Challenges for trapping and recycling phosphorus from agricultural run-off: Introduction to the P-TRAP project

Thilo Behrends, Sylvia Walter, & the P-TRAP Team
H2020-MSCA-ITN

Consortium:
16 participants
9 beneficiaries
7 partners
Objectives of P-TRAP

Improve quality status of surface waters by reducing the phosphate loading
Objectives of P-TRAP

Capture and recover phosphate from agricultural runoff

Reducing the internal phosphate loading of lakes
Context of P-TRAP

- mining
- fertilizer
- Labile pool
- leaching
- stabilization
- harvest

1970s
Global P scarcity

Figure: Neset, & Cordell  *J. Sci. Food Agriculture*, 2012 92, 2-6.
Excess P in surface waters

Figure: EEA Report No 7/2018

- General parameters
- Nutrient conditions
- Phosphorous conditions
- Nitrogen conditions
- Acidification status
- Transparency conditions
- Oxygenation conditions
- Salinity conditions
- Thermal conditions

- Less than good
- Good
- High
- Unknown
Reducing P fluxes to surface waters
Reducing P fluxes to surface waters

- Labile pool
- Stabilization
- Leaching
- Harvest
- Fertilizer
- WWT

- Avoiding application of fertilizer
P-budget Baltic Sea catchment

Legacy phosphorus

Legacy phosphorus

Legacy phosphorus

Figure: McCrackin et al. Global Biogeochemical Cycles, 2018 32, 1107-1122.
Objectives of P-TRAP

mining → fertilizer

Labile pool

stabilization → leaching

harvest → WWT

P-TRAP
The uniting element of P-TRAP

Approaches, technologies, and science investigated in P-TRAP are related to the close coupling of the biogeochemical cycling of Fe and P in natural systems.
Work Package 1

Capturing P in tile-drained agricultural watersheds

Convert captured P into marketable fertilisers
Capturing P from drainage water

Using Fe-containing by products from water treatment

Credits: Deltares and Arcadis
Recycling the Fe-bound P

\[ \text{Fe}^{3+}\sim\text{P} + \text{reductant} \rightarrow \text{vivianite} \quad [\text{Fe}_3(\text{PO}_4)_{2\circ}(\text{H}_2\text{O})_8] \]
Vivianite as a Fe and P source in soils


Flux of phosphate (P) from agricultural areas to surface waters is wasting a resource which is becoming scarce and is in conflict with the principles of a circular economy. Enhanced loading of surface water with P is the main cause for eutrophication and presents a key challenge in meeting the objectives of the EU Water Framework Directive.

P-TRAP as a European H2020 project targets both problems and develops new methods and approaches to trap P in drained agricultural areas and in the sediments of eutrophic lakes.
References


Use of iron sand in agricultural drain systems to prevent P run-off

Stefan Jansen
Phosphorus removal

- Chemical immobilization
- **Iron oxide coated sand**: side product from drinking water production from groundwater
  - Low cost
  - Strong phosphate binding
  - Good permeability
  - No side effects
Iron coated sand: pilot studies

• Various technological forms work
• Phosphorus removal rate can be high (80 – 90 %)
• Costs of maintenance and maximum lifetime varies
• Challenges:
  • Practical applicability
  • Stability of iron oxide coating at low redox potentials, high flow rate
  • Permeability
  • Costs
  • Experience
From field trials to actual application!

- 2 phosphate-removing drain systems installed at farms
- Cooperation between farmers, water authority, drainage contractors, supplier iron sand
Reducing phosphorus (P) losses from drained agricultural fields with iron coated sand (ICS) filters

Hui Xu

Department of Environment, Ghent University, Belgium

Advantages:

+ Low-tech solution
+ High P removal efficiency (80-90%)
+ Low cost of filter materials
+ Causes no other contaminations
+ No impact on accessibility and landscape

Key features:

- upward oriented outlet
- mesh netting at bottom & top
Iron oxide coated porous filter material for agricultural drainage water

Hans Christian Bruun Hansen¹, Lisa Heiberg², Changyong Lu¹, Adrian-Florin Florea¹

1) University of Copenhagen, Denmark
2) DiaPue AB, Sweden
**The challenge**

- Agricultural drainage water low phosphate (P) concentrations (0.1 – 1 (5) mg P/L that preferably should be taken to < 0.05 mg P/L!
- Water comes in huge volumes (up to 2000 m³/ha/year) ➞ high flow, short residence time
- Goal: end-of-pipe filter well that can bind soluble P.

