



# Decentralized Wastewater Treatment With Full Resource Recovery - Is it Worthwhile?

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## Introduction

Treatment of wastewater by decentralized treatment systems before releasing it into water bodies is important to preserve the aquatic ecosystem. On the other hand, wastewater could be used as sources of carbon and nutrients much more effectively than they are used today. Here we consider decentralized wastewater as a feedstock, from which valuable substances can be extracted in a suitable form and water is produced for reuse, e.g. irrigation. The operating model is based on physico-chemical unit operations, and can therefore be flexibly implemented in various scales locally or as seasonal solutions.

## Methods

The separation technology concept for valuables recovery and reuse water production was first developed by separately testing the performance of different units. The studied unit operations were flocculation enhanced belt filtration as a pre-treatment step for solids separation from liquid, phosphorous precipitation with lime ( $\text{Ca}(\text{OH})_2$ ), microfiltration (MF), nanofiltration (NF), reverse osmosis (RO), adsorption, activated carbon filtration (GAC), and evaporation. Hydrothermal carbonization (HTC) was studied for the centralized treatment of residue solids. Performances were assessed by measuring suspended solids (SS) and chemical oxygen demand (COD) for the pre-treatment, and ammonium nitrogen ( $\text{NH}_4\text{-N}$ ), phosphate phosphor ( $\text{PO}_4\text{-P}$ ) and COD for recoverable substances in the liquid phase. Municipal waste water was used in the tests.

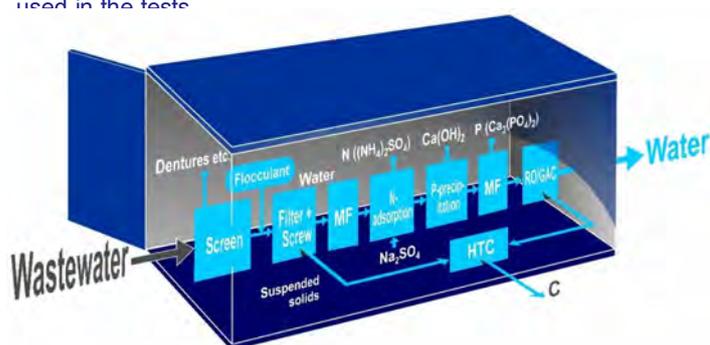


Figure 1. Tested concept.

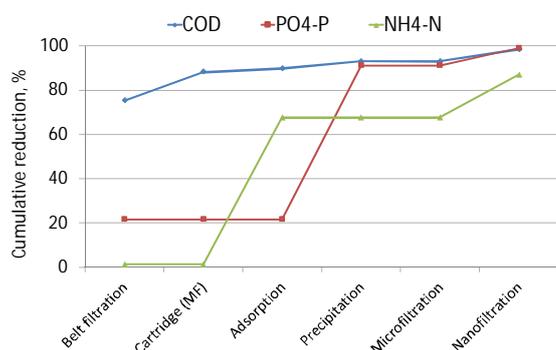


Figure 2. Separation efficiency of the studied unit operations.

## Results

The most functional concept contained flocculation, belt and cartridge filtration, adsorption, precipitation, MF and NF (Fig.1). Flocculation enhanced belt filtration removed 90% of SS. 70% of COD was removed among the solids, whereas 80% of  $\text{PO}_4\text{-P}$  and more than 99% of  $\text{NH}_4\text{-N}$  remained in the liquid (Fig. 2). Adsorption was found potential for  $\text{NH}_4\text{-N}$  recovery from the liquid fraction and lime/calcium precipitation for  $\text{PO}_4\text{-P}$  recovery. Tight NF concentrated efficiently all valorizable producing a very clean water fraction. Recovered suspended solids were separately treated by hydrothermal carbonization (HTC) to obtain good quality biochar. Wastewater from the HTC process was so small in volume that there were minor effect on the wastewater composition when returned back to wastewater treatment.

One main challenge was the cost effectiveness of recovery solutions for decentralized municipal wastewater treatment. Crucial factors were among others the capital charges, which for a 40 household plant correspond to 51% of the total costs (Fig. 3). The total production costs including the nutrient recovery were estimated 9.1 €/m<sup>3</sup> WW, whereas without nutrient recovery they were estimated 4.4 €/m<sup>3</sup> WW. Both estimations were carried out without HTC treatment.

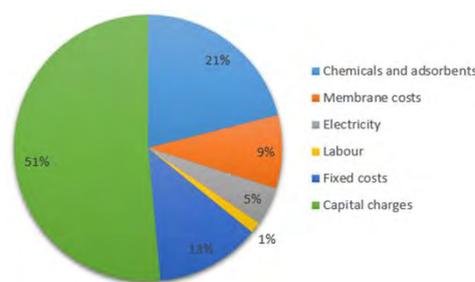
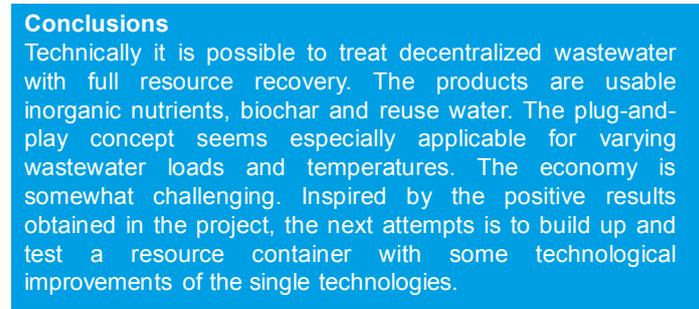


Figure 3. Cost breakdown of the tested concept.

## Conclusions

Technically it is possible to treat decentralized wastewater with full resource recovery. The products are usable inorganic nutrients, biochar and reuse water. The plug-and-play concept seems especially applicable for varying wastewater loads and temperatures. The economy is somewhat challenging. Inspired by the positive results obtained in the project, the next attempts is to build up and test a resource container with some technological improvements of the single technologies.



## Acknowledgements

The project was carried out as part of the Finnish RAKI programme by the Ministry of Environment. Other cooperation partners were Parainen, Kemira, Sarlin, Sofi Filtration, Aquaminerals, Dewaco, OWACO, Pöyry, Baltic Sea Action Group (BSAG) and Turku University of Applied Science.

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## Clay soil structure improvement and lime filters: engineered solutions to control phosphorus leakage

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Phosphorus discharged from compacted clay soils during heavy rain falls and snow melting periods contributes significantly to the eutrophication of lakes, rivers and finally the Baltic Sea. Thorough soil structure improvement by structure liming has a long term positive effect not only on eutrophication but also on soil water balance, plant nutrient intake and finally on crop yield.

In Nordkalk Fostop® structure lime concept, some key factors are in focus when clay soils' structure improvement is designed. Weather conditions are essential for success and it is preferable to schedule structure liming for early autumn, when the soil is not yet too wet and when the soil temperature is high. Blomquist *et al.* reported significantly better results for structure liming performed in August compared to one performed a month later. Drier clay soils are easier to cultivate efficiently after structure lime spreading and all structure reactions are faster in warm soils resulting in smaller clay aggregates.



The used lime product should have a guaranteed reactivity to ensure a fast and feasible structure improvement. This is essential to starting the chemical Pozzolan reactions and aggregate building. The dosing of structure lime should be based on existing soil fertility analysis, but we recommend a minimum dose of at least 7 – 8 t/ha of Nordkalk Fostop® Structure to secure a good result.



The reactive part of the product will act in aggregate building while the carbonate part will enhance mixing properties and ensure sufficient pH level maintenance. Later, traditional agricultural lime products can be used for pH level maintenance.

In those places where structure liming is not applicable, efficient phosphorus reduction can be achieved by using granulated calcium hydroxide in filter solutions. Nordkalk Fostop® filters consist of reactive Filtra G granules and effective limestone sand filters to reduce both particulate phosphorus and soluble phosphates due to precipitation with calcium in high pH. Efficient 50 – 80 % P reduction can be achieved in such filters.



Such/These filters perform best when combined with wetlands: wetland basins can be utilized as flow equalization basins, for sedimentation and even for neutralization. Finally, the filter material can be re-used on arable land as a phosphorus containing liming agent.



Key reference publications:

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Kirrkala T. *et al.* (2012), Long-Term Field-Scale Experiment on Using Lime Filters in an Agricultural Catchment, J. Environ. Qual. 41:410–419

Saulys V. and Bastiene N. (2007), The Impact of Lime Admixture into Trench Backfill on the Variation of Phosphorus in Drainage Outflow, Irrig. And Drain. 56: 99–105

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# Development of a method to track the organic phosphate compound 'phytate' during waste water treatment

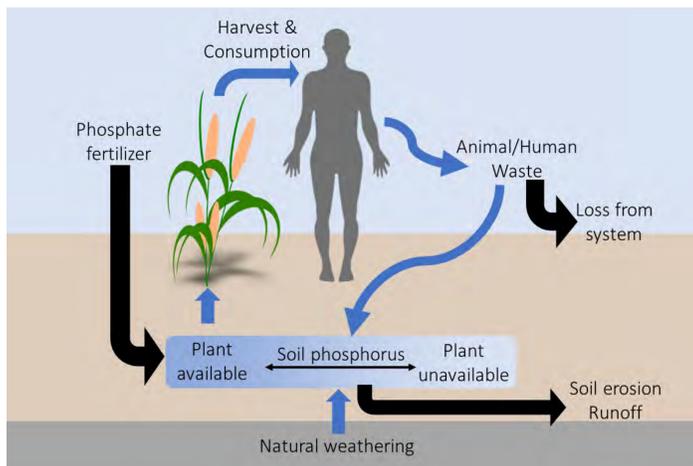
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## 1. Abstract

Current techniques for the recovery of phosphorus (P) from wastewater focus on the removal of inorganic phosphate, but the fates of organic phosphates are often overlooked. The organic phosphate compound 'phytate' is synthesized in plants and serves as the main P storage compound in grains, but when consumed by humans it is not digested and passes through into excreta. It is therefore likely that phytate is abundant in wastewater biosolids, but its fate throughout the treatment process is yet to be studied in detail. We describe the development of a technique that will be employed to trace the fate of phytate and lower inositol phosphates in a model wastewater treatment process. We present the straightforward synthesis of <sup>33</sup>P radiolabelled inositol phosphates, and the analysis of the synthesized product with <sup>31</sup>P NMR.

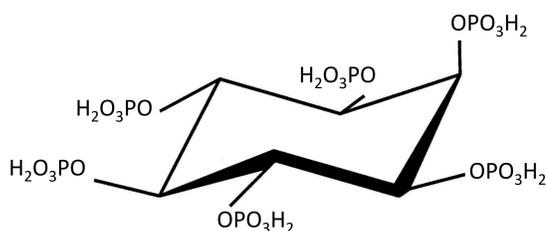
## 2. Introduction

- Global food production is completely dependent on phosphate rock
- Demand is growing annually with population growth & dietary change
- 'Peak Phosphorus expected in late 21<sup>st</sup> century [1]
- Transition from 'single use' system to circular economy model is essential
- Consequences include reduced yields, geo-political tensions & global hunger [2]



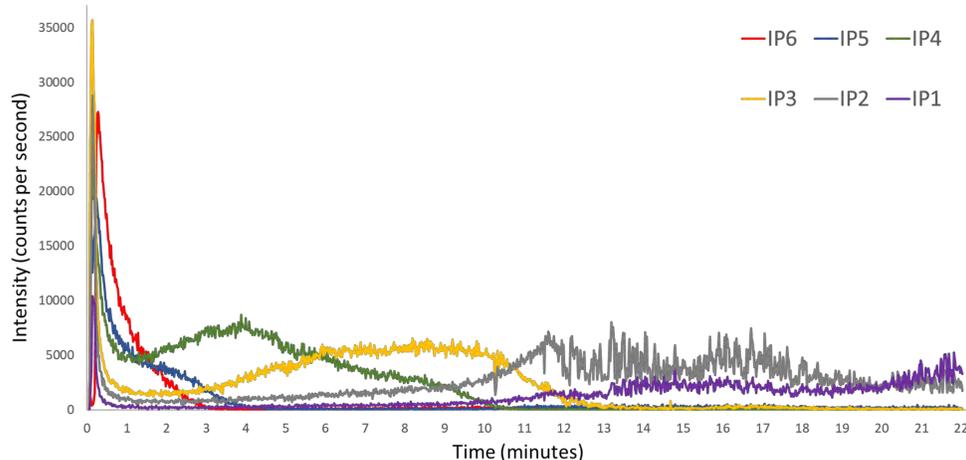
**Fig 1:** The agricultural phosphorus cycle. Arrows in blue represent the largely circular flows of P prior to the green revolution. Arrows in black represent the linear P flow since the green revolution, where large amounts of phosphate fertilizer are input annually, with much lost to water bodies

## 3. Phytate in waste water treatment



**Fig 2:** Chemical structure of phytate (inositol hexakisphosphate). Upon hydrolysis by phytase enzymes, inorganic phosphate groups are liberated.

- Organic phosphate synthesized in plants with 6-carbon inositol ring and 6 phosphate groups [3]
- Stored in grain but not digested by humans & other monogastric animals (swine, poultry, fish) due to absence of phytase enzyme
- Likely that phytate is abundant in excreta, but little known of its fate in wastewater treatment – does it survive anaerobic digestion?
- In the soil phytate is not available for plant uptake as it can become adsorbed to clays and form precipitates with cations, causing accumulation over time [4]

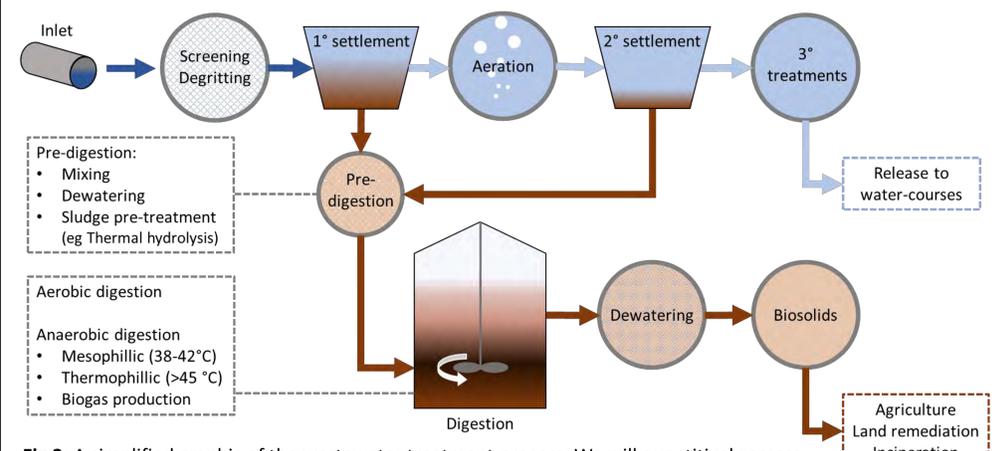


**Fig 3:** The step-wise dephosphorylation of phytate (IP6) by phytase enzyme from IP6>IP1. The progress of the reaction was captured by ESI Mass Spectrometry by continuous injection of the reaction through the mass spec.

- Phytate is dephosphorylated by phytase enzymes produced by microbes in environments such as soil & digestive tract of ruminants (cattle)
- Complex, multi-step reaction in which phosphates are sequentially cleaved
- If phytate is abundant in wastewater biosolids, can we harness this reaction to dephosphorylate phytate and liberate plant-available phosphate, thus improving P bioavailability in organic fertilisers?

## 4. Aims

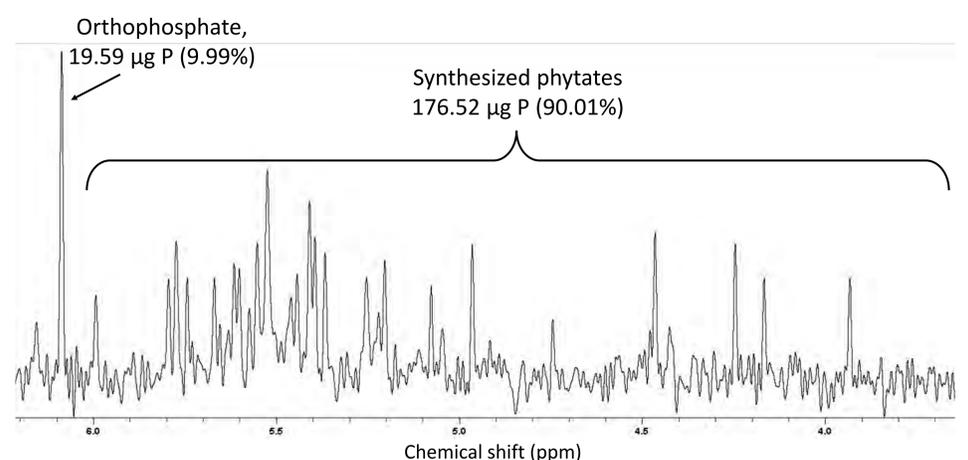
- Quantify phytate-P through the waste-water treatment process
- Employ <sup>33</sup>P radiolabelled phytates to track the behaviour and fate of phytate during microbial digestion steps of the wastewater treatment process
- Design a phytase enzyme treatment for sludge to liberate plant-available phosphate from phytate



**Fig 3:** A simplified graphic of the wastewater treatment process. We will quantitatively assess the behaviour of phytate at each stage of the process using <sup>33</sup>P radiolabelled phytate

## 5. Synthesis of <sup>33</sup>P radiolabelled phytates

- To track phytate through wastewater treatment, we have developed a method to synthesize <sup>33</sup>P radiolabelled phytates from myo-inositol and <sup>33</sup>P orthophosphoric acid
- Synthesized phytates are then purified on anion exchange column
- <sup>31</sup>P NMR analysis of parallel 'cold' synthesis <sup>33</sup>P showed production of 176.52 µg of phytate-P
- Equivalent to approximately 626 µg of fully phosphorylated phytate



**Fig 4:** <sup>31</sup>P NMR analysis of a cold synthesis of phytates run in parallel to radiolabelled synthesis. Numerous peaks were observed in the orthophosphate monoester region, signifying the synthesis of phytates at varying degrees of phosphorylation. Percentages represent P as a percentage of total P.

## 6. Summary & next steps

- We show the development of a straightforward synthesis that yields a mixture of <sup>33</sup>P radiolabelled phytates
- We will use this to trace the behaviour of phytate in a lab-based model wastewater treatment process
- Excreta can be spiked with <sup>33</sup>P phytate to track its structural integrity through anaerobic digestion to understand whether the microbial communities are able to scavenge phytate-P, or if it remains intact
- This data will then allow us to design a phytase-based treatment to recover and recycle phytate-P in the form of plant-available phosphate

# Phosphorus Elimination and Recovery from Wastewater and Process Water with Reusable Nanocomposite Magnetic Particles

## 01 MOTIVATION

### Phosphorus as an essential nutrient

- P is a non-substitutable element for the growth of organisms and a key nutrient for agriculture and global food security;
- Phosphate rock is a finite resource concentrated in a few countries worldwide;
- The quality of the remaining reserves is deteriorating (impurities: Cd, U);
- Countries with resource deficits face import dependency and insecurity;
- P-rock was declared a critical resource for the E.U. (EU Commission, 2014);
- P-recovery from secondary P-rich sources (e.g. wastewater) is of critical importance.

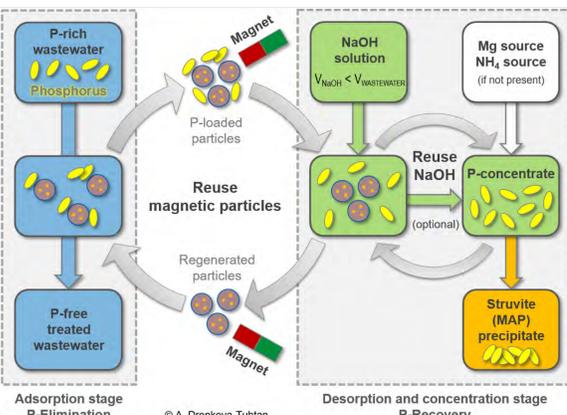
### Phosphorus as an environmental pollutant

- Causes eutrophication even at trace concentrations ( $\mu\text{g/L}$ ) of excess P;
- Negative impact and economic losses for fisheries, tourism, drinking water sources;
- E.U. discharge limit values (91/271/EEC):  $\text{max } 1 \text{ mg/L } P_{\text{tot}}$  (total phosphorus) for WWTP > 100 000 P.E.;
- U.S. guidelines:  $0.050 \text{ mg/L } P_{\text{tot}}$  at the point where streams enter a lake or a reservoir.

Ultra-low WWTP effluent concentrations (< 0.1 mg/L  $P_{\text{tot}}$ ) are unachievable with conventional P-removal techniques. The proposed sorption based technology progresses the field of wastewater treatment by providing an option for **advanced elimination and simultaneous recovery** of the valuable nutrient.

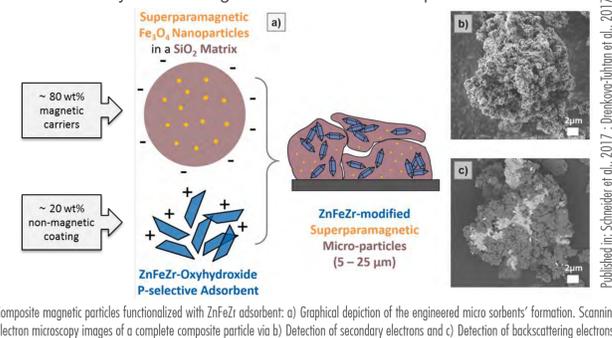
## 02 CONCEPT OF THE TECHNOLOGY

**Technology for reversible sorption of phosphorus** using nanocomposite magnetic carrier particles modified with a tailored P-selective adsorbent. Particles are extracted magnetically, regenerated in an alkaline solution, where P desorption and enrichment take place, and reused again. The P-rich solution serves as a source for further P-recovery. Ultra-low P concentrations < 0.005 mg/L  $\text{PO}_4\text{-P}$ , < 0.05 mg/L  $P_{\text{tot}}$  can be reached in the treated effluent.



### Characteristics of the engineered sorbent micro-particles:

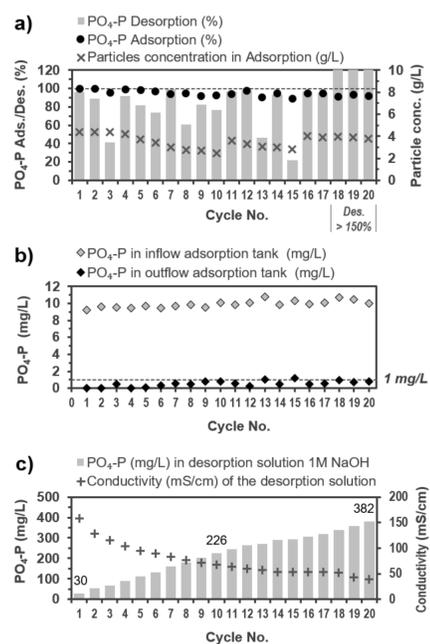
- Large surface area ( $\sim 100 \text{ m}^2/\text{g}$ ) and high selectivity for phosphorus;
- Separable in low magnetic field gradients with permanent magnets;
- Easy to re-suspend in water, do not retain remanent magnetization;
- Reusable after regeneration; Good chemical and mechanical stability;
- Low-cost synthesis using abundant and non-toxic precursors.



## 04 RESULTS AND DISCUSSION

### Pilot experiment at ISWA, Universität Stuttgart

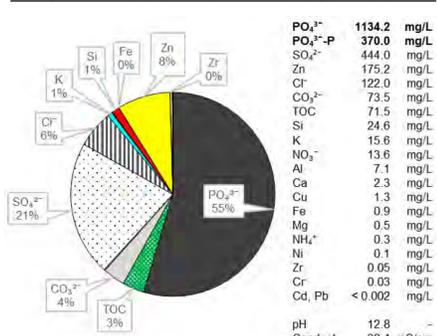
Removal, recovery and enrichment of phosphate from 1.5 m<sup>3</sup> wastewater (spiked SST effluent) over 20 cycles of particles reuse, loaded with 23 wt% ZnFeZr adsorbent. Initial adsorbent dose 1 g/L (4.4 g/L particles), adsorption pH 7, contact time 20 min.



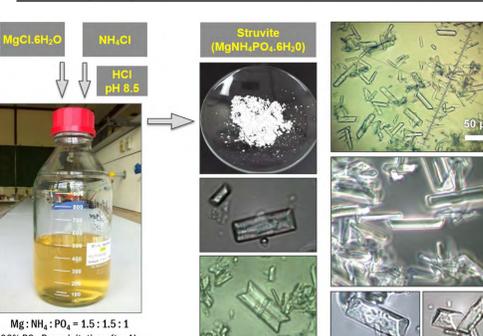
a) Efficiency of  $\text{PO}_4\text{-P}$  adsorption and desorption in every cycle;  
b) Concentrations of  $\text{PO}_4\text{-P}$  in wastewater before and after adsorption;  
c) Enrichment of phosphate ions in the NaOH desorption solution and conductivity drop due to particles' regeneration. Published in: Drenkova-Tuhtan et al., 2017a

Effluent concentrations < 0.005 mg/L  $\text{PO}_4\text{-P}$  could be achieved, i.e. > 99.9% P elimination. The overall P recovery efficiency after 20 runs was 82% (95.2% adsorption and 86% desorption efficiency), leading to 38 times P-enrichment of the final reclaimed eluate (382 mg/L  $\text{PO}_4\text{-P}$ ) compared to the initial phosphate concentration in the wastewater ( $\sim 10 \text{ mg/L } \text{PO}_4\text{-P}$ ).

