

**Supplemental Information File  
for**

**Nitrogen fertilization of soils fuels carbonate weathering and translocation in  
calcareous watersheds**

Beat Müller<sup>\*1</sup>, Joseph S. Meyer<sup>2,3</sup>, René Gächter<sup>1</sup>

<sup>1</sup> Eawag, Swiss Federal Institute of Aquatic Science and Technology, CH-6047 Kastanienbaum, Switzerland

<sup>2</sup> Department of Chemistry, Colorado School of Mines, Golden, Colorado 80401 USA

<sup>3</sup> Applied Limnology Professionals LLC, Golden, Colorado 80401 USA

\* Correspondence: beat.mueller@eawag.ch

February 25, 2020

Table S1. Nitrification of some common N-fertilizers (Walworth 2013) and several other pertinent chemical reactions in groundwaters and surface waters, in the absence and presence of carbonate minerals; and the associated molar  $\Delta[\text{HCO}_3^-]:\Delta[\text{NO}_3^-]$  and  $\Delta([\text{Ca}]+[\text{Mg}]):\Delta[\text{HCO}_3^-]$  ratios. --- = not listed if either the numerator or denominator is not part of the listed chemical reaction.

Mineral present	Chemical and transformation	Reactions	Molar $\Delta[\text{HCO}_3^-]:\Delta[\text{NO}_3^-]$ ratio	Molar $\Delta([\text{Ca}]+[\text{Mg}]):\Delta[\text{HCO}_3^-]$ ratio	Equation number
None	Anhydrous ammonia ( $\text{NH}_3$ ): Nitrification	$\text{NH}_3 + \text{H}_2\text{O} + 2\text{O}_2 = \text{NH}_4^+ + \text{OH}^- + 2\text{O}_2 = \text{NO}_3^- + 2\text{H}_2\text{O} + \text{H}^+$	---	---	S-1
	Ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ): Nitrification	$\text{NH}_4\text{NO}_3 + 2\text{O}_2 = 2\text{NO}_3^- + \text{H}_2\text{O} + 2\text{H}^+$	---	---	S-2
	Diammonium phosphate ( $(\text{NH}_4)_2\text{HPO}_4$ ): Nitrification	$(\text{NH}_4)_2\text{HPO}_4 + 4\text{O}_2 = 2\text{NO}_3^- + \text{HPO}_4^{2-} + 2\text{H}_2\text{O} + 4\text{H}^+$	---	---	S-3
	Ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ): Nitrification	$(\text{NH}_4)_2\text{SO}_4 + 4\text{O}_2 = 2\text{NO}_3^- + \text{SO}_4^{2-} + 2\text{H}_2\text{O} + 4\text{H}^+$	---	---	S-4
	Urea ( $(\text{NH}_2)_2\text{CO}$ ): Nitrification	$(\text{NH}_2)_2\text{CO} + 4\text{O}_2 = 2\text{NO}_3^- + \text{CO}_2 + \text{H}_2\text{O} + 2\text{H}^+ = 2\text{NO}_3^- + \text{HCO}_3^- + 3\text{H}^+$	0.5	---	S-5
	Nitric acid ( $\text{HNO}_3$ ): Dissociation	$\text{HNO}_3 = \text{NO}_3^- + \text{H}^+$	---	---	S-6
	Carbon dioxide / carbonic acid ( $\text{CO}_2 / \text{H}_2\text{CO}_3$ ): Dissolution & dissociation	$\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3 = \text{HCO}_3^- + \text{H}^+$	---	---	S-7
	Sugars ( $\{\text{CH}_2\text{O}\}$ ) <sup>c</sup> : Respiration	$\{\text{CH}_2\text{O}\} + \text{O}_2 = \text{CO}_2 + \text{H}_2\text{O} = \text{HCO}_3^- + \text{H}^+$	---	---	S-8
	Organic matter ( $\text{C}_{106}\text{H}_{263}\text{O}_{110}\text{N}_{16}\text{P}$ ) <sup>d</sup> : Mineralization	$\text{C}_{106}\text{H}_{263}\text{O}_{110}\text{N}_{16}\text{P} + 138\text{O}_2 = 16\text{NO}_3^- + \text{HPO}_4^{2-} + 106\text{CO}_2 + 122\text{H}_2\text{O} + 18\text{H}^+ = 16\text{NO}_3^- + \text{HPO}_4^{2-} + 106\text{HCO}_3^- + 16\text{H}_2\text{O} + 124\text{H}^+$	6.625	---	S-9
	Nitrate ( $\text{NO}_3^-$ ): Denitrification	$4\text{NO}_3^- + 5\{\text{CH}_2\text{O}\} = 2\text{N}_2(\text{g}) + 5\text{HCO}_3^- + 2\text{H}_2\text{O} + \text{H}^+$ or $2\text{NO}_3^- + 2\{\text{CH}_2\text{O}\} = \text{N}_2\text{O}(\text{g}) + 2\text{HCO}_3^- + \text{H}_2\text{O}$	-1.25	---	S-10
	Nitrate ( $\text{NO}_3^-$ ): Dissimilatory nitrate reduction to ammonia	$\text{NO}_3^- + 2\{\text{CH}_2\text{O}\} + \text{H}_2\text{O} = \text{NH}_4^+ + 2\text{HCO}_3^-$	-2.0	---	S-11