**The solution**

**Need:** Filter packed with larger particles (> 2 mm) that are porous and contains a P binder to allow high flow, and high (internal) P storage capacity

**Granular support:** Calcined diatomaceous earth (CDE), 2-4 mm, porosity 50 %

**Coating:** CDE impregnated with FeCl₃ (PIX111) solution followed by precipitation with NaOH.

**Product:** Sorbent granules where pore walls are covered with films of Fe oxides.
The filter

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe content (add)</td>
<td>%</td>
<td>3 – 10 %</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>5 - 7</td>
</tr>
<tr>
<td>SSA</td>
<td>m²/g</td>
<td>20-70</td>
</tr>
<tr>
<td>Bulk density</td>
<td>g/cm³</td>
<td>0.53</td>
</tr>
<tr>
<td>Solid density (ρ)</td>
<td>g/cm³</td>
<td>2.51</td>
</tr>
<tr>
<td>Total porosity#</td>
<td>%</td>
<td>79</td>
</tr>
<tr>
<td>Pore size</td>
<td>μm</td>
<td>&lt;1; &gt; 100</td>
</tr>
<tr>
<td>K_{sat}</td>
<td>m/s</td>
<td>0.0092</td>
</tr>
<tr>
<td>P sorption capacity</td>
<td>mg P/kg</td>
<td>&gt; 10,000</td>
</tr>
</tbody>
</table>

- High permeability; enables high flow.
- High long-term P sorption capacity and affinity (as for ferrihydrite)
- Filter support material is physically stable
- P can be recovered from the material
- Precaution: Sensitive to clogging by particulates which should be removed!

Filter material produced by DiaPure AB, Sweden
Magnetic MgFe LDH composites for phosphate removal - is the LDH sufficiently stable?
Changyong Lu and Hans Chr. Bruun Hansen
Department of Plant and Environmental Sciences-University of Copenhagen

Workshop on Iron – phosphorus interactions and opportunities for phosphorus stewardship
Background Information

How is the LDH stability?
What are the P sorption pathways under various conditions?
Conclusions

- MgFe LDH could be dissolved under constant acid and neutral pH.
- High concentration of phosphate anions could also stimulate the dissolution of MgFe LDH even at alkaline pH.
- The dissolution of MgFe LDH would lead to formation of poorly crystalized ferrihydrite, which has high phosphate sorption capacity.
- The phosphate was mainly sorbed via formation of magnesium phosphate precipitates at alkaline pH under high phosphate concentration.
- The instability of LDHs would hinder their practical application for wastewater treatment.
Acknowledgement

Department of Plant and Environmental Sciences
Environmental Chemistry group

Department of Chemistry
Prof. Jesper Bendix

SDU
UNIVERSITY OF SOUTHERN DENMARK

Department of Physics, Chemistry and Pharmacy
Prof. Ulla Gro Nielsen
Dr. Tae-Hyun Kim

DTU
Cen
Center for Electron Nanoscopy

Thank you for your attention!
Fe-P Coupling in Lake Sediments and Wastewater Treatment

Lena Heinrich, Michael Hupfer

Chemical Analytics and Biogeochemistry
Agenda: Fe-P coupling

Decreasing redox potential due to oxidation of biogenic material

Immobilization of P

Competition of P binding

P release

Water column

Depth (lake)

Sediment

Activated sludge

Sludge digestion

Research for the future of our freshwaters
Motivation: Fe-P coupling

- Prevent P release

- Prevent competition of P binding

- Prevent immobilization of P

- Decreasing redox potential

- Promote P release

Water column (lake) vs. activated sludge digestion

'Large Scale Laboratory'
P dissolution under anoxic conditions

Adapted from Stumm, Morgan 1995

Research for the future of our freshwaters
P dissolution under anoxic conditions

- Dissolution of Fe(II) and P
- Oxidation
- Reduction
- Insoluble Fe(III) [hydr]oxides bind P
- Sediment
- Water column
- Activated sludge
- Sludge digestion