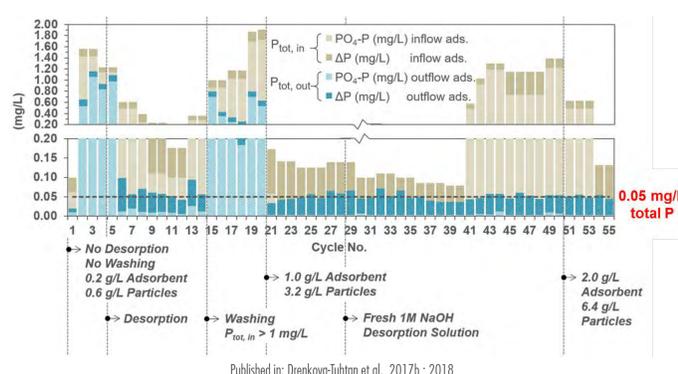
### Composition of the final P-rich desorption solution



### Struvite precipitation from the P-rich reclaimed solution

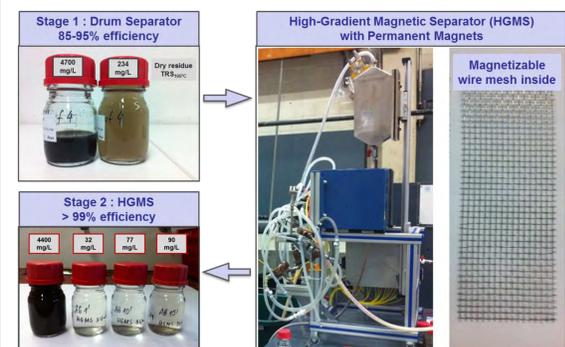
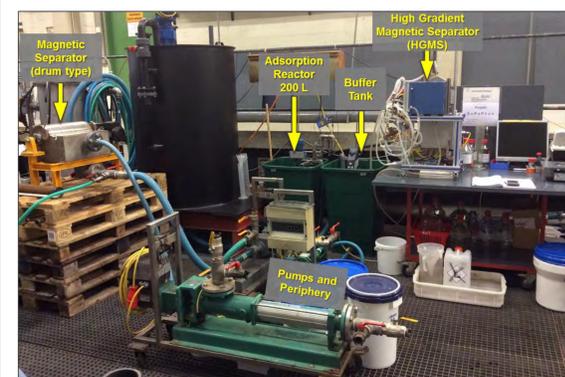


### Advanced phosphorus elimination and polishing of a municipal WWTP effluent, reaching ultra-low $P_{\text{tot}}$ concentration



The beige bars represent the total phosphorus  $P_{\text{tot},\text{in}}$  ( $\text{PO}_4\text{-P} + \Delta\text{P}$ ) concentrations in the wastewater to be treated (SST effluent) at inflow adsorption (pH 7, T = 20 min). The blue bars show the outflow total phosphorus  $P_{\text{tot},\text{out}}$  concentrations after the treatment with the particles. Remark: " $\Delta\text{P} = P_{\text{tot}} - \text{PO}_4\text{-P}$ " is the unreactive phosphorus fraction (dissolved and particulate). Other P-rich wastewaters with highly varying composition were tested as well. Overall, good treatment efficiency was achieved in all matrices after adjusting accordingly the process parameters.

## 03 EXPERIMENTAL SETUP



## 05 CONCLUSIONS

- Technology for simultaneous removal and recovery of phosphorus from wastewater; Potential for mainstream and side-stream implementation at a WWTP;
- Ultra-low effluent concentrations achievable < 50  $\mu\text{g/L}$  total P (dissolved + particulate), < 5  $\mu\text{g/L } \text{PO}_4\text{-P}$  due to significant reduction of the unreactive P fractions;
- Particles could be regenerated and reused throughout numerous loading cycles;
- Pilot test demonstrated proof-of-concept via successful upscaling / magnetic harvesting;
- Total efficiency of P-recovery > 90% under optimal conditions;
- Struvite crystals with high purity precipitated from the P-rich reclaimed solution;
- Most efficient performance in pre-treated wastewater (WWTP effluent). Possible application in other P-rich matrices (sludge liquor, filtrate, digestate, industrial WW) after adjustment of the process parameters;
- Particle performance highly matrix specific  $\rightarrow$  the cleaner the wastewater matrix, the purer the recovered product;
- Positive effects on existing WWTPs  $\rightarrow$  no EBPR or chemical precipitation necessary, savings on metal salts, reduced excess sludge volume, etc.;
- Potential for treating eutrophic water bodies.

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# Phosphorus platform founded in the Czech republic ... finally!

J. Duras, D. Kosour, M. Holba, V. Kočí, J. Pešta

## agriculture

### Situation

Soils are relatively poor in phosphorus in CZ, i.e.  
(a) not serious source of P for water ecosystems  
(b) lack of policy of sustainable management of P (losses by erosion)

### Themes

Improvement of soil quality → better nutrient cycle and lower losses  
P budget of farms  
Sustainable P (nutrient) management  
Retention of nutrients by semi-natural measures (wetlands, ponds) and recycling esp. of P

## water

### Situation

**Eutrophication** is the most important problem of surface waters in CZ, mainly due to P emissions from WWTP's:  
**6552 t of P per year**, i.e. 41 % of all P losses in CZ

### Themes

Improvement of legislation and technology towards reuse of P from wastewaters  
Retention of residual P in fishpond sediments  
- potential for recycling via application on arable land

**PHOSPHORUS IS A COMMON PROBLEM**  
-  
**SO LET'S SOLVE IT TOGETHER!**

### Situation

Still little awareness concerning circular economy, phosphorus, eutrophication  
**Only 10% of P is recycled in consumer sector in CZ**

### Themes

Education and involvement of public including farmers etc.  
Support changes in consumer sector  
Cooperation with universities and research institutes

## industry

### Situation

No systematic awareness concerning circular economy esp. to the topic of phosphorus  
**76% (23,2 kt) of P becomes a waste in CZ**  
→ it is irrecoverably lost

### Themes

Enhanced production of P free or P low detergents and ban P rich products for „Professional use“  
Faster introduction of circular economy

## society



Česká  
Fosforová  
Platforma

Czech  
Phosphorus  
Platform

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# Mg(OH)<sub>2</sub> tech - Closing the loop on phosphorus

Since five years, magnesium hydroxide is commonly used for precipitation of phosphorus in wastewater treatment plants. Phosphorus precipitated with magnesium ions can either be removed or discharged. In both cases it is possible to reuse phosphorus in fertilisers and thus, to close the loop on phosphorus.

## The phosphate challenge

Removing phosphorus is a challenge for many wastewater treatment plants. On one hand, uncontrolled formation of struvite can lead to scaling, which reduces capacity while increasing maintenance costs. On the other hand, discharge limits often require the conversion of soluble phosphates into extractable solids. As phosphorus is a valuable, ending natural resource, the importance to close the loop on phosphorus is increasing.

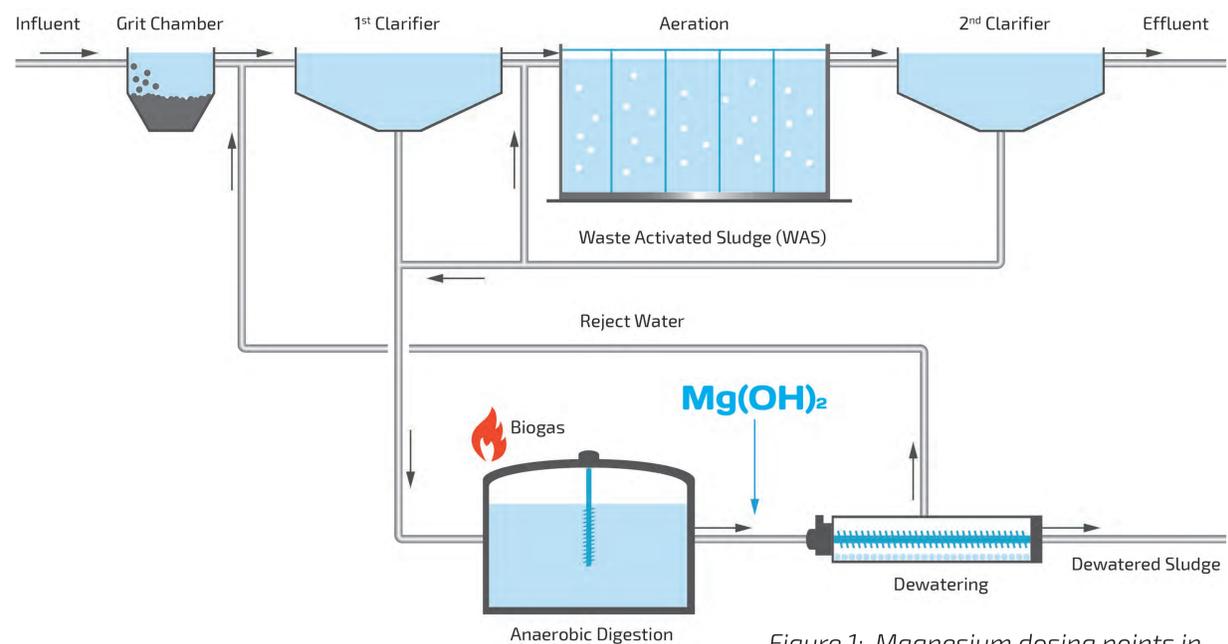


Figure 1: Magnesium dosing points in case of phosphate removal & recovery.

**“Addition of magnesium hydroxide to digested sludge leads to a significant cost reduction and major environmental benefits”**

## Case study: wastewater treatment at Harnaspolder

At the Dutch wastewater treatment plant Harnaspolder, located near The Hague, 225.000 m<sup>3</sup> wastewater from a million inhabitants and thousands of companies is treated daily. Harnaspolder is the largest wastewater treatment

plant in the Netherlands with 1.3 million population equivalents. Since 2015, phosphate removal and sludge dewatering have been optimised by adding magnesium hydroxide to the digested sludge buffer (figure 1). Results are described below.

### Benefits achieved:

- Improvement of reject water condition
- Operational cost reduction of 4% (ROI of 1.5 years)
- Increased dry matter content of dewatered sludge
- Opportunity to re-use phosphates
- Decrease in polymer usage by 25%
- No struvite scaling or blockage
- 42% reduction of iron chloride
- Reduction of chemical waste

## Nedmag B.V.

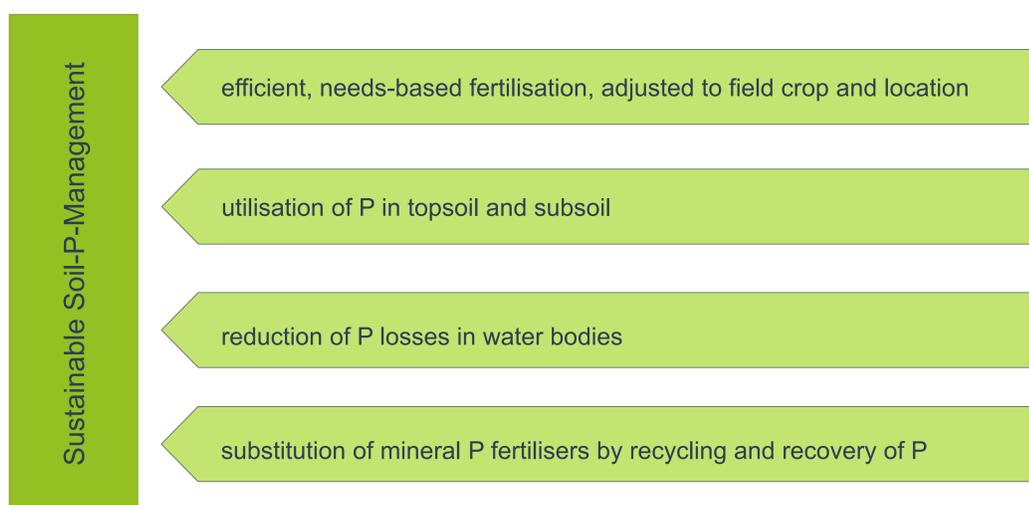
is a Netherlands based producer of magnesium oxide, magnesium hydroxide, magnesium chloride and calcium chloride. Main markets served by Nedmag are the refractories industry, pulp & paper industry, energy markets, food industries and environmental markets, with applications in wastewater treatment and flue gas treatment.



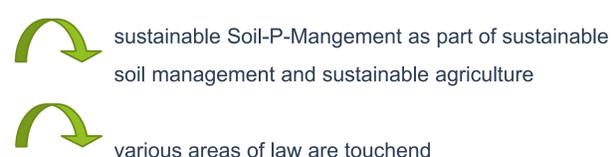
# Sustainable Soil-Phosphorus-Management in Environmental and Agricultural Law

Beatrice Garske / Jessica Stubenrauch / Felix Ekardt

## 1 Sustainable Soil-Phosphorus-Management



Although phosphorus is a vital and non-substitutable resource, the nutrient is used inefficiently. Soils with high P accumulation contrast with soils with P deficits. An appropriate Soil-Phosphorus-Management is necessary to close the P cycles, to avoid environmental damage, in particular the eutrophication of water bodies, to ensure the long-term preservation of all soil functions and to conserve the finite mineral P reserves and thus also to minimize Europe's dependence on P imports.



## 2 Starting Points of Sustainable Soil-Phosphorus-Management in German Law



## 3 Taxes, Cap-and-Trade-Schemes or Subsidies to Stimulate a Sound Use of Phosphorus

Besides the Common Agricultural Policy of the EU, the existing relevant law for P use on national and European level is dominated by **command-and-control law** which suffers from shortcomings like enforcement deficits, rebound effects and shifting effects. **Economic instruments as superior governance solutions** for quantitative environmental problems like P overuse enforce **higher prices** and/or absolute caps on (mineral) P use or other control parameters such as feed, land use or fossil fuels and can help to tackle disturbed nutrient cycles and further environmental problems such as soil degradation, water eutrophication, biodiversity loss and climate change.

## 4 Publications

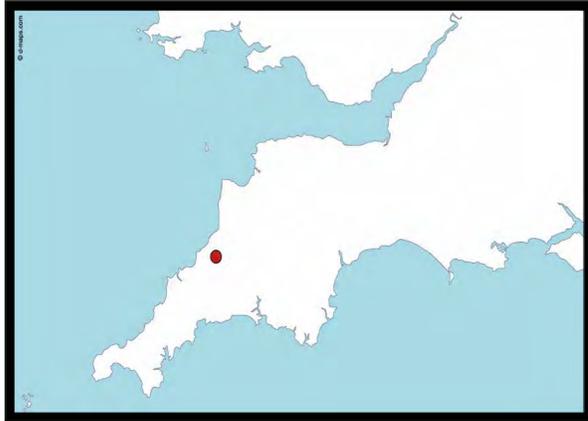
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# Investigating the impact of a dairy processing plant on a river catchment

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Location of study, in south-west England



Discharge point to river Inny



River Inny at bottom of study area

## Background

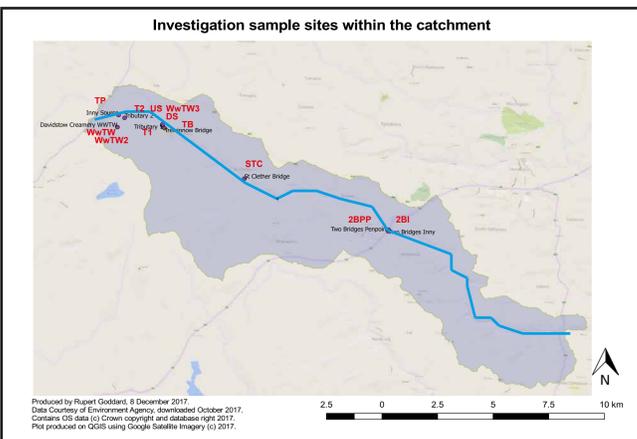
The south-west of England is an area rich in dairy farming. At Dairy Crest's Davidstow facility 500 million litres of milk sourced from Devon and Cornwall<sup>1</sup> are processed annually to produce 50,000 tonnes of cheddar style hard cheese. The plant has recently announced a significant investment to the plant to increase capacity to 77,000 tonnes per year<sup>2</sup>.

Liquid by-product waste (whey) from the primary process is demineralised on site to produce infant formula milk and galacto-oligosaccharide (GOS), a probiotic which helps to improve gut health. These processes produce a calcium phosphate cake as a waste product, which is co-mingled with other waste streams and used locally as a nutrient rich soil conditioner.

Liquid waste is piped 1000 metres away from the processing plant to the company's purpose built biological wastewater treatment works. Here, it is treated physically, biologically and chemically, including through dosing with ferric chloride. This enhances P removal before the treated effluent is discharged to the river Inny, a tributary of the river Tamar, 2000 metres from the water treatment works (middle photograph).

The Environment Agency controls permitted levels within the discharge for pH, phosphorus and suspended solids, ammoniacal nitrogen and organic load (measured as BOD5).

This study is investigating the impacts of the plant's waste discharge on the river catchment. Monthly analysis of water chemistry is undertaken. Tri-annual observations of fresh water invertebrate and diatom communities and an annual survey macrophyte communities will be made. The study area extends from the top of the Inny, 580 metres from its source to Two Bridges, 18 km from the source (right photograph). The outfall from the wastewater treatment works discharges into the river Inny 2.25 km from the source.



## Methodologies

Monthly water samples are collected to measure soluble reactive and total reactive phosphorus using the molybdenum blue method<sup>3</sup>, total phosphorus and total soluble phosphorus, by ICP-MS. On site field measurements of pH, conductivity and dissolved oxygen are collected.

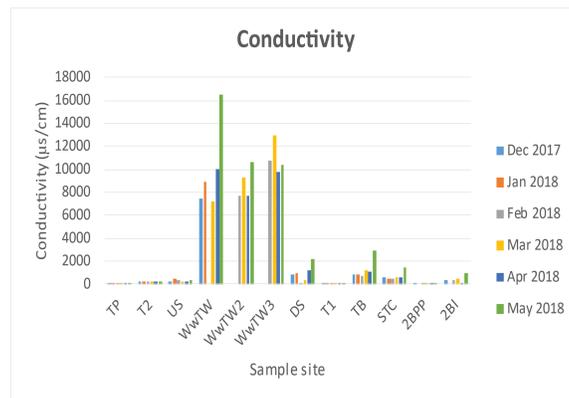
Tri-annual sampling for freshwater invertebrates is undertaken following UKTAG River Assessment methods for Benthic Invertebrate Fauna<sup>4</sup>.

Tri-annual sampling for diatoms is undertaken following Kelly et al.<sup>5</sup>, with samples being preserved and cleaned for mounting and preservation using the hot peroxide method.

## Early results

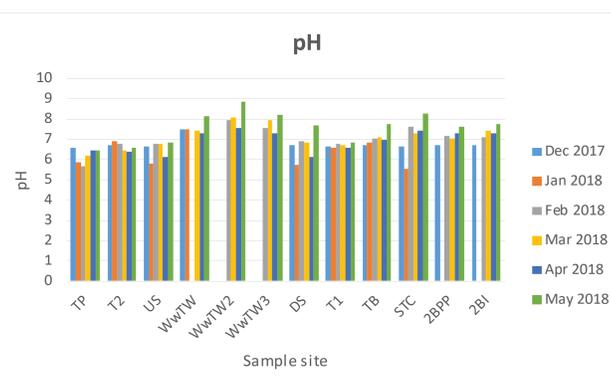
At the head waters of the River Inny, conductivity has been measured in the range 142 – 169  $\mu\text{s/cm}$ . Post-treatment, within the wastewater treatment works, conductivity has been measured in the range 7480 – 16493  $\mu\text{s/cm}$  and downstream of the discharge (site DS) within the range 107-2230  $\mu\text{s/cm}$ .

pH at the head water has been measured as 5.64 – 6.56, post-treatment, within the water treatment works between 7.26 and 8.15 and downstream of the discharge point between 5.74 and 7.65. The range of these results, taken monthly, covers the period December 2017 to May 2018.

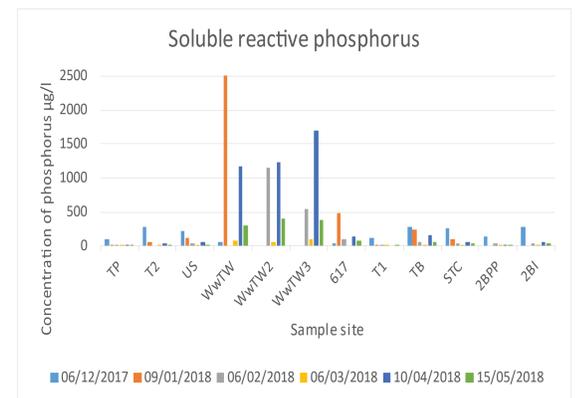
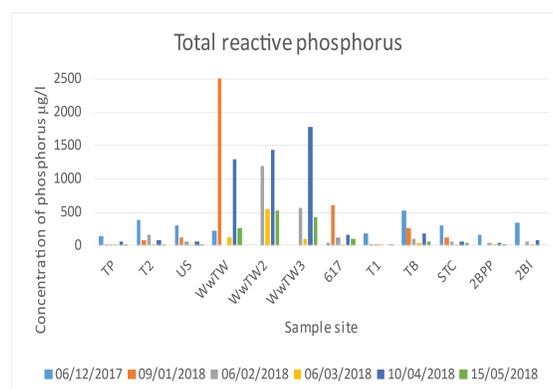


## Key to sample sites

- TP - Top of catchment
- T2 - Tributary 2
- US - Upstream of discharge
- WwTW - Post treatment
- WwTW2 - Post treatment, composite sample
- WwTW3 - Discharge to river
- DS - Downstream of discharge
- T1 - Tributary 1
- TB - Trewinnow Bridge
- STC - St Clether Bridge
- 2BPP - Two Bridges Penpoint waters
- 2BI - Two Bridges Inny

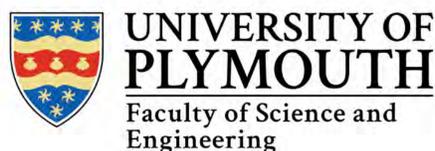
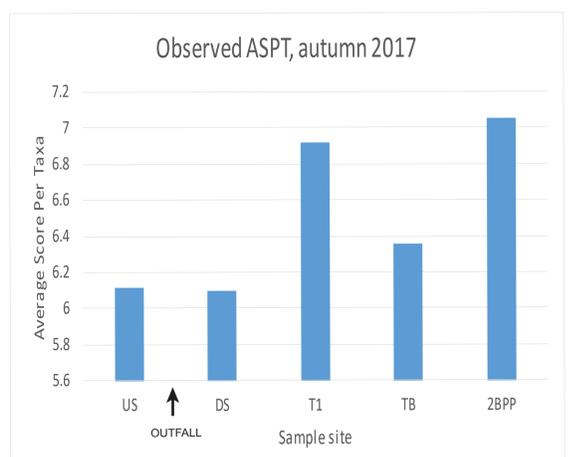
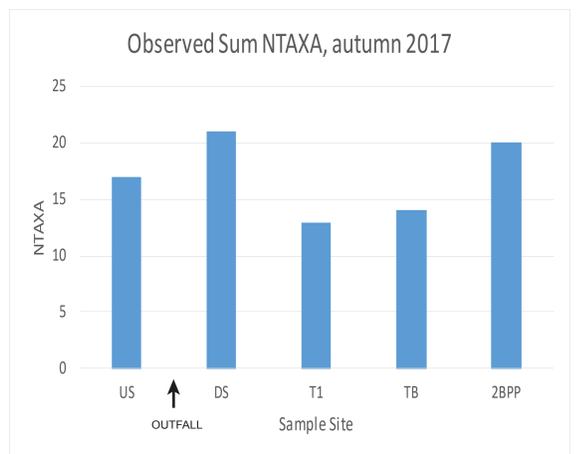


Concentrations of soluble reactive and total reactive phosphorus have been measured in the ranges 3 to 7117 and 4 to 7267  $\mu\text{g/l}$  P respectively, with the highest concentrations being measured within the water treatment works. The three sample points here all have lower SRP than TRP, showing that ferric oxide dosing is reducing the SRP load of waste being discharged. Concentrations of phosphorus downstream of the discharge point (WwTW3) have been measured in the range 35-490  $\mu\text{g/l}$  P for SRP and 15 to 617  $\mu\text{g/l}$  P for TRP, showing dilution once entering the channel.



Monitoring of invertebrates within the study is using models (eg RICT) to ascertain water quality, based on the sensitivity of invertebrate taxa to pollutants. At the time of production, the autumn invertebrate set has been identified to at least family level, but a bias correction to allow for identification errors has not yet been applied. Observed NTAXA is the sum of the number of different taxa listed within the table of benthic invertebrate taxa used for the RICT model<sup>4</sup>. Downstream (DS) of the water treatment works discharge, the score shows a higher number of listed taxa were found, compared to the head waters. Site 2BPP is a control site so is not impacted in any way by the water treatment works.

The observed average score per Taxa (ASPT) is again based on bias uncorrected data at this time so is purely for illustration. This score is calculated by dividing the sum of the pressure sensitivity score assigned to each taxon present, by the number of taxon present. A score of 10 indicates presence of very sensitive taxon. Here we can see little difference between downstream and upstream samples sets, suggesting little impact on the invertebrates from the dairy. This needs validating by comparison against a reference condition channel.



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# Flash Mixing for struvite precipitation - laboratory scale case study

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## Abstract

Ammonium nitrate removal from contaminated water stream as magnesium ammonium phosphate (MAP), or struvite, is particularly interesting as the reaction product can be further used as a fertilizer. The process is known to be slow and requiring a core structure to form. An innovative and more efficient solution for the precipitation process was studied as part of iFORMINE project. Aim of the project is to transfer the knowledge and technologies for handling large water flows from forest industry to mining industry. One promising case is TrumpJet® Flash Mixing, which increases efficiency and cuts chemical and water consumption in paper making remarkably. A special laboratory scale Flash Mixing Reactor was used to create optimal conditions for efficient struvite precipitation; faster, in smaller volumes and without the core structures. Batch experiments gave promising results with > 90 % ammonia removal.

## Introduction

Nitrogen release to mining wastewaters come from various sources, the major ones being the undetonated nitrate rich explosives and nitrogen containing chemicals used in enrichment processes. The reactive nitrogen compounds that end up in the receiving waters cause eutrophication and deterioration of water quality. There are number of physical-chemical and biological techniques available for the treatment of nitrogen containing waste streams. [1] However, an interesting process exist to convert ammonium nitrate into reusable fertilizing product and thus contributing overall nitrogen cycle. Magnesium ammonium phosphate (MAP) or struvite precipitation is an environmentally friendly process that removes ammonium nitrate from wastewater. Struvite contain both N and P and has a slow leaching rate, which makes it a good fertilizer. [2]

Previous studies has indicated that mixing has significant influence on the product quality in precipitation process [3, 4]. Struvite precipitation is a crystallization process and dependent on reaction kinetics such as nucleation, pH and molar ratio. However, aim is to optimize the precipitation conditions, but also generate a reusable product with high purity. [5]

## Materials and methods

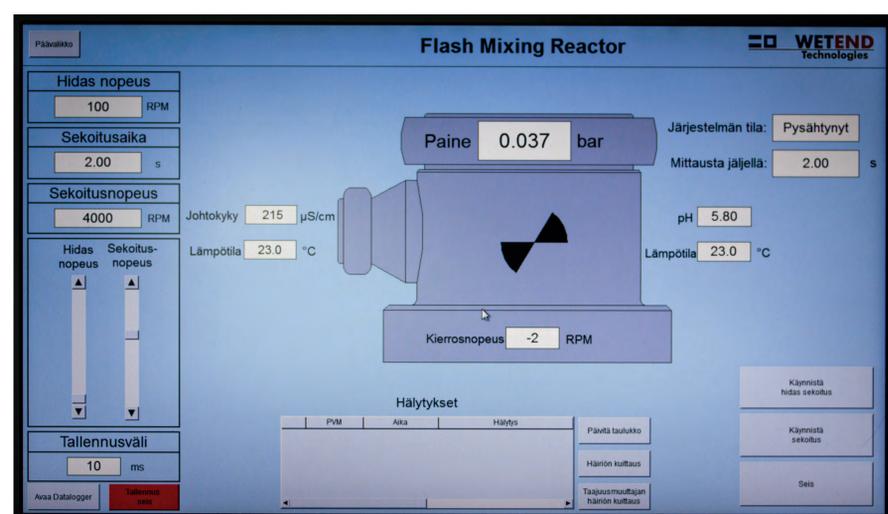
Three different water samples from a mill ground were studied. Ammonium concentrations were 480, 720 and 2250 mg NH<sub>4</sub>-N/l. Samples were free of suspended solids and pH level was 6-7.

