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1 Nitrogen fertilization of soils fuels carbonate weathering

2 and translocation in calcareous watersheds

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Abstract

In calcareous watersheds, groundwater alkalinity results largely from dissolution of carbonate minerals in soils. The alkalinity increases initially approximately in proportion to nitrate (NO_3^-) concentration and eventually approaches an apparent 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 fertilizer, (ii) exchange of OH^- and H^+ during the uptake of NO_3^- or ammonium by crop plants, and (iii) CO_2 released by roots as a result of fertilizer-stimulated plant growth. We suggest that the asymptotic approach to a maximum groundwater alkalinity at NO_3^- concentrations exceeding 0.25 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. Our analysis provides a general understanding and quantitative prediction of steady-state groundwater NO_3^- concentration, alkalinity, pH, the degree of CO_2 supersaturation in the soil, and soil CO_2 emissions to the atmosphere. The positive correlation between alkalinity and NO_3^- concentration observed in groundwaters persists in rivers and lakes. We conclude that an economically efficient agricultural practice that avoids over-fertilization might accelerate the in-soil carbonate weathering rate up to approximately 3-fold compared to unfertilized soils, but it will not jeopardize the use of aquifers for drinking water.

Keywords:

Groundwater, surface waters, alkalinity, nitrogen fertilizer, agriculture, Switzerland

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1 Introduction

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^-)] 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 (Raymond et al. 2008; Barnes and Raymond 2009; Kaushal et al. 2013; Müller et al. 2016; Lorenz and Lal 2018; Raymond and Hamilton 2018). 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 (Hamilton et al. 2007; Perrin et al. 2008; Li et al. 2013; Resplandy et al. 2018).

Biogeochemical processes in soils are the main sources of dissolved inorganic carbon in the interstitial waters, groundwaters and surface waters, and it is important to understand the factors generating and regulating these fluxes (Bauer et al. 2013). To evaluate the effect of N-fertilizers on the content of inorganic and organic carbon in soils, Dong et al. (2016) investigated the effect of 15 years of N-fertilization (0 to 600 kg N ha⁻¹ a⁻¹) on agricultural soils in the North China plains. They reported a loss of inorganic carbon from the soils as N-fertilization increased, and that loss was far higher than estimated from the proton release due to nitrification of the N-fertilizers. The additional loss of inorganic carbon was suspected to be caused by increased partial pressure of CO_2 due to increased soil respiration. In contrast, in field column experiments in which soils received various N-fertilizers (Song et al. 2017), carbonate dissolution was in stoichiometric balance with nitrification of NH_4^+ .

In addition to soils being deprived of their carbonate buffer, the worldwide increased mobilization of dissolved inorganic carbon affects surface waters and is of importance to the global carbon budget (Raymond and Hamilton, 2018). 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 discharge; and that enhanced export will continue to increase in the future (Ren et al. 2015). West and McBride (2005) estimated that 38% of the HCO_3^- transported by the Mississippi River originated from calcite dissolution induced by nitric acid (HNO_3). Although Stets et al. (2014) reported a trend of decreasing NO_3^- and sulfate (SO_4^{2-}) concentrations in the large rivers of the conterminous USA, indicating recovery from acidification, multiple processes appeared to contribute to the still increasing trends for alkalinity. Increasing alkalinity in French rivers was attributed to

nitrification of N-fertilizers by Perrin et al. (2008) and Brunet et al. (2011), and Guo et al. (2010) reported increased soil acidity as a consequence of the increasing use of N-fertilizers in China.

Apart from the steadily increasing partial pressure of CO₂ (pCO₂) in the atmosphere (NOAA, 2017), increasing soil temperature (Zobrist et al. 2018), and changes in runoff, a variety of other factors may affect groundwater and thus riverine alkalinity (Raymond et al., 2008). Those factors include (i) agricultural practices such as fertilization and liming (West and McBride, 2005; Oh and Raymond, 2006; Hamilton et al., 2007; Müller et al., 2016), (ii) mineral acid load originating from atmospheric deposition (e.g., HNO₃ [Equation S-6 in SI Table S1] and sulfuric acid (H₂SO₄)), (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 and in view of the approximately five-fold increase of anthropogenically-generated reactive N since 1960, Battye et al. (2017) posed the question “Is nitrogen the next carbon?”.

In this study, we use data from an extensive groundwater and surface-water monitoring program in calcareous agricultural Swiss watersheds to infer processes demonstrating a strong linkage between alkalinity and NO₃⁻ concentrations. The study aims to identify, quantify and relate in-soil processes that are fueled by the application of organic and inorganic nitrogen fertilizers and that affect groundwater and surface-water alkalinity. Microbial decomposition of manure, increased root respiration and nitrification are identified as the main driving forces linking the two constituents in groundwaters and surface waters. Further, we explain why in groundwater – at elevated NO₃⁻ concentrations – alkalinity reaches an apparent upper limit clearly below the solubility of calcite or dolomite.

2 Methods

2.1 The concept of alkalinity

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

$$\text{Alkalinity (as mmol L}^{-1}\text{)} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \quad (1)$$

where the brackets indicate concentrations of the designated ions (Stumm and Morgan 1996). At circumneutral pH, bicarbonate ion (HCO₃⁻) is the major component of alkalinity, with only minor contributions from carbonate

(CO₃²⁻) and the difference between hydroxyl (OH⁻) ions and protons (H⁺). In calcareous watersheds, alkalinity originates mainly from the dissolution of carbonate minerals [e.g., calcite (CaCO₃) and dolomite (Ca_xMg_(1-x)CO₃)] either by (i) protons, which are generated by dissociation of strong mineral acids [e.g., HNO₃ or H₂SO₄] (Equation 2), or (ii) by carbonic acid (H₂CO₃) that is formed by the solvation of CO₂ in water (Equation 3).