Research for the future of our freshwaters
**P immobilization under anoxic conditions**

Fe rich lake sediment

Fe dosing STP

0-2 cm

2-4 cm

4-6 cm

P-Fraction / Σ(P-Fractions)

P sequential extraction after Psenner et al. (1984)

Research for the future of our freshwaters
What does it say about Fe-P coupling?
P immobilization under anoxic conditions

Fe rich lake sediment

Fe dosing STP

0-2 cm

2-4 cm

4-6 cm

decreasing redox potential

Redox sensitive Fe bound P
Redox stable Fe bound P

activated sl

excess sl

digested sl

dissolved TP NH₄Cl TP BD TP NaOH SRP NaOH NRP HCl TP refractory P

Research for the future of our freshwaters
P immobilization under anoxic conditions

- Immobilization of P by Fe(II) mineral formation
- Diffusion of Fe(II) and P
- Oxidation
- Reduction
- Insoluble Fe(III) [hydr]oxides bind P
- P dissolution

- Water column
- Activated sludge
- Sediment
- Sludge digestion

Decreasing redox potential
Case studies: Fe amendment at Lake 1

Rothe, 2014, Biogeosciences 11(18): 5169-5180
Case studies: Fe amendment at Lake 2

Fe amendment (2000)
Case studies: Fe amendment at Lake 2

Fe amendment (2000)
Sulfidic conditions: Competition for Fe-P coupling

- Oxidation of Fe(II) and P
- Diffusion of Fe(II) and P
- Insoluble Fe(III) (hydr)oxides bind P
- P release
- Competition of P binding

- Fe(II)S_x precipitation
- Immobilization of P by Fe(II) mineral formation
- Decreasing redox potential due to oxidation of biogenic material

- Water column
- Sediment
- Activated sludge
- Sludge digestion
- Time (STP)

Research for the future of our freshwaters
Motivation: Fe-P coupling

- Insoluble Fe(III) [hydr]oxides bind P
- Diffusion of Fe(II) and P
- Competition of P binding
- Immobilization of P by Fe(II) mineral formation
- Prevent P release
- Prevent decreasing redox potential

- Prevent sediment water column
- Prevent sludge digestion

- Promote sulfate

- 'Large Scale Laboratory'

Research for the future of our freshwaters
Conclusions: Fe-P coupling

• Oxic water column prevents P dissolution to the water column and enables Fe(II)-P immobilization under anoxic conditions.

• Redox stable Fe-P mineral can form and immobilize P in anoxic sediments.

• Competitors like S need to be included in the planning of management measures using Fe.
Conclusions: Fe-P coupling

- Oxic water column prevents P release and enables Fe(II)-P immobilization under anoxic conditions.

- Redox stable Fe-P mineral can form and immobilize P in anoxic sediments.

- Competitors like S need to be included in the planning of management measures using Fe.
Phosphorus burial in coastal marine sediments: new insights in the role of Fe-P phases

Caroline P. Slomp
Classical view
Major burial sinks for P

- Organic P
- Fe-oxide P

HPO$_4^{2-}$

Authigenic minerals

Carbonate fluorideapatite (CFA)

Ruttenberg 1993
Alternative P sink: Fe(II) phosphates

- Organic P
- HPO$_4^{2-}$
- Authigenic minerals
- Water
- Sediment
- Fe-oxide P
- Carbonate fluorapatite (CFA)

Ruttenberg 1993

Fe(II) phosphates e.g. vivianite (Fe$_3$(PO$_4$)$_2$ * 8H$_2$O)

25% 
50% 
25%
When does vivianite form?

• Requirement: Excess Fe(II) over reduced S, sufficient PO$_4$

• Examples of environments:
  – Coastal systems with a low salinity
  – Below zone of anaerobic oxidation of CH$_4$ with SO$_4$

• Qualitative or indirect evidence, such as:
  – pore water profiles, saturation state calculations
  – sediment P enrichments
  – blue crystals
Why is vivianite so difficult to quantify?

