Supplemental Information File
for

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

Beat Müller[*1], Joseph S. Meyer[2,3], René Gächter[1]

[1] Eawag, Swiss Federal Institute of Aquatic Science and Technology, CH-6047 Kastanienbaum, Switzerland
[2] Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado 80401 USA
[3] Applied Limnology Professionals LLC, Golden, Colorado 80401 USA

* Correspondence: beat.mueller@eawag.ch

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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 $\Delta[HCO_3^-]:\Delta[NO_3^-]$ and $\Delta([Ca]+[Mg]):\Delta[HCO_3^-]$ ratios. --- = not listed if either the numerator or denominator is not part of the listed chemical reaction.

Mineral present	Chemical and transformation	Reactions	**Molar $\Delta[HCO_3^-]:\Delta[NO_3^-]$ ratio**	**Molar $\Delta([Ca]+[Mg]):\Delta[HCO_3^-]$ ratio**	Equation number
None	Anhydrous ammonia (NH_3): Nitrification	$NH_3 + H_2O + 2O_2 = NH_4^+ + OH^- + 2O_2 =$ $NO_3^- + 2H_2O + H^+$	---	---	S-1
	Ammonium nitrate (NH_4NO_3): Nitrification	$NH_4NO_3 + 2O_2 =$ $2NO_3^- + H_2O + 2H^+$	---	---	S-2
	Diammonium phosphate ($(NH_4)_2HPO_4$): Nitrification	$(NH_4)_2HPO_4 + 4O_2 =$ $2NO_3^- + HPO_4^{2-} + 2H_2O + 4H^+$	---	---	S-3
	Ammonium sulfate $(NH_4)_2SO_4$): Nitrification	$(NH_4)_2SO_4 + 4O_2 =$ $2NO_3^- + SO_4^{2-} + 2H_2O + 4H^+$	---	---	S-4
	Urea ($(NH_2)_2CO$): Nitrification	$(NH_2)_2CO + 4O_2 = 2NO_3^- + CO_2 + H_2O + 2H^+ =$ $2NO_3^- + HCO_3^- + 3H^+$	0.5	---	S-5
	Nitric acid (HNO_3): Dissociation	$HNO_3 =$ $NO_3^= + H^+$	---	---	S-6
	Carbon dioxide / carbonic acid (CO_2 / H_2CO_3): Dissolution & dissociation	$CO_2 + H_2O =$ $H_2CO_3 = HCO_3^- + H^+$	---	---	S-7
	Sugars ($\{CH_2O\}$) [c]: Respiration	$\{CH_2O\} + O_2 =$ $CO_2 + H_2O = HCO_3^- + H^+$	---	---	S-8
	Organic matter ($C_{106}H_{263}O_{110}N_{16}P$) [d]: Mineralization	$C_{106}H_{263}O_{110}N_{16}P + 138O_2 =$ $16NO_3^- + HPO_4^{2-} + 106CO_2 + 122H_2O + 18H^+ =$ $16NO_3^- + HPO_4^{2-} + 106HCO_3^- + 16H_2O + 124H^+$	6.625	---	S-9
	Nitrate (NO_3^-): Denitrification	$4NO_3^- + 5\{CH_2O\} =$ $2N_2(g) + 5HCO_3^- + 2H_2O + H^+$	-1.25	---	S-10
		or $2NO_3^- + 2\{CH_2O\} =$ $N_2O(g) + 2HCO_3^- + H_2O$	-1.0	---	S-11
	Nitrate (NO_3^-): Dissimilatory nitrate reduction to ammonia	$NO_3^- + 2\{CH_2O\} + H_2O =$ $NH_4^+ + 2HCO_3^-$	-2.0	---	S-12

Table S1 (continued).