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 due to the additional dissolution of carbonates (Gandois et al. 2011).

In SI Table S1, we calculated molar $\Delta[\text{HCO}_3^-]:\Delta[\text{NO}_3^-]$ and $\Delta([\text{Ca}]+[\text{Mg}]):\Delta[\text{HCO}_3^-]$ ratios of chemical reactions that likely occur in aquifers in the presence or absence of carbonate minerals. Ratios listed in that table are based on theoretical stoichiometry of the chemical reactions and might differ from ratios based on measured concentrations, because the resulting HCO₃⁻ concentration will be pH-dependent. Regardless, the $\Delta([\text{Ca}]+[\text{Mg}]):\Delta[\text{HCO}_3^-]$ ratio is a useful indicator of the underlying carbonate dissolution process(es) in a groundwater because, based on theoretical stoichiometry, 2 mol of HCO₃⁻ are released per mol of Ca plus Mg when CO₂ dissolves either CaCO₃ or Ca_xMg_(1-x)CO₃ (i.e., the $\Delta([\text{Ca}]+[\text{Mg}]):\Delta[\text{HCO}_3^-]$ ratio is 0.5; Equation 3, and Equation S19 in SI Table S1), but only 1 mol of HCO₃⁻ is released per mol of Ca plus Mg when H⁺ dissolves either CaCO₃ or Ca_xMg_(1-x)CO₃ (i.e., the $\Delta([\text{Ca}]+[\text{Mg}]):\Delta[\text{HCO}_3^-]$ ratio is 1.0; Equation 2, and Equation S18 in SI Table S1). Hamilton et al. (2007) demonstrated that, while carbonate dissolution with CO₂ (Equation 3) is a sink for CO₂, dissolution with sufficient strong acid (Equation 2) is a source of CO₂.

2.2 Datasets and data treatment

The datasets presented herein will be used as the basis to explain the observed correlation between the concentrations of NO₃⁻ and alkalinity in groundwaters, rivers and lakes, and to construct a conceptual model of the biogeochemical reactions of N-fertilizers with carbonate minerals in soils. The model will explain how alkalinity and NO₃⁻, as well as CO₂ emissions from the soil to the atmosphere, are related to agricultural production.

Aquifer and surface waters considered in this study are described in Table 1. The Swiss Federal Office for the Environment (FOEN) records the state of and changes in groundwater resources at monitoring sites in

131 Switzerland. The Swiss National Groundwater Quality Monitoring program (NAQUA, 2017) monitors and
132 reports on the development of groundwater resources and the drinking water quality. Data used in this study are
133 a subset of the NAQUA module ‘TREND’, which contains the chemical composition of the groundwaters. Four
134 to 12 samples per year were available from 53 monitoring sites in the time period 1997-2016. We specifically
135 targeted calcareous watersheds, thus excluding monitoring sites in clastic and crystalline rocks, resulting in 42
136 sites and a total of 2600 measurements. Data were averaged for each monitoring site. The Office of Waste,
137 Water, Energy and Air (WWEA) of the Canton of Zürich (Switzerland) provided data from 120 groundwater
138 sites within the Canton. We selected data from 1991 to 2016, resulting in 2670 data points. Data were averaged
139 for each site.

140 For calculations of the partial pressure of CO₂ (pCO₂) and saturation with respect to calcite (Ω_{CaCO_3}) in
141 groundwaters, we used pH measurements from the datasets and equilibrium constants adjusted to 8 °C with the
142 method of Plummer and Busenberg (1982). For calculations in river waters we used 15 °C.

143 At atmospheric pCO₂ ranging from 10^{-3.5} to 10^{-3.4} atm (i.e., CO₂ concentrations of approximately 300 to 400
144 ppm, the condition from approximately 1959 to present; NOAA, 2017) and in the absence of acids other than
145 H₂CO₃, an alkalinity concentration of 1.42 mmol L⁻¹ and a pH of 8.24 would be expected in water draining a
146 hypothetically N-free (and thus sterile) calcareous soil in equilibrium with calcite and atmospheric pCO₂,
147 assuming a temperature of 8 °C (see SI Table S3). Therefore, to avoid potentially confounding results from
148 waters not in considerable contact with carbonates, we included in this analysis only waters originating from
149 calcareous watersheds in which alkalinity exceeded 1.42 mmol L⁻¹. In all groundwater samples, O₂
150 concentrations exceeded 2 mg L⁻¹ (median 7.2 mg L⁻¹) and NH₄⁺ and nitrite (NO₂⁻) concentrations were below
151 detection limits.

152 Bi-weekly discharge-proportionally-collected river monitoring data from the NADUF program (National long-
153 term surveillance of Swiss rivers) are available from Eawag (2017). Concentrations measured in rivers were
154 averaged over the observation period.

155 Monitoring data from 21 lakes were obtained from the databank of FOEN (2017) for the years 1980-2015.
156 Reported concentrations of Ca²⁺, alkalinity, and NO₃⁻ in lakes are volume-weighted average values measured at
157 spring overturn, averaged over all years of observation. Trophic state of the lakes ranged from oligotrophic to
158 eutrophic, and only one lake was meromictic with a permanently anoxic hypolimnion.