SEDEX extraction procedure

- Extractant: 1 M MgCl₂
  Extracted: Loosely bound P
- CDB (pH = 7.6)
  Extracted: Fe-bound P
- Acetate buffer pH = 4.0
  Extracted: Authigenic Ca–P, Biogenic Ca–P, CaCO₃-bound P
- 1 M HCl
  Extracted: Detrital Ca–P
- Ashing 550 °C 1 M HCl
  Extracted: Organic P

Extraction of both Fe-oxide bound and Vivianite P in one step

Ruttenberg, 1992
Goal of our studies:

Detect and quantify vivianite in coastal sediments using SEDEX extractions combined with (micro-)XRF, XANES, SEM and/or XRD & understand conditions of formation
Fe and P rich sediments of the Bothnian Sea (oxic bottom waters)

Slomp et al., 2013; Egger et al., 2015
Bothnian Sea: US5B

Shallow sulfate-methane-transition zone (SMTZ)

High porewater Fe$^{2+}$ and PO$_4$

Egger et al., 2015
SEDEX extraction

Fe-oxides

Vivianite?

Fe-P

Depth [cm]

SMTZ

Egger et al., 2015
Distinct Fe-P enrichments

Table top micro-XRF

Synchotron-based micro-XRF

Egger et al., 2015
Synchroton-based K-edge P-XANES

Egger et al., 2015
Blue crystals

Optical Light Microscopy

Scanning Electron Microscopy

Egger et al., 2015
XRD-analysis: vivianite

Egger et al., 2015
Quantitative importance of vivianite

- Combination of SEDEX and Iron extractions
- Fraction of total P associated with P enrichments based on the Desktop µXRF maps for P:

=> Vivianite responsible for 40-50% of total P burial at this site
Upward shift of SMTZ due to eutrophication

Egger et al., 2015 ES&T; Rooze et al. 2016
Higher P burial and more vivianite at lower salinities

(a) Phosphorus burial rates (mol P m$^{-2}$ yr$^{-1}$) vs. Salinity

(b) Phosphorus burial forms (Percentage) vs. Salinity

Model sensitivity analyses for Bothnian Sea sediments

Lenstra et al., 2018
Conclusions

• Fe(II)-phosphates
  - can be identified using a range of geochemical techniques
  - are likely important (but variable) sinks for phosphorus in coastal seas

• Shifts in the sulfate-methane transition zone caused by eutrophication or freshening may enhance Fe(II)-P formation
Acknowledgements

- Funding: ERC STG+Synergy, NWO Vici
- Beamline scientists Diamond, ESRF (Camille Rivard)
- Matthias Egger, Nikki Dijkstra, Wytze Lenstra et al.
Use of iron and aluminium coagulants in wastewater treatment

Phosphorus removal and challenges of phosphorus recovery

13th of July 2020
Jean-Christophe Ades
Aluminium and iron salts are essential elements for water treatment, paper manufacturing, fertiliser production and other industries.

**INCOPA - the European Inorganic Coagulants Producers Association**

- 29 PRODUCERS
- 80 PRODUCTION SITES
- 85% of the European PRODUCTION CAPACITY
Better recycle than waste: P recovery from waste water

FROM A **LINEAR** WORLD

Mined P fertilizer → Food → Wastewater → Sludge disposal

TO **CIRCULAR** ECONOMY

Food

Agriculture

Wastewater

Coagulants

Recovered P

Recovered Fe & Al

Recycled raw materials
P recovery starts always with removal

- Ultra low level of phosphorus discharge
- Lowest carbon footprint of all P-removal processes
- Use of coagulant manufactured from recycled raw materials
- Low CAPEX
- Protect waterways from eutrophication
- Most effective and cost-efficient solution
- Phosphorus chemical precipitation

Lowest carbon footprint of all P-removal processes
Inorganic coagulants can achieve ultra low levels of phosphorus – Finnish case

Only with chemical phosphorus removal, levels below 0.2 mg/l in the effluent can be consistently achieved

Removal rate of phosphorus
(Source: Environment.fi)
Precipitation of phosphorus leads to high recovery potential as well

