Alkalinity and nitrate concentrations in calcareous watersheds: Are they linked, and is there an upper limit to alkalinity?

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Abstract. Data from aquifers in calcareous watersheds in Switzerland demonstrate that alkalinity initially increases approximately in proportion to nitrate (NO_3^-) concentration in the groundwater and eventually approaches an apparent
10 maximum of approximately 8 mmol L^{-1} at high NO_3^- concentrations. This close positive relationship between alkalinity and NO_3^- concentration appears to be predominantly a result of three processes: (i) mineralization of organic nitrogen (N) fertilizer, (ii) exchange of OH^- and H^+ during the uptake of NO_3^- or ammonium (NH_4^+), and (iii) CO_2 released by roots as a result of fertilizer-stimulated plant growth. Atmospheric deposition of N and strong acids (H_2SO_4 and HNO_3) play a minor role. We suggest that the asymptotic approach to a maximum groundwater alkalinity at NO_3^- concentrations exceeding 0.25
15 mmol L^{-1} may be caused by (i) a maximum possible areal crop production at excessive N fertilization and (ii) an increasing CO_2 loss to the atmosphere due to the increasing CO_2 production in the soil. Thus, we estimate that the fertilizer-intensive agriculture of Switzerland generates an annual flux from the soil to the atmosphere of at least 0.26 Mt CO_2 a^{-1}. This analysis provides a general understanding and quantitative prediction of steady-state groundwater NO_3^- concentration; equilibrium groundwater alkalinity, pH, and pCO_2; and soil CO_2 emissions to the atmosphere based on quantitative and qualitative
20 information on the supply of N and acidity to the soil by atmospheric deposition and N fertilization. The positive correlation between alkalinity and NO_3^- concentration in groundwaters persists in rivers and lakes. However, due to the diffusive loss of CO_2 to the atmosphere, subsequent precipitation of calcite, dilution with surface water, input of wastewater discharges and NO_3^- consumption by aquatic photoautotrophs, the correlation is less distinct.

1 Introduction

25 To enhance crop production, farmers supply nitrogen (N) in the form of inorganic and organic fertilizers (Walworth, 2013) and/or manure to fields. Because nitrification [the oxidation of ammonium (NH_4^+) to nitrate (NO_3^-)] of reduced-N compounds produces protons (H^+) that can dissolve carbonate minerals (Equations S-1 to S-5 and S-13 to S-17 in SI Table S1), the effects of N-fertilizers on dissolved inorganic carbon (DIC) concentrations and fluxes in lotic systems have been investigated (Semhi et al., 2000; Raymond and Cole, 2003; Raymond et al., 2008; Barnes and Raymond, 2009; Kaushal et
30 al., 2013; Müller et al., 2016). Additionally, the potential for a resulting release of CO_2 to the atmosphere and its consequences for global climate change have been of special concern (West and McBride, 2005; Perrin et al., 2008; Li et al., 2013).

Alkalinity is a measure of the acid-neutralizing capacity of water. In freshwater systems, it is generally defined as:

35 $$\text{Alkalinity (as mmol } L^{-1}) = \left[HCO_3^-\right] + 2\left[CO_3^{2-}\right] + \left[OH^-\right] - [H^+] \tag{1}$$

where the brackets indicate concentrations of the designated ions (Stumm and Morgan, 1996). At circumneutral pH, bicarbonate ion (HCO_3^-) is the major component of alkalinity, with only minor contributions from carbonate (CO_3^{2-}) and

hydroxyl (OH^-) ions. In calcareous watersheds, alkalinity originates mainly from the dissolution of carbonate minerals [e.g., calcite ($CaCO_3$) and dolomite ($Ca_xMg_{(1-x)}CO_3$)] either by i) protons, which are generated by dissociation of strong mineral acids [e.g., nitric (HNO_3) or sulfuric (H_2SO_4)], or ii) by carbonic acid (H_2CO_3) that is formed by the solvation of biogenic CO_2 in water (Equations 2 and 3).

5

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^- \qquad\qquad (2)$$

$$CaCO_3 + H_2CO_3 = Ca^{2+} + 2HCO_3^- \qquad\qquad (3)$$
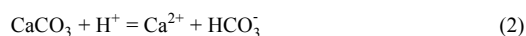
Therefore, in calcareous soils, in-soil production of CO_2 (e.g., due to root respiration and heterotrophic mineralization of
10   organic matter) and/or generation of protons by nitrification result in an increased alkalinity concentration. In contrast, in the absence of carbonate minerals, alkalinity is expected to decrease in proportion to the amount of nitrification and in-soil CO_2 production (Perrin et al., 2008).

Changes in alkalinity can be of importance to the global carbon budget. For example, the alkalinity export of the Mississippi River (USA) to the Gulf of Mexico increased between 1950 and 2000, in excess of the simultaneously increasing water
15   discharge (Raymond and Cole, 2003). West and McBride (2005) estimated 38% of the HCO_3^- transported by the Mississippi River originated from calcite dissolution induced by HNO_3. Similarly, Semhi et al. (2000), Perrin et al. (2008), Probst (1986) and Brunet et al. (2011) have attributed increasing alkalinity observed in French rivers to nitrification of N-fertilizers, and Guo et al. (2010) observed increased soil acidity as a consequence of the increasing use of N-fertilizers in China.