We applied the geochemical speciation software ChemEQL Version 3.2 (Müller 2015) to calculate pH, alkalinity, $p\text{CO}_2$, and Ca^{2+} concentrations in groundwater that would be 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 assumed equilibrium of the groundwater with soil $p\text{CO}_2$. Initial conditions were as follows: temperature = 8 °C, atmospheric CO_2 = 400 ppm 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 $\Omega_{\text{CO}_2} = p\text{CO}_2(\text{aq})/p\text{CO}_2(\text{atm})$, where $p\text{CO}_2(\text{aq})$ is the partial pressure of CO_2 in the water (in atm) and $p\text{CO}_2(\text{atm})$ is the partial pressure of CO_2 in the atmosphere (in atm). $p\text{CO}_2(\text{aq})$ was calculated from the reported pH and alkalinity using Equation 6 in Müller et al. (2016). To produce conservative (i.e., minimum) estimates of Ω_{CO_2} , we assumed a value of 400 μatm for $p\text{CO}_2(\text{atm})$, which is the 2015 annual average in the Mauna Loa dataset (NOAA 2017).

The saturation index for calcite solubility was calculated as

$$\Omega_{\text{calcite}} = \frac{\{\text{Ca}^{2+}\} \times \{\text{CO}_3^{2-}\}}{K_{\text{calcite}}} \quad (4)$$

where braces denote the ChemEQL-predicted chemical activity of Ca^{2+} or CO_3^{2-} , 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 and cations. We calculated Ω_{calcite} only for the NAQUA-groundwaters and rivers, because Ca^{2+} concentrations were not available for the lake waters and Canton 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 $p \leq 0.05$.

3 Results

Groundwater alkalinity increased as NO_3^- concentration increased (Figure 1a). In the concentration range 0-0.25 mmol NO_3^- L⁻¹, the initial slope of alkalinity *versus* NO_3^- concentration for groundwater was 17.0 mmol

184 alkalinity L^{-1} / $\text{mmol NO}_3^- \text{L}^{-1}$ and the alkalinity-axis intercept was 2.44 mmol L^{-1} (Table 2). At NO_3^-
 185 concentrations exceeding 0.25 mmol L^{-1} , the alkalinity *versus* NO_3^- slope decreased nearly 10-fold to only 1.8
 186 $\text{mmol alkalinity L}^{-1}$ / $\text{mmol NO}_3^- \text{L}^{-1}$ (Table 2). All groundwater samples were distinctly supersaturated with
 187 respect to atmospheric CO_2 (up to 90-fold; Figure 1b). Ω_{CO_2} increased rapidly as NO_3^- concentration increased
 188 from 0 to approximately 0.25 mmol L^{-1} , but leveled-off at higher NO_3^- concentrations. As NO_3^- concentration
 189 increased from 0 to 0.25 mmol L^{-1} in the groundwaters, pH tended to decrease but then leveled-off to
 190 approximately circumneutral values at higher NO_3^- concentrations (Figure 1c). Ranging from 0.51 to 0.72, the
 191 molar $([\text{Ca}]+[\text{Mg}]) : [\text{HCO}_3^-]$ ratio in the aquifer waters increased significantly as NO_3^- concentration increased
 192 (slope = $0.079 / \text{mmol NO}_3^- \text{L}^{-1}$, $p < 0.001$; Figure 1d). However, NO_3^- only accounted for 15% of the variation
 193 of this ratio, suggesting that the majority of that variation depended on other factors. Most groundwaters were
 194 slightly undersaturated with respect to CaCO_3 solubility ($\Omega_{\text{CaCO}_3} < 1$; Figure 1e).

195 In surface waters, NO_3^- concentration did not exceed 0.2 mmol L^{-1} . As observed in groundwaters, alkalinity
 196 increased with increasing NO_3^- concentrations (Figure 2a); but contrary to groundwaters, all surface waters were
 197 supersaturated with respect to calcite solubility, and Ω_{CaCO_3} tended to increase as NO_3^- concentration increased
 198 (Figure 2b).

199 Table 3 summarizes quantitative information about the various sources, sinks, and pathways affecting the N
 200 budget of agricultural Swiss soils. The total N supply of $233 \text{ kg N ha}^{-1} \text{a}^{-1}$ and removal of only $148 \text{ kg N ha}^{-1} \text{a}^{-1}$
 201 results in an excess deposition of $85 \text{ kg N ha}^{-1} \text{a}^{-1}$.

202 In Figure 3 we present annual fluxes of N, H^+ and CO_2 generated and/or consumed by fertilization, atmospheric
 203 deposition, primary production, denitrification and CO_2 loss from the soil to the atmosphere. Three different
 204 C:N ratios of terrestrial plants were considered to cover a representative range. The estimated net input of N, H^+ ,
 205 and CO_2 together with the annual average groundwater generation of $5000 \text{ m}^3 \text{ ha}^{-1} \text{a}^{-1}$ results in a NO_3^-
 206 concentration of 0.3 mmol L^{-1} , pH 7.08, alkalinity of 5.74 mmol L^{-1} and CO_2 supersaturation Ω_{CO_2} of 55 (round
 207 yellow markers in Figures 1a-1d) that are well in the range observed in groundwaters.