Ammonium concentrations of the water samples were measured using Spectroquant photometric test (2-150 mg NH<sub>4</sub>/l) after 0,45 µm filtration. Water samples were diluted with distilled water if necessary. Particle size distribution of struvite crystals was determined using Malvern Mastersizer 2000.

Phosphoric acid solution was used as a concentration of 250 g H<sub>3</sub>PO<sub>4</sub>/l. Magnesium hydroxide solution was used as a concentration of 350 g MgO/l. The required amount of H<sub>3</sub>PO<sub>4</sub> was calculated by using stoichiometric coefficient 1,2 for PO<sub>4</sub><sup>3-</sup> in equation Mg<sup>2+</sup> + PO<sub>4</sub><sup>3-</sup> + NH<sub>4</sub><sup>+</sup> → MgNH<sub>4</sub>PO<sub>4</sub>. Desired final pH (8-9) of precipitation quantified the required amount of magnesium hydroxide solution (stoichiometric coefficient of Mg<sup>2+</sup> was 13-16).

Struvite precipitation tests were accomplished by using Wetend Technologies Flash Mixing Reactor (Figure 1). The reactor has a mixing chamber (volume 3 l) with adjustable mixing speed (100...4000 rpm). Phosphoric acid solution was added first, then magnesium hydroxide solution. After reaction chemicals added to water (2 l), mixing sequence was first 100 rpm (2 s), then 4000 rpm (2 s) and finally 100 rpm (5 s). The precipitation time after mixing was 5 min. After the analyzes a remaining sample of struvite slurry was dried in 105 °C temperature and crushed manually using a mortar to get a powdered sample (Figure 2). Figure 1. Operation sheet of Flash Mixing Reactor.

Figure 1. OPERATION SHEET OF FLASH MIXING STATION



## Acknowledgements

This research was conducted as part of iFORMINE –project (Innovative forest technology based water treatment and eco-efficient solutions for mining industry), funded by the European Regional Development Fund.

## Results and discussion

The final ammonium concentrations are presented in table 1. Reductions of concentrations are 94-99%. Ammonium can be precipitated fast and almost completely with the help of flash mixing. On the other hand, high amount of magnesium hydroxide is required for pH control. Also Mg(OH)<sub>2</sub> can precipitate and pure struvite is not generated.

Particle size distribution of precipitated crystals (sample 2) is presented in Figure 3. Approximately 58% of crystal sizes are less than 10µm. High portion of small particles can make the separation difficult in large-scale operations. SEM image of precipitated crystals is presented in Figure 4.

Table 1. RESULTS OF PRECIPITATION TESTS USING FLASH MIXING.

Water sample n:o	Initial NH <sub>4</sub> -N mg/l	Added H <sub>3</sub> PO <sub>4</sub> g/l	Added Mg(OH) <sub>2</sub> gMgO/l	Final pH	Final NH <sub>4</sub> -N mg/l
1	480	3.9	17.9	8.4	25
2	720	5.8	27.3	8.0	13
3	2250	18.1	102.9	8.3	10

Figure 2. POWDERED STRUVITE SAMPLE.



Figure 3. PARTICLE SIZE DISTRIBUTION OF PRECIPITATED CRYSTALS (SAMPLE 2).

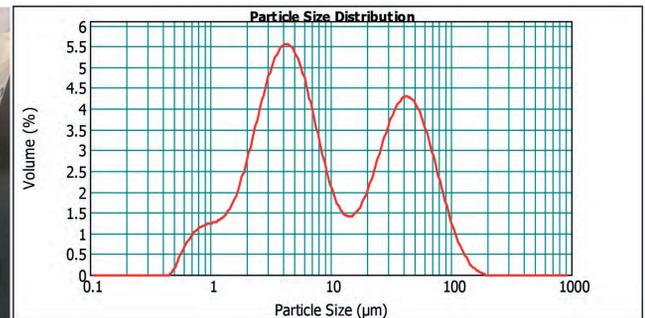
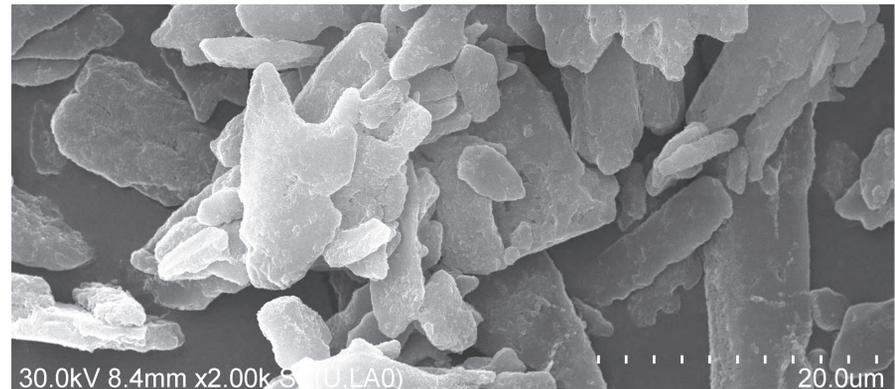


Figure 4. SEM IMAGE OF PRECIPITATED CRYSTALS.



## Conclusions

- Ammonium can be precipitated as struvite fast and almost completely with the help of flash mixing.
- Consumption of magnesium hydroxide is high due to required pH level (8-9).
- Pure struvite is not generated because of precipitated Mg(OH)<sub>2</sub>.
- Separation of crystals in large scale can be difficult due to small particle size.

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Leväsieppari

# Nutrient recovery from wastewater by microalgae



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The Leväsieppari project (2018-2019) is funded by the Ministry of the Environment. The project contributes to Finland's action programmes concerning river basin and marine area management that set down the measures to achieve a good status of waters. The project also implements the Government key programme 'Breakthrough to a circular economy and adoption of clean solutions'.

## OBJECTIVES

- Demonstrate algal cultivation in various wastewaters both *in situ* and *in vitro* (see Experiment 1-4)
- Study the optimization of the cultivation conditions
- Study the suitability of the algae biomass as fertilizer for plant production (Experiment 5)
- Estimate the potential of nutrient harvesting with microalgae from wastewaters in Finland
- Estimate the potential to reduce nutrient load to wastewater treatment plants as well as to recipient water courses
- Disseminate the results

### Experiment 1

#### Algal cultivation in treated municipal wastewater

At Lammi WWTP of HS-Vesi, we will estimate to which extent nutrient loading from the WWTP into water courses could be reduced by algal cultivation in a constructed wetland.



Photos: Lammi Biological Station



Experiments are carried out in 1 m<sup>3</sup> containers by the Helsinki University Lammi Biological Station in Lammi, Hämeenlinna.

### Experiment 2

#### Algal cultivation in human urine

In a new residential area in Hiedanranta, City of Tampere, composting toilets are used and human urine is drained separately and then used for algal growth. This experiment is carried out in raceway ponds by Tampere University of Technology.



Photo: Priitika Chatterjee

## BACKGROUND

- Present wastewater treatment wastes nutrients by binding phosphorus in chemical compounds recalcitrantly available for plant production, whereas most of nitrogen is degassed into the atmosphere.
- A remarkable portion of the nutrients entering the wastewater treatment plants (WWTP) could be captured by harvesting with microalgae near the source.
- Additionally, algal cultivation can be applied as tertiary treatment at WWTP after the initial treatment process to reduce nutrient loads to recipient water courses even further.
- In the algal biomass, nutrients are in optimal proportions in organic form and can readily be used as fertilizer and in soil amelioration.

This poster illustrates 5 examples of the experiments carried out in the project.

### Experiment 3

#### Algal cultivation in landfill leachate

At Karanoja landfill area of Kiertokapula in Hämeenlinna, algae are grown in the leachate in a raceway pond. This experiment is carried out by the HAMK University of Applied Sciences.



Photo: HAMK

### Experiment 4

#### Algal cultivation in reject water of biogas production plant

Reject water from Gasum biogas production plant is used for algal growth in an experiment carried out by the Finnish Environment Institute in Helsinki. An analysis on how algal cultivation could be incorporated into biogas production processes follows.

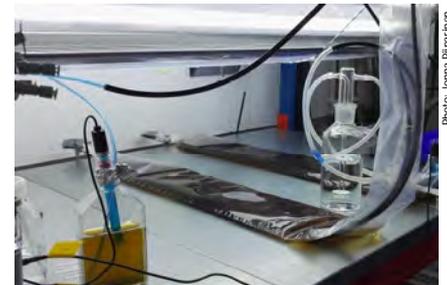


Photo: Jonna Piiparinen

### Experiment 5

#### Algal biomass as a fertilizer

After the different kinds of algal biomasses have been grown and harvested in experiments 1-4, they are tested for their fertilizer qualities in growth experiments. The biomasses are applied to the substrate in varying proportions, and different types of plants are grown in the substrate. This experiment is carried out by the HAMK University of Applied Sciences.



Photo: HAMK

**RESULTS SCHEDULE** The experiments on different locations are starting in May-June 2018. First results are expected by autumn 2018. Complete results will be available by end of 2019.



# INHIBITION OF PHYTASE ACTIVITY BY POLYPHENOL-RICH EXTRACTS FROM SORGHUM, IN RELATION TO PHOSPHORUS SUSTAINABILITY

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## Abstract

The antinutritive effect of phytic acid is tackled by using phytase in the animal feed, but there is no solution for the polyphenols' antinutritive effect. For this project, polyphenols were extracted from different sorghum varieties and the polyphenol-rich extracts were used to estimate their effect on the activity of a commercially used phytase. The results showed a negative impact of the polyphenol-rich extract on the phytase activity. As a result, less phosphates are cleaved from the phytic acid, which has a series of negative effects. Less phosphate released, therefore inorganic phosphate supplementation is required in the feed. Amidst current concern over the longevity of global phosphate reserves, this is an unsustainable practice. Finally, the inefficiency of phytase leads to higher levels of phosphorus present in the animal's excreta that must be eliminated since it is then released in the waste water stream and ends up in rivers.

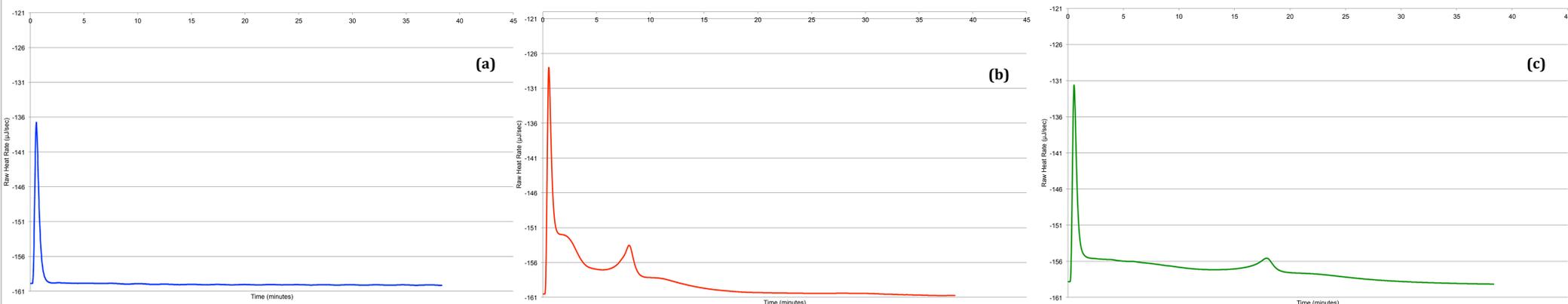
## 1 Introduction

- Phosphorus security is emerging as one of the twenty-first century's greatest global sustainability challenges.
- It is essential to improve the phosphorous efficiency for agricultural use to contribute to the reduction of demand for fossil P resources [1].
- The use of phytase to de-sequester phosphate from phytic acid in animal feed has resulted in a reduction in P excretion by 25–50% dependent on type of animal, species and activity of added phytase [2].
- Polyphenols are present in grains and their natural aim is to deter ingestion to animals. It is believed that they interact with digestive enzymes and proteins and subsequently decrease their efficiency.
- The anti-nutritive effect of polyphenols is profound, but not all the interactions causing this effect are known. For the purpose of this project, the effect of the polyphenol-rich extracts on the phytic acid-phytase reaction was estimated.

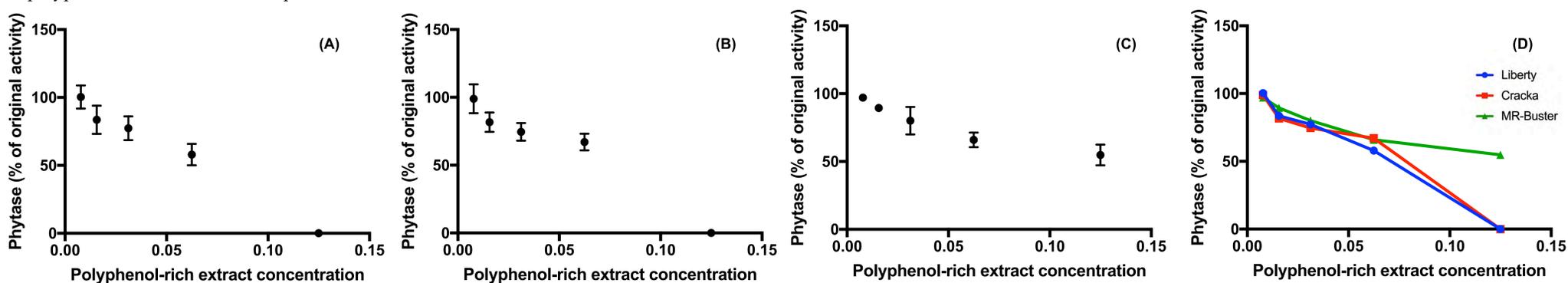
## 2 Materials and Methods

- The polyphenol-rich extract was isolated from a red sorghum, mai.<sup>(b)</sup>, the bran, using 70% aqueous acetone.
- Phytase was incubated with the sorghum polyphenolic extract for 25 minutes.
- The enzyme assay used a TA Instruments NanoITC; injecting 5  $\mu$ L of 20 mM phytate into 0.125  $\mu$ M Hiphos in 5% ethanol and a series of different concentrations of the polyphenol-rich extract (0-0.125mg/ml).
- The inverse of the time for 90% completion of the phytase catalysed reaction to occur was used as activity in this assay.<sup>(c)</sup>
- Experiments on ITC were conducted at 30°C and 285 rpm. Note, the ethanol is present to solubilise the polyphenolic extract and does not affect the assay.

## 3 Results



**Figure 1:** Thermograms obtained by single injection Isothermal titration calorimetry experiment of: (a) 5  $\mu$ L of 20 mM Phytic acid into 300  $\mu$ L of 0.109 mg/ml of polyphenol-rich extract in 5% aqueous ethanol, (b) 5  $\mu$ L of 20 mM Phytic acid into 300  $\mu$ L of 0.125  $\mu$ M phytase in 5% aqueous ethanol and (c) 5  $\mu$ L of 20 mM Phytic acid were titrated into 300  $\mu$ L 0.125  $\mu$ M phytase and 0.109 mg/ml of polyphenol-rich extract in 5% aqueous ethanol.



**Figure 3:** The relative reduction in phytase activity in the presence of acetone extracts from the sorghum varieties (A) Liberty, (B) Cracka, (C) MR-Buster and (D) their comparison.

## 4 Discussion & Conclusions

- As shown in Figure 2, the enzymatic reaction of phytic acid and phytase is inhibited or prolonged by the addition of polyphenol-rich extract, compared to the reaction without any additives.
- With 0.125mg/ml there was a complete inhibition of the phytase by the Liberty and Cracka extracts and a 45% decreased enzymatic activity with the extract from MR-Buster.
- At lower concentrations (0.013 mg/mL) the polyphenolic extract from Cracka had the highest effect on the phytase activity (18.5% decrease), followed by the Liberty extract (16.5%), followed by MR-Buster (10.5%).
- Therefore, preventing the inhibition of phytase by the polyphenol-rich extract could improve the monogastrics nutrition, which would lead to higher phytase efficiency and reduced fossil P used as an additive to the animal feed.
- With less P excreted, there will be a reduction in the amount of P entering watercourses as a pollutant.

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# RECYCLING PHOSPHORUS FROM THE WATERBODIES INTO PLANT PRODUCTION: SEDIMENT Fe/P RATIO IS THE KEY



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## Importance and Objective



The aim of this research was to compare different ways of sediments applications to soil to quantify their effects on root growth, yield, and nutrient uptake by ryegrass.

## Methods



Restoration of Heavily Eutrophicated Lake, Viljandi, EE.



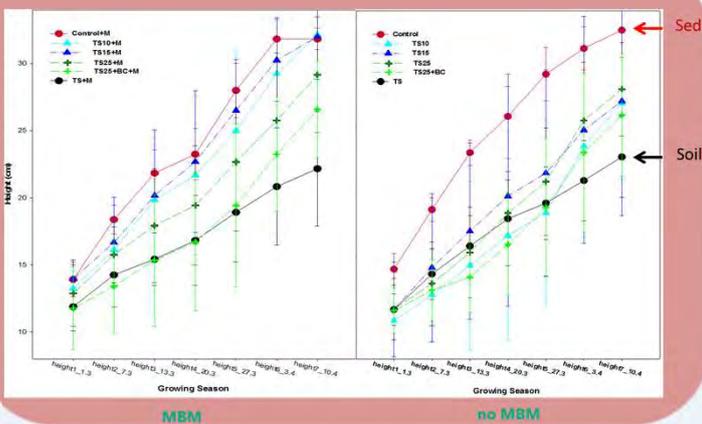
Collecting Soil and Sediment from the Storage Site Near the Lake Shore.



Treatments in Lysimeter Study.

## Results (sediment Fe/P ratio is the key)

### 1. Ryegrass Height



### 2. Biomass and Leachate

Table 1 - Analysis of variance for dry above-ground biomass (ton ha<sup>-1</sup>) and leachate (mm) in 2017 for lysimeter study.

Treatment	dry above-ground biomass (ton ha <sup>-1</sup> )				Leachate (mm)			Total
	1 <sup>st</sup> cut	2 <sup>nd</sup> cut	3 <sup>rd</sup> cut	Total	Leachate 1	Leachate 2	Leachate 3	
Sediment (S)	0.000**	0.000**	0.000**	0.000**	0.000**	0.091	0.020*	0.023*
Fertilizer (F)	0.468	0.245	0.591	0.232	0.046*	0.211	0.797	0.578
S * F	0.190	0.623	0.604	0.437	0.981	0.501	0.527	0.510
<b>Sediment</b>								
control	8.69 a	6.15 a	4.65 b	19,47 a	48.14 a	18.43	8,76 ab	75,33 a
TS10	3.72 b	6.01 a	7,06 a	16,80 a	28.89 b	25.89	7,99 ab	62,77 ab
TS15	4.39 b	6.00 a	5,69 ab	16,09 a	26.49 bc	17.36	17,35 ab	61,20 ab
TS25	3.89 b	6.93 a	6,39 ab	17,20 a	23.84 bc	7.55	2,23 b	33,61 ab
TS25BC	3.85 b	7.66 a	6,81 a	18,32 a	23.30 bc	5.97	0,31 b	29,59 b
TS	2.89 b	2.48 b	2,43 c	7,79 b	22.21 c	7.08	25,43 a	54,72 ab
SEM	0.68	0.809	0.687	1.760	1.481	7.851	7.520	
<b>Fertilizer</b>								
MBM	4.78	6.23	5,60	16,60	30.07 a	10.07	10,64	50,77
noMBM	4.37	5.51	5,41	15,29	27.55 b	17.36	10,06	54,97
SEM	0.40	0.330	0.280	0.718	0.855	3.205	3,070	5,846

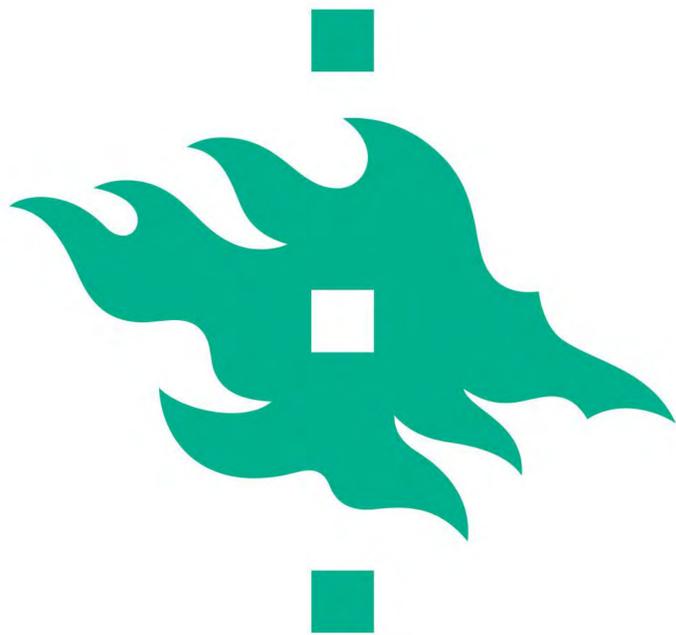
## Conclusion

- We found that the treatment containing 75cm of sediments on topsoil had initially the greatest ryegrass aboveground biomass and height.
- The P fraction results of fresh soil and sediment samples revealed that unlike the previous research on sediment P availability, there is more available P in sediment than in soil samples.
- Our small case study results can be upscaled to larger lakes with similar sediment properties which will aid in reducing transformation of nutrients to water bodies and facilitate the disposal of dredged sediments in agriculture and environmental engineering.

**Acknowledgements:** We are grateful for technical assistance by Merike Kissa, Miia Collander, & Sepehr Fatemi. Also, many thanks to our funding sources:

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**GOVERNMENT  
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# AGROECOLOGICAL SYMBIOSIS – INTEGRATING BIOGAS PRODUCTION INTO NUTRIENT RECYCLING

Agroecological Symbiosis (AES) is a food production model based on theories of Industrial symbiosis and Industrial ecology.

## PALOPURO CASE STUDY

The first AES is emerging in the village of Palopuro, Southern Finland. The centre of Palopuro AES is Knehtilä Farm, which is an organic cereal farm. Other farms include a henhouse and a vegetable farm. The biogas plant will start to operate in autumn 2018 and future construction of a bakery is also planned for processing grain into bread onsite at the farm.

Both nutrient flows and the amount of energy produced from green manure leys and manures were studied. The AES system was modelled as if in full operation and compared to the current situation.

## INCREASED PRODUCTION WITH REDUCED LOSSES

Circulating the grass biomass and manure through the biogas plant increased crop production by reducing nutrient losses from the system. Phosphorus surplus were reduced by 3.7 kg ha<sup>-1</sup> compared to the current situation.

The most substantial phosphorus input was derived from the hennerly. This was due to imports of chicken feed concentrate. Also, horse manure contributed a substantial amount of phosphorous to the system. In addition to increased food production, biogas production converted the system from energy consumer to an energy producer (2800 Mwh).

Results demonstrated the potential of biogas production based on utilizing biomasses available with-in the farming system to increase primary production in farming, reduce nutrient losses, and produce renewable energy in excess while enhancing nutrient recycling.

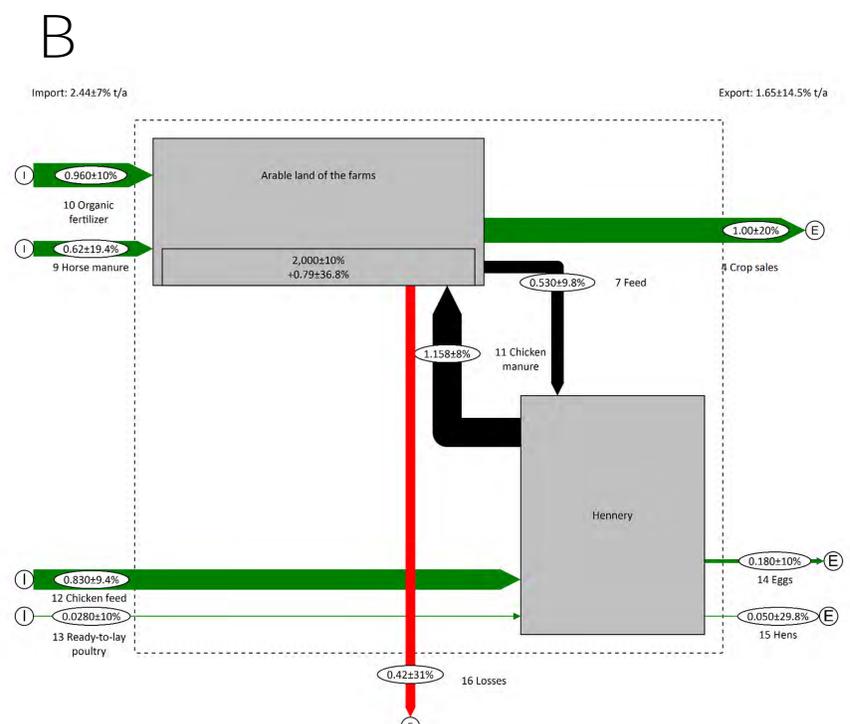
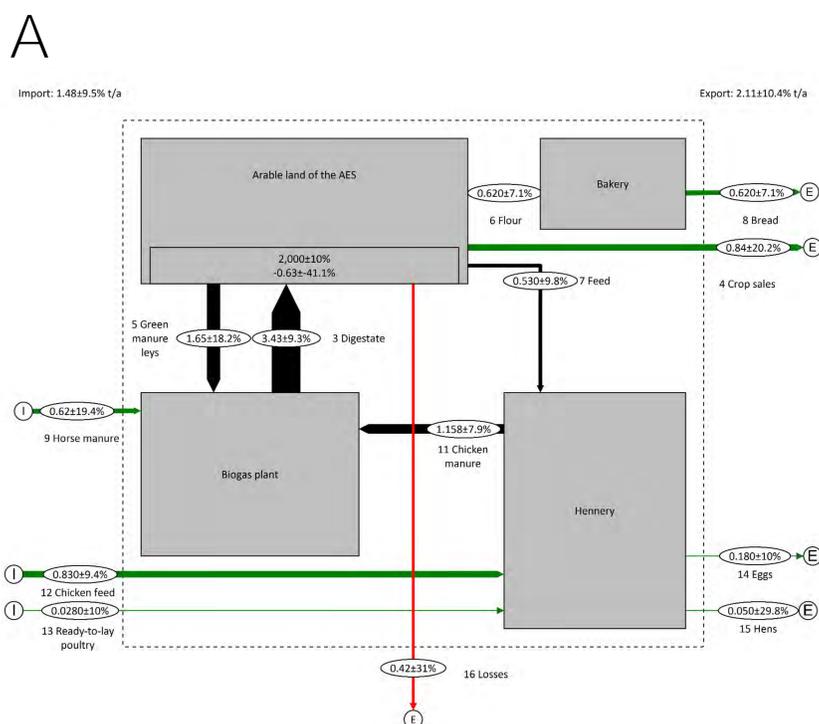
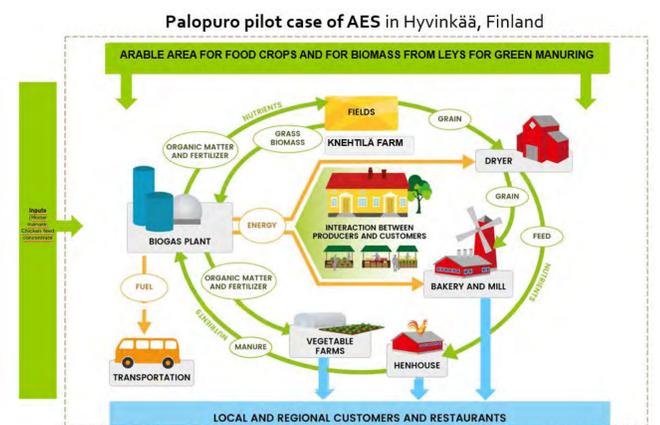


Figure: Phosphorus flows (tn a<sup>-1</sup>) in the AES (A) and in the current system (B). The width of the arrow is proportional to rate of the flow. Green arrows illustrate imports to the system and exports out of the system, red arrows illustrate the losses from the system and black arrows are the flows within the system. (Source: Koppelmäki et al. 2018. Manuscript submitted to Agricultural System).