Apart from the increasing partial pressure of CO_2 (pCO_2) in the atmosphere (NOAA, 2017), increasing soil temperature
20   (Zobrist et al., 2018) and changes in runoff, a variety of factors may affect groundwater and thus riverine alkalinity (Raymond et al., 2008). Those factors include (i) agricultural practices such as fertilization and liming (Müller et al., 2016; West and McBride, 2005; Oh and Raymond, 2006), (ii) mineral-acid load originating from atmospheric deposition (e.g., HNO_3 [Equation S-6 in SI Table S1] and H_2SO_4), (iii) changes in microbial activity, (iv) acid mine drainage (Kaushal et al., 2013), and (v) sewage effluents (Barnes and Raymond, 2009). Because N plays a leading role in many of these interactions
25   with soil water, groundwater and surface waters globally, and in view of the approximately five-fold increase of anthropogenic reactive N since 1960, with uncertain consequences, Battye et al. (2017) posed the question "Is nitrogen the next carbon?".

In this study, we

- present data from extensive groundwater and surface-water monitoring programs in calcareous agricultural Swiss
30   watersheds demonstrating a strong linkage between alkalinity and NO_3^- concentrations,

- identify agricultural N fertilization fueling terrestrial primary production as the main driving force linking the two constituents in ground and surface waters.

- explain why alkalinity reaches an apparent upper limit at elevated NO_3^- concentrations in groundwater, and

- estimate the contributions of the Swiss farming activities to the global CO_2 accumulation and to the alkalinity load
35   of downstream surface waters.

2 Methods

Aquifer and surface waters considered in this study are described in Table 1. At atmospheric pCO_2 ranging from $10^{-3.5}$ to $10^{-3.4}$ atm (the condition from approximately 1959 to present; NOAA, 2017) and in the absence of acids other than H_2CO_3, an
40   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 °C. Therefore, to avoid potentially confounding

results from waters not in considerable contact with carbonates, we included in this analysis only waters originating from calcareous watersheds in which alkalinity exceeded 1 mmol L^{-1}. If a titrated alkalinity was not reported, we approximated it as the reported molar concentration of HCO_3^-.

In SI Table S1, we calculated theoretical molar $\Delta[HCO_3^-]:\Delta[NO_3^-]$ and $\Delta([Ca]+[Mg]):\Delta[HCO_3^-]$ ratios of chemical reactions

5   that likely occur in aquifers in the presence or absence of carbonate minerals. Additionally, we applied the geochemical speciation software ChemEQL Version 3.2 (Müller, 2015) to calculate pH, alkalinity, pCO_2, and Ca^{2+} concentrations in groundwater in equilibrium with calcite, into which we computationally titrated the CO_2, NO_3^-, and H^+ resulting from the estimated loads of these compounds as used in Swiss agriculture. For these computational titrations, we neglected the exchange of soil/groundwater CO_2 with the atmosphere and assumed equilibrium of the groundwater with soil pCO_2. Initial

10   conditions were as follows: temperature = 8 °C, atmospheric pCO_2 = 0.0004 atm in equilibrium with calcite, and NO_3^- = 0 mmol/L, resulting in pH = 8.24 and alkalinity = 1.42 mmol L^{-1}.

We calculated the CO_2 saturation index of water as Ω_{CO_2} = $CO_2(aq)/CO_2(atm)$, 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 (in atm). $CO_2(aq)$ was calculated from the reported pH and alkalinity using Equation 6 in Müller et al. (2016). Reported concentrations of Ca^{2+}, alkalinity, and NO_3^-

15   in lakes represent values observed at spring overturn averaged over all years of observation. Concentrations measured in rivers were averaged over the observation period. To produce conservative (i.e., minimum) estimates of Ω_{CO_2}, we assumed a value of 4×10^{-4} atm (400 ppm) for $CO_2(atm)$, which is the 2015 annual average in the Mauna Loa dataset (NOAA, 2017). The saturation index for calcite solubility was calculated as

20    $$\Omega_{calcite} = \frac{\{Ca_2^+\} \times \{CO_3^{2-}\}}{K_{calcite}} \qquad (4)$$

where braces denote the ChemEQL-predicted chemical activity of Ca^{2+} or CO_3^{2-}, respectively, and $K_{calcite}$ is the solubility product of calcite (3.95×10^{-9} at 8 °C for groundwaters; 3.71×10^{-9} at 15 °C for rivers). Ion activities were estimated with the Debye-Hückel approximation (Stumm and Morgan, 1996) for an ionic strength calculated from the sum of measured anions

25   and cations. We calculated $\Omega_{calcite}$ only for the NAQUA-groundwaters and rivers, because Ca^{2+} concentrations were not available for lake waters and Zürich well waters.

Linear regressions of alkalinity *versus* NO_3^- concentration were performed with the statistical software program Stata Version 14 (StataCorp LLC, College Station, Texas, USA). Regression coefficients were inferred to be statistically significant when $p \leq 0.05$.

30

3 Results

Alkalinity increased systematically with increasing NO_3^- concentrations in groundwater as well as in surface waters (Figures 1a and 1b). In the concentration range 0-0.25 mmol NO_3^- L^{-1}, initial slopes of alkalinity *versus* NO_3^- concentration for groundwater and surface waters were 17.0 and 12.5 mmol alkalinity L^{-1} / mmol NO_3^- L^{-1}, respectively (Table 2). The

35   alkalinity-axis intercepts for the aquifer and surface waters were 2.44 and 1.74 mmol L^{-1}, respectively (Table 2). At NO_3^- concentrations exceeding 0.25 mmol L^{-1}, the alkalinity *versus* NO_3^- slope decreased in the aquifer waters nearly 10-fold to only 1.8 mmol alkalinity L^{-1} / mmol NO_3^- L^{-1} (Table 2, Figure 1a). Because NO_3^- concentrations in the surface waters did not exceed 0.25 mmol L^{-1} (Figure 1b), we could not test for an analogous decrease of the slope at elevated NO_3^- concentrations in those waters.