208

209 4 Discussion

210 Based on the N balance in Swiss agriculture (Table 3) and considering chemical in-soil interactions of the
211 biologically-generated CO₂ and protons with solid carbonates, we develop a conceptual biogeochemical model
212 (Figure 3) that quantitatively explains the observed covariance of groundwater alkalinity with groundwater NO₃⁻
213 concentration shown in Figure 1 as a consequence of N-fertilizer application.

214 Because in all aquifer waters included in this analysis, (i) alkalinity exceeded 1.42 mmol L⁻¹, the concentration
215 expected in calcite-saturated, air-equilibrated water (Figure 1a), (ii) pH was considerably less than the
216 equilibrium-predicted value of 8.24 (Figure 1c), and (iii) CO₂ concentrations were highly supersaturated with
217 respect to the atmosphere (Figure 1b), all aquifer waters appear to have been at least partially protected from
218 contact with the atmosphere.

219 Because the equations in Table S1 show that the stoichiometric molar ([Ca]+[Mg]) : [HCO₃⁻] ratio (i) equals 0.5
220 if carbonates are dissolved only as a result of interaction with CO₂ (Equations S-19 and S-20) but (ii) exceeds
221 0.5 if protons generated by nitrification or supplied by acid precipitation (Equations S-1 to S-6) contribute to the
222 dissolution of carbonates (Equations S-13 to S-18), the observed ([Ca]+[Mg]) : [HCO₃⁻] ratios between
223 approximately 0.5 and 0.7 (Figure 1d) suggest that protons generated by in-soil processes or atmospheric
224 deposition of acids must have contributed partly but not extensively to the generation of alkalinity. Accordingly,
225 in agreement with Hamilton et al. (2007) and Dong et al. (2016), we conclude that carbonate weathering in soils
226 is a net sink and not a net source of CO₂ emissions to the atmosphere. However, as summarized in Figure 3,
227 despite this CO₂ sequestration, about 90% of the in-soil CO₂ production escapes to the atmosphere.

228 Despite high pCO₂ in the groundwaters, those waters were only saturated to slightly-undersaturated with respect
229 to calcite solubility (Figure 1e), likely due to slow, diffusion-limited kinetics of calcite dissolution in the
230 relatively quiescent soil water (Plummer et al. 1979).

231 4.1 Origin of N in Swiss groundwaters

232 Swiss legislation (Art. 14 Abs. 4 GSchG) restricts N fertilization of crop fields and meadows to a maximum of
233 315 kg N ha⁻¹ a⁻¹ (22.5 kmol N ha⁻¹ a⁻¹). Based on the nationwide N balance for Swiss agriculture (Table 3), the
234 total N-fertilizer supply on average amounts to 206 kg N ha⁻¹ a⁻¹, seed adds 1 kg N ha⁻¹ a⁻¹, and atmospheric
235 deposition contributes 26 kg N ha⁻¹ a⁻¹. However, only 148 kg N ha⁻¹ a⁻¹ are harvested as crops, resulting in an
236 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 ($22 \text{ kg N ha}^{-1} \text{ a}^{-1}$) and to the atmosphere ($63 \text{ kg N ha}^{-1} \text{ a}^{-1}$) by way of denitrification to N_2 and/or N_2O (Table 3). Given the annual rate of groundwater generation of approximately $5000 \text{ m}^3 \text{ ha}^{-1} \text{ a}^{-1}$ in Switzerland, we therefore expected an average groundwater NO_3^- concentration of $22 \text{ kg N}/5000 \text{ m}^3 \text{ a}^{-1} = 4.4 \text{ mg N L}^{-1}$ ($0.31 \text{ mmol N L}^{-1}$). This value is in the mid-range of the observed NO_3^- concentrations (Figure 1).

4.2 CO_2 and acidity production by organic N fertilization

In Switzerland, liquified manure (i.e., a slurry of dry manure suspended in water) is the predominant form of fertilizer applied to fields, and croplands in the calcareous watersheds included in this study are not usually limed. However, elemental C:N:P ratios for liquid manure are difficult to find in the literature. According to Table 3 in the Alberta Manure Composting Handbook (2005), the atomic C:N ratios equal $18.6 : 1$ and $23.1 : 1$ for liquid dairy and pig manure, respectively. In their Table 39, Flisch et al. (2009) report atomic N:P ratios of the same two manure types as $11.9 : 1$ for dairy manure and $7.8 : 1$ for pig manure. After combining those two sets of estimates, we postulate an atomic C:N:P ratio of $201 : 10 : 1$ for a mixed liquid manure in Switzerland. Thus, a generalized formula for the manure and its complete mineralization is:

Consequently, complete oxic mineralization of a manure load containing $8.9 \text{ kmol N ha}^{-1} \text{ a}^{-1}$ (Table 3) causes a CO_2 load to the soil of $179 \text{ kmol ha}^{-1} \text{ a}^{-1}$ and a H^+ load of $10.7 \text{ kmol ha}^{-1} \text{ a}^{-1}$.