## Phosphate Recovery research theme

Research at Wetsus is clustered in research themes. These themes are IP clusters with participation of industrial partners. One of the 22 themes of Wetsus is dedicated to P recovery. Core competence of the research theme is the understanding of **interactions of phosphate with iron** in complex organic matrices like sewage sludge and manure.



## Vivianite recovery

The majority of municipal wastewater treatment plants (WWTP's) use **iron salts** to co-precipitate iron phosphates. This method of operation is popular as it presents low investment costs and is easier to operate. Incineration is the only available method to recover phosphate from these types of WWTP's.

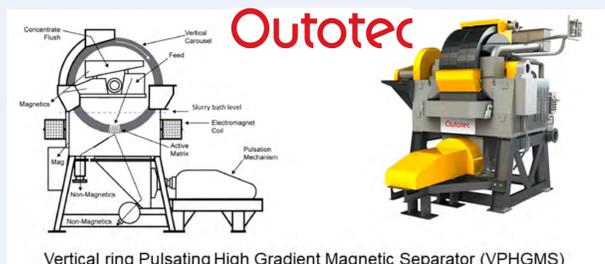
Unfortunately, this technique presents limitations like the lack of ash treatment facilities and the required investment costs to realize an incineration facility.

Research at Wetsus showed that almost all phosphorus in sludge is present as **vivianite**, provided that enough iron is present and the sludge is digested. This discovery opened new perspectives for phosphorus recovery from sludge and possibly also for manure.



Fig. 2 Image of a vivianite sample from an STP and SEM image of a vivianite particle recovered from digested sludge.

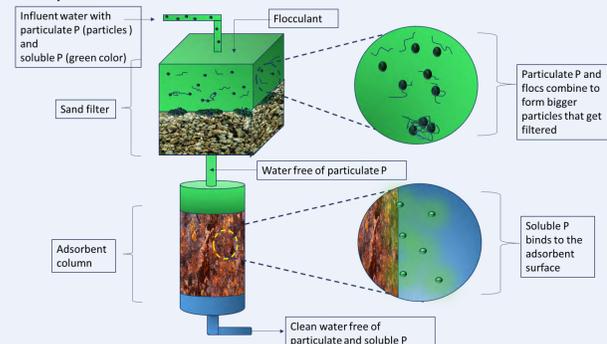
Within the VivIMAG project magnetic separation of vivianite from sewage sludge will be piloted using standard magnetic separators from the mining industry. In addition research is performed to understand the crystallization mechanisms of vivianite formation.



**Wetsus**, European centre of excellence for sustainable water technology is a facilitating intermediary for trendsetting know-how development. Wetsus creates a unique environment and strategic cooperation for development of profitable and sustainable state of the art water treatment technology. The inspiring and multidisciplinary collaboration between companies and research institutes from all over Europe in Wetsus results in innovations that contribute significantly to the solution of the global water problems. Wetsus' scientific research program is defined by the private and public water sector and conducted by leading universities. Wetsus is part of WaterCampus Leeuwarden. WaterCampus Leeuwarden is the physical core of the Dutch water technology sector and has the ambition to play a sector uniting role for the rest of Europe as well.

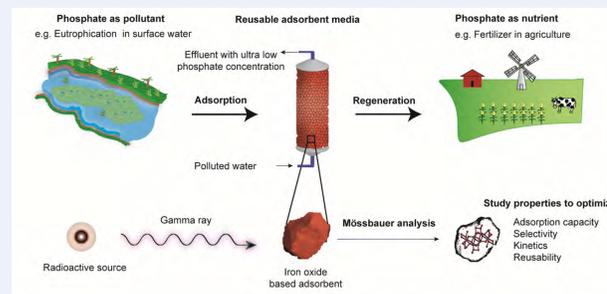
## Phosphorus removal and recovery to ppb level

Excess phosphorus is the main cause for eutrophication and (toxic) algae blooms. This is a world wide problem. To combat this, phosphorus needs to be removed to ultra low concentrations at a reasonable cost. Wetsus has developed the **NaFRad** technology that can do exactly this with a very small footprint.



Wetsus NaFRad is a two-step approach where phosphorus is removed through **flocculation** to remove particulate phosphorus and **adsorption** to remove the soluble phosphorus. This approach has a very small plot size and low operational costs. The adsorbent can be regenerated to recover the phosphorus.

Research at Wetsus focusses on understanding the fundamentals of adsorption and regeneration of the adsorbent as this is key to an economic application. Wetsus uses advanced **Mössbauer** facilities to study the iron based adsorbent and the interaction with phosphate.



## George Barley prize winner!

The Everglades Foundation has commissioned a 10 M\$ prize contest to stimulate technologies that can remove phosphorus economically down to 10 ppb. The Wetsus team won stage 1 and 2 of this prize contest and was 1 of the 9 teams participating in stage 3, a 3 month pilot test in Ontario, Canada.



[www.barleyprize.org](http://www.barleyprize.org)

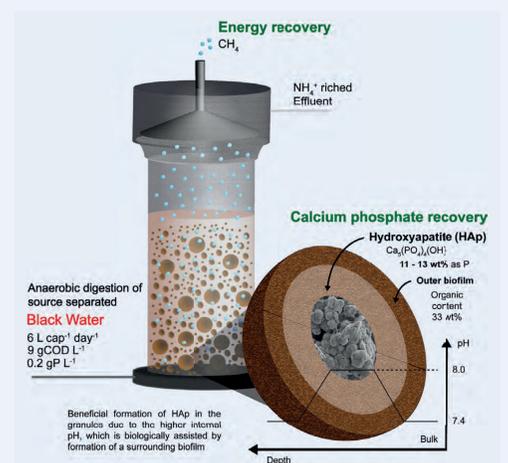


## More P-recovery technologies

Also other research clusters within the Wetsus network develop new approaches to P recovery

### Calciumphosphate formation in anaerobic digestion

Wetsus research shows that one can stimulate the formation of **calciumphosphate** granules in a UASB type digester of source separated black water. In this way phosphate recovery can be combined with energy production. The technology also holds interesting promises for compact **manure** digestion.

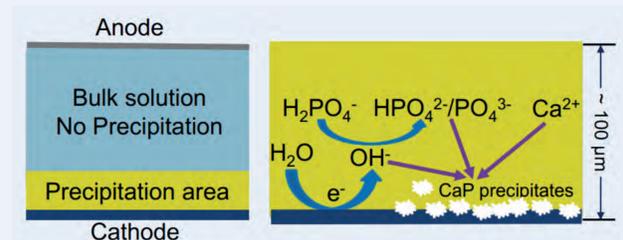


### Membranes for phosphate removal and recovery

This research focusses on the modification of **anion exchange membranes** to make them more selective for phosphate transport. The main challenge of the project is to find a combination of materials (receptor and membrane) and methods that allows to selective binding and recovery of phosphate.

### Electrochemical recovery of phosphorus by calcium phosphate precipitation

This a promising method for removal of phosphate from waste streams because it can stimulate calcium phosphate precipitation without the need to change the bulk pH of the waste water, thus minimizing the chemical uses. In addition less crystalline products can be formed that are more suitable as a fertilizer.



### Closed loop phosphonate recovery and usage optimization

Phosphonates belong to the most widely used antiscalants in RO desalination processes. A closed loop adsorption process can prevent discharge of the phosphonates and recover them at the same time.

# Manure phosphorus surplus from fur animal production in Ostrobothnia, Finland

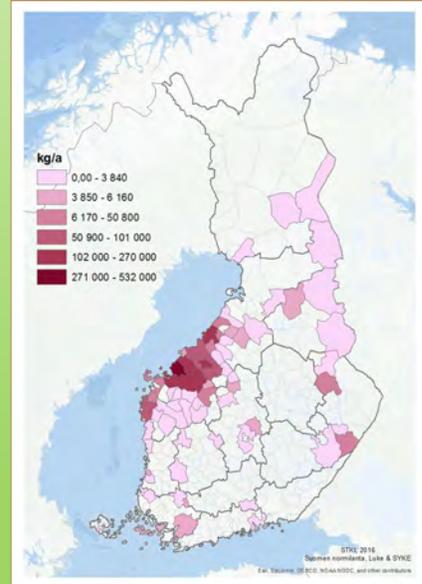
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## BACKGROUND

- Fur animal production is highly concentrated in a region, which also hosts other intensive animal production
- Fur animal manure is rich in nutrients ( $P_{tot}$  and  $N_{tot}$  up to  $20 \text{ kg t}^{-1}$ ) due to the feed consisting mostly of fish and slaughtering by-products
- Of the total manure P in Finland, 16% is produced in fur farms mostly located in this region (Fig. 1)
- Fur farms rarely cultivate crops and their manure should be utilized by other farms



**Fig. 1. Manure phosphorus from fur animals (kg/year).**

## OBJECTIVES

- To create comprehensive concepts for manure processing to decrease regional imbalance of manure-based nutrients
- Special attention given to improved nutrient management in fur production

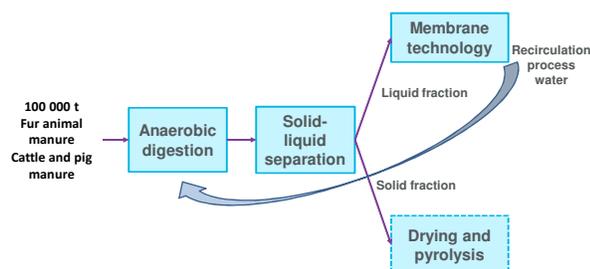
## METHODS

Manure processing demonstrations

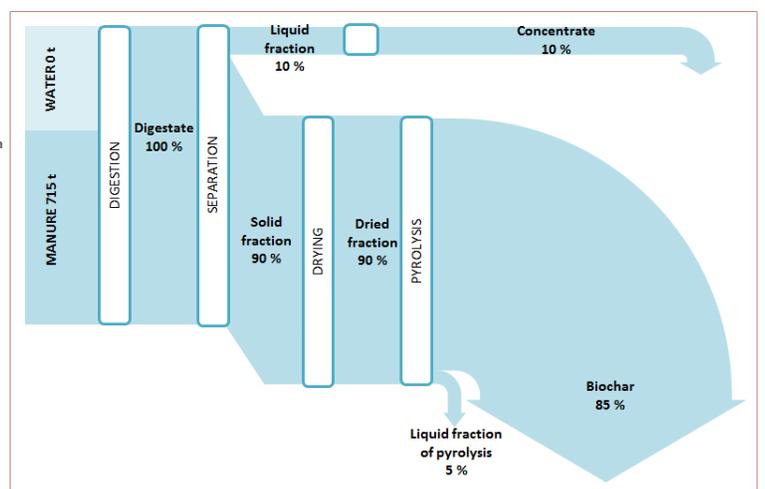
- Biogas production and digestate post-processing to new fertilizer products
- Pyrolysis of fur animal manure and characterisation of produced biochar, liquid and gas fractions (See poster Sarvi et al.: Pyrolysis as a method for improved phosphorus recycling of fur animal manure)

## MANURE PROCESSING EXAMPLE

Biogas production and digestate post-processing:



- 85% of manure P in biochar (Fig. 2), representing <5% of total manure mass processed
- 75% of N recovered as a concentrate from membranes



**Fig. 2. Distribution of P in digestate fractions after processing.**

## FURTHER ACTIONS

Life cycle environmental impacts and economic potential will be assessed.

# Feeds and soil improvers from vegetable by-products

GOVERNMENT  
KEY PROJECTS

Marja Lehto, Marketta Rinne, Eila Järvenpää, Minna Kahala, Hilikka Siljander-Rasi, Tapio Salo, Terhi Suojala-Ahlfors, Natural Resources Finland (Luke)

SivuHyöty project funded by the Ministry of the Environment in the RAKI program examined the handling of vegetable by-products as feeds and soil improvers.

## Background

Vegetable by-products come from warehouse waste, sorting sources, peeling of root vegetables, preparation for sale, and the production of salads and other vegetable products. Vegetable by-products contain nutrients and organic matter, and are well suited for feed and soil improvers.

## Feed

Vegetable by-products used for feed must meet nutritional and hygienic requirements. Carrot by-products are wet and up to half of the dry matter are sugars. Fresh by-products are suitable e.g. for cattle and the stability of them can be improved by chemical preservatives such as formic, propionic and benzoic acids to extend the delivery intervals.

Two case studies involved carrot by-product ensiling using lactic acid bacteria inoculants and formic acid based additives. The pH of all samples ranged from 3.4 to 3.8 after a 3 to 4-week ensiling period. Organic acid content of ensiled control and inoculated samples were similar, but acid effectively restricted production of lactic and acetic acids while promoting ethanol production (Figure 1).



Carrot by products have high moisture and sugar contents, which makes them a challenging material to utilize. Photo: Luke / Marketta Rinne.

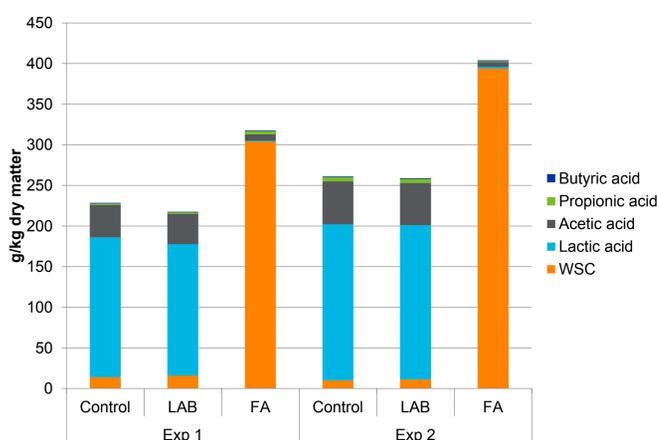


Figure 1. Sugars in carrot by-products were vigorously fermented into lactic and acetic acids in spontaneously fermented or lactic acid bacteria (LAB) inoculated carrot by-product materials during ensiling period of 4 (Exp. 1) or 3 (Exp. 2) weeks. The fermentation could efficiently be restricted by formic acid (FA) addition. WSC = Water soluble carbohydrates.



Photo Johanna Rihtilä / Luke

## Soil Improver

The vegetable material contains 85-90% water, so the dry support material has to be abundant, if composting is used. Various bedding materials of compost were tested: peat, reed canary grass, biochar and cardboard. Composts were tested in pot and field experiments.

In pot experiment composts were tested for their nitrogen (N) availability. In all composts, total N was added 300 mg/l soil, that lead soluble N additions of 10-70 mg/l. Ryegrass growth was compared against inorganic N additions (N: 0, 100, 200 and 300 mg/l soil). The growth responses and N uptakes of composts were related to their content of soluble N (Figure 2) and no negative growth effect or increased growth due to organic N mineralisation was observed in three ryegrass yields. Field experiment was conducted on barley, and the total N applications were 85 kg/ha which lead to soluble N additions of 3-20 kg/ha. These soluble N additions had a slight increase on barley yield. Vegetable composts supply organic matter, phosphorus and potassium, and are well suited for soil improvement, but nitrogen fertilization has to be supplemented with mineral fertilizers.



Ryegrass growth in pot experiment. Treatments from left to right: 0 mg/l N, Peat compost (N 66 mg/l), 100 mg/l N and 200 mg/l N. Photo: Luke / Tapio Salo.

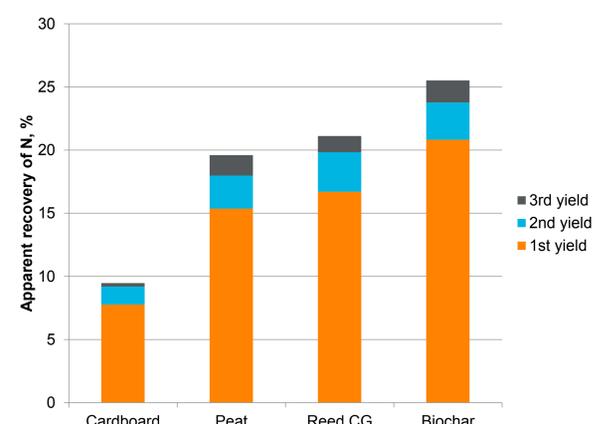


Figure 2. Apparent recovery of applied total N [(N uptake of treatment – N uptake of non-fertilised yield)/ applied total N] of the four studied vegetable by-product composts.

# Pasrea composting system with heat and ammonia reclamation for animal shelters

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## Introduction

The transport of manure to large scale processing plants for treatment is typically unfeasible or unrewarding for the farmer, and application to local fields is not always possible due to excess manure volumes or great distances. Simultaneously, with intensifying agricultural practices, the efficient reuse of manure is limited by its increasing volume, and its low potential for value.

Composting lowers the mass of manure, makes its nutrients more plant available, and allows its sale as compost, but a lot of its potential is lost as gaseous releases and heat.

For an economically viable solution, a local treatment method capable of reclaiming this lost potential is needed.

## Materials and methods

We aimed to develop an integrated composting solution, with under pressure aeration, that could be built into an animal shelter, and which allowed the reclaiming of heat and gaseous nitrogen releases from the composting manure in an economically viable way onsite.

The concept was tested on multiple levels, with compost unit sizes ranging from small scale pre-experiments of <math><1\text{ m}^3</math> and

The full system was built into a animal shelter, with the floor laid from perforated hollow core concrete slabs. Air-water heat pump units were installed inside the slabs.

For further heat efficiency, incoming replacement air of the animal shelter was warmed through nested airpipes which formed an air-air heat exchangers.

## Conclusions

- Forced under pressure aeration allows composting of dry bedded manure without mixing
- Heat reclamation is possible with both air to air, and air to water heat exchangers
- There is potential for nitrogen collection from the reclamation systems condensation water

## Acknowledgements

This research was done with financing as a government key project, coordinated by the Centre for Economic Development, Transport and the Environment, of south Ostrobothnia



Centre for Economic Development, Transport and the Environment

**GOVERNMENT  
KEY PROJECT**

## System functionality

In order to enhance the composting, a under pressure was formed inside the hollow core slabs (or perforated steel mesh in smaller units), causing a continuous flow through the floor, and the accumulating straw bedded manure on it. This airflow was directed out of composter. In the full scale system gaseous nitrogen emissions were collected from the air outflow pipes outside the animal shelter.

In the small scale systems, ammonia concentrations were measured from condensation water from the heat reclamation systems, while in the full scale system, both a biochar based, and an acid based methods of nitrogen collection were tested.

## Results

The pre-experiments showed, that while the under pressure system allowed a short term temperature development of the composters, without mixing the single fill units compacted during composting, which lead to low heat generation in the units (Fig 1). The concentrations of nitrogen in the condensation water varied from 0.2 g/l to 1.2 g/l.

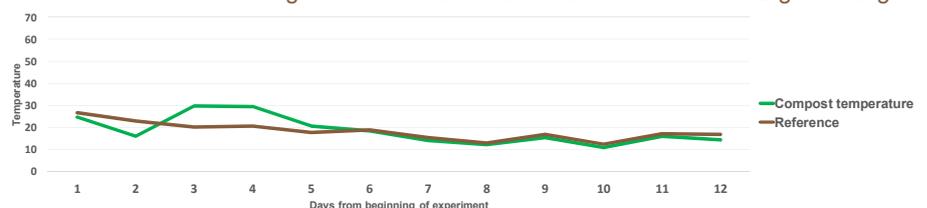


Fig. 1 Temperature development of the <math><1\text{ m}^3</math> scale compost units

The

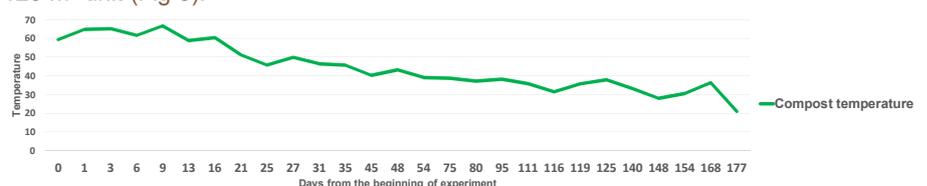


Fig. 2 Temperature development of the

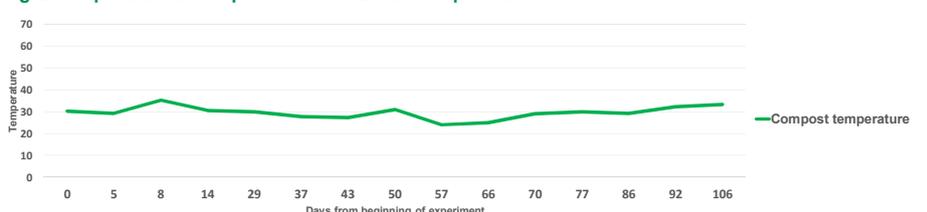


Fig. 3 Temperature development of the

# The impact of biochars prepared from brewery wastes on phosphorus availability and growth of maize

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## INTRODUCTION

Biochar is a product derived from pyrolysis of biomass that could be utilized as a soil amendment. Biochars can have essential macro- and micro-nutrients, such as N, P, K and Ca, which can be used by plants (1). Other benefits of biochar application to soil include increase of soil organic content, water holding capacity, soil aeration, CEC, nutrient retention and availability and decrease of fertilizer needs and nutrient leaching (2).

## OBJECTIVES

- To assess the effects of biochars from brewery wastes, as amendments in a calcareous soil.
- To investigate the effect of these amendments on phosphorus availability and plant growth of maize.

## MATERIALS AND METHODS

### Biochar production:

Biochars were produced using a muffle furnace at pyrolysis temperature 300°C.

### Pot experiments:

The pot experiment took place in an open-sided greenhouse.

- Control soils (soils without amendment)
- Soils treated with 2% (w/w) biochar produced from either brewery spent grains (BC-BSG-2%) or brewery surplus yeast (BC-BSY-2%)
- Soils treated with 5% (w/w) biochar produced from either brewery spent grains (BC-BSG-5%) or brewery surplus yeast (BC-BSY-5%)
- Soils treated with 1% (w/w) biochar produced from brewery spent grains *plus* 1% (w/w) biochar produced from brewery surplus yeast (BC-BSG+BSY-1%+1%).
- Soils treated with 2.5% (w/w) biochar produced from brewery spent grains *plus* 2.5% (w/w) biochar produced from brewery surplus yeast (BC-BSG+BSY-2.5%+2.5%).