Table S1 (continued).

Mineral present	Chemical and transformation	Reactions	Molar $\Delta[\text{HCO}_3^-]:\Delta[\text{NO}_3^-]$ ratio	Molar $\Delta([\text{Ca}]+[\text{Mg}]):\Delta[\text{HCO}_3^-]$ ratio	Equation number
Carbonates $(\text{Ca}_x\text{Mg}_{(1-x)}\text{CO}_3)^e$	Anhydrous ammonia ( $\text{NH}_3$ ): Nitrification	$\text{Ca}_x\text{Mg}_{(1-x)}\text{CO}_3 + \text{NH}_3 + \text{H}_2\text{O} + 2\text{O}_2 = \text{Ca}_x\text{Mg}_{(1-x)}\text{CO}_3 + \text{NH}_4^+ + \text{OH}^- + 2\text{O}_2 = x\text{Ca}^{2+} + (1-x)\text{Mg}^{2+} + \text{NO}_3^- + \text{HCO}_3^- + 2\text{H}_2\text{O}$	1.0	1.0	S-13
	Ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ): Nitrification	$2\text{Ca}_x\text{Mg}_{(1-x)}\text{CO}_3 + \text{NH}_4\text{NO}_3 + 2\text{O}_2 = 2x\text{Ca}^{2+} + 2(1-x)\text{Mg}^{2+} + 2\text{NO}_3^- + 2\text{HCO}_3^- + \text{H}_2\text{O}$	1.0	1.0	S-14
	Diammonium phosphate ( $(\text{NH}_4)_2\text{HPO}_4$ ): Nitrification	$4\text{Ca}_x\text{Mg}_{(1-x)}\text{CO}_3 + (\text{NH}_4)_2\text{HPO}_4 + 4\text{O}_2 = 4x\text{Ca}^{2+} + 4(1-x)\text{Mg}^{2+} + 2\text{NO}_3^- + \text{HPO}_4^{2-} + 4\text{HCO}_3^- + 2\text{H}_2\text{O}$	2.0	1.0	S-15
	Ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ): Nitrification	$4\text{Ca}_x\text{Mg}_{(1-x)}\text{CO}_3 + (\text{NH}_4)_2\text{SO}_4 + 4\text{O}_2 = 4x\text{Ca}^{2+} + 4(1-x)\text{Mg}^{2+} + 2\text{NO}_3^- + \text{SO}_4^{2-} + 4\text{HCO}_3^- + 2\text{H}_2\text{O}$	2.0	1.0	S-16
	Urea ( $(\text{NH}_2)_2\text{CO}$ ): Nitrification	$3\text{Ca}_x\text{Mg}_{(1-x)}\text{CO}_3 + (\text{NH}_2)_2\text{CO} + 4\text{O}_2 = 3x\text{Ca}^{2+} + 3(1-x)\text{Mg}^{2+} + 2\text{NO}_3^- + 4\text{HCO}_3^-$	2.0	0.75	S-17
	Nitric acid ( $\text{HNO}_3$ ): Dissociation	$\text{Ca}_x\text{Mg}_{(1-x)}\text{CO}_3 + \text{HNO}_3 = x\text{Ca}^{2+} + (1-x)\text{Mg}^{2+} + \text{NO}_3^- + \text{HCO}_3^-$	1.0	1.0	S-18
	Carbon dioxide / carbonic acid ( $\text{CO}_2 / \text{H}_2\text{CO}_3$ ): Dissolution & dissociation	$\text{Ca}_x\text{Mg}_{(1-x)}\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} = x\text{Ca}^{2+} + (1-x)\text{Mg}^{2+} + 2\text{HCO}_3^-$	---	0.5	S-19
	Sugars ( $\{\text{CH}_2\text{O}\}$ ) <sup>c</sup> : Respiration	$\text{Ca}_x\text{Mg}_{(1-x)}\text{CO}_3 + \{\text{CH}_2\text{O}\} + \text{O}_2 = x\text{Ca}^{2+} + (1-x)\text{Mg}^{2+} + 2\text{HCO}_3^-$	---	0.5	S-20
	Organic matter ( $\text{C}_{106}\text{H}_{263}\text{O}_{110}\text{N}_{16}\text{P}$ ) <sup>d</sup> : Mineralization	$124\text{Ca}_x\text{Mg}_{(1-x)}\text{CO}_3 + \text{C}_{106}\text{H}_{263}\text{O}_{110}\text{N}_{16}\text{P} + 138\text{O}_2 = 124x\text{Ca}^{2+} + 124(1-x)\text{Mg}^{2+} + 16\text{NO}_3^- + \text{HPO}_4^{2-} + 230\text{HCO}_3^- + 16\text{H}_2\text{O}$	14.375	0.539	S-21
	Nitrate ( $\text{NO}_3^-$ ): Denitrification	$\text{Ca}_x\text{Mg}_{(1-x)}\text{CO}_3 + 4\text{NO}_3^- + 5\{\text{CH}_2\text{O}\} = x\text{Ca}^{2+} + (1-x)\text{Mg}^{2+} + 2\text{N}_2(\text{g}) + 6\text{HCO}_3^- + 2\text{H}_2\text{O}$ or $\text{Ca}_x\text{Mg}_{(1-x)}\text{CO}_3 + 2\text{NO}_3^- + 2\{\text{CH}_2\text{O}\} = x\text{Ca}^{2+} + (1-x)\text{Mg}^{2+} + \text{N}_2\text{O}(\text{g}) + 3\text{HCO}_3^- + \text{OH}^-$	-1.5	0.167	S-22
Nitrate ( $\text{NO}_3^-$ ): Dissimilatory nitrate reduction to ammonia		$\text{Ca}_x\text{Mg}_{(1-x)}\text{CO}_3 + \text{NO}_3^- + 2\{\text{CH}_2\text{O}\} + 2\text{H}_2\text{O} = x\text{Ca}^{2+} + (1-x)\text{Mg}^{2+} + \text{NH}_4^+ + 3\text{HCO}_3^- + \text{OH}^-$	-3.0	0.333	S-24

