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

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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.

<table>
<thead>
<tr>
<th>Mineral present</th>
<th>Chemical and transformation</th>
<th>Reactions</th>
<th>Molar $\Delta$[HCO$_3^-$]:$\Delta$[NO$_3^-$] ratio</th>
<th>Molar $\Delta$([Ca]+[Mg]):$\Delta$[HCO$_3^-$] ratio</th>
<th>Equation number</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>Anhydrous ammonia (NH$_3$): Nitrification</td>
<td>$\text{NH}_3 + \text{H}_2\text{O} + 2\text{O}_2 = \text{NH}_4^+ + \text{OH}^- + 2\text{O}_2$</td>
<td>---</td>
<td>---</td>
<td>S-1</td>
</tr>
<tr>
<td></td>
<td>Ammonium nitrate (NH$_4$NO$_3$): Nitrification</td>
<td>$\text{NH}_4\text{NO}_3 + 2\text{O}_2 = $</td>
<td>---</td>
<td>---</td>
<td>S-2</td>
</tr>
<tr>
<td></td>
<td>Diammonium phosphate ((NH$_4$)$_2$HPO$_4$): Nitrification</td>
<td>(NH$_4$)$_2$HPO$_4 + 4\text{O}_2 = $</td>
<td>---</td>
<td>---</td>
<td>S-3</td>
</tr>
<tr>
<td></td>
<td>Ammonium sulfate (NH$_4$)$_2$SO$_4$): Nitrification</td>
<td>(NH$_4$)$_2$SO$_4 + 4\text{O}_2 = $</td>
<td>---</td>
<td>---</td>
<td>S-4</td>
</tr>
<tr>
<td></td>
<td>Urea ((NH$_2$)$_2$CO): Nitrification</td>
<td>(NH$_2$)$_2$CO + 4O$_2 = 2\text{NO}_3^- + \text{CO}_2 + \text{H}_2\text{O} + 2\text{H}^+$</td>
<td>0.5</td>
<td>---</td>
<td>S-5</td>
</tr>
<tr>
<td></td>
<td>Nitric acid (HNO$_3$): Dissociation</td>
<td>HNO$_3 = $</td>
<td>---</td>
<td>---</td>
<td>S-6</td>
</tr>
<tr>
<td></td>
<td>Carbon dioxide / carbonic acid (CO$_2$ / H$_2$CO$_3$): Dissolution &amp; dissociation</td>
<td>CO$_2 + \text{H}_2\text{O} = $</td>
<td>---</td>
<td>---</td>
<td>S-7</td>
</tr>
<tr>
<td>Sugars ({CH$_2$O})$^6$: Respiration</td>
<td>(CH$_2$O) + O$_2 = $</td>
<td>CO$_2 + \text{H}_2\text{O} = \text{HCO}_3^- + \text{H}^+$</td>
<td>---</td>
<td>---</td>
<td>S-8</td>
</tr>
<tr>
<td>Organic matter (C$<em>{106}$H$</em>{203}$O$<em>{110}$N$</em>{16}$P$^{6}$): Mineralization</td>
<td>C$<em>{106}$H$</em>{203}$O$<em>{110}$N$</em>{16}$P$^{6}$ + 138O$_2 = $</td>
<td>6.625</td>
<td>---</td>
<td>---</td>
<td>S-9</td>
</tr>
<tr>
<td>Nitrate (NO$_3^-$): Denitrification</td>
<td>4NO$_3^- + 5$(CH$_2$O) =</td>
<td>-1.25</td>
<td>---</td>
<td>---</td>
<td>S-10</td>
</tr>
<tr>
<td></td>
<td>or 2NO$_3^- + 2$(CH$_2$O) =</td>
<td>-1.0</td>
<td>---</td>
<td>---</td>
<td>S-11</td>
</tr>
<tr>
<td>Nitrate (NO$_3^-$): Dissimilatory nitrate reduction to ammonia</td>
<td>NO$_3^- + 2$(CH$_2$O) + H$_2$O =</td>
<td>-2.0</td>
<td>---</td>
<td>---</td>
<td>S-12</td>
</tr>
</tbody>
</table>
Table S1 (continued).