## RESULTS

Table 1: Feedstock and biochar characterization (mean ± std., n=4)

Characteristics	BSY	BSG	BC-BSY	BC-BSG
C <sup>a</sup> (%)	46.4±2.04	44.95±1.25	54.54±4.24	50.62±4.07
TOC (%)	44.74±2.39	40.68±3.53	42.15±0.93	36.10±1.15
TN <sup>a</sup> (%)	8.4±0.95	4.77±1.09	10.56±0.72	7.83±0.54
Ash <sup>b</sup> (%)	6.64±1.05	9.45±1.6	18.64±3.55	17.66±3.7
pH	5.5±0.28	4.75±0.06	6.26±0.19	5.14±0.07
EC (dS m <sup>-1</sup> )	3.49±0.28	0.61±0.22	2.15±0.79	0.78±0.02
NO <sub>3</sub> -N (mg kg <sup>-1</sup> )	2148.25±173.69	3395±114.9	196.44±9.24	308.53±23.22
NH <sub>4</sub> -N (mg kg <sup>-1</sup> )	2818.75±280.07	3405.75±964.88	390.21±163.04	501±133.04
P (g kg <sup>-1</sup> )	16.31±3.33	5.59±0.57	30.29±0.98	22.29±2.14
Mg (g kg <sup>-1</sup> )	1.57±0.37	2.33±0.29	3.83±0.32	5.44±0.54
K (g kg <sup>-1</sup> )	10.02±0.05	0.30±0.13	21.18±3.10	0.64±0.07
Ca (g kg <sup>-1</sup> )	1.41±0.06	2.74±0.24	3.57±0.8	6.55±0.79
Mn (mg kg <sup>-1</sup> )	10.66±3.63	51.34±5.33	23.59±5.44	129.03±30.22
Fe (mg kg <sup>-1</sup> )	98.68±5.80	95.47±13.82	210.4±35.59	219.93±24.74
Zn (mg kg <sup>-1</sup> )	96.37±11.84	143.57±22.53	199.25±54.21	420.79±121.69
Cu (mg kg <sup>-1</sup> )	31.3±7.92	17.8±1.74	19.72±1.44	17.52±2.57

<sup>a</sup>As received basis <sup>b</sup>Dry basis, TOC: Total Organic Carbon, TN: Total Nitrogen, EC: Electrical Conductivity

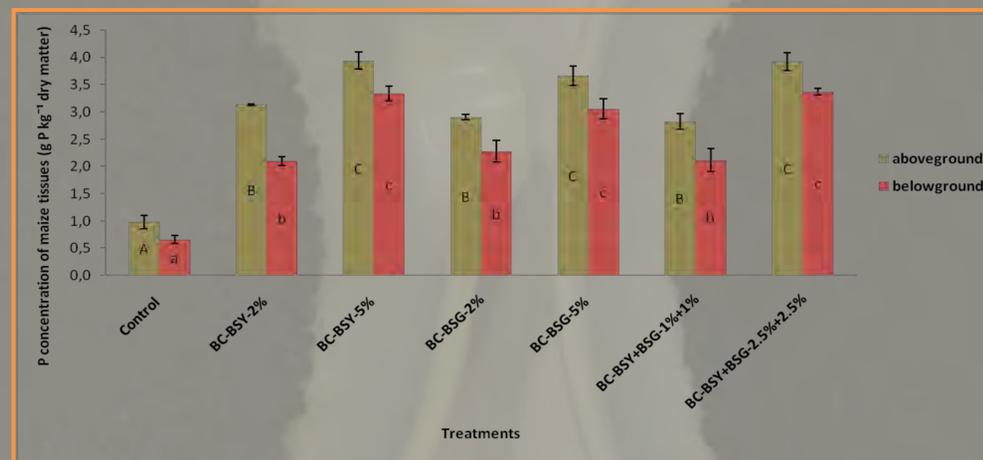


Figure 1: P concentration of maize aboveground and belowground tissues 30 d after seedling emergence (mean ± std., n=3). Values not sharing the same letter indicate a significant difference (Tukey HSD  $p \leq 0.05$ ). Upper- and lower-case letters indicate that statistical testing was done separately for each type of tissue.

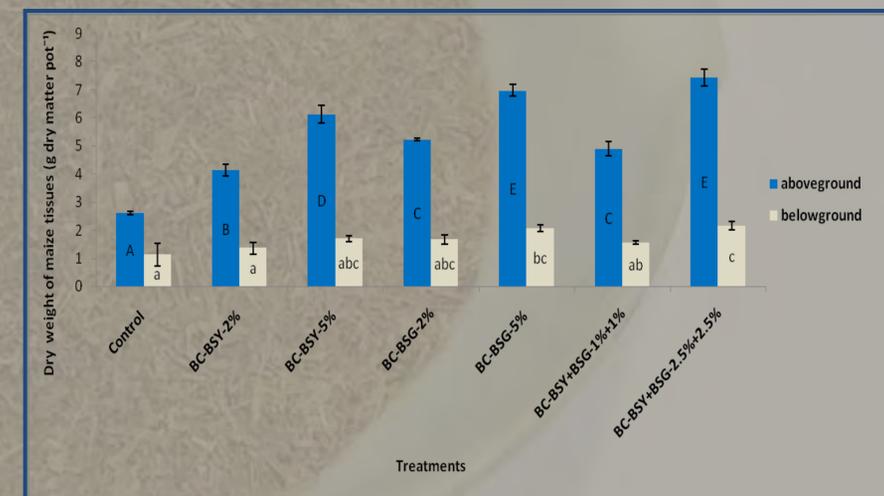


Figure 2: Dry weight (g pot<sup>-1</sup>) of aboveground and belowground tissues of maize 30 d after seedling emergence (mean ± std., n=3). Values not sharing the same letter indicate a significant difference (Tukey HSD  $p \leq 0.05$ ). Upper- and lower-case letters indicate that statistical testing was done separately for each type of tissue.

## CONCLUSIONS

- The addition of biochars significantly increased the aboveground and belowground dry weight of maize.
- The highest increase of aboveground and belowground weight of maize was detected at 5% application rate.
- P concentration of tissues was significantly enhanced by biochars individually or in a mixture.
- The highest increase of P concentration in maize aboveground tissues was detected by biochar from brewery surplus yeast at 5% application rate.

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# Recovery of concentrated fertilizer product from biogas plant reject water

Kristian Melin, Eliisa Järvelä, Anja Oasmaa and Mona Arnold  
VTT Technical Research Centre of Finland Ltd

## Background

- Substituting fossil fuels with biogas reduces significantly greenhouse gas emissions, generate extra income and business opportunities.
- However, applying the digestate from biogas plants on fields, can cause eutrophication of rivers and lakes, particularly in wet conditions and when all the nutrients cannot be used by the growing plants.
- The digestate from biogas plants using municipal waste water plants sludge as feedstock cannot be applied on the fields, but separate management and disposal/utilisation is needed.
- The digestate is typically treated, by first separating it into reject water and solids. The nitrogen content of the reject water needs to be reduced before the water is discharged to the environment.
- Challenges with existing nitrogen recovery methods include high treatment costs, operational challenges and low N-concentration of the recovered product.

## Methods

**Feedstock:** Reject water from a biogas plant treating mainly sewage sludge and biodegradable waste from food industry

**Additives:**  $\text{Na}_2\text{CO}_3$  to increase pH,  $\text{K}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$  in membrane distillation.

**Procedure:** Two methods to recover reject water nitrogen were compared:

- Direct evaporation employing sodium carbonate to increase pH at different temperatures and vacuum.
- Direct membrane distillation with acidified potassium sulfate solution on the permeate side

**Analysis:** pH, Total ammonia, inorganic ammonia nitrogen, total organic carbon, sodium and potassium content.

**Calculations:** Fraction of ammonia and water removed from reject water, flux of inorganic nitrogen in membrane distillation. Estimated energy needed for evaporation, area required for membrane, rough estimate of operation and capital cost for a full scale system connected to a real biogas plant.



Figure 1. Rotavapor equipment used for the evaporation experiments

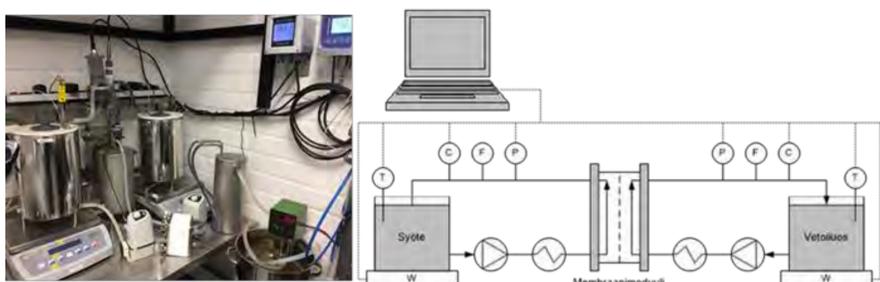


Figure 2. Membrane distillation equipment

## Results

Effect of vacuum on  $\text{NH}_4$ -content of residue (80 °C, 30 min)

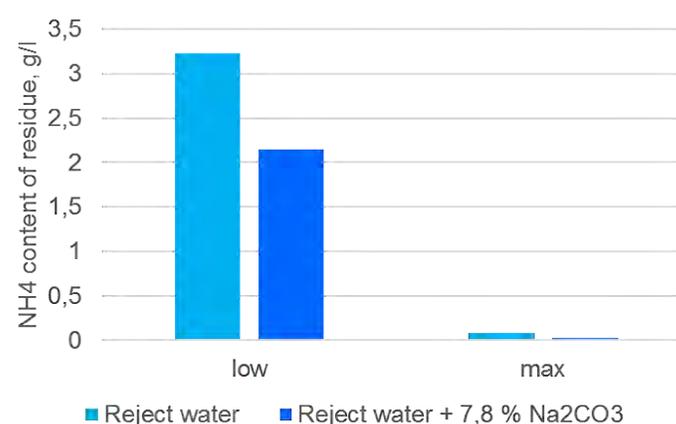


Figure 3. The effect of vacuum and addition of sodium carbonate on the residual  $\text{NH}_4$  content of reject water

- In direct evaporation over 99 % ammonium nitrogen was removed, however also more than 40 % of water evaporated, meaning that the condensate from evaporation has a low concentration < than 1 % of  $\text{NH}_4\text{-N}$

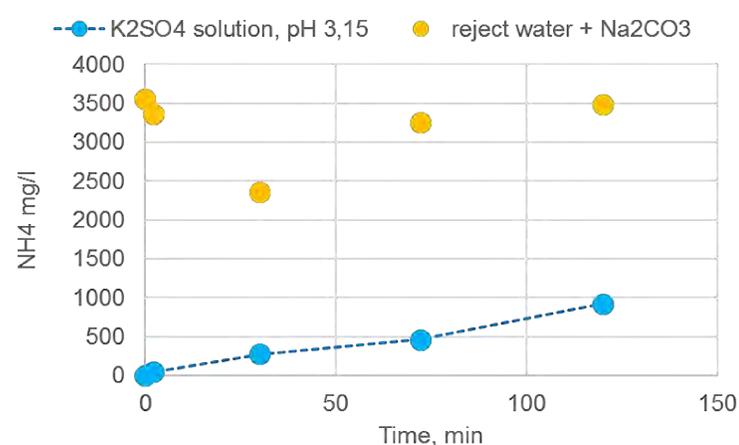


Figure 4. The concentration of reject water and permeate side as function of time in membrane distillation experiment

- The flux of  $\text{NH}_3$  through the membrane was about  $0.1 \text{ kg/m}_2/\text{h}$
- The flux of water was roughly 6 times higher than  $\text{NH}_3$
- After test, pure water flux was 37 % lower than before test indicating that some fouling might have taken place

## Conclusions

- A significantly more selective separation of water and ammonia was achieved with membrane distillation compared to evaporation, however the membrane should be tested with a more concentrated product on the permeate side.
- Membrane distillation seems attractive from techno-economic point of view compared to evaporation. However, further work should be done to improve membrane resistance to fouling and optimize the overall system from energy consumption and cost point of view.

## Contacts

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# NPHARVEST – Solution for converting wastewater nutrients into eco-friendly fertilizer

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## BACKGROUND

We produce large amounts of liquid waste with valuable nutrients. By harvesting nitrogen from these waste streams, we will significantly decrease energy consumption. Recycling phosphorus is a step towards sustainability.

## OBJECTIVES

Developing an improved nitrogen and phosphorus recovery process for different concentrated liquid waste streams. Our emphasis is on the end-product quality and resource optimization during recovery process.

## ACTIONS

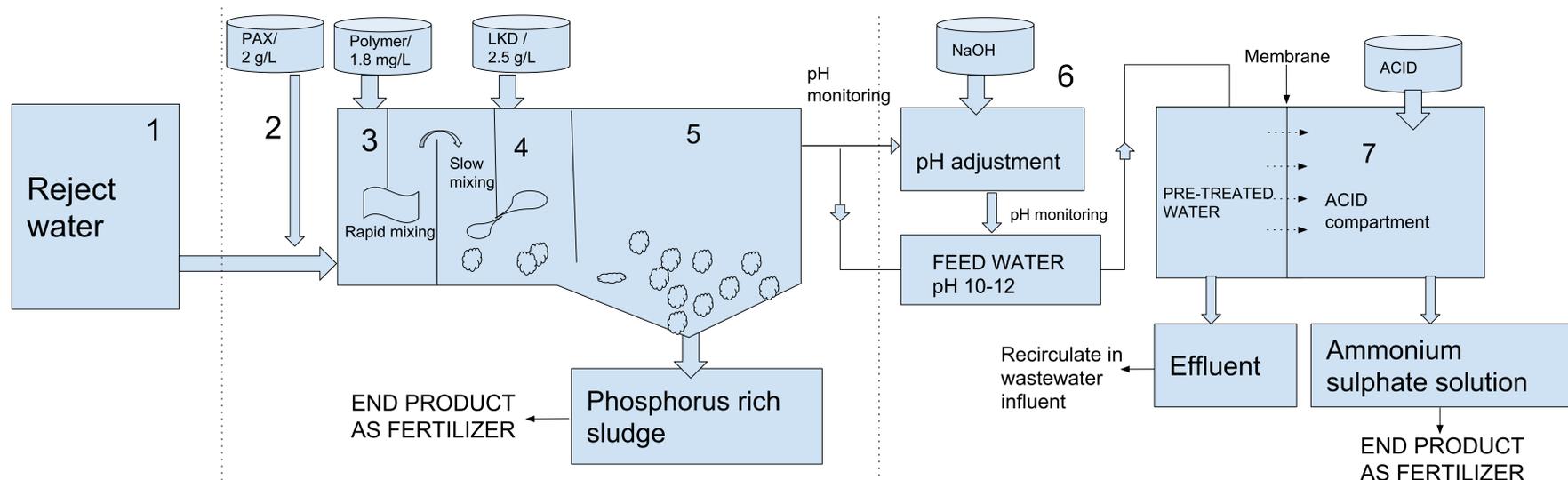
### Technical Path

- Membrane reactor optimization
- Pretreatment development
- End-product optimization
- End-product quality tests
- On-site piloting
- Large-scale piloting

### Commercial Path

- Market potential of different waste streams
- End-product value chain studies
- Business model development

## TECHNICAL PROCESS



RAW WATER	PRETREATMENT	NUTRIENT RECOVERY
1. High nitrogen and phosphorus content in liquid waste	<p>2. Coagulation: Suspended and colloidal matter are destabilized and are more likely to form bigger structure by using PAX XL 100 (2 g/L)</p> <p>3. Flocculation: Aggregation of destabilized particles into larger particles by using Polymer A 120 (1.8 mg/L)</p> <p>4. Ballasted settling: By using LKD (Lime kiln dust) (2.5 g/L) flocs get heavier and settled quicker.</p> <p>5. Separation process: Flocs are separated by gravity in a settling tank and removed periodically. Sediment is called as phosphorus rich sludge.</p>	<p><i>Pre-treated water further processed for nitrogen recovery</i></p> <p>6. pH adjustment: Addition of sodium hydroxide to increase pH 10-12.</p> <p>7. Nitrogen recovery: In this tank pre-treated water and sulfuric acid is separated with hydrophobic gas permeable membrane. The concentration gradient is the driving force for ammonia to transfer through the membrane. Ammonia is captured in sulphuric acid, where it reacts to form ammonium sulphate solution. This solution is raw material for nitrogen fertilizer.</p>

## FURTHER ACTIONS

Piloting of the process has started at Viikinmäki waste water treatment plant in Helsinki. The economical feasibility and process performance will be further developed.

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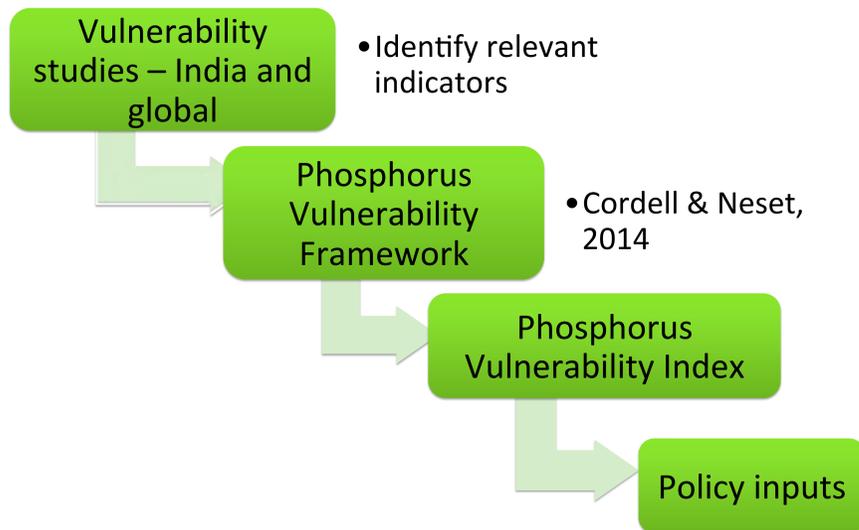
# Phosphorus Vulnerability Index (PVI) as a tool for Phosphorus security

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## PVI AS A POLICY TOOL



## PVI CALCULATION

$$PVI = \sum_{i=0}^n I_{i,std.} \times w_{i,std.}$$

$$w_{i,std.} = \frac{w_i}{\sum_{i=0}^n w_i} \quad I_{i,std} = \frac{I_t}{I_{t,max}} \times 100$$

i – indicators (23 priority indicators out of 81 total indicators)

w – weights assigned based on consultation with 6 categories of stakeholders

## P VULNERABILITY FOR INDIA

1. Agrarian economy – Large population, further growth expected in coming years
2. Majority group of small and marginal farmers
3. More than 80% districts low in soil Phosphorus
4. Nearly 90% requirement of Phosphorus is met through imports (raw material and/or fertilizer)

## OUTCOMES AND KEY FINDINGS FOR INDIA

**PVI = 34.04 (scale of 1-100) implying high vulnerability**

- **Very High** impacting vulnerability indicators for India are high dependence on imports; low purchasing power of farmers; poor soil fertility
- **High** impacting vulnerability indicators are limited access to formal credit; predominantly marginal farmers; low GDP; rural population growth
- Gaps were found in useful data for deriving Phosphorus vulnerability due to lack of focus by the government. These are phosphorus governance, potential of alternative phosphorus resources in the country, and others.

**Table 1: Status of PVI Indicators for India**

Indicator (unit) – weight	Value for India (Ref.) (I <sub>t</sub> )	Degree of vulnerability				
		Very low 1 (I <sub>t,max</sub> )	Low 2	Medium 3	High 4	Very high 5
1 Dependence on indigenous production (%) – 5	10 (Indian Bureau of Mines, 2017)	>81	61–80	41–60	21–40	1–20
2 Farmer's purchasing power (US dollars per year) – 5	1200 (FAO, 2008)	>7000	5000–7000	3000–5000	1500–3000	<1500
3 Proportion of farm income spent on items other than fertilizers (%) – 5	76.7 <sup>1</sup>	>85	80–85	75–80	70–75	<70
4 Soil fertility (% districts in which soils show high P content) – 5	9 (Reddy, 2011)	>81	61–80	41–60	21–40	1–20
5 National importance of P (qualitative) – 5	3 (stakeholders' opinion)	1	2	3	4	5
6 Marginal farmers' access to credit (%) – 4	28.6 <sup>1</sup>	>81	61–80	41–60	21–40	<20
7 Livestock population per head but limited to marginal farmers (no. of cows and buffaloes) – 4	1.7 <sup>1</sup>	3.1–4.0	2.1–3.0	1.1–2.0	0.1–1.0	<0.1
8 Effectiveness of governance (rank) – 4	56.25 (The World Bank, 2016a)	>81	61–80	41–60	21–40	<20
9 GDP/capita PPP (constant international prices in US dollars in 2011) – 3	6093 (World Bank, 2016b)	>20,000	15,000–20,000	10,000–15,000	5,000–10,000	<5000
10 Level of urbanization (%) – 3	31 <sup>1</sup>	>81	61–80	41–60	21–40	1–20
11 Proportion of the non-poor in rural population (%) – 3	28 (Rangarajan, 2010)	>81	61–80	41–60	21–40	<20
12 Share of groundwater-irrigated area in total irrigated area (%) – 2	61 <sup>1</sup>	>81	61–80	41–60	21–40	1–20
13 Share of land holdings larger than 1 hectare (%) – 2	23 <sup>1</sup>	>81	61–80	41–60	21–40	1–20
14 Rural literacy (% farmers with at least five years of schooling) – 2	69 <sup>1</sup>	>81	61–80	41–60	21–40	1–20
15 Proportion of area under cereal crops to total cultivated area (%) – 2	54 <sup>1</sup>	>81	61–80	41–60	21–40	<20
16 Proportion of cultivated area to total geographical area (%) – 2	42.5 <sup>1</sup>	>81	61–80	41–60	21–40	<20
17 Negative growth of rural population (%) – 2	–0.6 (The World Bank, 2016c)	>2	0.5 to 2	–0.5 to 0.5	–0.5 to –2	<–2
18 Proportion of rural households owning telephones to total number of rural households (%) – 1	54.4 <sup>1</sup>	>81	61–80	41–60	21–40	1–20

## ILLUSTRATION OF POLICY IMPACTS ON PVI

No.	Policy measure	Indicator/s influenced	Predicted value of indicator	PVI
1	Soil health card	➤ Soil fertility	50%	38.44
		➤ Proportion of indigenous production	75%	
		➤ Proportion of income spent on items other than fertilizers	90%	
2	Doubling farmers' incomes	➤ Farmers' purchasing power	2400 USD per year	35.42
3	Farm credit package and farmer's credit card	➤ Marginal farmers' access to credit	50%	35.77
4	Combination of above three measures	➤ All of the above	Sum of all of the above policies	42.61

**Soil Health Card Scheme:** Launched in 2015, the scheme is expected to lower the cost of agriculture production by 16%–25%

**Doubling farmer's income by 2022:** top-down policy from the PM office, aims at improving supply chain, using resources more efficiently, switching to high value crops, assured MSPs for marginal farmers and rural infrastructure improvement

**Farm credit package and farmer's credit card:** Farm credit package since 2004 and Kisan credit card since 1998 aim at effective disbursement of loans to farmers

**Individual schemes can only improve PVI marginally; combined effective implementation of all the schemes is important to improve vulnerabilities for India**

## USEFUL READINGS

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# Switzerland - Current status and outlook for the world-wide first national implementation of mineral phosphorus recovery

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## Summary

The Swiss disposal infrastructure and the technical and institutional developments related to the implementation of phosphorus recovery until 2026 are presented. A material flow analysis scenario based on these data indicates that Switzerland will become net exporter of fertilizer and phosphoric acid and reduce P to landfill/cement by 70%. Swiss recycling will likely be implemented on time and be influenced by pending decisions of federal authorities.

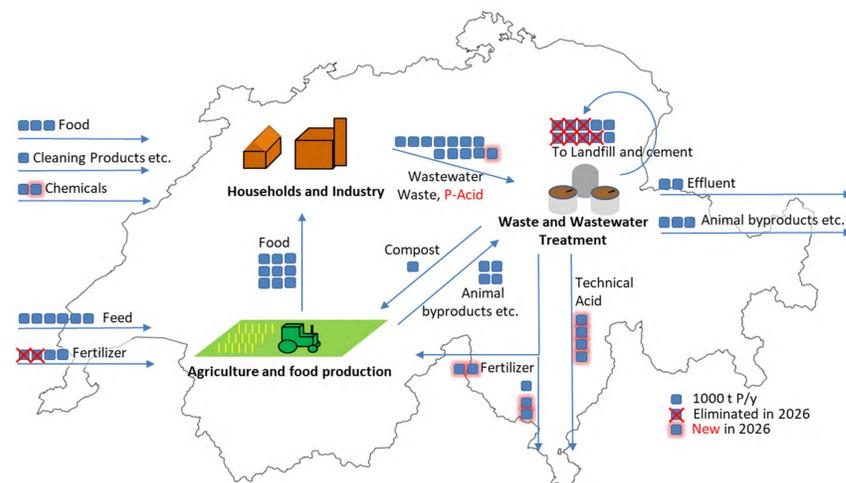


Figure 1: Current Swiss P-Flows and projection for implementation until 2026. Current state adapted from Mehr, Jedelhauser & Binder (2018).

## Background

In 2016, Switzerland was the first country in the world to introduce the obligation to recycle phosphorus from sewage sludge and meat and bone meal (Figure 1). Within a transitional period of 10 years the phosphorus should be recycled. A prediction of the results of the implementation based on these developments will be made and consequences will be discussed.

Disposal today (Figure 2):

- Sewage sludge is mainly mono-incinerated but also co-incinerated in municipal solid waste incineration (MSWI) plants or dried and subsequently incinerated in cement works
- Slaughterhouse waste is mostly exported, but about 40% including the category 1 material, is processed to meat and bone meal, dried and incinerated in cement works.
- The MSWI co-incineration is gradually being replaced by mono-incineration and mono-incineration of the meat and bone meal is planned. This disposal transition will thus gradually increase the fraction of phosphorus in form of mono-incineration ash suitable for recovery.

### Swiss phosphorus network

The Swiss phosphorus network ([www.pxch.ch](http://www.pxch.ch)) started by organizing the European nutrient event in Basel in 2017. The network supports the implementation of phosphorus recovery in Switzerland's different language regions. It provides neutral and publicly available information for all concerned parties in collaboration with associations and authorities. It also brokers contacts within Switzerland and with the rest of Europe.

## Demonstrating and evaluating recovery technologies for Switzerland

There are five types of processes that can be used to recover the Swiss phosphorus (Figure 2). Five main demonstration projects are pursued in Switzerland (Table 1).

The Canton Zürich initiated an information exchange regarding the P-recovery implementation with plant operators responsible for the treatment of over 60% of the Swiss sewage sludge. In a "Process Technology Market Analysis" (VTMA) the five Swiss demonstration projects as well as Ecophos and Extraphos were evaluated through questionnaires and a hearing (final report L. Morf et al., 2018 on [www.pxch.ch](http://www.pxch.ch)).

The VTMA concluded there is not yet enough available information for choosing appropriate technologies today. The very dynamic stakeholder groups plan to develop the different processes further for a new VTMA in 2020. Among the key requirements identified by the VTMA were coordination of disposal capacity and clarification of the financing of the phosphorus recovery. The Federal office for the Environment (FOEN) was asked to define technology requirements (e.g. yield) and on what terms P-recovery abroad is allowed.

Cost of disposal is about 80 EUR/t of dewatered sludge today and this would increase by between 0 EUR/t to 45 EUR/t according to the last estimations (Sources: VTMA, Pyrophos, P-REX <http://doi.org/10.5281/zenodo.242550>).

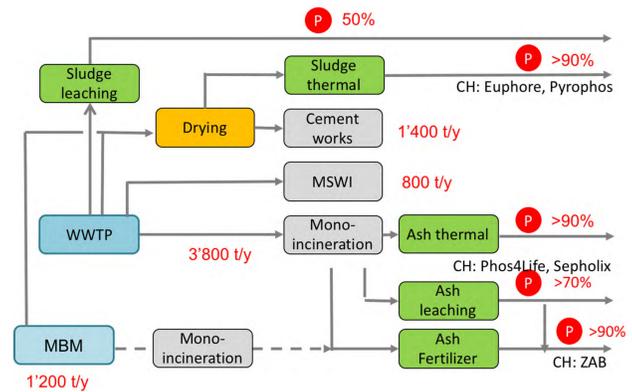


Figure 2: Volumes of current Swiss disposal routes (Source: VBSA). Phosphorus recovery routes with yields and Swiss demonstration projects indicated.

Table 1: Swiss recovery technology demonstration projects. See also [www.pxch.ch](http://www.pxch.ch).

