400 μatm)

RESPONSE: We change that sentence to: “At atmospheric pCO₂ ranging from 10^{-3.5} to 10^{-3.4} atm (approximately 300-400 ppm; the condition from approximately 1959 to present; NOAA, 2017)”. We think the “At atmospheric pCO₂” at the beginning of the sentence helps avoid confusion, but the exponential form of reporting these partial pressures is more helpful if one wants to perform speciation calculations (leaving the ppm concentration in parentheses for those more comfortable with the simple form for expressing concentrations). _____

p.2 L39-41 ”... in the absence of acids other than H₂CO₃, 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 80C.” Which assumptions have been made? (I guess Ω_{calcite} = 1, equilibrium of CO₂ partial pressures, alkalinity ≈ [HCO₃⁻] + 2 [CO₃²⁻] ≈ Ca) Can you give a reference? Which equilibrium constants did you use?

RESPONSE: The calculation was performed with the chemical speciation software

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ChemEQL (referenced on p. 11, lines 14-16, free download). We assumed equilibrium with calcite and atmospheric $p\text{CO}_2$. Alkalinity was not approximated but was calculated according to eqs. 1 to 3 in the manuscript. However, we have now noticed that we did not report all the equations considered in the calculation, and the equilibrium constants used. We will report them in the revised version of the supplemental file (SI Table S3). The text in the manuscript will be extended accordingly. _____

p.3 L12-13: "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 $\text{CO}_2(\text{aq})$ is the partial pressure of CO_2 in the water (in atm) and $\text{CO}_2(\text{atm})$ is the partial pressure of CO_2 in the atmosphere ..." I suggest to use the notation $p\text{CO}_2$ for partial pressures.

RESPONSE: We will change the expression. _____

p.6: "As $p\text{CO}_2$ increases and as pH concurrently decreases, the extent to which H_2CO_3 dissociates into HCO_3^- and CO_3^{2-} decreases (because increasingly greater percentages of the DIC remain as H_2CO_3 as the H^+ concentration increases)." This could be quantified and illustrated by a Bjerrum plot.

RESPONSE: We will extend the sentence indicating that this process is best illustrated by a Bjerrum plot and refer the reader to Stumm and Morgan (1996, p. 160). _____

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 $\beta \pm \text{SE}$ or more extreme values for the slope, β , under the null hypothesis H_0 : 'slope β is zero'. The null hypothesis is rejected if $p < \alpha$ where α is the level of significance (commonly chosen as $\alpha = 0.05$). Same for the intercept.

RESPONSE: The reviewer is correct; and that incorrect wording also appears in footnote a in Table 2. In both places, in order to avoid extensive rewording, we will revise the incorrectly-worded clause to the following: "p" is the Type I error probability for a

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test of the null hypothesis that the slope (or intercept) equals 0. _____

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