All waters were distinctly supersaturated with respect to atmospheric CO_2 (up to 90-fold in groundwaters and up to 11-fold in surface waters; Figure 1c). In the groundwaters, Ω_{CO_2} increased rapidly as NO_3^- concentration increased from 0 to approximately 0.25 mmol L^{-1}, but leveled-off at higher NO_3^- concentrations. In the surface waters, the trend of increasing Ω_{CO_2} with increasing NO_3^- concentration was less distinct.

5   As NO_3^- concentration increased from 0 to 0.25 mmol L^{-1} in the groundwaters, pH tended to initially decrease but then leveled-off to approximately circumneutral values at higher NO_3^- concentrations (Figure 1d). In surface waters, pH ranged between 7.7 and 8.3, seemingly unrelated to the NO_3^- concentration (Figure 1d).

Ranging from 0.51 to 0.72, the molar ($[Ca]+[Mg]$) : $[HCO_3^-]$ ratio in the aquifer waters increased significantly as NO_3^- concentration increased (slope = 0.079 / mmol NO_3^- L^{-1}, $p < 0.001$; Figure 1e). However, NO_3^- only accounted for 15% of

10   the variation of this ratio, suggesting that the majority of that variation depended on other factors. In the surface waters, the molar ($[Ca]+[Mg]$) : $[HCO_3^-]$ ratio ranged from 0.47 to 0.74, without a trend analogous to the groundwater trend across the narrower range of NO_3^- concentrations in the surface waters (Figure 1f).

Contrary to most groundwaters being slightly undersaturated with respect to $CaCO_3$ solubility (Ω_{CaCO_3} = 0.5-1.2; Figure 1g), 21 of the 22 river waters were supersaturated (Ω_{CaCO_3} = 1.2-8.4; Figure 1g).

15   Table 3 summarizes quantitative information about the various sources, sinks and pathways affecting the nitrogen budget of agricultural Swiss soils.

4 Discussion

4.1 Aquifer Waters

Because in all aquifer waters included in this analysis, (i) alkalinity exceeded the 1.42 mmol L^{-1} concentration expected in
20   calcite-saturated, air-equilibrated water (Figure 1a), (ii) pH was considerably below the equilibrium-predicted value of 8.24 (Figure 1d), and (iii) CO_2 concentrations were highly supersaturated (Figure 1c), the aquifer waters appear to be at least partially protected from contact with the atmosphere.

The equations in Table S1 show that the stoichiometric molar ($[Ca]+[Mg]$) : $[HCO_3^-]$ ratio (i) equals 0.5 if carbonates are dissolved only as a result of interaction with CO_2 (Equations S-19 and S-20), (ii) exceeds 0.5 if protons generated by
25   nitrification or supplied by acid precipitation (Equations S-1 to S-6) contribute to the dissolution of carbonates (Equations S-13 to S-18), and (iii) only slightly exceeds 0.5 (Equation S-21) if mineralization of organic matter (e.g., $C_{106}H_{263}O_{110}N_{16}P$, per Stumm and Morgan, 1996) is responsible for the carbonate dissolution. In all the groundwaters, the ($[Ca]+[Mg]$) : $[HCO_3^-]$ ratio slightly exceeded 0.5 (Figure 1e), suggesting that protons generated by in-soil nitrification or atmospheric deposition of acids must have contributed partly but not extensively to the generation of alkalinity in the groundwaters.

30   Despite high pCO_2 in the groundwaters, those waters were only saturated to slightly undersaturated with respect to calcite solubility (Figure 1g), likely due to slow, diffusion-limited kinetics of calcite dissolution in the relatively quiescent soil water (Plummer et al. 1979).

4.1.1 Origin of nitrogen in Swiss groundwaters

35   Swiss legislation (Art. 14 Abs. 4 GSchG) restricts fertilization of crop fields and meadows to a maximum of 315 kg N ha^{-1} a^{-1} (22.5 kmol N ha^{-1} a^{-1}). Table 3 and Figure 2 display that on average the total N-fertilizer supply in Switzerland amounts to 206 kg N ha^{-1} a^{-1}, seed adds 1 kg N ha^{-1} a^{-1}, and atmospheric deposition contributes 26 kg N ha^{-1} a^{-1}. On the other hand, only 148 kg N ha^{-1} a^{-1} are harvested as crops, resulting in an annual surplus of 85 kg N ha^{-1} a^{-1} to the soil. Because N does not accumulate in soils, this excess supply must result in losses to the groundwater (22 kg N ha^{-1} a^{-1}) and to the atmosphere (63

kg N ha^{-1} a^{-1}) by way of denitrification to N_2 and/or N_2O (Table 3). These inputs via fertilizer and atmospheric deposition and losses via crops and denitrification are summarized in Figure 2 (green arrows).

Because the annual groundwater generation rate is approximately 5000 m^3 ha^{-1} a^{-1}, we estimate an average groundwater NO_3^- concentration of 22 kg N/5000 m^3 a^{-1} = 4.4 mg N L^{-1} or 0.31 mmol N L^{-1}. This value is in the mid-range of the observed

5 NO_3^- concentrations in Figure 1.

4.1.2 CO_2 and acidity production by organic nitrogen fertilization

As indicated in Table 3, in Switzerland most of the N-fertilizer is applied as manure (124 kg ha^{-1} a^{-1}) or by way of N fixation by Leguminosae (32 kg ha^{-1} a^{-1}). Because approximately 20% of the 50 kg ha^{-1} a^{-1} of commercial N-fertilizer (i.e., 10 kg ha^{-1} a^{-1}) is supplied as urea (FOAG, 2016), a total of 166 kg N ha^{-1} a^{-1} or 11.9 kmol N ha^{-1} a^{-1} of organic N needs to be

10 mineralized annually before becoming bioavailable to plants. According to Equations S-5 and S-9 in SI Table S1, this mineralization produces totals of 11.9 kmol NO_3^- ha^{-1} a^{-1}, 74.2 kmol CO_2 ha^{-1} a^{-1} and 13.3 kmol H$^+$ ha^{-1} a^{-1} (Fig. 2).