Name (contact)	Process	Product	Characteristics
Euphore (ERZO)	Thermal treatment of sludge in kiln respectively fluidized bed	Ash as fertilizer raw material.	Low cost, but must fulfil Swiss fertilizer regulation
Pyrophos (CTU)			
Phos4Life (AWEL, Zürich)	Ash leaching followed by purification by liquid-liquid extraction	Technical grade phosphoric acid	90% of P, Fe and inerts recovered
Sephohix (CIMO)	Ash leaching followed by precipitation with calcium hydroxide	Calcium phosphate for fertilizer	Will use onsite precipitation capacity. Leaching still in lab
ZAB (Bazenheid)	Co-incineration of sewage sludge and MBM, acidulation and granulation of ash to fertilizer	Triple superphosphate or NPK fertilizer	Finished fertilizer for Swiss partners or export

## Scenario of phosphorus flows

Based on the current infrastructure, the development of the projects and the discussions during the VTMA we estimate a possible implementation scenario (Figure 1):

- The co-incineration in MSWI would mostly be replaced by mono-incineration.
- The dried sludge incinerated in cement works would previously be leached to fulfil the recycling obligation. Part of the current volume would instead be thermally processed, perhaps with Euphore/Pyrophos.
- A large leaching plant would process most of the mono-incineration ash. A smaller leaching plant would be built at the CIMO site.
- ZAB would become the largest fertilizer producer of Switzerland, processing about 2000 t P/y. The remaining MBM would also be processed to fertilizer.

An overall recovery yield of almost 90% from sewage sludge ash and MBM would result and the products would fall into three categories:

- Fertilizer for the domestic market
- Fertilizer/fertilizer raw materials for export
- Technical grade phosphoric acid for export

Thus, Switzerland would become a net exporter of fertilizers. The amount of phosphorus that goes to landfill/cement would be reduced drastically (by 70%).

## Conclusions and Outlook

In Switzerland loosely formed stakeholder groups are already demonstrating technically viable technologies that can likely be implemented to fulfil the obligation until 2026.

The effect of the transition on Swiss disposal in cement works is unclear and will depend on the success of compatible recovery technologies and requirements from the FOEN.

Less phosphorus will be lost to landfill and cement, and instead likely be exported as fertilizer and phosphoric acid. This development will depend on decisions of federal authorities, e.g. on the recycling fertilizer limits and conditions for export of sewage sludge ash for recovery.

### Mineral Recycling Fertilizer Category

In 2017 the Swiss Federal Office of Agriculture (FOAG) defined a new fertilizer category for mineral recycled fertilizers. These have a higher nutrient content than recycling fertilizers such as compost and therefore the pollutant limits per amount of dry matter is higher. The category will thus facilitate the recycling of phosphorus into agriculture. However, due to the ALARA approach used, the limits are considerably lower than in the upcoming European fertilizer regulation and risk complicating international trade in recovered phosphorus. The limits are due for publication end of 2018 ([www.pxch.ch](http://www.pxch.ch)).

# Enhancement of nutrient recycling by a local bio-cycle-model- BioCycle

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## Current state – local biomass and phosphorus hotspots

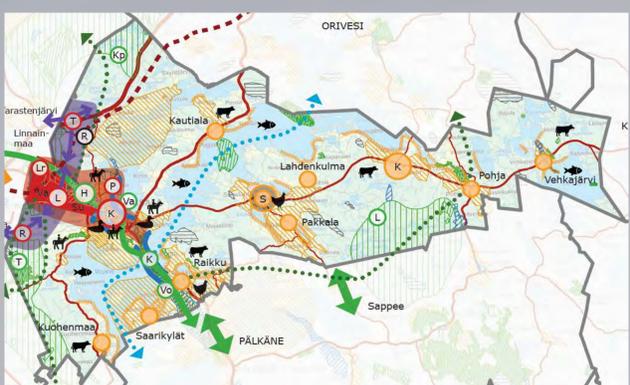


Figure 1 – “Strategic master plan 2040”. Various domestic animals - for livestock and hobby are important part of Sahalahti (Kangasala) region's economy. Agriculture, industry and suburban overlap on the region.[1].

**Sahalahti (Kangasala) region:**  
Concentration of food industry, agriculture, especially poultry farms, and horticulture.

- Significant amount of biobased sidestreams and biowaste concentrated on a small area
- Uneven distribution of available phosphorus resources

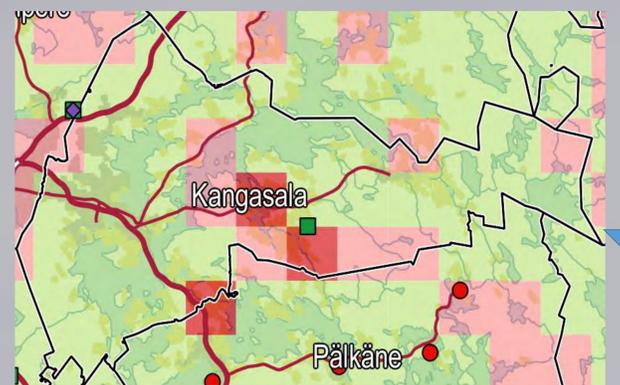


Figure 2 – Hotspots of phosphorus surplus/deficit on Kangasala area based on the crop need. Pink and red squares – phosphorus surplus, light green and dark green squares – phosphorus deficit. [2].

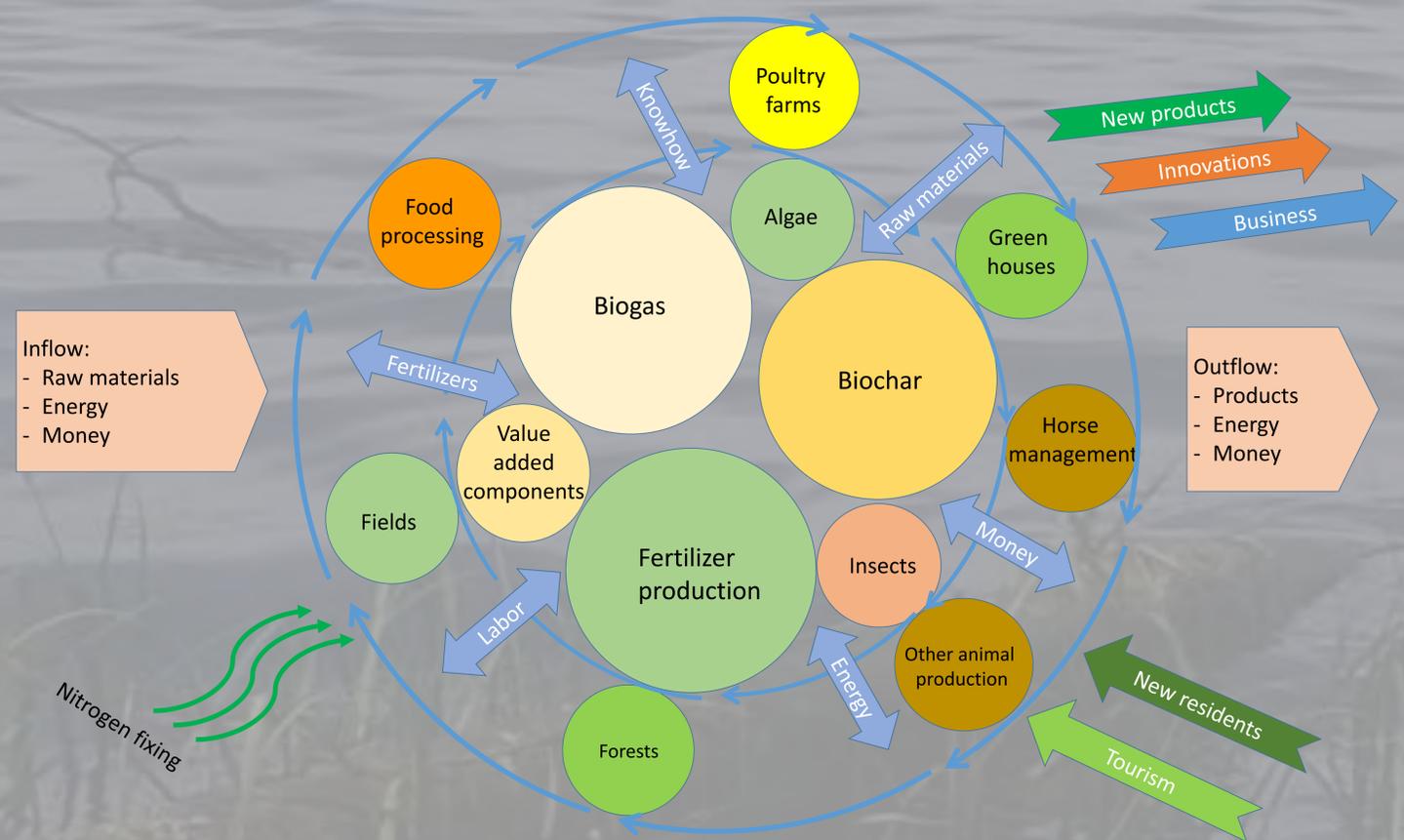
## Methods – options for sustainable nutrient catchment and recycling

- Microalgae cultivation:**
- nutrient catchment from process sidestreams
  - for feed and food ingredient
- Biochar production**
- integration biochar and bioenergy production
  - for nutrient catchment (e.g. leachate and manure emissions)



- Biogas production**
- nutrient catchment from manure, biowaste and processing residues
  - bioenergy
  - fertilizers
- Insect economy**
- nutrient catchment from process residues
  - feed and food ingredients
- Value added components**
- target for a cascade model

## Model – a comprehensive circulation model



**References:** [1] City of Kangasala, Kangasalan strateginen yleiskaava 2040 (“strategic master plan 2040”), Referred to: [http://kangasala-fi-bin.aldone.fi/@Bin/c31cf744d0ac4a209cb115051480022b/1528187686/application/pdf/6833978/31\\_Kaavaluonnos%2024%2010%202016.pdf](http://kangasala-fi-bin.aldone.fi/@Bin/c31cf744d0ac4a209cb115051480022b/1528187686/application/pdf/6833978/31_Kaavaluonnos%2024%2010%202016.pdf), October .2016, Pages 24. [2] Pirkanmaan ELY-keskus; Pirkanmaan ravinnekartoitus, Sweco Ympäristö Oy, 2017, Page 20.

**Acknowledgements:** BioCycle project (2017-2019) is funded by the Ministry of the Environment. The project contributes to the Finnish Government project *Breakthrough to a circular economy and adoption of clean solutions*. Several companies and stakeholders are acknowledged for the support

# NEW SUSTAINABLE PRODUCTS FROM THE SOLID SIDE STREAMS OF THE CHEMICAL PULP MILLS

NSPPulp

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## Introduction

Carbon content of agricultural soils is declining in Finland (Heikkinen et al. 2013). Soil organic carbon is an essential input for sustainable food production as it improves plant growth in general by increasing a soil's water holding capacity and cation exchange capacity, and reduces adverse environmental effects of agriculture, e.g. nutrient leaching. Pulp and paper industries produce annually large quantities (420 000 t DM) of agriculturally useable organic side streams.

In NSPPulp-project we investigate the ability of pulp mill side streams to stabilize soil aggregate structure, and consequently reduce erosion and nutrient leaching through a clay soil profile.

## Material and methods

Field experiment was established in autumn 2015 on a loamy clay, amended with 1) composted pulp mill sludge (CPMS), 2) lime-stabilized pulp mill sludge (LPMS), both derived from a waste water treatment process of the factory, and 3) fiber sludge (FS). Application rates were 23-26 tn DM ha<sup>-1</sup> (with about 8 tn org. C ha<sup>-1</sup>).

Large undisturbed soil columns were taken from the field in spring 2016 and 2017, following rainfall simulation tests (as described in Uusitalo et al., 2012).

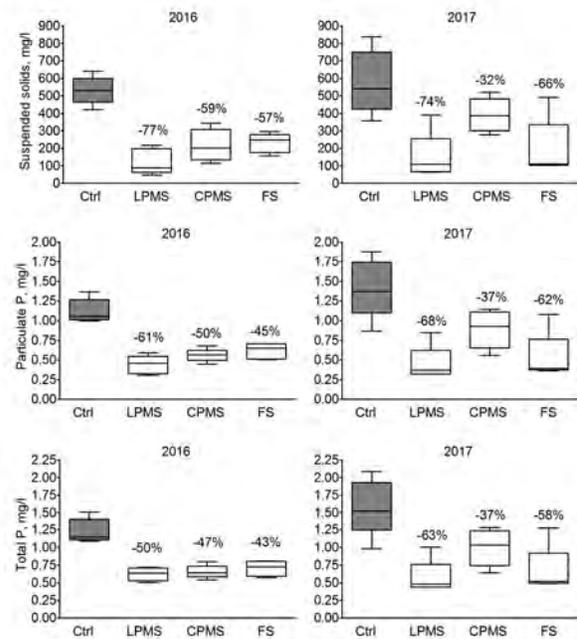
**Table 1.** The amounts of total (Tot-N), soluble organic (Sol-N org) and soluble inorganic (Sol-N inorg) nitrogen, total phosphorus (P), potassium (K), sulphur (S), calcium (Ca) and magnesium (Mg) applied to soil (kg ha<sup>-1</sup>) in the amendments.

Material	Tot-N	Sol-N org	Sol-N inorg	P	K	S	Ca	Mg
LPMS (Lime-stabilized Sludge)	250	32	1	49	28	121	2010	51
CPMS (Composted Sludge)	214	35	3	42	37	104	900	38
FS (Fibre Sludge)	13	1	0	2	1	7	2206	19

## Results

In the first study year, all materials reduced concentration of suspended solids in percolation water more than 57-77% compared to the unamended control soil (Fig. 1). In the second year the reduction was 66-74% for LPMS and FS and 32% for CPMS. Consequently, concentrations in percolation water of particle-bound P and total P were reduced more than 43% in the first and for CPMS and FS more than 58% in the second year.

FS reduced wheat yield in the first year compared to control, but in the second year oat yields were at the same level.



**Figure 1.** Concentrations of suspended solids, particle-bound phosphorus, and total phosphorus in percolation water after simulated rain in spring 2016 and 2017 (9 and 21 months after amendment applications). Treatment codes are given in Table 1.

## Conclusions

All of the tested pulp mill side-streams clearly decreased mobilization and transport of erosion material and phosphorus through soil monoliths. Eight months after application the effect was equally good for all materials.

In the second year (20 mo after application), the effect seemed to have sustained slightly better when Ca-containing organic amendments (LPMS and FS) were used.

Reduced erosion tendency and P transport through soil monoliths will be tested for two further years in a follow-up project called "Ravinnekuitu".



## Acknowledgements

Funding for this research was provided through a TEKES (Business Finland) project by UPM-Kymmene Oyj, Stora Enso Oyj, Metsä Fiber Oyj, Tyynelän maanparannus Oy (Soilfood), Biolan Oy, Ekokem Oyj (Fortum) and Outotec Oyj.

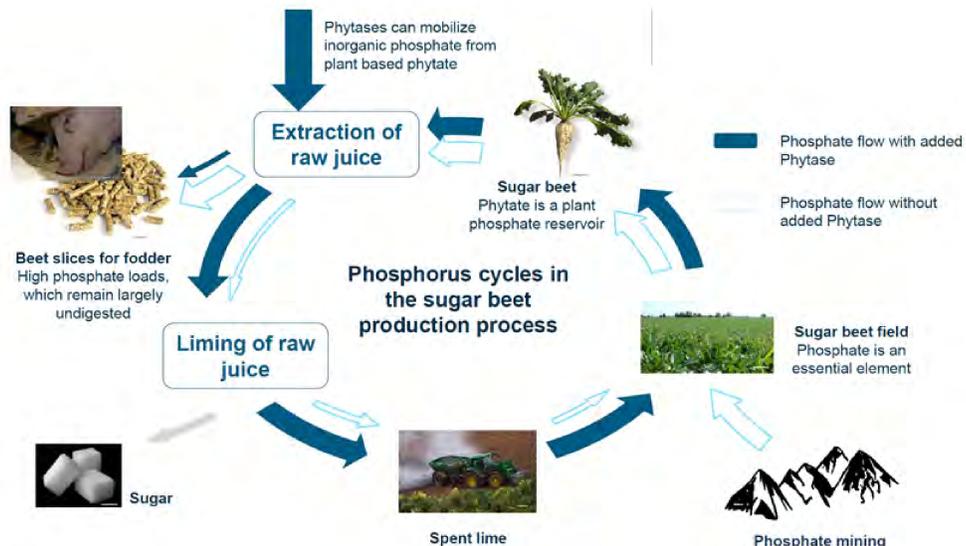
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 Uusitalo, R., Ylivainio, K., Hyväluoma, J., Rasa, K., Kaseva, J., Nylund, P., Pietola, L., Turtola, E. 2012. The effects of gypsum on the transfer of phosphorus and other nutrients through clay soil monoliths. *Agricultural and Food Science* 21: 260-279.

## ABSTRACT

PhytaPhoS aims at creating phytases that are supplied to the sugar extraction process and cleave phytate phosphate from sugar beet slices. The isolated phosphorus is transferred to spent lime and subsequently added back to the fields as fertilizer. The P availability of enriched spent lime (SL) was investigated at different plant species and plant growth stages, and its effect was compared to the commercial fertilizer-TSP. Results show the possibility to use the recycled P source as a fertilizer, optimizing the P-cycle and reducing P losses in agricultural waste streams.

Schema of the current (light blue) and optimized (dark blue) phosphorus cycle in the sugar beet production process

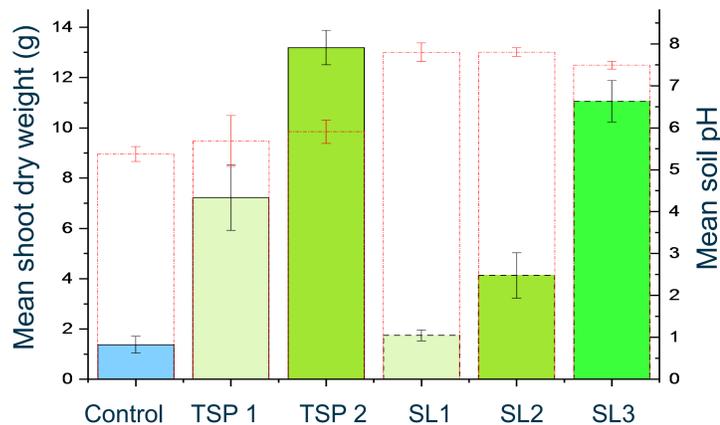


## TEST IN MAIZE AS REFERENCE SPECIES

### Plant availability of P enriched spent lime



### Effect of enriched spent lime on shoot dry weight



- Production of Phosphorus enriched spent lime (SL1 – SL3) by adding Calcium dihydrogen phosphate ( $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ) and water-soluble  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  reacts to insoluble Dicalcium phosphate



- However, as demonstrated in our pot experiment, Dicalcium phosphate in spent lime is still plant available

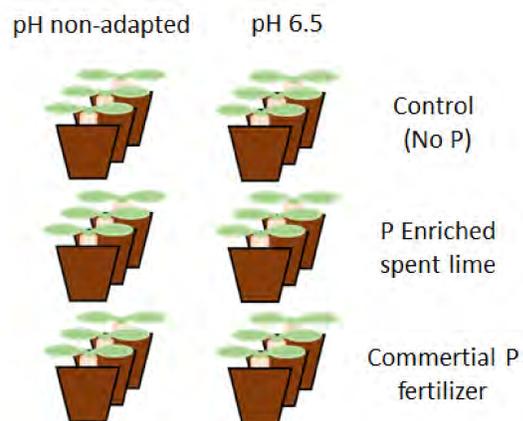
- Comparison with commercial P showed that the increase in pH (red line) is correlated with lower shoot dry weight in SL-treated plants

- Comparison with commercial P fertilizers is not possible without adapting the pH

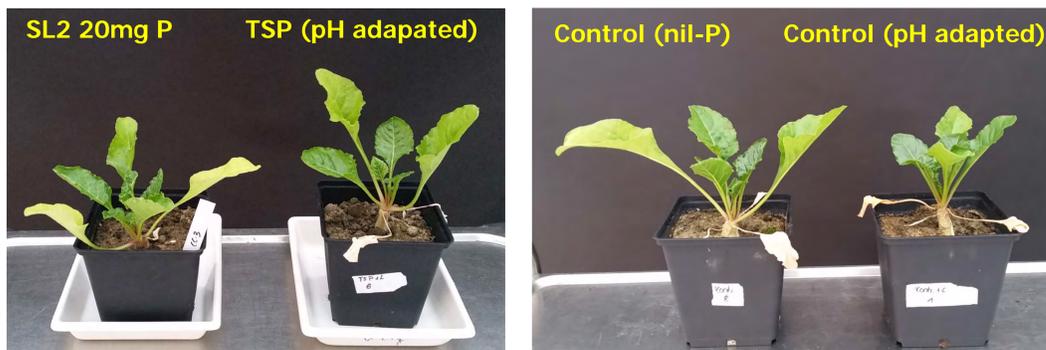
- SL3 performed better than SL2. However, the production of SL3 is more difficult

## TEST IN SUGAR BEETS

### Experimental design adapting the pH to the optimal for sugar beet



### Effect of enriched spent lime on plant performance



- SL-treated plants don't perform as well as TSP-treated plants, even following pH adaptation
- In control plants with no P addition, the increase of pH (pH adapted-plants) reduced the plant growth
- Upcoming analyses aim at determining the effect of SL on plant nutrient uptake

## Next steps/ Follow-up projects

- The recycling potential of the new technology will be calculated including economic assessment
- It is planned in a Follow-up project to implement the new technology into the running processes of a sugar beet plant under praxis conditions.

## Consortium

Prof. M. Becker, Dr. U. Arnold, Dr. M. Trimborn, INRES, Bonn

Prof. U. Schurr, Dr. S. D. Schrey, **Dr. A.A. Robles-Aguilar**

Dr. N.D. Jablonowski, IBG-2, Jülich

Prof. U. Schwaneberg, Prof. A. Pich, Dr. A.J. Ruff, Biotech, Aachen

# RAVITA



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**GOVERNMENT  
KEY PROJECT**

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## INTRODUCTION

Phosphorus is a limited resource essential for all life on Earth. Phosphorus fertilizers are needed for feeding the increasing human population but the main source of phosphorus, the phosphate rock, has been announced as a critical raw material by European Commission [1]. A potentially significant alternative source of phosphorus could be recycled phosphorus from municipal wastewater and especially sewage sludge. Recovery technologies available today require biological phosphorus removal or sludge incineration. In Finland and other Nordic countries, strict phosphorus discharge limits require chemical precipitation thus biological phosphorus removal alone is not sufficient. Furthermore, sludge incineration is not common. Ammonium recovery from wastewater is not that often discussed. However, recovery from WWTP's reject waters would decrease the energy demand of ammonium synthesis and the energy demand of WWTP's biological process.

HSY has developed a new process called RAVITA where phosphorus and nitrogen recovery are combined in order to produce phosphoric acid ( $H_3PO_4$ ) and ammonium phosphate ( $(NH_4)_3PO_4$ ) [2].

## RAVITA Process

The main idea in RAVITA process is to recover phosphorus directly from the water phase by post-precipitation (Fig 1.). Produced chemical sludge is processed to  $H_3PO_4$

### Pros&Cons of the process

- + No need for biological phosphorus removal, sludge incineration or digestion
  - + Nutrients are not integrated to the sludge
  - + Fits all kinds of WWTPs
  - + Size Neutral
  - + Maximizes Phosphorus Recovery
  - + Enables nutrient harvesting
  - + Enables precipitation chemical circulation
  - + Combination process with nitrogen recovery (MAP/DAP)
  - +  $H_3PO_4$  is valuable in many applications
  - + Low concentrations of hazardous substances
- Increased risk for phosphorus leakages due to tertiary treatment process phase
    - Risk management: two-step precipitation
  - Process is in piloting phase (TRL 5-6)

## METHODS

Research has been done both in laboratory and pilot scale (1000 PE) in 2016-2017.

Piloting is done in the facilities of HSY's Viikinmäki WWTP (1 100 000 PE) in Helsinki (Fig 2.). The objects are:

- optimize the precipitation process
- find the most suitable processes for the chemical sludge treatment

In laboratory scale processing of the chemical sludge is researched. The objective is to:

- Study and optimize the dissolution process
- Optimize the separation process (solvent-solvent extraction)
- To gain information for pilot plant design

## HAZARDOUS SUBSTANCES

Hazardous substances are one of the main concerns in municipal based recycled nutrients

- Main part of the micro pollutants are already biologically degraded or attached to the sludge before RAVITA's precipitation step
- Post-precipitation do not precipitate those substances, but some are attached to the chemical sludge
- Heavy metal and organic micropollutant concentrations in RAVITA sludge are low (Fig 3., Table 1)

## FUTURE STEPS

In 2018 RAVITA DEMO plant will be constructed in Viikinmäki WWTP. This plant will consist the chemical sludge processing units and  $H_3PO_4$  production.