- From 50% to over 90% phosphorus recovery
- Phosphorus can be recovered
  - from sludge
  - from tertiary treatment unit
  - from ash
- Cost efficient solution with minor influence on OPEX, and low CAPEX requirement are available

Recovered thermally dried aluminium phosphate
Exemples of phosphorus recovery processes when using inorganic coagulants

Phosphorus recovery from sludge
- Depending on technology, iron or aluminium coagulant can be used and recovered as well
- It can be dosed flexibly to the primary, secondary or tertiary treatment
- Needs chemical extraction of phosphorus or physical separation methods or biological pathways

Phosphorus recovery from tertiary treatment
- The recovery unit is easily installed to the existing wastewater treatment plant
- Coagulant is dosed to the tertiary treatment
- Both iron or aluminium coagulant can be used and recovered as well

Phosphorus recovery from sewage sludge ash
- Normally a very high recovery yield of phosphorus
- Most extraction processes also recover aluminium and iron coagulant
- Mono-incineration of sludge required
Carbon footprint of different wastewater treatment plant configurations

Magnus Rahmberg, Sofia Andersson, Erik U Lindblom and Kristin Johansson, IVL
Scope & Effluent limits

Evaluate 3 WWTP processes from a LCA perspective:

- Pre-precipitation
- Simultaneous precipitation
- Biological P removal

Effluent Limits

Baseline:
TP 1 mg/l, TN 10 mg/l, BOD 25 mg/l

Stricter:
TP 0.3 mg/l, TN 10 mg/l, BOD 25 mg/l
Global Warming Potential with / without coagulants

With coagulants

Without coagulants

With coagulants

Without coagulants

GWP

kg CO₂-eq. per m³ treated water

PrePrec

SimPrec

Bio-P

Baseline

Stricter
Conclusions of the IVL study

- Chemical pre-treatment clearly gives a lower GWP than the other configurations
- Pre-precipitation generates most biogas
- Energy source important factor for several impact categories
- A more stringent effluent limit leads to a higher carbon footprint
Role of inorganic coagulants in the circular economy

Inorganic coagulants used in wastewater treatment:
- Are needed to achieve ultra low levels of phosphorus discharged in the environment
- Guarantee high phosphorus recovery rate (> 50%)
- Allow higher energy recovery from organic waste and hence lead to a lower carbon footprint
- Have been part of the circular economy for many years
THANK YOU VERY MUCH!
WATER TREATMENT WITH MAGNETITE & FERRIC PELLETS

Denise Roberts, LKAB Minerals UK & Ireland
Derrick Emms, Sustainable Water Company
WATER TREATMENT APPLICATIONS WITH MAGNETITE

• Used as a flocculant to weigh down particulates from the water
• Ferric Sulphate Coagulants
• Filtration media used whilst backwashing through a filtration system
SWEDISH MAGNETITE PROPERTIES

• Black, hard mineral with a rough surface texture mined in Northern Sweden
• Chemical Composition – Iron Oxide – Fe₃O₄
• High Fe content (65-70%) with ferrimagnetic properties
• No heavy metals
• Chemically inert (pH neutral), non-hazardous and durable
• Resistant to leaching (Deltasres report 2014)
• Low water absorption < 0.3%

• New pellet for reed bed systems to remove phosphate
  – Project with Derek Emms
WATER TREATMENT USING FERRIC

Background

- Objective to achieve a “good ecological status” for all waters
- Phosphorous removal technique from domestic wastewater before discharging into receiving water bodies
- For small communities localised upstream of catchment areas or in zones sensitive to eutrophication
- Rural communities often choose to treat their wastewater with extensive treatment systems which can be expensive
- Using natural wetlands will be easier to operate and maintain
- Research focused on adsorption and/or precipitation mechanisms on specific reactive materials

Solution

- Treatment of Phosphorous
- By-product from the water industry to produce a pelletised media embracing a closed loop technology
- Utilising a sensitive binder ensures minimal spikes in pH (tested at 7.8 after 24 hours)
ADVANTAGES