4.1.3 Nitrate supply and acidity production due to the application of inorganic nitrogen fertilizer

If the remaining 40 kg N ha^{-1} a^{-1} (2.86 kmol N ha^{-1} a^{-1}) of commercial fertilizer is applied as NH_4NO_3, its nitrification results in production of 2.86 kmol H$^+$ ha^{-1} a^{-1} and 2.86 kmol NO_3^- ha^{-1} a^{-1} (Equation S-2 in SI Table S1, and Figure 2).

15 ### 4.1.4 Contribution of atmospheric nitrogen, acid and CO_2 deposition to alkalinity production

Strong acids in the atmosphere originate from combustion of fuels that generates NO_x and SO_2, which in contact with atmospheric water droplets oxidize to nitric and sulfuric acids. The average atmospheric deposition of acidity in Switzerland (Swiss plateau, Jura and pre-alps) is estimated to be 1.34 kmol H$^+$ ha^{-1} a^{-1} (Graf Pannatier et al., 2011, their Table 3).

In Switzerland, approximately one-third of the 26 kg N ha^{-1} a^{-1} (1.86 kmol N ha^{-1} a^{-1}) of atmospheric deposited N consists of

20 NO_3^- and two-thirds of NH_4OH (NABEL, 2016). Nitrification of the latter in aerated soil or groundwater generates 1.24 kmol acidity ha^{-1} a^{-1} (Equation S-1). Thus, the atmospheric acid deposition results in a total acidity load of 1.34 + 1.24 = 2.6 kmol H$^+$ ha^{-1} a^{-1}.

At a pCO_2 of 4×10^{-4} atm, approximately 10^4 m^3 ha^{-1} a^{-1} of rain water (FOMC, 2018) saturated with CO_2 imports 0.26 kmol CO_2 ha^{-1} a^{-1} into the soil.

25 ### 4.1.5 Nitrate and acidity removal, and CO_2 generation due to crop production

In the process of NO_3^- assimilation, plants take up protons from the soil water in order to maintain charge balance (Haynes, 1990):

$$106CO_2 + 16\ NO_3^- + HPO_4^{2-} + 122H_2O + 18H^+ \Leftrightarrow \{C_{106}H_{263}O_{110}N_{16}P\} + 138O_2 \qquad (5)$$

where $C_{106}H_{263}O_{110}N_{16}P$ is a generic formula for organic matter (eg. Stumm and Morgan, 1996). Accordingly, an annual net

30 primary production of 148 kg N ha^{-1} (10.6 kmol N ha^{-1} a^{-1}) removes 11.9 kmol acidity ha^{-1} a^{-1} from the soil.

In addition, growth-dependent root respiration of crop plants can contribute 12-62% of the total in-soil CO_2 production in temperate-zone crop fields, grasslands, and forests (Raich and Tufekcioglu, 2000). Using sunflower as a model plant, root respiration amounts to approximately 20% of net assimilation (Cheng et al., 2000). Assuming a molar C:N ratio of 106:16, the net assimilation of 10.6 kmol N ha^{-1} a^{-1} corresponds to a net carbon production of 70.2 kmol C ha^{-1} a^{-1} and thus suggests

35 an in-soil CO_2 production by crop plants of approximately 14 kmol CO_2 ha^{-1} a^{-1}.

4.1.6 Alkalinity and nitrate concentrations as well as CO_2 emissions from the soil to the atmosphere are directly related to agricultural production

Growth-dependent N uptake by crop plants increases with increasing N fertilization but eventually reaches a maximum at elevated concentrations in the soil solution (Baule, 1917). Mineralization of increasing amounts of manure stimulates growth-dependent N uptake that results in increased groundwater NO_3^- and alkalinity concentrations, mainly due to the coupling of plant growth and root respiration. But as expected from the concept of a maximum of growth-dependent N

5   uptake and as empirically demonstrated in Figure 1a, alkalinity asymptotically approaches a maximum at elevated NO_3^- concentrations. This result suggests that crop production is no longer limited by N when groundwater concentrations exceed approximately 0.25 mmol NO_3^- L^{-1}. The tolerance limit for drinking water (0.4 and 0.7 mmol NO_3^- L^{-1} in Switzerland and USA, respectively) exceeds this value by approximately two- to three-fold. Accordingly, ecologically- and economically-efficient agricultural practice avoiding over-fertilization with N (i.e., not exceeding 0.25 mmol NO_3^- L^{-1}) in no way is a risk

10   for a groundwater drinking-water supply.

Apart from these biological processes, the increase of CO_2 oversaturation (Figure 1c) and the accompanying decrease in pH (Figure 1d) as NO_3^- concentration increases suggest that at least two physical-chemical processes might also contribute to the leveling-off of alkalinity at high NO_3^- concentrations. First, in a partly closed groundwater system, not all of the biogenic CO_2 and protons are consumed by carbonate-dissolution reactions. As pCO_2 increases and as pH concurrently decreases, the

15   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). Thereby, alkalinity increases at a decreasing rate as pCO_2 increases. Second, as pCO_2 increases in soil water, the rate of diffusive losses of CO_2 through air channels in the soil increases. That tendency to diffusively lose CO_2 to the atmosphere at increasingly faster rates slows the rate of alkalinity increase, as NO_3^- concentration and associated biogenic CO_2 production increase.