<table>
<thead>
<tr>
<th>Mineral present (Ca$<em>{x}$Mg$</em>{1-x}$CO$_3$)</th>
<th>Chemical and transformation</th>
<th>Reactions</th>
<th>$\Delta$[HCO$_3^-$]:$\Delta$[NO$_3^-$] ratio</th>
<th>$\Delta$<a href="">(Ca+Mg)</a>:$\Delta$[HCO$_3^-$] ratio</th>
<th>Equation number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonates</td>
<td>Anhydrous ammonia (NH$_3$):</td>
<td>Ca$<em>x$Mg$</em>{1-x}$CO$_3$ + NH$_3$ + H$_2$O + 2O$_2$ =</td>
<td>1.0</td>
<td>1.0</td>
<td>S-13</td>
</tr>
<tr>
<td></td>
<td>Nitrification</td>
<td>Ca$<em>x$Mg$</em>{1-x}$CO$_3$ + NH$_4^+$ + OH$^-$ + 2O$_2$ =</td>
<td>xCa$^{2+}$ + (1-x)Mg$^{2+}$ + NO$_3^-$ + HCO$_3^-$ + 2H$_2$O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonium nitrate (NH$_4$NO$_3$):</td>
<td>Nitrification</td>
<td>2Ca$<em>x$Mg$</em>{1-x}$CO$_3$ + NH$_4$NO$_3$ + 2O$_2$ =</td>
<td>1.0</td>
<td>1.0</td>
<td>S-14</td>
</tr>
<tr>
<td></td>
<td>Diammonium phosphate ((NH$_4$)$_2$HPO$_4$):</td>
<td>4Ca$<em>x$Mg$</em>{1-x}$CO$_3$ + (NH$_4$)$_2$HPO$_4$ + 4O$_2$ =</td>
<td>2.0</td>
<td>1.0</td>
<td>S-15</td>
</tr>
<tr>
<td></td>
<td>Ammonium sulfate (NH$_4$)$_2$SO$_4$):</td>
<td>4Ca$<em>x$Mg$</em>{1-x}$CO$_3$ + (NH$_4$)$_2$SO$_4$ + 4O$_2$ =</td>
<td>2.0</td>
<td>1.0</td>
<td>S-16</td>
</tr>
<tr>
<td>Urea ((NH$_2$)$_2$CO):</td>
<td>Nitrification</td>
<td>3Ca$<em>x$Mg$</em>{1-x}$CO$_3$ + (NH$_2$)$_2$CO + 4O$_2$ =</td>
<td>2.0</td>
<td>0.75</td>
<td>S-17</td>
</tr>
<tr>
<td>Nitric acid (HNO$_3$):</td>
<td>Dissociation</td>
<td>Ca$<em>x$Mg$</em>{1-x}$CO$_3$ + HNO$_3$ =</td>
<td>1.0</td>
<td>1.0</td>
<td>S-18</td>
</tr>
<tr>
<td>Carbon dioxide / carbonic acid</td>
<td>(CO$_2$ / H$_2$CO$_3$): Dissolution &amp; dissociation</td>
<td>Ca$<em>x$Mg$</em>{1-x}$CO$_3$ + CO$_2$ + H$_2$O =</td>
<td>...</td>
<td>0.5</td>
<td>S-19</td>
</tr>
<tr>
<td>Sugars ((CH$_2$O))$^c$:</td>
<td>Respiration</td>
<td>Ca$<em>x$Mg$</em>{1-x}$CO$_3$ + (CH$_2$O) + O$_2$ =</td>
<td>...</td>
<td>0.5</td>
<td>S-20</td>
</tr>
<tr>
<td>Organic matter (C$<em>{108}$H$</em>{208}$O$<em>{110}$N$</em>{18}$P$^d$):</td>
<td>Mineralization</td>
<td>124Ca$<em>x$Mg$</em>{1-x}$CO$<em>3$ + C$</em>{108}$H$<em>{208}$O$</em>{110}$N$_{18}$P + 138O$_2$ =</td>
<td>14.375</td>
<td>0.539</td>
<td>S-21</td>
</tr>
<tr>
<td>Nitrate (NO$_3^-$):</td>
<td>Dentitrification</td>
<td>Ca$<em>x$Mg$</em>{1-x}$CO$_3$ + 4NO$_3^-$ + 5(CH$_2$O) =</td>
<td>-1.5</td>
<td>0.167</td>
<td>S-22</td>
</tr>
<tr>
<td></td>
<td>Dissimilatory nitrate reduction to ammonia</td>
<td>Ca$<em>x$Mg$</em>{1-x}$CO$_3$ + 2NO$_3^-$ + 2(CH$_2$O) =</td>
<td>-3.0</td>
<td>0.333</td>
<td>S-24</td>
</tr>
</tbody>
</table>

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$^a$ {CH$_2$O} = generic chemical formula for sugars (e.g., glucose, C$_6$H$_{12}$O$_6$).

$^b$ Based on Redfield ratio; equivalent to (CH$_2$O)$_{108}$(NH$_4$)$_{18}$(NH$_4$HPO$_4$) (Stumm and Morgan 1996: page 887).

$^c$ Generic formula for a mixture of calcium- and magnesium-containing carbonates.

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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.

<table>
<thead>
<tr>
<th>Waters</th>
<th>NO$_3^-$ range for regression (mmol/L)</th>
<th>Slope</th>
<th>Intercept</th>
<th>Regression R$^2$</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Value (meq Alk/ mmol NO$_3^-$)</td>
<td>p</td>
<td>Value (meq/L)</td>
<td>p</td>
</tr>
<tr>
<td>Swiss groundwaters</td>
<td>&lt;0.25</td>
<td>14.23 (10.66 - 17.81)</td>
<td>&lt;0.001</td>
<td>2.44 (1.94 - 2.94)</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td></td>
<td>&gt;0.25</td>
<td>2.78 (0.24 - 5.32)</td>
<td>0.034</td>
<td>4.75 (3.67 - 5.83)</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Canton Zürich well waters</td>
<td>&lt;0.25</td>
<td>17.46 (12.78 - 22.14)</td>
<td>&lt;0.001</td>
<td>2.57 (1.80 - 3.34)</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td></td>
<td>&gt;0.25</td>
<td>1.51 (0.39 - 2.64)</td>
<td>0.009</td>
<td>5.86 (5.36 - 6.35)</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Swiss lakes</td>
<td>&lt;0.25</td>
<td>17.00 (12.05 - 21.95)</td>
<td>&lt;0.001</td>
<td>1.69 (1.29 - 2.08)</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Swiss rivers</td>
<td>&lt;0.25</td>
<td>11.82 (10.38 - 13.25)</td>
<td>&lt;0.001</td>
<td>1.57 (1.41 - 1.72)</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>