<sup>a</sup>  $\{\text{CH}_2\text{O}\}$  = generic chemical formula for sugars (e.g., glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ ).<sup>b</sup> Based on Redfield ratio; equivalent to  $(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4)$  (Stumm and Morgan 1996: page 887).<sup>c</sup> Generic formula for a mixture of calcium- and magnesium-containing carbonates.

Table S2. Regressions of alkalinity *versus* nitrate ( $\text{NO}_3^-$ ) for the Swiss groundwaters, Canton Zürich well waters, Swiss lakes, and Swiss rivers in Figure 1 in the accompanying text. 95% confidence intervals of slopes and intercepts are in parentheses; “p” is the type 1 error probability for a test of the null hypothesis that the slope (or intercept) equals 0 (i.e.,  $p < 0.05$  indicates significant difference from zero); Alk = alkalinity.

Waters	$\text{NO}_3^-$ range for regression (mmol/L)	Slope		Intercept		Regression $R^2$	n
		Value (meq Alk/ mmol $\text{NO}_3^-$ )	p	Value (meq/L)	p		
Swiss groundwaters	<0.25	14.23 (10.66 - 17.81)	<0.001	2.44 (1.94 - 2.94)	<0.001	0.785	21
	>0.25	2.78 (0.24 - 5.32)	0.034	4.75 (3.67 - 5.83)	<0.001	0.216	21
Canton Zürich well waters	<0.25	17.46 (12.78 - 22.14)	<0.001	2.57 (1.80 - 3.34)	<0.001	0.628	36
	>0.25	1.51 (0.39 - 2.64)	0.009	5.86 (5.36 - 6.35)	<0.001	0.080	84
Swiss lakes	<0.25	17.00 (12.05 - 21.95)	<0.001	1.69 (1.29 - 2.08)	<0.001	0.731	21
Swiss rivers	<0.25	11.82 (10.38 - 13.25)	<0.001	1.57 (1.41 - 1.72)	<0.001	0.937	22