20

4.1.7 Synthesis

According to the compilation shown in Figure 2 for Switzerland, fertilization (including atmospheric deposition) of the soil contaminates groundwater with 1.52 kmol N ha^{-1} a^{-1}. This results in an average groundwater NO_3^- concentration of 0.30 mmol L^{-1} and in a net-production of 2.36 kmol H^+ ha^{-1} a^{-1} and 94.1 kmol CO_2 ha^{-1} a^{-1}. Subsequent equilibration of the 2.36

25   kmol H^+ and 94.1 kmol CO_2 in 5000 m^3 water in contact with solid $CaCO_3$ results in pH 7.14, 5.56 mmol L^{-1} alkalinity and a pCO_2 of 0.019 atm (1.1 mmol L^{-1}). These estimates (light blue circles in Figures 1a, c, d and e) agree well with the actual groundwater measurements.

Alternatively, assuming a scenario in which i) fields are neither fertilized nor harvested, ii) atmospheric deposition (currently 1.86 kmol N ha^{-1} a^{-1}) is the only N source, and iii) denitrification removes the same fraction of N as in the fertilized scenario

30   (74%), the resulting NO_3^- loss via exfiltrating groundwater would be 0.48 kmol N ha^{-1} a^{-1} (i.e., a groundwater concentration of 0.097 mmol NO_3^- L^{-1}). This value is 3.1 times lower than the fertilization scenario and is in the mid-rage of the minimum NO_3^- concentrations measured in Swiss groundwaters (Figure 1a). Assuming that the resulting production of CO_2 and acidity as well as denitrification in the soil would be 3.1-fold lower than shown in Figure 2, the original groundwater concentrations would be 4.58 mmol CO_2 L^{-1} and 0.23 mmol acidity L^{-1} before reaction with soil carbonates. Equilibration with the soil

35   carbonates would then result in an alkalinity of 3.30 mmol L^{-1}, a pH of 7.54, a Ω_{CO_2} of 11.5 and a $[Ca^{+2}]/[HCO_3^-]$ ratio of 0.54. These values, shown as light blue squares in Figures 1a, c, d, and e, also agree well with the observed data.

Finally, our dataset allows to assess the effect of Swiss farming practice on the atmospheric CO_2 budget (Figure 3). As shown in Figure 2 (blue arrows), the soil is exposed to a total annual CO_2 load of 94.1 kmol CO_2 ha^{-1} a^{-1}. Because CO_2 neither accumulates infinitely nor is assimilated in soils, it must leave the aquifer as gaseous CO_2 or dissolved in the

40   exfiltrating groundwater either as $H_2CO_3^*$ (= H_2CO_3 + CO_2(aqueous)) or as dissolved $Ca(HCO_3)_2$. In the 47-fold supersaturated groundwater, the $H_2CO_3^*$ concentration equals 1.1 mol m^{-3}. Multiplication with the volume of the annually exfiltrating groundwater (5000 m^3 ha^{-1} a^{-1}) results in a $H_2CO_3^*$ export of 5.5 kmol ha^{-1} a^{-1}.

In addition, 27.8 kmol ha^{-1} a^{-1} of alkalinity is exported with the groundwater. This is partly due to the 2.36 kmol H$^+$ ha^{-1} a^{-1} introduced to the system, which generates an equal amount of alkalinity by dissolution of carbonates (Equation 2). However, the remaining 25.44 kmol ha^{-1} a^{-1} of exported alkalinity must have resulted from the reaction of 12.72 kmol ha^{-1} a^{-1} of CO_2 (predominantly present as H_2CO_3 in the water) with carbonates (Equation 3). Subtracting the sum of these two CO_2 losses

5   via groundwater (5.5+12.72=18.22 kmol ha^{-1} a^{-1}) from the total CO_2 exposure (94.1 kmol CO_2 ha^{-1} a^{-1}) results in a gaseous CO_2 loss to the atmosphere of 75.9 kmol CO_2 ha^{-1} a^{-1}.

On the other hand, crop production extracts 10.6 kmol N ha^{-1} a^{-1} from the soil, corresponding to a 70.2 kmol CO_2 ha^{-1} a^{-1} net consumption from the atmosphere. Consequently, Swiss agricultural activities burden the atmosphere annually with 5.7 kmol CO_2 ha^{-1} a^{-1}. Extrapolation to the total Swiss agricultural area yields an annual accumulation of 0.26 Mt CO_2 a^{-1}. This is a

10   very conservative estimate, because it neglects the CO_2 emissions from CO_2-supersaturated surface waters and does not consider that a large fraction of the harvest serves as food for animals, which generate additional CO_2.

4.2. Surface Waters

Although groundwater exfiltrates to riverbeds or lakes, surface-water quality is in addition subjected to surface runoff and wastewater discharges.

15   When CO_2-supersaturated groundwater exfiltrates and becomes surface water, much of the above-saturation CO_2 diffuses into the atmosphere. Additionally, photoautotrophic organisms may assimilate some of the CO_2. Both processes lead to the observed higher pH and lower Ω_{CO_2} values in rivers and lakes than in groundwaters at similar NO_3^- concentrations (Figures 1c and d). Nevertheless, CO_2 concentrations in the river and lake waters did not reach equilibrium with the atmospheric pCO_2, possibly because of heterotrophic mineralization and slow diffusional loss of the CO_2 to the atmosphere (Hotchkiss et

20   al., 2015).

Calcite would be expected to precipitate due to the loss of CO_2 and the rising pH when groundwater exfiltrates. However, as demonstrated in Figure 1g, it remains oversaturated in surface waters, indicating that precipitation of calcite often is kinetically constrained (Plummer et al., 1979) and/or at least partly inhibited (e.g., by elevated phosphate concentrations; Langmuir, 1997: p. 222; Müller et al., 2016).

