Nutrient recovery from wastewater streams:

new perspectives and technical solutions

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Programme for Sustainable Growth and Jobs

KAMK • University of Applied Sciences

KOKKOLA
MATERIAL
WEEK

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the EU
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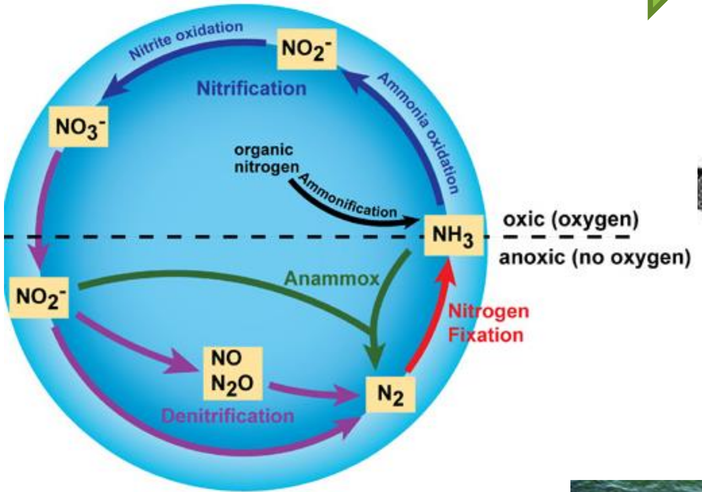
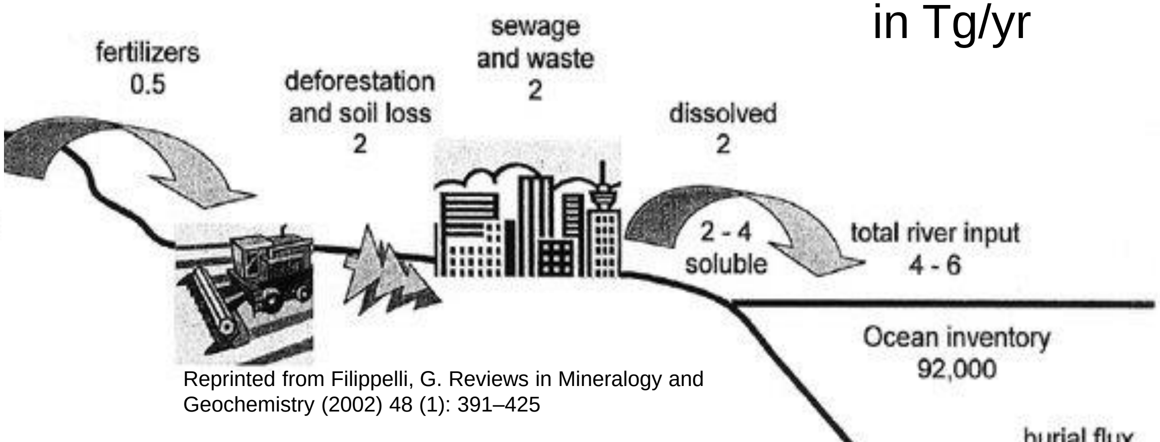
Motivation

The human alteration of nitrogen and phosphorus global natural cycles → heavily unbalanced



Reprinted from Bernhard, A. (2010) The Nitrogen Cycle: Processes, Players, and Human Impact. Nature 3(10):25

in Tg/yr



Reprinted from Filippelli, G. Reviews in Mineralogy and Geochemistry (2002) 48 (1): 391–425

Price?
annually

U.S. **$2.2 billion** (Dodds et al. 2009)
UK **$160 million** (Pretty et al. 2003)
Baltic sea **€ 200 million** (HELCOM)