Nitrogen fixation by Leguminosae contributes $32 \text{ kg N ha}^{-1} \text{ a}^{-1}$ ($2.3 \text{ kmol N ha}^{-1} \text{ a}^{-1}$) to fertilization (Table 3). If that amount of N is added to the soil as, for example, alfalfa hay with a C:N ratio of 25:1 (USDA National Resources Conservation Service 2011), its oxic mineralization results in $2.3 \text{ kmol NO}_3^- \text{ ha}^{-1} \text{ a}^{-1}$, $57.5 \text{ kmol CO}_2 \text{ ha}^{-1} \text{ a}^{-1}$, and $4.6 \text{ kmol H}^+ \text{ ha}^{-1} \text{ a}^{-1}$. In addition, $10 \text{ kg N ha}^{-1} \text{ a}^{-1}$ ($0.71 \text{ kmol N ha}^{-1} \text{ a}^{-1}$) are supplied as urea $[(\text{NH}_2)_2\text{CO}]$ that reacts with O_2 as described in Equation S-5 in SI Table S1. Consequently, the application of urea supplies $0.71 \text{ kmol NO}_3^- \text{ ha}^{-1} \text{ a}^{-1}$, $0.71 \text{ kmol H}^+ \text{ ha}^{-1} \text{ a}^{-1}$, and $0.355 \text{ kmol CO}_2 \text{ ha}^{-1} \text{ a}^{-1}$ to the soil. Because the N supplied with seeds is finally harvested with the crop, its addition does not result in a net change in protons or CO_2 . To sum up, biological N-fixation plus fertilization with urea results in $3 \text{ kmol NO}_3^- \text{ ha}^{-1} \text{ a}^{-1}$, $57.9 \text{ kmol CO}_2 \text{ ha}^{-1} \text{ a}^{-1}$, and $5.3 \text{ kmol H}^+ \text{ ha}^{-1} \text{ a}^{-1}$.

4.3 Nitrate supply and acidity production due to the application of inorganic N fertilizer

264 If 40 kg N ha⁻¹ a⁻¹ (2.86 kmol N ha⁻¹ a⁻¹) of commercial fertilizer is applied as NH₄NO₃ (Table 3), its
 265 nitrification results in the production of 2.86 kmol H⁺ ha⁻¹ a⁻¹ and 2.86 kmol NO₃⁻ ha⁻¹ a⁻¹ (Equation S-2 in SI
 266 Table S1, and Figure 3).

267 4.4 Contribution of atmospheric N, acid, and CO₂ deposition to alkalinity production

268 Strong acids in the atmosphere originate from combustion of fuels that generates NO_x and SO₂, which in contact
 269 with atmospheric water droplets oxidize to nitric and sulfuric acids (Tanner 1990). The average atmospheric
 270 deposition of acidity in Switzerland (Swiss plateau, Jura and pre-alps) is estimated to be 1.34 kmol H⁺ ha⁻¹ a⁻¹
 271 (Graf Pannatier et al. 2011, their Table 3).

272 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
 273 N consists of NO₃⁻ and two-thirds of NH₄OH (NABEL, 2016). Nitrification of the latter in aerated soil or
 274 groundwater generates 1.24 kmol acidity ha⁻¹ a⁻¹ (Equation S-1 in SI Table S1). Thus, the atmospheric acid
 275 deposition results in a total acidity load of 1.34 + 1.24 = 2.6 kmol H⁺ ha⁻¹ a⁻¹. At a pCO₂ of 4x10⁻⁴ atm,
 276 approximately 10⁴ m³ ha⁻¹ a⁻¹ of rain water (FOMC, 2018) saturated with CO₂ imports 0.26 kmol CO₂ ha⁻¹ a⁻¹
 277 into the soil.

278 4.5 Nitrate and acidity removal, and CO₂ generation due to crop production

279 Assuming the median observed atomic ratios C:N = 32 and C:P = 799 (Elser et al., 2000), the organic matter of
 280 terrestrial autotrophs can be characterized as (CH₂O)₇₉₉(NH₃)₂₅(H₃PO₄). The USDA Natural Resources
 281 Conservation Service (2011) reported somewhat lower C:N mass ratios ranging from 11 to 25, corresponding to
 282 atomic C:N ratios of 13:1 to 29:1, respectively, for legume hay, alfalfa hay, and hairy vetch cover. To
 283 incorporate a representative range, we assumed atomic C:N ratios of 32, 29 and 13, resulting in organic matter
 284 stoichiometries for terrestrial plants of (CH₂O)₇₉₉(NH₃)₂₅(H₃PO₄), (CH₂O)₇₉₉(NH₃)₂₈(H₃PO₄), and
 285 (CH₂O)₇₉₉(NH₃)₆₁(H₃PO₄). Equations 6a to 6c conceptually describe the synthesis of these organic substances.

289 As indicated by the N mass balance in Table 3, the annual crop production in Switzerland consumes 148 kg N
 290 ha⁻¹ a⁻¹ (10.57 kmol N ha⁻¹ a⁻¹). According to Equations 6a to 6c, this NO₃⁻ assimilation is accompanied by

proton consumption of 11.41, 11.32, and 10.91 kmol H⁺ ha⁻¹ a⁻¹, respectively. Furthermore, Cheng et al. (2000) reported root respiration equaled about 20% of primary production. Thus, crop production is expected to contribute 67.6, 60.3, and 27.7 kmol CO₂ ha⁻¹ a⁻¹ to the annual CO₂ load of the soil, depending on the C:N ratio of the harvested organic matter.

Furthermore, it follows that the assimilation of 10.57 kmol NO₃⁻ ha⁻¹ a⁻¹ results in CO₂ assimilation rates of 338 (Equation 6a), 302 (Equation 6b), and 138 kmol ha⁻¹ a⁻¹ (Equation 6c). That is, the lower the atomic C:N ratio of the harvested crop material is, the less organic carbon that can be produced with a given amount of N.