25   Wastewater loads to a river may alter its groundwater-derived alkalinity-NO_3^- relationship in several ways. First, introduction of NH_4^+-containing wastewater into well-oxygenated river water results in nitrification that increases the NO_3^- concentration but simultaneously decreases the pH and alkalinity if carbonate minerals are not present (Equation S-1 in SI Table S1) or do not dissolve fast enough, thus contributing to an additional release of CO_2 to the atmosphere. Second, the introduction of large amounts of wastewater-derived dissolved organic matter stimulates microbial respiration, resulting in

30   low O_2 concentrations that favor denitrification and/or dissimilatory NO_3^- reduction to ammonia, both of which decrease NO_3^- concentrations but increase alkalinity even in the absence of carbonate minerals (Equations S-10 to S-12 in SI Table S1).

Consequently, as demonstrated by Abril et al. (2000) and Abril and Frankignoulle (2001) in the highly-polluted Scheldt Basin (Belgium and Netherlands), large wastewater loads can induce N transformations in river water and change its acid-

35   base properties to the extent that the positive relationship between alkalinity and NO_3^- concentration observed in calcareous soils completely reverses in a river. Although that reversal did not occur in the Swiss surface waters, a trend toward lower alkalinity at a given NO_3^- concentration is apparent (Figure 1b).

5 Conclusions

As illustrated in Figure 2 and discussed above, N-limited terrestrial primary production plays a dominant role in the linking of alkalinity and NO_3^- concentrations in aquifer and surface waters. From a global perspective, application of N-fertilizers fueling the production of short-lived organic matter contributes to a net increase of atmospheric CO_2 concentrations via

5 release of CO_2 that otherwise would remain sequestered in carbonate minerals in soils (West and McBride, 2005; Perrin et al., 2008; Li et al., 2013), and accelerates the translocation of DIC from calcareous soils to downstream reaches in surface waterways and eventually to the oceans.

As atmospheric CO_2 concentrations increase and thus riverine, lake, and oceanic pH values decrease through time, the proportion of the DIC that precipitates as $CaCO_3$ after CO_2-oversaturated aquifer waters ex-filtrate to surface-water bodies

10 will decrease, and the proportion that is released to the atmosphere as CO_2 will increase. Therefore, continued N-fertilization will contribute to the ongoing global CO_2 enrichment of the atmosphere and will promote in-soil calcite dissolution.

Information about the Supplement

Table S-1 lists chemical reactions for the nitrification of some common N-fertilizers and several other processes in groundwaters and surface waters in the presence and absence of carbonate minerals. Table S-2 reports results of regressions of alkalinity *versus* NO_3^- concentration in Swiss groundwaters, Canton Zürich well waters, and Swiss lakes and rivers.

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Author contributions. BM, JSM, and RG contributed equally to the manuscript. BM performed ChemEQL speciation calculations.

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Table 1: Data sources.

Dataset	Description	Range of NO$_3^-$ (mmol L^{-1})	Range of alkalinity (mmol L^{-1})
Aquifers	Groundwaters and well waters in carbonaceous watersheds in Switzerland with alkalinity ≥1 mmol L^{-1}. Groundwater data from 42 watersheds during 1997-2016 (NAQUA, 2017); averages were calculated over all years. Well-water data from 120 wells along rivers in the Canton of Zürich during 1991-2016 (AWEL, 2017); averages were calculated over all years.	0.004 - 0.905	2.08 - 7.88
Surface waters	Lake and river waters in carbonaceous watersheds in Switzerland with alkalinity ≥1 mmol L^{-1}. Lake data from 21 lakes (0.2-580) km^2 during 1980-2015 (BAFU, 2017); based on volume-weighted mean concentrations at winter/spring lake overturn averaged over all years. Only 16 of the lakes had Ca and Mg data. River data from 22 stations on 12 rivers during 5- to 44-year monitoring periods (Eawag, 2017); based on concentrations at lake overturn averaged across all years.	0.017 - 0.219	1.52 - 5.03

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Table 2: Regressions of alkalinity *versus* nitrate (NO_3^-) concentration for the Swiss aquifer and surface-water data in Figure 1.[a]

| Waters | NO_3^- range for regression (mmol L^{-1}) | Slope | | | Intercept | | | |
		Value (mmol Alk/ mmol NO_3^-)	p		Value (mmol L^{-1})	p	Regression R^2	n
Aquifers	<0.25	17.04 (13.89 - 20.19)	<0.001		2.44 (1.95 - 2.93)	<0.001	0.681	57
	>0.25	1.79 (0.72 - 2.86)	0.001		5.62 (5.15 - 6.09)	<0.001	0.097	105
Surface waters [b]	<0.25	12.48 (9.67 - 15.29)	<0.001		1.74 (1.48 - 2.00)	<0.001	0.662	43

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[a] 95% confidence intervals of slopes and intercepts are in parentheses; "p" is the probability value of the slope or intercept being equal to 0 (i.e., p < 0.05 indicates significant difference from zero); Alk = alkalinity.

[b] None of the surface waters had an NO_3^- concentration >0.25 mmol L^{-1}.

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**Table 3:** Averaged nitrogen budget for agricultural soils (10'490 km^2) in Switzerland. (FOAG, 2018).