This will give opportunity to:

- Optimize and study dissolution and separation processes in pilot scale (1000 PE)
- Increase TRL (now 5 - 6)
- Calculate more accurate energy and mass balances
- Cost estimations
- More analyses of the end product quality (hazardous substances and microplastics)

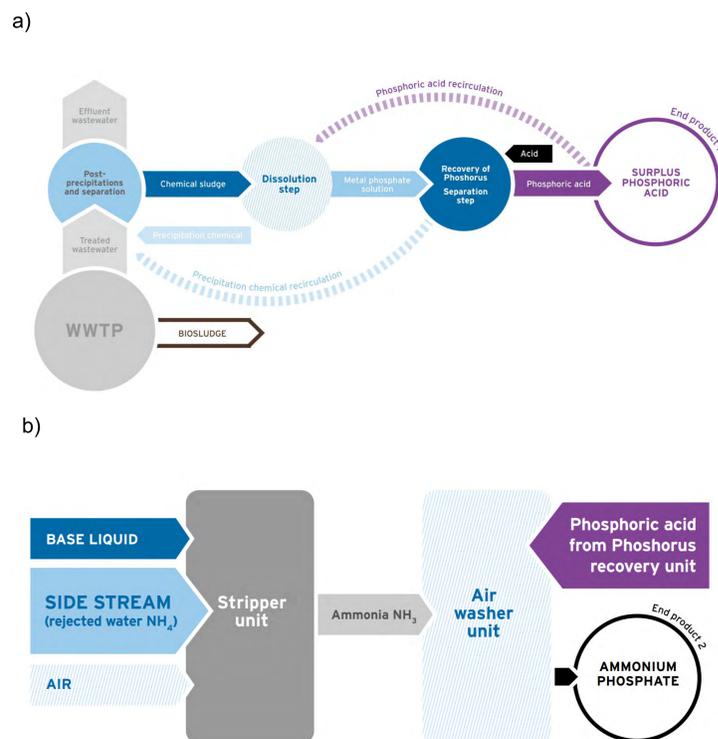


Fig 1. RAVITA a) Phosphorus recovery step b) Nitrogen recovery step



Fig 2. Pilot plant at Viikinmäki wastewater treatment plant in Helsinki

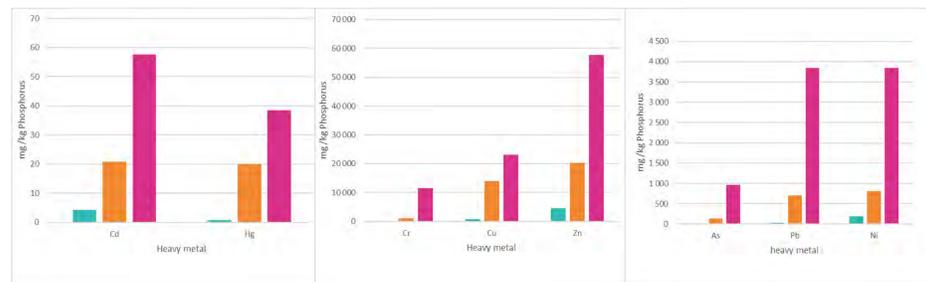


Fig 3. Heavy metal concentrations: ■ RAVITA sludge ■ Viikinmäki WWTP sludge ■ Legislative limit in Finland

Table 1. Organic micropollutant concentrations

Results (mg/kg DM)	RAVITA sludge	Sweden [3]	Norway [3]	Viikinmäki WWTP Dried sewage sludge
<b>tetraBDE#47</b>	0,000 550	N.A	N.A	N.A
<b>pentaBDE#99</b>	0,000 540	0,050	0,025	0,016
<b>decaBDE#209</b>	0,008 400	0,300	0,400	0,490
<b>(meta+para)-cresol</b>	8,9	N.A	N.A	28

[1] European Commission (2018). COMMISSION STAFF WORKING DOCUMENT -Report on Critical Raw Materials and the Circular Economy, SWD(2018) 36.

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[3] Kasurinen V., Munne P., Mehtonen J., Türkmen A., Seppälä T., Mannio J., Verta M., Äystö L. (2014). Organic micropollutants in sewage sludge (In Finnish). Suomen ympäristökeskuksen raportteja 6/2014.

The RAVITA project has granted funding from the Finnish Ministry of the Environment RAKI Programme 2014-2017.

The RAKI RAVITA DEMO plant has been chosen as a part of the Finnish Government's key project on the circular economy 2017-2018

RAVITA Process was selected as one of the three winners in BONUS Return competition in 2018.

RAVITA won the SITRA Award on Municipal Recycling Act in 2018.

# Pyrolysis as a method for improved phosphorus recycling of fur animal manure

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## BACKGROUND

Fur animal manure is rich in nutrients. Finnish fur production is concentrated to Western coast (Ostrobothnia regions) with other intense animal production. The region has a significant surplus of manure-based phosphorus (P) (see poster Laakso et al.: Manure phosphorus surplus from fur animal production in Ostrobothnia, Finland).

Pyrolysis was tested as an option for processing fur animal manure into P-fertilizer products transportable to other regions in need of phosphorus for plant production.

## MATERIALS AND METHODS

Fox and mink manure were pre-dried (50-60°C) and pyrolyzed with batch-type laboratory scale equipment at 350 or 450 °C.

Suitability of the char fraction for P-fertilizing was assessed by Hedley fractionation scheme and growth experiment (rye-grass).

Gas main compounds (CO<sub>2</sub>, CH<sub>4</sub>, CO, H<sub>2</sub>) were analysed and the lower heating value (LHV) of them were calculated.

For liquids, LHV was analysed only for liquids from 450 °C pyrolysis.

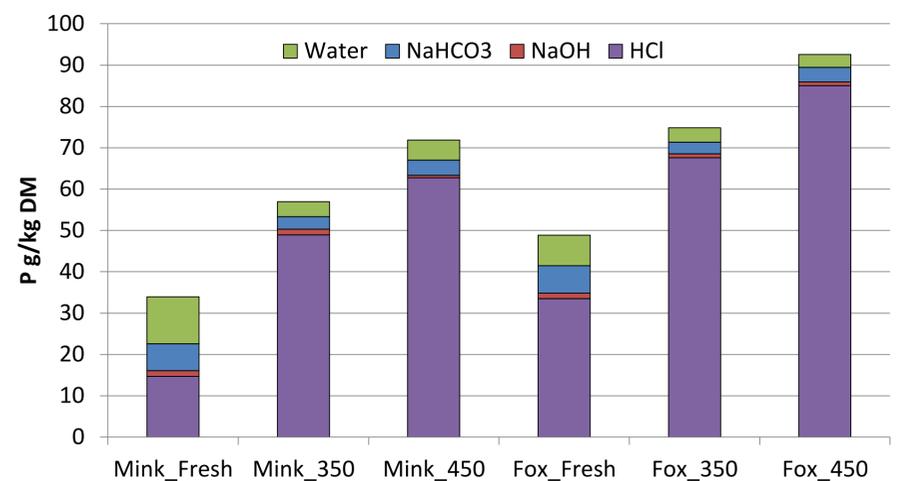


Fig. 1. P concentrations according to Hedley fractionation in fresh and pyrolyzed mink and fox manures. Water- and NaHCO<sub>3</sub>-extractable P represents bioavailable P, whereas NaOH- and HCl-fractions are less bioavailable.

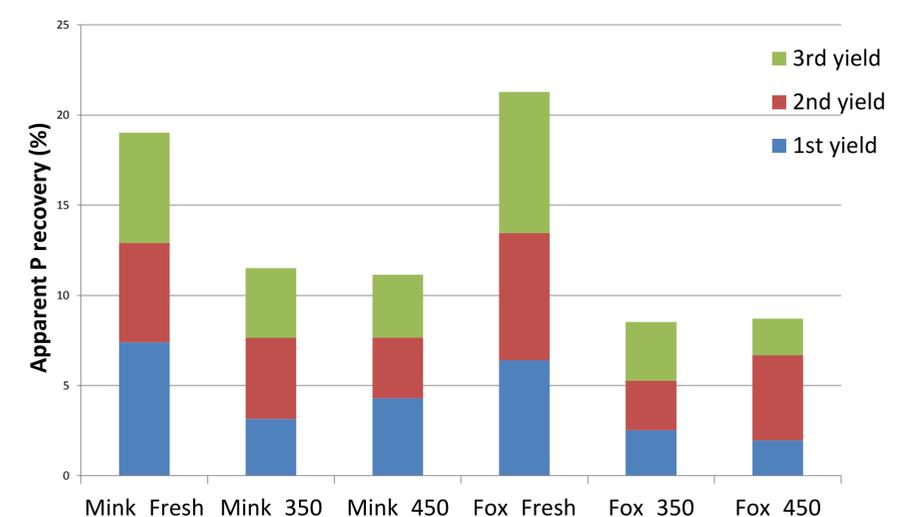


Fig. 2. Apparent P recovery in tested manures in three ryegrass yields. Apparent recovery is (P uptake of manure – P uptake without P fertilizer)/ applied P \* 100%.

## RESULTS

### Char fraction



- Manure mass halved
- P concentrated (Fig. 1)
- Share of water-soluble P-content decreased and less soluble P fraction (HCl) increased (Fig. 1)
- Apparent P recovery decreased with a higher reduction in fox manure char (Fig. 2)

### Gas and liquid fractions

- CO<sub>2</sub> as the main gas component
- LHV of pyrolysis gas and liquid of mink manure higher than for fox manure (Table 1)

Table 1. Energy content (LHV) of pyrolysis gas and liquid.

	Gas		Liquid	
	MJ/m <sup>3</sup>	MJ/kg dried manure	MJ/kg	MJ/kg dried Manure
Fox_450	3.7	0.15	27.95	9.00
Mink_450	4.5	0.19	35.70	14.72

## CONCLUSIONS

Pyrolysis may be a promising technique to develop transportable P-fertilizers from fur animal manure. More research and tests in industrial scale are needed. Utilization possibilities of liquid fraction and nitrogen recovery from pyrolysis and pre-drying should be further investigated.

# Consumption of Estonian phosphorite

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## INTRODUCTION

Active phosphate mining operation goes on in Finland at Siilinjärvi deposit with limited resources in European Union (EU). [1] In this context it is important that **Estonia holds the largest unused sedimentary phosphate rock reserve (about 800 Mt P<sub>2</sub>O<sub>5</sub> [2])** in EU. Estonian phosphate is a sedimentary rock (**Figure 1**) composed of variegated sandstone that contains abundant remains of phosphatic brachiopod shells. [3] Phosphate enriched beds occur stratigraphically at the transition between Cambrian and Ordovician and the phosphatic sandstones belong to Kallavere formation.



Figure 1. Tremadocian shelly phosphorite coquina. Photo: H. Bauert

The biogenic phosphate is dominated by carbonate-fluorapatite mineral phase (**Table 1**). The **P<sub>2</sub>O<sub>5</sub> content of the sandstone beds is quite low varying between 6...20%**. However, the **brachiopod shells and detritus contain up to 35...37% of P<sub>2</sub>O<sub>5</sub>**, the content of **U and Cd is quite low in ore (~20 and <3 ppm, respectively)** and sandstone is weakly cemented that allows quite efficient enrichment of the phosphate ore. [2,4]

Table 1. Average mineral and chemical composition of Estonian phosphorite. [2]

Mineral composition, wt%		Chemical composition, wt%	
Apatite:	29,3	ore	shells
in shells	28,3	P <sub>2</sub> O <sub>5</sub>	12,70 33,97
in quartz beads	1,0	CaO	18,12 47,38
Carbonates	1,5	MgO	0,76 0,46
Pyrite	1,3	F	1,01 2,64
Hydrogoethite	0,6	SiO <sub>2</sub>	55,3 2,49
Glauconite	0,3	Al <sub>2</sub> O <sub>3</sub>	2,32 0,26
Clay minerals	1,7	Fe <sub>2</sub> O <sub>3</sub>	2,52 1,67
Quartz	64,5	CO <sub>2</sub>	1,74 3,39

Despite of its economical and social importance, **Estonian phosphate rock is currently not mined or explored** due to concerns over the ecological impact of mining. The main concern is the environmental effects of the rock mining in the inhabited area with numerous settlements and intensive agricultural use.



Figure 2. The abandoned Maardu chemical factory. Photo: Google street view 2016

## BENEFICIATION AND PROCESSING OF ESTONIAN PHOSPHORITE

**Estonian phosphorite is principally a siliceous phosphate ore.**

Available data currently existing in the field of **beneficiation of Estonian phosphorite rocks** was generated and collected by research institutions of the former Soviet Union in the period of about 40 years ago.

The full-scale **flotation plant was operated in Maardu (Figure 2) using Swedish cationic flotoreagents (Figure 3)** during some years in 1970-ies. [5] **The concentrate was used in the second stage of triple superphosphate production in Russia.**

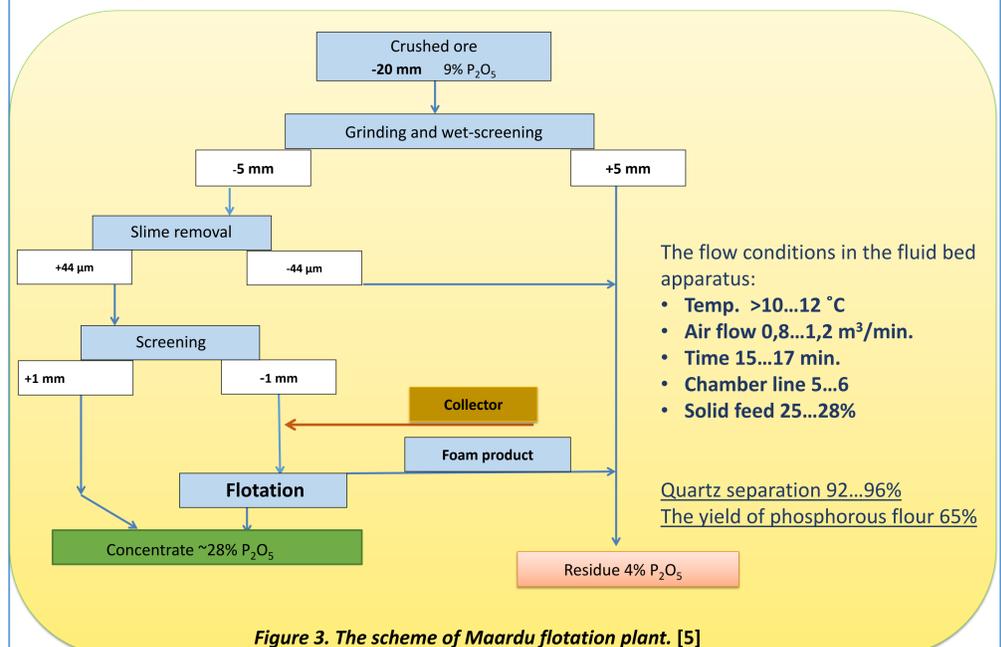


Figure 3. The scheme of Maardu flotation plant. [5]

The application of the **wet acid H<sub>3</sub>PO<sub>4</sub> process for Estonian phosphorite** is originates from laboratory scale investigations at **Tallinn University of Technology (TTÜ)** in the period of **1978-1985**.

The **suitability of Estonian phosphate concentrates for processing them into H<sub>3</sub>PO<sub>4</sub> as well as into triple superphosphate, thermophosphates and complex fertilizers** has been shown by **lab-scale investigations at TTÜ in the period 1965-1985**.

## CONCLUSIONS

**Estonia has:**

- **noticeable resources of natural phosphates;**
- **earlier experience of industrial-level mining, enrichment and processing of phosphorites;**
- **large experience of lab-scale chemical, physical and technological characterization of phosphorite concentrates for production of H<sub>3</sub>PO<sub>4</sub>, thermophosphates and complex fertilizers;**
- **initiated new activities in this field have been initiated on the state level**

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- [4] Kuusik, R. and Kallemeets K., Preconditions for the processing of Estonian phosphorus, 2014. <https://eestifosforiit.ee/cms-data/upload/uuringud/seminar-p-rkuusik-140107.pdf>
- [5] Tatarskii, A.E., Podvigin, M.A., Shuvalova, N.K., Suhanova, V.G. and Gubanov, A.F., Introduction of new technology in the enrichment of Maardu phosphorite, Obogachenie rud, 1982, 1, pp. 12-13.

## ACKNOWLEDGEMENTS

This work was supported by the Estonian Research Council grant (PUTJD705, IUT33-19) and by the Estonian Ministry of Education and Research grant (RITA1/01-01-11). In addition, this research was financially supported the Geological Survey of Estonia which are gratefully acknowledged.



GEOLOGICAL SURVEY OF ESTONIA



Eesti Teadusagentuur  
Estonian Research Council



## NUTRIENT NEUTRAL MUNICIPALITY

The **nutrient neutral municipality concept** was developed with six Finnish pilot municipalities between the years 2015 - 2017. The concept is a way for municipalities to find their role in nutrient recycling and in circular economy.

The development project was a part of the Ministry of the Environment's RAKI programme. The study was conducted in Finland, but its principles are suitable for municipality-level work anywhere.

The work continues in a new project (2018-2020) by the Finnish government's key projects funding and its main target is to encourage all Finnish municipalities take responsibility for nutrient recycling and find ways to make most of it.

Municipalities can act as partners to other operators, and nutrient recycling will also benefit the municipalities in return.

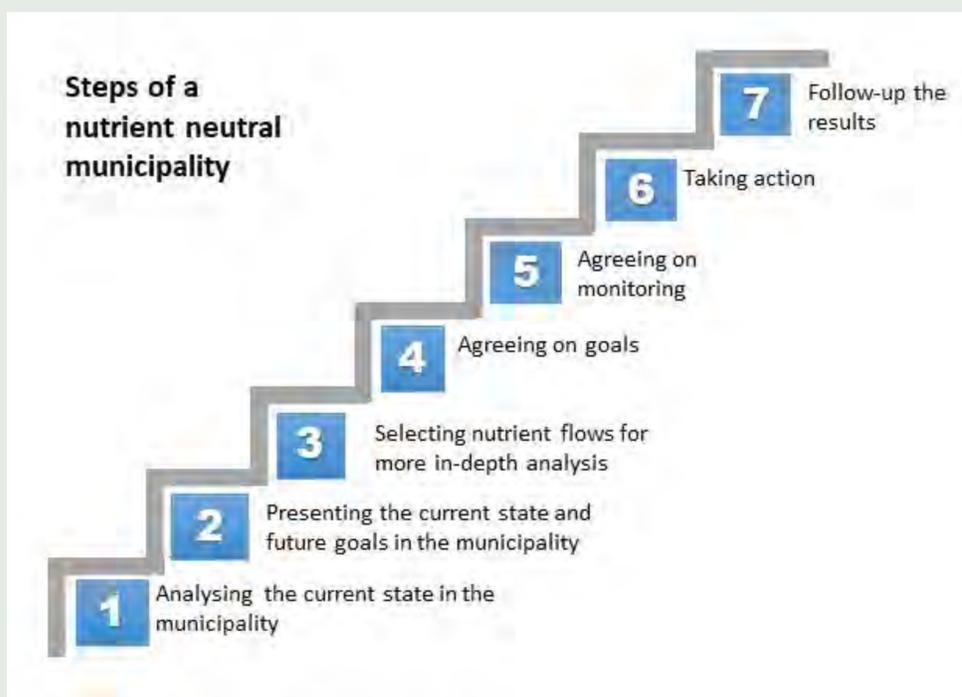


### Nutrient neutral municipality

- \* is an active nutrient recycling operator
- \* is aware of the local nutrient flows and their potential utilisation
- \* encourages others with its own example towards sustainable activities
- \* promotes nutrient recycling and circular economy with administrative decisions and measures

### Nutrient neutral municipality concept

- is an opportunity for municipalities and other regional actors
- \* to take an additional step towards sustainable development
- \* to support the innovative nutrient recycling business
- \* to promote and maintain good environment



### The seven steps

The Nutrient Neutral Municipality concept is a seven-step approach for organizations to implement nutrient recycling in their everyday activities and decision-making processes

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[http://www.ymparisto.fi/en-US/Nutrient\\_Neutral\\_Municipality](http://www.ymparisto.fi/en-US/Nutrient_Neutral_Municipality)

# Understanding the soil-like behaviour of secondary P-source – a necessity prior to agricultural use

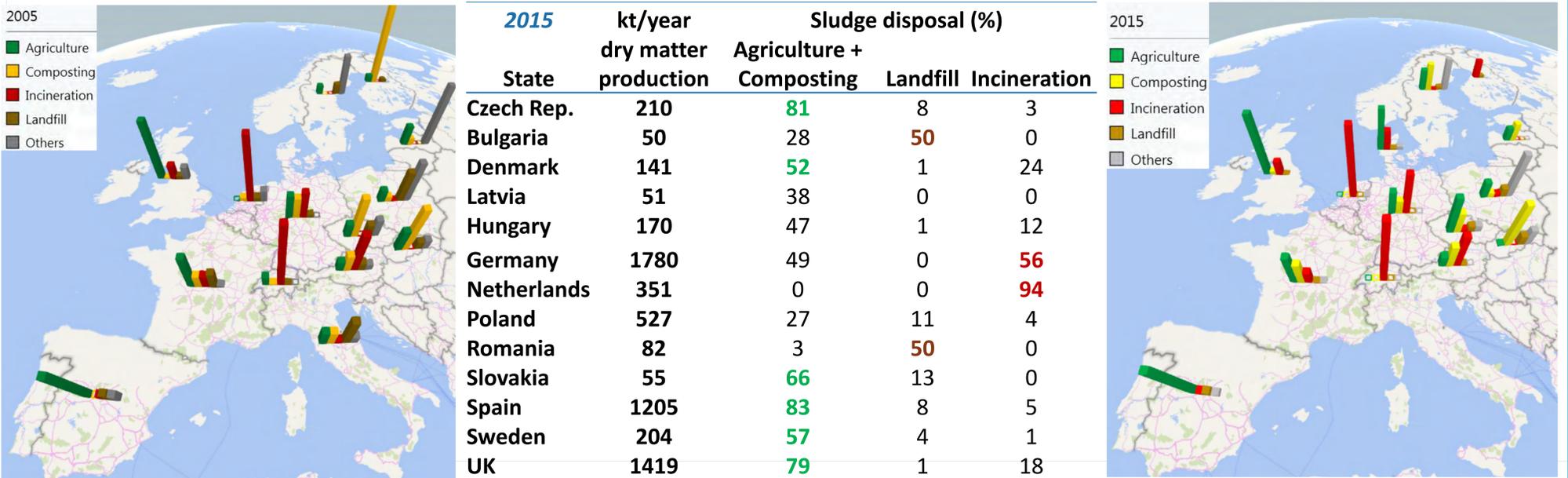
Šárka Václavková, Michal Šyc

Department of Environmental Engineering, Institute of Chemical Process Fundamentals of the Czech Academy of Sciences, Prague, Czech Republic

## Introduction

The common practise of sewage sludge agricultural application is diminishing. Consequently, variety of phosphorus recovery technologies produce phosphorus rich secondary sources. These are often examined according to rules designed for phosphate rock based fertilizers. In our studies we are questioning the suitability and correspond value of these test, when considering agricultural application of secondary P-sources.

## Sewage sludge handling in Europe



## Demands on different materials when applied on agricultural land

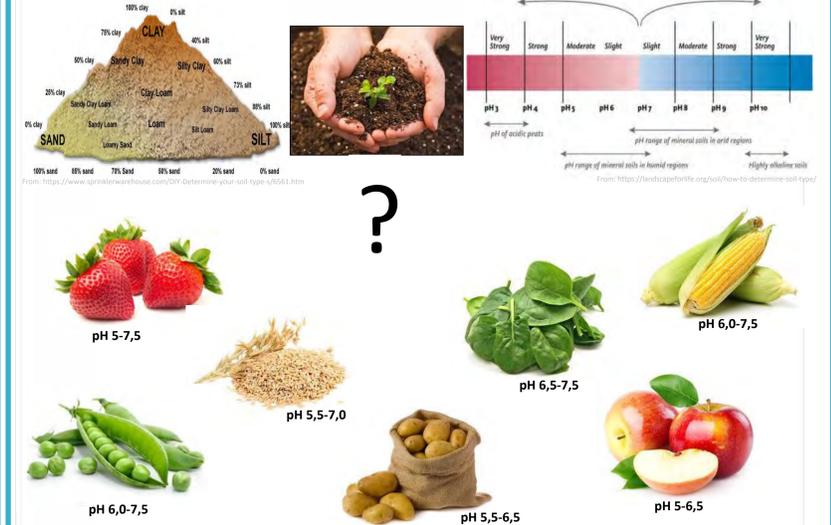
### Fertilizers (mineral) with > 5%wt. of P<sub>2</sub>O<sub>5</sub>

maximal concentration	EC proposal (2016/0084 COD)
As [mg/kg <sub>fertdrymatter</sub> ]	60
Cd [mg/kg <sub>P2O5</sub> ]	60/40 (3 years)/20 (12years)
Hg [mg/kg <sub>fertdrymatter</sub> ]	2
Cr/Cr <sup>VI</sup> [mg/kg <sub>fertdrymatter</sub> ]	- /2
Ni [mg/kg <sub>fertdrymatter</sub> ]	120
Pb [mg/kg <sub>fertdrymatter</sub> ]	150
Biuret (C <sub>2</sub> H <sub>5</sub> N <sub>3</sub> O <sub>2</sub> ) [mg/kg <sub>fertdrymatter</sub> ]	12
Perchlorate (ClO <sub>4</sub> -) [mg/kg <sub>fertdrymatter</sub> ]	50

### Sewage sludge

maximal concentration [mg.kg <sup>-1</sup> <sub>drymatter</sub> ]	Czech decree 437/2016
As	30
Cd	5
Cr	200
Cu	500
Hg	4
Ni	100
Pb	200
Zn	2500
AOX	500
PCB	0,6
PAU	10

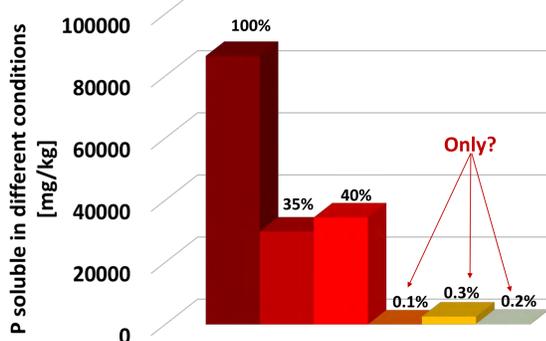
## Soils



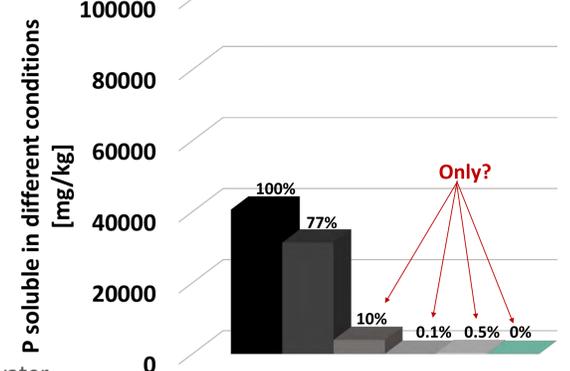
## Products of sewage sludge thermal treatment behaviour seen as fertilizers and as soil P-source



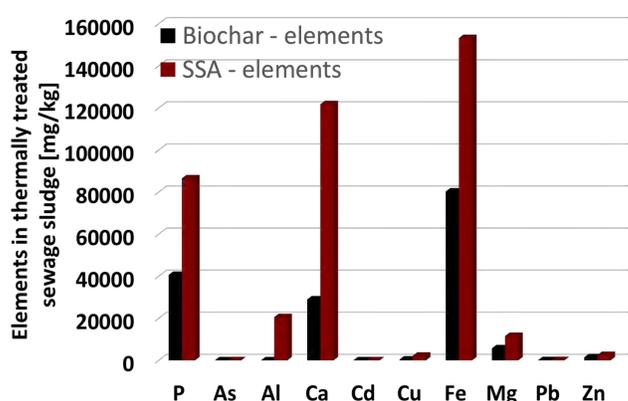
- SSA - total content
- SSA - acid soil fertilizer
- SSA - acid soils
- SSA - neutral soil fertilizer
- SSA - neutral soils
- SSA - immediate mobility - water



- Biochar - total content
- Biochar - neutral soil fertilizer
- Biochar - acid soil fertilizer
- Biochar - neutral soils
- Biochar - acid soils
- Biochar - immediate mobility - water



## Elements in products of sewage sludge thermal treatment



## Conclusion

- For both products of sewage sludge thermal treatment standardized fertilizer test shows promising long-term phosphorus bio-availabilities thus efficiencies of materials as P source
- These efficiencies estimated by methods common for testing of phosphate rock based fertilizers and soil amendments are however giving false positive P solubilities, thus bio-availabilities, compared to what we have seen in soil-like environment simulated by standardized soil tests such as the Olsen test (neutral to calcareous soils) or the Mehlich3 extraction test (acid soils)
- Standardized soil tests seems to give more realistic view on efficiency of sewage sludge based secondary P – sources

## Acknowledgements

- This work was conducted within the Waste-to-Energy Competence Centre (project no. TE02000236) with support from the Technology Agency of the Czech Republic.