4.6 Nitrate and acidity removal, and CO₂ generation due to denitrification

According to the N mass balance shown in Table 3, agricultural soils in Switzerland lose 4.5 kmol NO₃⁻ ha⁻¹ a⁻¹ via denitrification. Although all of the groundwaters included in this analysis were oxic, anoxic zones must exist locally in most soils in order to allow denitrification. In that process, organic matter (generically represented as CH₂O) is oxidized with NO₃⁻ as the electron acceptor, as follows:

Thus, acidity is removed as NO₃⁻ is transformed to N₂, tending to decrease carbonate dissolution (i.e., decreasing Equation 2); but more CO₂ is released than H⁺ is consumed, tending to result in a net increase of carbonate dissolution and an increase of alkalinity (Equation 3).

4.7 Agricultural soils emit CO₂ to the atmosphere

Because all groundwater samples in this analysis were supersaturated with respect to their CO₂ concentration (Figure 1b), the CO₂ content of the soil gas must have greatly exceeded the atmospheric pCO₂ as a consequence of i) mineralization of organic manure, ii) root respiration, iii) denitrification, and iv) respiration by heterotrophic soil organisms (neglected in Figure 3). Due to the difference in pCO₂ between soil and atmosphere, soils act as a CO₂ source to the atmosphere. For example, CO₂ emission rates reported in the literature range from 300 and 1200 kmol ha⁻¹ a⁻¹ (Haber 1957; Duiker et al. 2000; Jacinthe et al. 2002; Jones et al., 2005; Schulte-Bisping et al. 2012; Hagedorn et al. 2018).

We estimated the average soil CO₂ emission rate (transfer of CO₂ from soil to atmosphere) of Swiss farmland, as follows:

- i) Given the estimated NO_3^- and proton loads of the groundwater (Figure 3), we determined the amount of CO_2 that would dissolve in the water annually draining a calcareous watershed ($5000 \text{ m}^3 \text{ ha}^{-1} \text{ a}^{-1}$), in order to result in circumneutral groundwater with an alkalinity of approximately 6 mmol L^{-1} .
- ii) Applying a solubility product of $\text{pK}_{\text{so}} = 8.404$ at 8°C , ChemEQL speciation predicts a groundwater pH of 7.08 and an alkalinity of 5.74 mmol L^{-1} , if 18 kmol CO_2 and $5.6\text{--}6.1 \text{ kmol H}^+$ annually dissolve in 5000 m^3 of water for all three C:N scenarios (yellow circles in Figures 1a-d).
- iii) Assuming that the annual in-soil CO_2 production equals the total annual losses to the atmosphere and the draining groundwater, we then subtracted the CO_2 consumed by calcite dissolution from the total loads estimated from Equations 6a-c (Figure 3).

The resulting soil emission rates of 292 (Equation 6a), 286 (Equation 6b) and $252 \text{ kmol CO}_2 \text{ ha}^{-1} \text{ a}^{-1}$ (Equation 6c) range at the lower end of the rates reported in the literature (see above), likely because the CO_2 balance sketched in Figure 3 neglects CO_2 production by heterotrophic organisms of higher trophic levels. Additionally, those other authors measured emission rates experimentally with flux chambers covering a soil area of only about 1 m^2 , whereas we indirectly estimated an average emission rate based on nationwide information about the agricultural N balance. Although many physical and biogeochemical processes can contribute to the inorganic carbon balance in fertilized agricultural soils, we believe the agreement of groundwater measurements and our modeled estimates (yellow points in Figure 1) is a strong indication that we have considered the main processes.

4.8 Why alkalinity and nitrate concentrations as well as CO_2 emissions from the soil to the atmosphere are 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). As sketched in Figure 3, mineralization of increasing amounts of manure stimulates growth-dependent N uptake but also results in increased groundwater NO_3^- and alkalinity concentrations, mainly due to the coupling of in-soil CO_2 and proton production with manure mineralization, plant growth, and denitrification.

Consequently, according to the concept of nutrient-limited growth, groundwater alkalinity must asymptotically approach a maximum at elevated NO_3^- concentrations, as empirically demonstrated in Figure 1a, when crop production is no longer limited by N availability. Thus, the results presented in Figure 1 suggest that manure

345 application resulting in soil-water concentrations exceeding $0.25 \text{ mmol NO}_3^- \text{ L}^{-1}$ no longer fuels N assimilation
 346 by crop plants but only results in an increasing loss of NO_3^- to the aquifer. Consistent with this hypothesis, the
 347 maximum groundwater alkalinity reported by Hamilton et al. (2007) in intensively-fertilized and -limed
 348 agricultural systems in Michigan, USA was only slightly less than the maximum in the Swiss groundwaters [6-7
 349 meq L^{-1} (equivalent to 6-7 $\text{mmol HCO}_3^- \text{ L}^{-1}$) in the Michigan groundwaters versus 7-8 $\text{mmol HCO}_3^- \text{ L}^{-1}$ in the
 350 Swiss groundwaters], even at NO_3^- concentrations greater than 10-fold higher than in the Swiss groundwaters
 351 (i.e., up to 10-11 $\text{mmol NO}_3^- \text{ L}^{-1}$ *versus* up to 0.8-0.9 $\text{mmol NO}_3^- \text{ L}^{-1}$).