Input/output	annual N flux	reference
	kg N ha^{-1} a^{-1}	
Total N supply	**233**	FSO (2014)
Fertilizer supply	**206**	FSO (2014)
Manure	124	FSO (2014)
Leguminosae	32	FSO (2014)
Org/inorg commercial fertilizer	50	FSO (2014)
$\quad$ NH$_4$NO$_3$ (60%)	30	FOAG (2016)
$\quad$ Urea (20%)	10	FOAG (2016)
$\quad$ Other (20%)	10	FOAG (2016)
N deposition with seeds	**1**	FSO (2014)
Atmospheric N deposition	**26**	FSO (2014)
Atm. NO$_3^-$ deposition	8.7	
Atm. NH$_4^+$ deposition	17.3	
Nitrogen removal with crop	**148**	FSO (2014)
Excess nitrogen deposition	**85**	FSO (2014)
N removal by groundwater to surface waters	22	Hürdler et al. (2015a)
N load to the atmosphere by denitrification to N$_2$ and/or N$_2$O	63	

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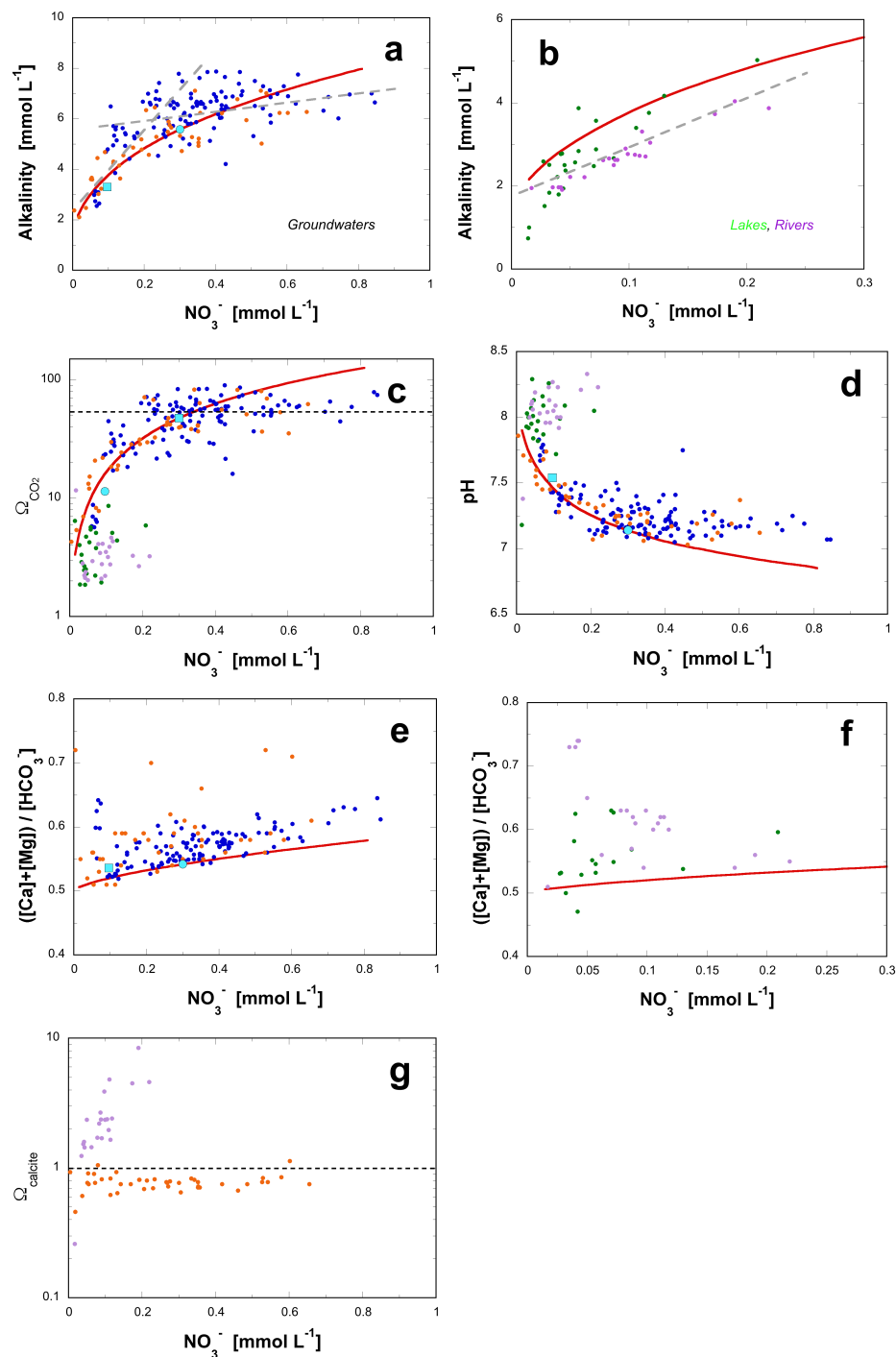
Figure 1:

Figure 1: Relationships between NO_3^- concentration and (a and b) alkalinity, (c) Ω_{CO_2} (CO_2 saturation index), (d) pH, (e and f) molar ($[Ca]+[Mg]$)/$[HCO_3^-]$ ratio, and (g) $\Omega_{calcite}$ (calcite $[CaCO_3]$ saturation index) in aquifers and surface waters in calcareous catchments in Switzerland that had alkalinity ≥ 1 mmol L^{-1}. These include 42 groundwaters across the country (orange), 120 wells in the Canton of Zürich (blue), 21 lakes (green), and 22 stations on 12 rivers (purple) (Table 1). The light blue circle depicts the resulting alkalinity for the estimated average loads of 1.52 kmol N ha^{-1} a^{-1}, 2.36 kmol H^+ ha^{-1} a^{-1} and 94.1 kmol CO_2 ha^{-1} a^{-1} (see Synthesis section) and a groundwater formation rate of 5000 m^3 ha^{-1} a^{-1}. The solid red curve is the ChemEQL-predicted relationship assuming the NO_3^- : CO_2 : H^+ ratio of the above loads in a system open to the air in the soil in the presence of calcite. The light blue square depicts the alkalinity and NO_3^- concentration in a natural system without fertilization and without crop harvest, but with the current atmospheric N deposition of 1.86 kmol ha^{-1} a^{-1}. The speciation calculation was performed considering the activities of the ions (Debye-Hückel-approximation), which was essential for the appropriate estimation of the dissolution of calcite. Note the difference in scale for the horizontal axis between panels b) and f) and the other five panels. Linear-regression slopes and intercepts shown by the black lines in panels a) and b) are listed in Table 2.

