Should we focus only on P load when aiming to reduce eutrophication in a P-limited aquatic system?

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Phosphorus was discovered by an alchemist.

‘The Discovery of Phosphorus’
by Joseph Wright (1734-1797)
Highly productive aquatic system

Gulf of Finland: ~3000 t y\(^{-1}\) BAP

PO\(_4\), NO\(_3\)

CO\(_2\)

Algae
\((\text{CH}_2\text{O})_{106}(\text{NH}_3)^{16}(\text{H}_3\text{PO}_4)\)

"Alchemy"
\(P, (N) \rightarrow \text{Org. C} \rightarrow P\)
**External sources**
- Dissolved: $\text{SO}_4^{2-}$
- Particulate: Fe(III) (hydr)oxides

**Algae**

**Morphology**

**Hydrodynamics**

**$O_2$**

**Sediment depth**

**Aerobic oxidation**

Denitrification: $4 \text{NO}_3^- + 5 \text{CH}_2\text{O} + 4 \text{H}^+ \rightarrow 2 \text{N}_2 + 5 \text{CO}_2 + 7 \text{H}_2\text{O}$

Manganese reduction: $2 \text{MnO}_2 + \text{CH}_2\text{O} + 4 \text{H}^+ \rightarrow \text{Mn}^{2+} + \text{CO}_2 + 3 \text{H}_2\text{O}$

Nitrate reduction: $\text{NO}_3^- + 2 \text{CH}_2\text{O} + 2 \text{H}^+ \rightarrow \text{NH}_4^+ + 2 \text{CO}_2 + \text{H}_2\text{O}$

Iron reduction: $4 \text{Fe(OH)}_3 + \text{CH}_2\text{O} + 8 \text{H}^+ \rightarrow 4 \text{Fe}^{2+} + \text{CO}_2 + 11 \text{H}_2\text{O}$

Sulphate reduction: $\text{SO}_4^{2-} + 2 \text{CH}_2\text{O} + 2 \text{H}^+ \rightarrow \text{H}_2\text{S} + 2 \text{CO}_2 + 2 \text{H}_2\text{O}$

**Reduction rates limited by the availability of electron acceptors**

Methanogenesis: $2 \text{CH}_2\text{O} \rightarrow \text{CO}_2 + \text{CH}_4$

**Anaerobic oxidation**

**P**
Microbial Fe(III) oxide reduction

Chemical Fe(III) oxide reduction

Potential effects of $SO_4$ and Fe(III) oxides

• "Alchemy"
  – Org. C + $SO_4$ $\rightarrow$ much P from sediments
  – Fresh-water $\rightarrow$ "Sea water"

• Hypothesized "alchemy"
  – Org. C + $SO_4$ + Fe(III) oxides $\rightarrow$ less P from sediments
Sediments taken from a eutrophic estuary
Incubated for ~ 2 months (10 °C, dark)
• Low and high SO$_4$ concentration
• Organic C (acetate, lactate)
Concentrations in the overlying water

Uncoupled Fe and P cycling

Coupled Fe and P cycling
Agriculture and SO$_4$ losses

<table>
<thead>
<tr>
<th>SO$_4$ losses</th>
<th>kg ha$^{-1}$ y$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Finland</td>
<td>Agricultural catchments</td>
<td>42–180</td>
</tr>
<tr>
<td></td>
<td>Acid sulphate soil</td>
<td>920</td>
</tr>
<tr>
<td>Norway</td>
<td>Lysimeter (cereals, fallow)</td>
<td>24, 27</td>
</tr>
<tr>
<td>Texas &amp; Oklahoma</td>
<td>Agricultural catchments</td>
<td>0.2–18.9</td>
</tr>
</tbody>
</table>

- Riverine SO$_4$ fluxes correlate with field percentage in Finland (Korkman 1973, Mattsson et al. 2007)
- Lake SO$_4$ concentrations correlate with field percentage (unpubl. data)
- *The effect of agricultural SO$_4$ load on eutrophication?*

Graph redrawn from Mattsson et al. (2007)

Potential effect of Fe(III) oxides
Sources of Fe(III) oxides

Concentrations of Fe in riverine suspended solids

- 4.8% (Worlds major rivers, Martin & Meybeck 1979)
- 6.1–6.5% (Finnish agricultural rivers, Mäkiaho 2007)
- 2.7–7.3% (USA, Canfield 1997)

Fe is present e.g.

- As poorly crystallized oxides (microbially reactive)
- As crystalline oxides (sulphide reactive)
- In silicates (largely inert)
Erosion

- Does the Fe(III) oxide in eroded soil maintain coupled Fe and P cycling in sulphidic waters?
- Effect of erosion control on eutrophication?
  + Bioavailable particulate P decreases
  - Sediment ability to bind P may decrease

- The effect of agricultural Fe(III) oxide load on eutrophication?
Day 16: Surface soil (sandy clay) + acetate and lactate + SO$_4$
Phosphorus release from a clay soil in a 141-d anaerobic incubation

\[ P = 0.45 \cdot (1 - e^{-0.71 \text{Carbon}}) \]

Extraction with buffered dithionite

Water extraction
Should we focus only on P load when aiming to reduce eutrophication in a P-limited aquatic system?

- $SO_4$ weakens the ability of sediments to bind P by enhancing “an adverse” sediment mineralization pathway ($SO_4$ reduction)
- Agriculture appears to be a source of $SO_4$
- Fe(III) oxides may increase the ability of sediments to bind P by inhibiting $SO_4$ reduction
- Soil erosion is a source of Fe(III) oxides
- **In addition to P load, we should focus on the fluxes of electron acceptors**
Thank you!

Photo: EteläSaimaa, Mika Strandén
Runoff $SO_4$ concentrations in an agricultural catchment amended with gypsum

Ekholm P, Valkama P, Jaakkola E, Tattari S, Kiirikki M, Pietola L (unpubl.)