352 In addition, the increase of CO_2 supersaturation (Figure 1b) and the accompanying decrease in pH (Figure 1c) as
 353 NO_3^- concentration increases suggest that at least two physical-chemical processes might also contribute to the
 354 leveling-off of alkalinity at high NO_3^- concentrations.

355 1. Not all of the biogenic CO_2 and protons are consumed by carbonate-dissolution reactions. As $\text{pCO}_2(\text{aq})$
 356 increases and pH concurrently decreases, the extent to which H_2CO_3 dissociates into HCO_3^- and CO_3^{2-}
 357 decreases because increasingly greater percentages of the DIC remain as H_2CO_3 as the H^+
 358 concentration increases. This is best illustrated by a Bjerrum plot (e.g., Stumm and Morgan 1996: p.
 359 160). Thereby, alkalinity increases at a decreasing rate as $\text{pCO}_2(\text{aq})$ increases.

360 2. As pCO_2 increases in the soil, the rate of diffusive losses of CO_2 to the atmosphere increases.

361 4.9 Surface Waters

362 Because groundwater exfiltrates to riverbeds and then flows via the rivers into the lakes, alkalinity and NO_3^- are
 363 also positively correlated in calcareous surface waters (Figure 2a). When CO_2 -supersaturated groundwater
 364 exfiltrates and becomes surface water, much of the above-saturation CO_2 diffuses into the atmosphere.
 365 Additionally, photoautotrophic organisms may assimilate some of the CO_2 . Both processes lead to the observed
 366 higher pH and lower Ω_{CO_2} values in rivers and lakes than in groundwaters at similar NO_3^- concentrations.
 367 Nevertheless, CO_2 concentrations in the river and lake waters did not reach equilibrium with the atmospheric
 368 pCO_2 , most likely because of heterotrophic mineralization and slow diffusional loss of the CO_2 to the
 369 atmosphere (Hotchkiss et al. 2015).

370 Calcite would be expected to precipitate due to the loss of CO_2 and the rising pH when groundwater exfiltrates.
 371 However, it remained oversaturated in surface waters (Figure 2b), indicating that precipitation of calcite often is

372 kinetically constrained (Plummer et al. 1979) and/or at least partly inhibited (e.g., by elevated phosphate
373 concentrations; Langmuir 1997: p. 222; Müller et al. 2016).

374 In addition, surface-water quality is subjected to surface runoff and wastewater discharges. Wastewater loads to
375 a river may alter its groundwater-derived alkalinity- NO_3^- relationship in several ways. First, introduction of
376 NH_4^+ -containing wastewater into well-oxygenated river water results in nitrification that increases the NO_3^-
377 concentration but simultaneously decreases pH and alkalinity if carbonate minerals are not present (Equation S-
378 1 in SI Table S1) or do not dissolve fast enough, thus contributing to an additional release of CO_2 to the
379 atmosphere. Second, the introduction of large amounts of wastewater-derived dissolved organic matter
380 stimulates microbial respiration, resulting in low O_2 concentrations that favor denitrification and/or
381 dissimilatory NO_3^- reduction to ammonia, both of which decrease NO_3^- concentrations but increase alkalinity
382 even in the absence of carbonate minerals (Equations S-10 to S-12 in SI Table S1).

383 Consequently, as demonstrated by Abril et al. (2000) and Abril and Frankignoulle (2001) in the highly-polluted
384 Scheldt Basin (Belgium and Netherlands), large wastewater loads can induce N transformations in river water
385 and change its acid-base properties to the extent that the positive relationship between alkalinity and NO_3^-
386 concentration observed in calcareous soils completely reverses in a river.

387

388 **5. Summary and Conclusions**

389 Alkalinity clearly increases with increasing NO_3^- concentrations in Swiss groundwater (Figure 1a). Based on the
390 N balance for Swiss agriculture (Table 3), a conceptual model inter-relating the biogeochemical processes
391 permits a semi-quantitative understanding of why and how alkalinity depends on N-fertilizer application. As a
392 result, we demonstrate that N-fertilizer application i) increases groundwater alkalinity and thereby accelerates
393 carbonate weathering rate about four-fold, and ii) results in a minimum soil emission of approximately 250
394 $\text{kmol CO}_2 \text{ ha}^{-1} \text{ a}^{-1}$. This is likely a conservative estimate, because it does not consider CO_2 production by all
395 heterotrophic soil organisms and neglects that CO_2 -supersaturated groundwater releases CO_2 to the atmosphere
396 after exfiltration to the surface.

397 As atmospheric CO_2 concentrations increase and thus riverine, lake, and oceanic pH values decrease through
398 time, the proportion of the DIC that precipitates as CaCO_3 after CO_2 -oversaturated aquifer waters exfiltrate to

399 surface-water bodies will decrease, and the proportion that is released to the atmosphere as gaseous CO₂ will
400 increase. Therefore, continued N-fertilization will contribute to ongoing global CO₂ enrichment of the
401 atmosphere and will promote in-soil calcite dissolution; thus, it will accelerate the translocation of DIC from
402 calcareous soils to downstream reaches in surface waterways and eventually to the oceans.