Mineral present	Chemical and transformation	Reactions	**Molar $\Delta[HCO_3^{-}]:\Delta[NO_3^{-}]$ ratio**	**Molar $\Delta([Ca]+[Mg]):\Delta[HCO_3^{-}]$ ratio**	Equation number
Carbonates ($Ca_xMg_{(1-x)}CO_3$) [e]	Anhydrous ammonia (NH_3): Nitrification	$Ca_xMg_{(1-x)}CO_3 + NH_3 + H_2O + 2O_2 =$ $Ca_xMg_{(1-x)}CO_3 + NH_4^+ + OH^- + 2O_2 =$ $xCa^{2+} + (1-x)Mg^{2+} + NO_3^- + HCO_3^- + 2H_2O$	1.0	1.0	S-13
	Ammonium nitrate (NH_4NO_3): Nitrification	$2Ca_xMg_{(1-x)}CO_3 + NH_4NO_3 + 2O_2 =$ $2xCa^{2+} + 2(1-x)Mg^{2+} + 2NO_3^- + 2HCO_3^- + H_2O$	1.0	1.0	S-14
	Diammonium phosphate ($(NH_4)_2HPO_4$): Nitrification	$4Ca_xMg_{(1-x)}CO_3 + (NH_4)_2HPO_4 + 4O_2 =$ $4xCa^{2+} + 4(1-x)Mg^{2+} + 2NO_3^- + HPO_4^{2-} + 4HCO_3^- + 2H_2O$	2.0	1.0	S-15
	Ammonium sulfate ($(NH_4)_2SO_4$): Nitrification	$4Ca_xMg_{(1-x)}CO_3 + (NH_4)_2SO_4 + 4O_2 =$ $4xCa^{2+} + 4(1-x)Mg^{2+} + 2NO_3^- + SO_4^{2-} + 4HCO_3^- + 2H_2O$	2.0	1.0	S-16
	Urea ($(NH_2)_2CO$): Nitrification	$3Ca_xMg_{(1-x)}CO_3 + (NH_2)_2CO + 4O_2 =$ $3xCa^{2+} + 3(1-x)Mg^{2+} + 2NO_3^- + 4HCO_3^-$	2.0	0.75	S-17
	Nitric acid (HNO_3): Dissociation	$Ca_xMg_{(1-x)}CO_3 + HNO_3 =$ $xCa^{2+} + (1-x)Mg^{2+} + NO_3^- + HCO_3^-$	1.0	1.0	S-18
	Carbon dioxide / carbonic acid (CO_2 / H_2CO_3): Dissolution & dissociation	$Ca_xMg_{(1-x)}CO_3 + CO_2 + H_2O =$ $xCa^{2+} + (1-x)Mg^{2+} + 2HCO_3^-$	---	0.5	S-19
	Sugars ($\{CH_2O\}$) [c]: Respiration	$Ca_xMg_{(1-x)}CO_3 + \{CH_2O\} + O_2 =$ $xCa^{2+} + (1-x)Mg^{2+} + 2HCO_3^-$	---	0.5	S-20
	Organic matter ($C_{106}H_{263}O_{110}N_{16}P$) [d]: Mineralization	$124Ca_xMg_{(1-x)}CO_3 + C_{106}H_{263}O_{110}N_{16}P + 138O_2 =$ $124xCa^{2+} + 124(1-x)Mg^{2+} + 16NO_3^- + HPO_4^{2-} + 230HCO_3^- + 16H_2O$	14.375	0.539	S-21
	Nitrate (NO_3^-): Denitrification	$Ca_xMg_{(1-x)}CO_3 + 4NO_3^- + 5\{CH_2O\} =$ $xCa^{2+} + (1-x)Mg^{2+} + 2N_2(g) + 6HCO_3^- + 2H_2O$ or $Ca_xMg_{(1-x)}CO_3 + 2NO_3^- + 2\{CH_2O\} =$ $xCa^{2+} + (1-x)Mg^{2+} + N_2O(g) + 3HCO_3^- + OH^-$	-1.5 -1.5	0.167 0.333	S-22 S-23
	Nitrate (NO_3^-): Dissimilatory nitrate reduction to ammonia	$Ca_xMg_{(1-x)}CO_3 + NO_3^- + 2\{CH_2O\} + 2H_2O =$ $xCa^{2+} + (1-x)Mg^{2+} + NH_4^+ + 3HCO_3^- + OH^-$	-3.0	0.333	S-24

[a] $\{CH_2O\}$ = generic chemical formula for sugars (e.g., glucose, $C_6H_{12}O_6$).
[d] Based on Redfield ratio; equivalent to $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)$ (Stumm and Morgan 1996: page 887).
[e] Generic formula for a mixture of calcium- and magnesium-containing carbonates.

Table S2. Regressions of alkalinity *versus* nitrate (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 probability value of the slope or intercept being equal to 0 (i.e., $p < 0.05$ indicates significant difference from zero); Alk = alkalinity; NS = not significant.

Waters	NO_3^- range for regression (mmol/L)	Slope			Intercept			Regression R^2	n
		Value (meq Alk/ mmol 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