• Phosphate reduction from 1.05 > 0.45mg/L after 24 hours
• Pellets negate the need for additional treatments (such as pH acid treatments)
• Trials ongoing with customer to prove retention time
• Low cost solution
• Sustainable
  • Produced from by-product (closed loop)
  • Self running system (gravity fed)
  • No power needed in treatment process
  • Long term solution
Industrial phosphates

for iron phosphates workshop, July 13-14, 2020

Willem Schipper
World usage of phosphorus

Worldwide 21 Mt/y P

- fertilizers
- feed phosphates
- food phosphates
- detergents, technical phosphates
- glyphosate
- other true P$_4$ derivatives

Non-fertilizer P$_4$

- feed phosphates
- food phosphates
- detergents and technical phosphates
- glyphosate
- other true P$_4$ derivatives
Value chain – the element phosphorus

phosphate rock → P₄ → sulfides, oxides, chlorides, thermal acid

P₄ → true derivatives

P₄ → (poly)phosphates

P₄ → feed phosphates, technical

P₄ → fertilizers

P₄ → (poly)phosphates, technical

P₄ → thermal acid

P₄ → true derivatives

H₃PO₄, impure → fertilizers

H₃PO₄, pure → (poly)phosphates

H₃PO₄, pure → technical

H₃PO₄, pure → feed phosphates

other P derivatives

phosphate

phosphates

Consulting
phosphates: main uses

• fertilizers
• feed additive
• food additives (moisture retention, preservation, acidity...)
• detergents
main phosphates types

- **H^+**
  - phosphoric acid (precursor to salts, food additive, etchant)

- **NH₄^+**
  - ammonium (MAP, DAP)

- **Na^+**
  - sodium (food, detergents)

- **K^+**
  - potassium (food)

- **Ca^{2+}**
  - calcium (food, feed, toothpaste, polymerization, implants...)

- **Mg^{2+}**
  - magnesium (feed)
iron phosphates (ferric/ferrous)

• not in any major producer’s portfolio
• not described in market studies e.g. CRU
iron phosphates (ferric/ferrous)

• niche: organic molluscicide – market < 5 kt/y
iron phosphates (ferric/ferrous)

specialty: LiFePO₄

cathode material in Li ion batteries
alternative for LiCoO₂

- better voltage stability
- lower energy density
- lower conductivity
- higher stability

FePO₄ + Li⁺ ↔ LiFePO₄

ferric (3+)
ferrous (2+)
same structure

ULTRA HIGH PURITY MATERIALS
vivianite $\text{Fe}_3(\text{PO}_4)_2 \cdot 8 \text{H}_2\text{O}$

- historical use as a pigment
- limited applications

Vermeer, The Procuress (De Koppelaarster)
iron phosphating

• important for rust protection and as paint adhesion primer
• iron phosphate film on iron
• application exclusively through phosphoric acid
iron phosphates from recovered sources

- usually impure
- largely incompatible with the existing applications
- these are quite limited anyway

no large promising 1:1 industrial pathways for recovered phosphates
Thank you for your kind attention

willemschipper@wsconsulting.nl
« Get More P » : New Technology For Di-Calcium Phosphate Production From Low Grade Phosphate Sources

ESPP Conference
13th July 2020

Alexandre WAVREILLE – Hubert HALLEUX
Context

- Continuous demographic expansion -> Increased demand for phosphatic nutrients
- Decrease of raw material quality + demand for P-recycling
  - Difficult to use in traditional phosphoric acid processes
  - Need for new process routes
The new process consists of two main steps:

① Attack of the rock by diluted sulfuric acid
② Precipitation of the DCP
Preliminary results

- Lab and pilot scale tests on various rocks and secondary phosphate sources
- Mainly calcium phosphates tested with $P_2O_5$ recovery around 90%
- Production of by-product (gypsum) with major part of impurities
- Possibility to produce Di-Calcium phosphate up to animal feed grade

Tests on iron phosphate:
- Lower recovery: +- 60%
- Precipitation of iron phosphate during pre-neutralization ->
  $P_2O_5$ losses in the gypsum cake
- Higher Calcium carbonate consumption as the raw material is not a calcium phosphate
- Need for more tests to confirm feasibility