403 Dissolution of calcite appears to cease in these mostly manure-fertilized Swiss soils when the groundwater NO₃⁻
404 concentration exceeds 0.3 mmol L⁻¹ (Figure 1a), likely because additional fertilization does not further fuel
405 primary production and thus root respiration. However, addition of NH₄-containing commercial fertilizers could
406 further increase proton production and NO₃⁻ concentrations, thus increasing the maximum calcite dissolution
407 even further. Tolerance limits for drinking water (0.4 and 0.7 mmol NO₃⁻ L⁻¹ in Switzerland and USA,
408 respectively) exceed the 0.3 mmol NO₃⁻ L⁻¹ break-point concentration by up to approximately two-fold.
409 Accordingly, ecologically meaningful and economically efficient agricultural practice that would avoid over-
410 fertilization with N (i.e., not exceeding 0.25 mmol NO₃⁻ L⁻¹) would pose no risk for a groundwater drinking-
411 water supply.

412

413

414 **Information about the Supplement**

415 Table S-1 lists chemical reactions for the nitrification of some common N-fertilizers and several other processes
416 in groundwaters and surface waters in the presence and absence of carbonate minerals. Table S-2 reports results
417 of regressions of alkalinity *versus* NO₃⁻ concentration in Swiss groundwaters, Canton Zürich well waters, and
418 Swiss lakes and rivers.

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

421 *Competing interests.* The authors declare that they have no conflict of interest.

422 *Data availability.* The groundwater datasets analyzed during the current study are not publicly available because
423 they belong to the Canton of Zürich and the Swiss Federal Office for the Environment (FOEN), but they are
424 available from the corresponding author on reasonable request.

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 574

575 **Table 1:** Data sources.

576

577

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 >1.42 mmol L ⁻¹ . Groundwater data were from 42 watersheds during 1997-2016 (NAQUA, 2017); averages were calculated over all years. Well-water data were from 120 wells along rivers in the Canton of Zürich during 1991-2016 (WWEA, 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 >1.42 mmol L ⁻¹ . Lake data were from 21 lakes (0.2-580 km ²) during 1980-2015 (FOEN, 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 were from 22 stations on 12 rivers during 5- to 44-year monitoring periods (Eawag, 2017).	0.017 - 0.219	1.52 - 5.03

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Table 2: Regressions of alkalinity *versus* nitrate (NO₃⁻) concentration for the Swiss aquifers in Figure 1a.^a

NO ₃ ⁻ range for regression (mmol L ⁻¹)	Slope		Intercept		Regression R ²	n
	Value (mmol Alk/ mmol NO ₃ ⁻)	p	Value (mmol L ⁻¹)	p		
<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

^a 95% confidence intervals of slopes and intercepts are in parentheses; “p” is the Type 1 error probability in a test of the null hypothesis that the slope (or intercept) equals 0; Alk = alkalinity.

589 **Table 3:** Averaged nitrogen (N) budget for agricultural soils (10,490 km²) in Switzerland (FOAG, 2018).
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Input/output	Annual N flux kg N ha ⁻¹ a ⁻¹	Reference
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)
NH ₄ NO ₃ (60%)	30	FOAG (2016)
Urea (20%)	10	FOAG (2016)
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	
N removal with crop	148	FSO (2014)
Excess N deposition	85	FSO (2014)
N removal by groundwater to surface waters	22	Hürdler et al. (2015)
N load to the atmosphere by denitrification	63	

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594 **Figure 1:**

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599 **Figure 1:** Relationships between nitrate (NO_3^-) concentration and (a) alkalinity, (b) Ω_{CO_2} (CO_2 saturation
600 index), (c) pH, (d) molar $([\text{Ca}]+[\text{Mg}])/[\text{HCO}_3^-]$ ratio, and (e) Ω_{calcite} (calcite $[\text{CaCO}_3]$ saturation index) in
601 aquifers in calcareous catchments in Switzerland that had alkalinity >1.42 mmol L⁻¹. These include 42
602 groundwaters across the country (red) and 120 wells in the Canton of Zürich (blue) (Table 1). The yellow circle
603 depicts the resulting alkalinity for the estimated average loads of 1.52 kmol N ha⁻¹ a⁻¹ and 5.8 kmol H⁺ ha⁻¹ a⁻¹,
604 and p CO_2 of 0.022 atm (see section 4.7 in the text) and a groundwater formation rate of 5000 m³ ha⁻¹ a⁻¹. The
605 yellow square depicts the alkalinity and NO_3^- concentration in a natural system without fertilization and without

606 crop harvest, but with the current atmospheric N deposition of $1.86 \text{ kmol ha}^{-1} \text{ a}^{-1}$. The yellow diamond depicts
 607 the situation of pure water in equilibrium with calcite and the pCO_2 of the atmosphere. The speciation
 608 calculations were performed considering the activities of the ions (Debye-Hückel-approximation), which was
 609 essential for the appropriate estimation of the dissolution of calcite. Linear-regression slopes and intercepts
 610 shown by the dashed black lines in panel a) are listed in Table 2.

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614 **Figure 2:**

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618 **Figure 2:** (a) Alkalinity increases with increasing nitrate (NO_3^-) concentrations in lakes and rivers in calcareous
 619 catchments in Switzerland. (b) River water is always supersaturated with respect to calcite (Ω_{calcite} = calcite-
 620 saturation index).

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Figure 3:

Figure 3: Postulated nitrogen (N), proton (H^+) and CO_2 balances for Swiss agricultural soil based on a total annual application of manure, Leguminosae, urea, and inorganic N-fertilizers corresponding to 14.8 kmol N ha⁻¹ a⁻¹. Green indicates fluxes of N, red indicates fluxes of H^+ , and blue indicates fluxes of CO_2 . Numbers are given in [kmol ha⁻¹ a⁻¹]. Consult the text for additional explanation.