Figure 2:
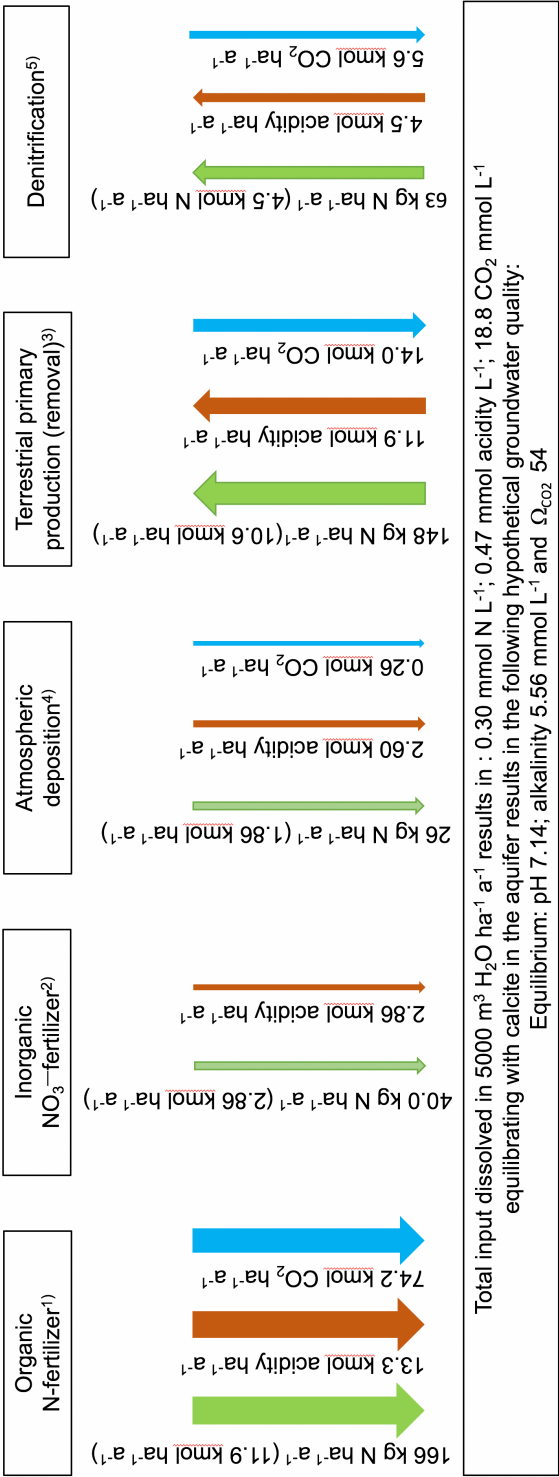
1) Mineralization of organic N-fertilizer generates $106 CO_2$ and $18 H^+$ per $16 NO_3^-$ (eq. S-9)
2) Nitrification of NH_4NO_3 generates $2H^+$ and NO_3^- per mol NH_4NO_3 (eq. S-2))
3) Primary production (annual crop – annual seed) i) consumes $18 H^+$ and ii) generates $21.2 CO_2$ (due to root respiration) per $16 NO_3^-$ removal (eq. S-9)
4) At a pCO_2 of 4×10^{-4} atm, 10^4 m^3 ha^{-1} a^{-1} rain water saturated with CO_2 import 0.26 kmol CO_2 $ha^{-1}a^{-1}$.
   About $1/3$ of the atmospheric N-deposition is NO_3^- and $2/3$ is NH_4^+, which is nitrified and generates 1 equivalent of acidity per mol of oxidized NH_3 (eq. S-1).
   Hence, 1.34 kmol H^+ $ha^{-1}a^{-1}$ originates from nitrification of deposited NH_4^+.
5) According to $1.25 CH_2O + NO_3^- + H^+ = 1.25 CO_2 + 0.5 N_2 + 1.75 H_2O$ denitrification of 1 mol NO_3^- generates 1.25 mol CO_2 and consumes 1 mol H^+

Figure 2: Compilation and overview of areal deposition rates of nitrogen, acidity, and CO_2 in agricultural soils of Switzerland, interacting in the carbonaceous soil- groundwater system.
Concentrations were estimated assuming a groundwater formation rate of 5000 m^3 ha^{-1} a^{-1}.

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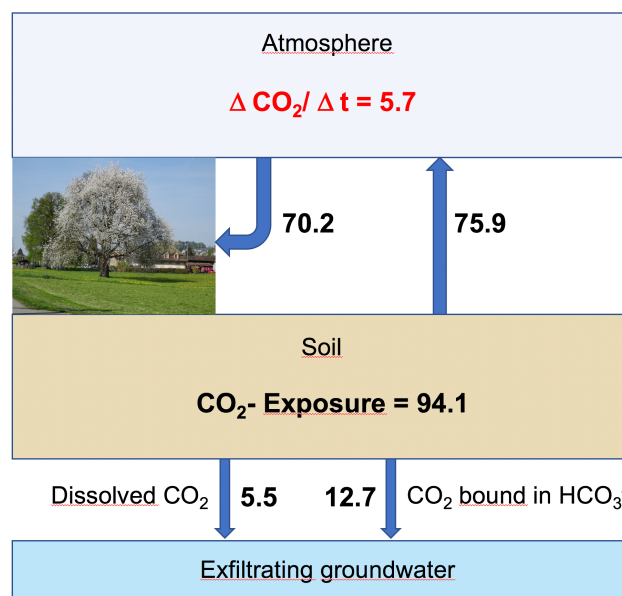
Figure 3:

Figure 3: CO_2 budget of Swiss agricultural soils. Fluxes in kmol CO_2 ha^{-1} a^{-1}.