A new modified clay for the removal of dissolved phosphorus from aquatic systems

National Cyanobacterial Workshop

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Focus of research

Past 15 years focused on two aspects:

• Limit terrestrial P movement
• P-inactivation in aquatic ecosystems
• Not about cyanobacteria per se
• Method to reduce P
  - at source
  - in-situ

1990’s
Phoslock™

2000’s
Soil amendments

2010’s
New modified clays

Eutrophication management
Mining by-products as a soil amendment

- NUA added as a 5% by mass on a turf farm
- 97% P and 82% N retention over four years
Phosphorus removal

Mining by-products as a filtration media

- Various combinations of mining by-products (>50% removal in red)

<table>
<thead>
<tr>
<th>Column contents</th>
<th>DOC</th>
<th>DON</th>
<th>TN</th>
<th>PO₄-P</th>
<th>TP</th>
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<tbody>
<tr>
<td>Steel by-product</td>
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<td>NUA/activated carbon</td>
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<tr>
<td>Red sand</td>
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<tr>
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<tr>
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<tr>
<td>NUA/red sand</td>
<td>43</td>
<td>27</td>
<td>51</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
Phosphorus removal

Mining by-products as filtration media – nutrient lim

• >99% P reduction
• Change from potential N- to potential P-limitation
Phosphorus inactivation – aquatic systems

The recent past/present:

Phoslock™, a lanthanum-modified clay
• Developed, patented and commercialised by CSIRO in the 1990’s
• Now used in over 20 countries
• One of few effective methods to remove dissolved P from eutrophic systems
• Used in Serpentine/Hyde Park prior to London Olympics*

But (Back to the Future):

• Recent research focus - shifted to alternative methods of P inactivation
• New method of modification of clay minerals for dissolved P uptake
• Why: clays, cheap, abundant, common (environmental compatibility)
Phosphorus removal/inactivation

A new modified clay:

- Development of a clay-hydrotalcite nanohybrid
- Substantial P uptake capacity (0.5-4% P by mass)
- Can be used in fresh and saline waters
- May also remove dissolved P from various sewage effluents
- Prospect for use as soil, riparian zone or wetland amendment
What are hydrotalcites (HT)?

• HT - Mg-Al sub-class of Layered Double Hydroxides (LDH)/anionic clays

• HT - natural and synthetically produced

• Structure: positively-charged mixed Me-OH layers - interlayers host H₂O + exch anions
How do we make hydrotalcites?

Use low-cost clays as feedstock and modify

- Preferably a clay that contains abundant Mg and Al but low Fe
- Acid leach to liberate Mg + Al, but also Fe (fourgerite) and Si (anion ex capacity)
- Augment with additional Mg and Al if required, complex out Fe and Si
- Neutralise (carefully) and precipitate
- Remnant clay acts as a substrate for HT nucleation (+ particle size and density)
- Age as solids-rich suspension
- Apply as slurry, powder or pellets
What do hydrotalcites look like?

Hydrotalcite botryoids and aggregates

Detail of hydrotalcite precipitates

Al-element map: hydrotalcite aggregate

Mg-element map: hydrotalcite aggregate
HT and phosphate - carbonate speciation

• HT - Strong gradient in anion selectivity:
  • $\text{CO}_3^{2-} > \text{HPO}_4^{2-} > \text{HCO}_3^{-}$
    $>> \text{SO}_4^{2-}, \text{NO}_3^{-}, \text{Cl}^{-}$ etc
  • pH is also important
    $\text{CO}_3^{2-} \leftrightarrow \text{HCO}_3^{-}$ vs $\text{H}_2\text{PO}_4^{-} \leftrightarrow \text{HPO}_4^{2-}$
  • “Sweet spot” for P-uptake
    (mostly as $\text{HPO}_4^{2-}$), but with low $\text{CO}_3^{2-}$
• A wider operational pH range in practice (+ increase application rate)
P-uptake – natural waters

- Sample matrix: Swan River (estuarine and freshwater tributaries), coastal seawater, lakes, ponds

- Range of pH and salinity

- Range of DOC concentrations (~0 – 50 mg/L)

- Range of P concentrations (~20 – 300 µg/L)
• Strong relationship between P-uptake and salinity

• ~30% (saline), ~ 50 - 70% (fresh)

• Apply additional clay-hydrotalcite nanohybrid (initial trials only used stoichiometric quantities)

\[ R^2 = 0.82 \]
P-uptake – sewage effluents

- Range of sewage effluents (Vic, ACT, WA)
- Complex matrix, l - h SPM, high DOC etc.
- pH adjusted to 8.0 ± 0.1 (7.2 – 7.6)
- EC range (~680 – 7800 µs/cm)
- Large range of P concentrations (~1 – 270 mg/L)
P-uptake – sewage effluents

- Very efficient P uptake (1 – 271 mg/L)
- Much better P uptake (red dots) (~94 – 99%)
- (~1.5 times stoichiometric reqmt)

\[ R^2 = 0.32 \]

\[ R^2 = 0.82 \]
Future research

• Further laboratory evaluation/performance testing

• Scale-up to pre-commercial quantities (2012-14)

• Stability and ecotox testing

• Field trials: WA initially - DoW, but other possibilities (2012-14)

• STP trials: Aust Water Recycling Centre of Excellence (2012 - ??)

• Make widely available/commercialise?

• Estimate real cost: Assume 2% P uptake, clay-hydrotalcite nanohybrid is
  ~ $1000/tonne, so ~ $50/kg P (+ transport, application, etc.)
Thank you

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Summary

- Clay-hydrotalcite nanohybrid developed over past two years
- Range of possible applications in fresh and saline waters
- P-uptake partially dependent on pH and EC but possible to optimise or add additional material to compensate
- Excellent P-uptake for a range of sewage effluents
- Next two years pivotal – field trials, STP trials, performance validation