

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.

Beat Müller et al.

beat.mueller@eawag.ch

Received and published: 17 December 2018

We agree that the title is not very straight-forward and requires some interpretation. We will change the title to “Nitrogen fertilization of soils fuels carbonate weathering in calcareous watersheds”. When we noticed the stunning correlation between alkalinity and nitrate concentrations in groundwaters, lakes and rivers, and the asymptotic approach to a maximum groundwater alkalinity at nitrate concentrations exceeding 0.25 mmol L⁻¹, it was not at all evident what the linking processes were. No such correlation exists for other anions such as sulfate or nitrite. Ammonium was absent in virtually all samples, because all ground- and surface waters in our dataset contained measurable

Printer-friendly version

Discussion paper



oxygen. (We will add this information to the Results chapter, end of the 1st paragraph). Thus, we have no reason to expect the reduction of sulfate, iron or manganese etc. to play a significant role in the soil system. This is also supported by the observation that the ratio of calcium + magnesium vs. alkalinity was close to 0.5, indicating the origin of alkalinity was mainly the dissolution of Ca/Mg-carbonate minerals. The main effect of the groundwater (or hypolimnetic lake water) being “closed” to the atmosphere (i.e. not in equilibrium with the atmospheric CO₂ partial pressure) was that the partial pressure increased due to aerobic mineralization of organic matter, which subsequently decreased pH and thus affected the dissolution of carbonate minerals. The solubility product of calcite indeed appears to determine the concentrations of calcium ions and carbonate ions (CO₃²⁻) in the groundwaters as is shown in Figure 1g and commented on lines 10-11 of page 4. Lake and river waters, however, are often supersaturated with respect to calcite (Küchler-Krischun and Kleiner, *Aquatic Sci*, 52, 176-197, 1990; Müller et al., *Limnol. Oceanogr.* 61, 341-352, 2016) for reasons that are still debated (e.g., inhomogeneities initiating the formation of initial nuclei (Obst et al., *Geobiol.* 7, 324-347, 2009), retardation by phosphate sorption (Giannimaras and Koutsoukos, *J. Coll. Intf. Sci.* 166, 423-430, 1987)). Moreover, the solubility of calcite is not a fixed upper limit to alkalinity. Instead, that upper limit increases as pH decreases, explaining in part why increases in H⁺ and CO₂ as agricultural fertilization is increased can increase the alkalinity in a calcareous watershed, as we have documented in Swiss soils.

The model: We agree that the generic Redfield ratio for phytoplankton (C:N:P = 106:16:1) is not strictly applicable for land plants, because they have a higher C:N ratio. A generally applicable value is difficult to determine, however. An alternative attempt could be the use of the stoichiometry for “soil” suggested by Cleveland & Liptzin (*Biogeochem.* 85, 235-252, 2007) (C:N:P = 186:13:1). We currently screen the literature for element ratios and will redo our calculations more convincingly in the revised version of the manuscript. However, our main aim is to demonstrate the link between increased agricultural fertilization and increased alkalinity with a conceptual model in which the precise C:N ratio would not significantly alter our line of argument, for the

[Printer-friendly version](#)[Discussion paper](#)

following reasons: The numbers in Table 3, which Figure 2 is based on, reflect the Swiss nitrogen budget. It does not contain assumptions on the coupling between the CO₂ and nitrogen cycles. In Figure 2, a correction towards a higher C:N ratio in the manure would increase the CO₂ production due to mineralization in the item “Organic N-Fertilizer” as would a higher C:N crop plant ratio in the item “Terrestrial primary production”, because root respiration has been shown to increase in proportion to CO₂ assimilation. Hence, at the given nitrogen budget, higher C:N ratios would even further increase the dissolution of carbonates driven by agricultural activities.

Minor issues: 1. How is pH defined and in what scale? pH is defined as $-\log(H^+$ activity) according to IUPAC convention. The scale is standard units.

2. Explain "CO₂ bound in HCO₃⁻" in the caption for Fig. 3. Calcite dissolves using 1 equivalent of CO₂ and H₂O to produce Ca²⁺ and 2 HCO₃⁻. Hence, 0.5 equivalents of CO₂ were consumed per each equivalent of dissolved HCO₃⁻ (thus being incorporated into HCO₃⁻). We will explain this term in the figure caption.

3. The groundwater has a pH range of 7.1-7.8 so I question the average value of 7.14 used for the model Minimum and maximum pH values in the groundwater dataset are 7.05 and 7.83, respectively, and the median pH is 7.22. The pH calculated by the speciation equilibrium program ChemEQL (chapter 4.1.7, 1st paragraph) using the estimated concentrations of H⁺, CO₂ in equilibrium with calcite results in a pH of 7.14 (blue circle in Figure 1d), which we think agrees quite well with the measured values.

Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2018-461>, 2018.

Printer-friendly version

Discussion paper