# Restoring nutrient cycles in food systems – a regional perspective

Bernou van der Wiel, Cees Buisman<sup>1,3,7</sup>, Jan Weijma<sup>1,3,9</sup>, Corina van Middelaar<sup>1,4,8</sup>, Matthias Kleinke<sup>2,6,9</sup> and Florian Wichern<sup>2,5,9</sup>

1 Wageningen University and Research, 2 Rhine-Waal University of Applied Sciences,

3 Environmental Technology group, 4 Animal Production Systems group, 5 soil science and plant nutrition,

6 environmental technology, 7 promotor, 8 co-promotor, 9 supervisor

This PhD research project runs from Sept. 2017 till Oct. 2021



## Problem definition

Globalization, intensification and specialization of food production have collectively unbalanced nutrient cycles, as food and waste production became decoupled from consumption. In turn this has resulted in environmental, economic and social issues. Regional nutrient management has to focus on restoring circularity to minimize losses, inefficient use of available nutrients and dependency on non-renewable resources.

## Research objective

Assessing options to decrease the dependency of regional food production on non-renewable nutrient resources and minimizing nutrient losses while maintaining local economic viability and food security.

## Research questions

How can N, P, K and C cycles be restored in regional food production systems?

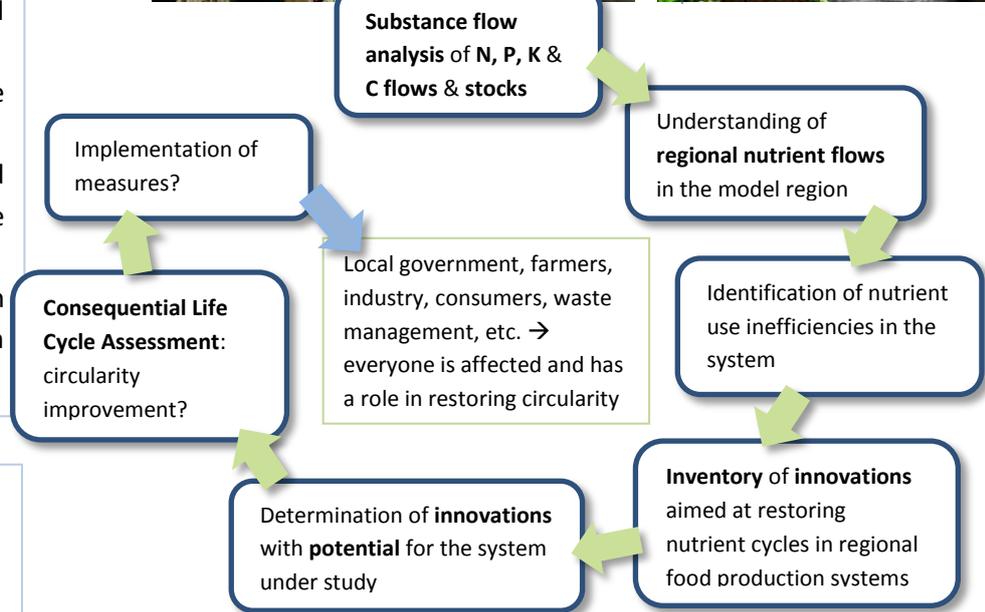
- Where are points of nutrient use inefficiencies?
- Which system innovations aimed improving nutrient circularity are available?
- What is the effect of innovations on circularity of nutrient management in regional food production systems?

## Materials and Methods

- Stakeholder meetings, modelling, literature review to obtain flows
- Stakeholder meetings and literature review to make an inventory of innovations
- Consequential Life Cycle Assessment

## Model region

Kleve, North Rhine-Westphalia, Germany: nutrient surplus area, negative impacts of nutrient losses, high livestock density, biogas production, horticulture, import of organic waste from the Netherlands



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Rhine-Waal University  
of Applied Sciences

WAGENINGEN  
UNIVERSITY & RESEARCH

# NUTRIENT RECOVERY WITH SOURCE SEPARATION OF URINE – ENVIRONMENTAL BENEFITS AND FERTILIZER POTENTIAL

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## BACKGROUND

Source separated human urine and faeces are nutrient-rich biomasses and could be utilised more efficiently as fertilisers. Many factors, however, are hindering the nutrient recovery on a large scale. For example, the logistical chain, including storage, transport and spreading, as well as legislative barriers require solutions as well.

## OBJECTIVES AND ACTIONS

The feasibility of source separation of urine, management and potential as a fertilizer was examined in this study. The fertilizer efficiency of source-separated urine was tested in field-scale experiments. Additionally nutrient potential as well as environmental impacts of source-separation in three alternative scenarios were examined using mass balance calculation and comparative LCA.

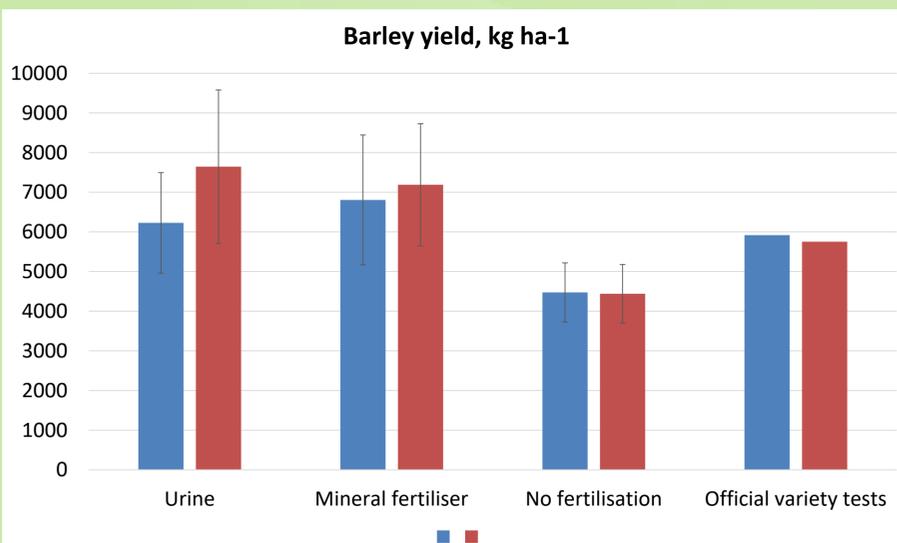


Figure 1. Total grain yield ( $\pm$ SD) of barley (*Hordeum vulgare*, var. Wolmari and Harbinger) (kg ha<sup>-1</sup>) with urine, mineral fertiliser and non-fertilised treatments.

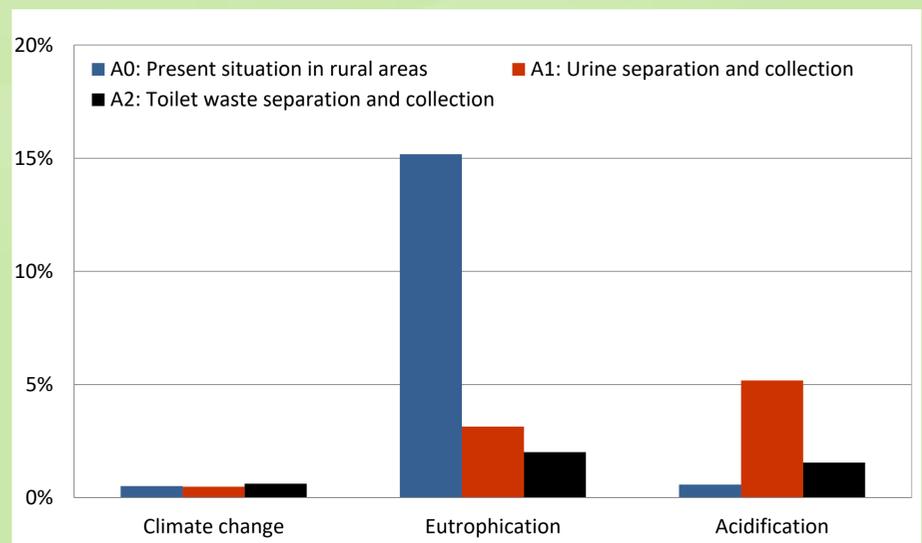


Figure 2. Environmental impacts of source separation of urine normalized by the European average annual emissions of the consumption.

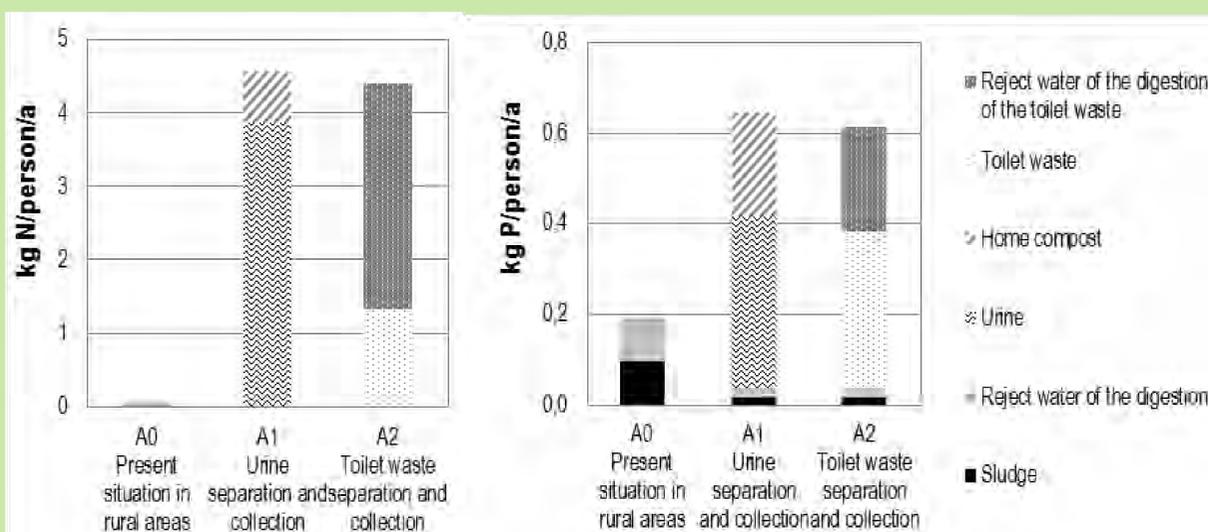


Figure 3. The nutrient potential of alternative scenarios with source separation of urine compared to the present onsite wastewater treatment methods in rural areas.

## RESULTS

Four times more P and over ten times more N could be recovered with source separation and utilisation of urine

Eutrophication impact is reduced down to one fifth

Urine was found to be as effective as mineral fertiliser

## CONCLUSIONS

Based on the results, environmental and economic benefits support the source separation and fertiliser use of urine. There are, however, strong opinions also against the fertiliser use of urine. Therefore, the acceptance of urine as a fertiliser and alternative technologies for nutrient recovery should be promoted.

Ongoing project: [www.hierakka.fi](http://www.hierakka.fi)

# THE CONTENT OF PHOSPHORUS IN THE SOIL IN THE CZECH REPUBLIC

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**Abstract:** Phosphorus is an essential nutrient both as a part of several key plant structure compounds and as a catalysis in the conversion of numerous key biochemical reactions in plants. Nevertheless, when phosphorus enters surface waters in substantial amounts it becomes a pollutant, contributing to the excessive growth of algae, and thus to the accelerated eutrophication of lakes and reservoirs. Practices to reduce phosphorus loadings must be based on an understanding of phosphorus sources, the forms of phosphorus added to soils, and the availability of phosphorus in soils. A long-term system of agrochemical soil testing in the Czech Republic has been running since the 1960s. The extraction procedure Mehlich 3 is the official analytical method currently used for the determination of the content of available phosphorus. However, it has turned out that the determination of phosphorus by Mehlich 3 in soils having a pH above 7,2 is not completely accurate. The current maps of the content of phosphorus in the soil in the Czech Republic were compiled based on the results obtained by the Mehlich 3 method. This project is working to refine the criteria for evaluating the content of available phosphorus in soils (especially carbonate soils - with a pH above 7,2) according to the Mehlich 3 method, so that the results are realistic and applicable in agricultural practice for the determination of real doses of single-purpose fertilizer.

**Phosphorus in the Soil.** The majority of P in most soil is in essentially insoluble forms, and unavailable to plants. In fertile soil a significant portion of the total P is in moderately soluble forms, which act as a "ready reserve" to replenish the pool of soluble P as it is depleted by and other organisms. Because phosphorus is essentially immobile in most soils, any factor that reduces normal root growth and function, for example soil compaction, will likely result in a P deficiency in those plants. This occurs even on soils with adequate to high P tests. Plant roots take up nearly all P as either the primary or secondary orthophosphate anion ( $H_2PO_4^-$  or  $HPO_4^{2-}$ , respectively). Primary orthophosphate is the form that is dominant in acid soils and is taken up about 10 times as readily as the secondary orthophosphate form. At a soil pH of 7,0 there is approximately equal amounts of the two P forms and as the soil pH increases above pH 7,0, the secondary orthophosphate ion becomes the dominant form of available P. The fertilizer form of P is referred to as  $P_2O_5$  (phosphorous pentoxide), however, no such compound actually exists in fertilizer or the soil. This is simply a uniform way of equating the various forms of P to each other. To convert P to  $P_2O_5$  multiply P  $\times$  2,3. To convert  $P_2O_5$  to P, either divide  $P_2O_5$  by 2,3 or multiply  $P_2O_5 \times 0,435$ .

## Soil reactions - pH / CaCl<sub>2</sub> solution - agricultural soil.

Replaceable soil reaction is one of the most important factors influencing soil fertility. Soil reaction is mainly for mooring and accessibility of nutrients to improve the structural condition of the soil and thus to a better circulation of water and air in the soil, on soil microbial activity, the formation of humus and the mobility risk elements in the soil.

The average value of farmland soil reaction in the Czech Republic is a pH of 6,1. Soil with an extremely acidic, strongly acidic and acidic soil reaction (with pH up to 5,5) represents more than 29,7% of the tested area. Another 39,8% of agricultural soil has a weakly acidic soil reaction (pH 5,6 to 6,5). Regularly liming (at least with a maintenance dose) would require a total of nearly 70% of agricultural soil. The share of alkaline soils with pH above 7,2 occupies about 13,4% of the area of agricultural soil.

**The content of accessible phosphorus.** According to the results the average availability of accessible phosphorus in the agricultural land of the Czech Republic is 89 mg.kg<sup>-1</sup>. Soil with a low supply of phosphorus, which needs intensive fertilization, representing more than 25,9% of the area of the Czech Republic. High and very high supply of available phosphorus was found on 24,3% of the area of the Czech Republic.

The average pH values and the percentage of acidic and alkaline soils for the territorial units of the Czech Republic

Table 1

Region	Average value pH	Soil share, [%]	
		Acid reaction (up to 5,5)	Alkaline reaction (over 7,2)
Praha - hl. město	6,2	19,10	7,51
Středočeský	6,3	20,82	20,09
Jihočeský	5,6	49,80	0,34
Plzeňský	5,6	49,04	0,14
Karlovarský	5,6	55,81	0,72
Ústecký	6,8	9,09	39,18
Liberecký	5,9	33,37	1,93
Královéhradecký	6,2	20,15	10,67
Pardubický	6,0	31,31	6,42
Vysočina	5,6	49,68	0,72
Jihomoravský	6,7	12,37	41,01
Olomoucký	6,3	19,47	11,21
Zlínský	6,3	17,87	11,67
Moravskoslezský	5,9	32,54	1,37
<b>Czech Republic</b>	<b>6,1</b>	<b>29,74</b>	<b>13,35</b>

Resource: Central Institute for Supervising and Testing in Agriculture

Accessible phosphorus, Mehlich III extract - agricultural soil.

Table 2

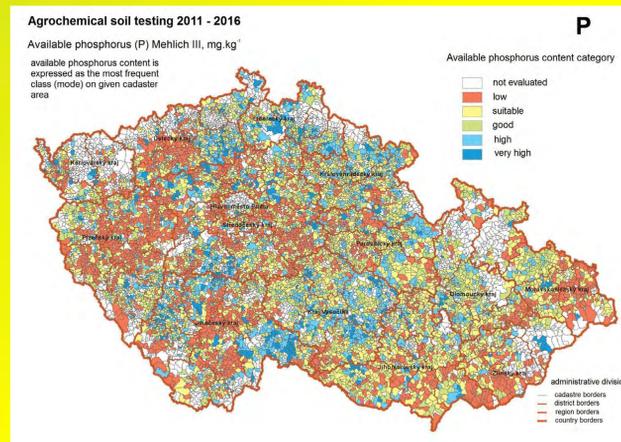
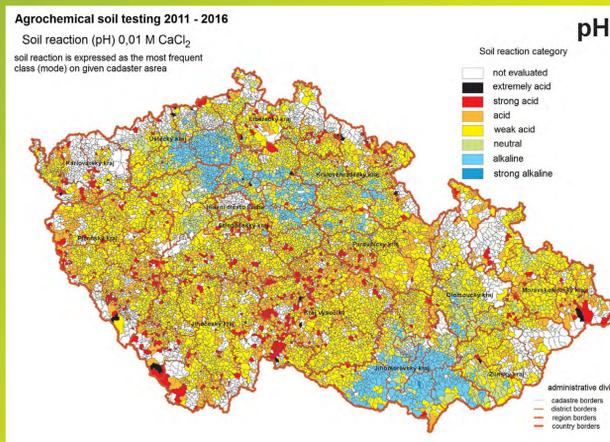
Region	Average value P (mg.kg <sup>-1</sup> )	Soil share, [%]	
		Low content	High and very high content
Středočeský	92	29,15	23,85
Jihočeský	87	28,92	26,11
Plzeňský	71	37,17	17,18
Karlovarský	77	31,66	22,10
Ústecký	101	27,20	29,63
Liberecký	119	10,13	45,91
Královéhradecký	96	16,82	28,37
Pardubický	86	22,06	21,78
Vysočina	99	16,49	30,49
Jihomoravský	90	28,06	21,29
Olomoucký	94	19,73	25,56
Zlínský	78	31,07	17,69
Moravskoslezský	78	26,41	16,80
<b>Czech Republic</b>	<b>89</b>	<b>25,86</b>	<b>24,30</b>

Resource: Central Institute for Supervising and Testing in Agriculture

**Principle of Mehlich III extract.** The soil is extracted with an acidic solution containing ammonium fluoride to increase solubility of different forms of phosphorus bonded to iron and aluminum. Ammonium nitrate is also present in the solution, which has a beneficial effect on the desorption of potassium, magnesium and calcium. The acidic reaction of the leaching solution is adjusted with acetic acid and hydrochloric acid.

The leach solution simulates accessibility of the soil. K, Mg, Ca is determined in the leachate by means of atomic absorption spectrometry and phosphorus photometrically as phosphomolybdate blue (Mehlich 1984).

For analysis, a soil sample is used which is dried or dried in air at the soil is extracted with an acidic solution containing ammonium fluoride, ammonium nitrate and EDTA (ethylenediaminetetraacetic acid), which is prepared according to ČSN ISO 11464. The acidic reaction of the leach solution is set acetic acid and nitric acid.



Resource: Central Institute for Supervising and Testing in Agriculture

There are no maximum phosphorus application limits or other P restrictions in the Czech Republic. The regulations affecting phosphorus application and losses are indirect, e.g. by manure N restriction in the Nitrates Directive, erosion control and buffer zone directives, and agri-environmental programmes. In the latter, farmers can have a free soil P measurement (every 5 or 6 years, organised by a state agency) and P fertilisation recommendation (not mandatory).

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# Probabilistic environmental risk assessment – comparing primary and secondary phosphate-fertilizer application (Example: Cadmium)

Malte Zamzow, Fabian Kraus

## Approach

- Risk characterisation of harmful effects on humans and the environment by inorganic pollutants and pharmaceutical residues caused by fertilizer application
- Quantification of risk via *Risk Quotient (RQ)* =  $\frac{\text{Predicted Environmental Concentration (PEC)}}{\text{Predicted No Effect Concentration (PNEC)}}$  in three different compartments

### Pathways and Endpoints

Hazard application → Soil concentration → Soil organisms

Hazard application → Soil concentration → Soil pore water → Leaching → Groundwater

Hazard application → Soil concentration → Plant uptake (wheat) → Humans

### PEC

Average soil concentration (30 days after applications)

Average pore water concentration (30 days after application)

Pollutant intake due to wheat consumption

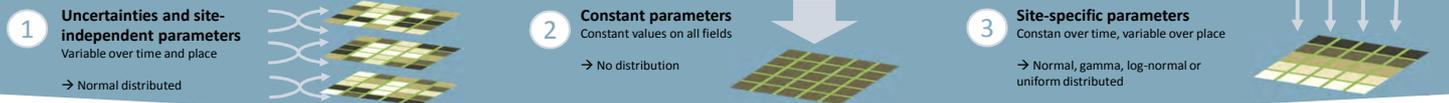
### PNEC

PNEC<sub>Soil</sub>

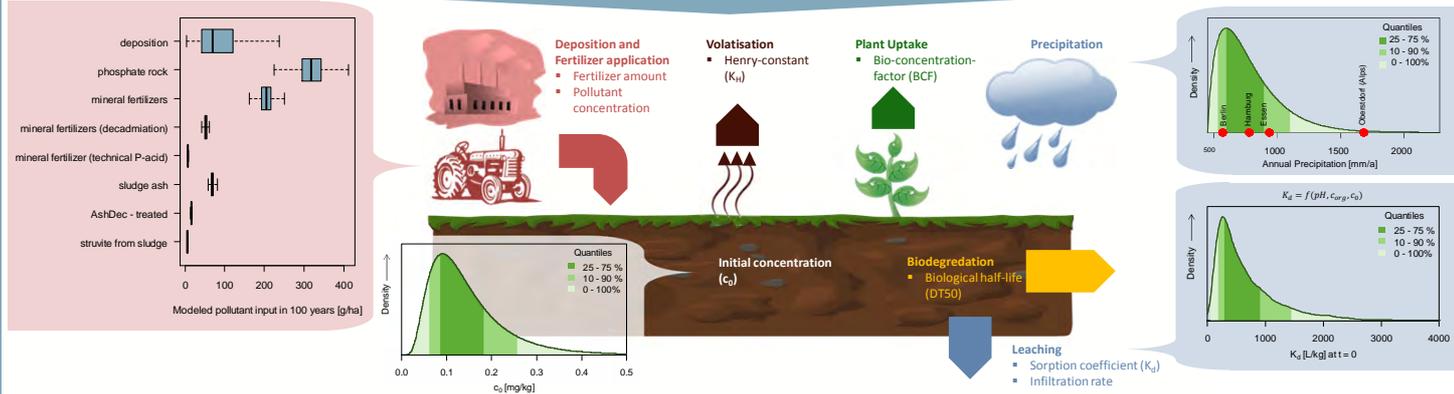
PNEC<sub>Water</sub>, Groundwater minor threshold values

0.5 · Tolerable daily intake (TDI)

Challenges: High variability depending on environmental conditions and high uncertainties about toxicity data and pollutant behaviour



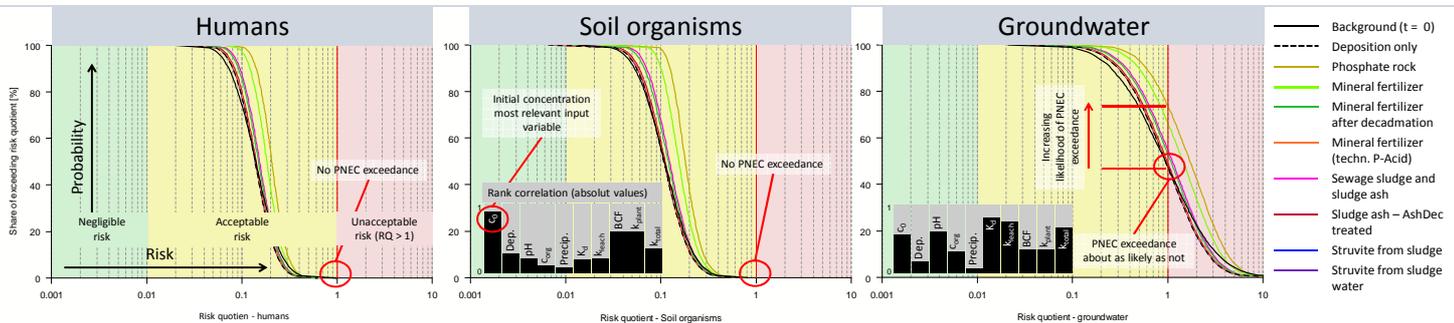
## Exposure assessment



- Based on *Technical Guidance Document on Risk Assessment (TGD)* of the European Commission, extended by output „plant uptake“ and pH-related leaching
- Simulation runs over 100 years - no change of surrounding conditions (e.g. legislative conditions, improvements of wastewater treatment not considered, etc.)

## Cadmium Results

## Risk characterisation



## Conclusions

- Groundwater is the most sensitive endpoint
- Exceedance of the PNEC is likely after 100 years of mineral fertilizer or phosphate rock application (despite low assessment factor for Cd-PNEC)
- Decadmatation of conventional fertilizers reduces the RQ significantly
- Initial concentration and sorption coefficient (pH-related) are the most relevant variables of the model

## Outlook

- Risk assessment on further inorganic and organic substances and pharmaceutical residues:
  - Arsenic, Chromium, Copper, Mercury, Nickel, Lead, Zinc, Uranium
  - PAK, PCDD/F + dl-PCB
  - 17α-Ethinylestradiol, 17β-Estradiol, Bezafibrate, Carbamazepine, Cefuroxim, Ciprofloxacin, Clarithromycin, Diclofenac, Levofloxacin, Metoprolol, Sulfamethoxazole,

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