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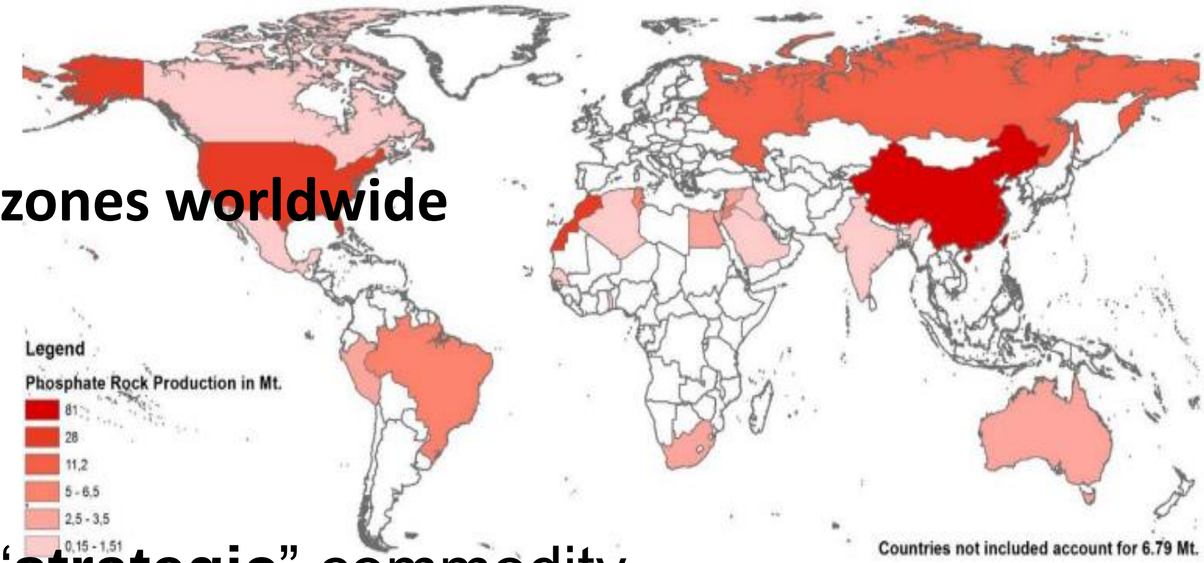
Motivation

- >400 coastal **dead zones worldwide**



Source: Based on Jasinski (2013).

- Phosphorus is a “**strategic**” commodity

located in just few countries and deposits

included into the list of critical materials in **2014**

up 80% of mined phosphorus is lost the extraction process

- Recovery could be valuable in near future

will be depleted within the next 45–100 years

as discharge limits become stricter

- Possibility to cover **50% of a P-market**

Motivation

– developing less energy-demanding process for nitrogen capturing – Haber-Bosch process accounts for approximately **1% of global energy consumption**;

– to **reduce GHG emission**: substantial concomitant as Haber-Bosch process and WWTP facilities (biological treatment, 3% of all GHG globally);

– to reduce nutrient leaching into natural water bodies

– transition to **circular economy**

Benefits

Renewable fertilizers or industry feedstocks
Protecting and improving water quality
Improving operation and performance at WWTP
Improving food security and social equity
Business opportunities

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Nutrient-contaminated streams

Agriculture, fishery, forestry

- Facultative lagoons
- Air purification cattle farms
- Overfertilized fields
- Aquaculture operations
- Ditches and peat bogs

Municipal and urban wastewaters

- Run-off and storm waters
- Wastewater treatment plants

Industrial waste-
and processing waters

- Reject waters of biogas stations
- Landfill leachates
- Textile industry processing waters
- Paper mills grey waters
- Food industry (meat and beverage)

Low-laden or High-laden with nutrients

Diffuse or centralized source

Emerging pollutants

Complexity of matrix

Energy demand

Public perception and acceptance

Legislation

N/P ratio

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Nutrients in municipal wastewater

Globally

380 billion m^3/a of wastewater

Major nutrients in wastewater, worldwide, annually:

16.6 million metric tonnes of N

6.3 million metric tonnes of K

3 million metric tonnes of P

Recovered these nutrients could offset of global demand:

14.4% for N;

6.8% for P

18.6% for K

Nationally*

0.5 billion m^3/a of wastewater

Nitrogen load in sewage systems **32 670** ton/a and **66%** of it is removed and **lost** in current treatment processes, **rest** in inland waters

Phosphorous load in sewage systems **4 300** ton/a and **3%**** of this was recycled

In 2017, a total of app.155 tonnes of **P** and app. 11,090 tonnes of **N** were discharged from municipal wastewater treatment plants.

theoretically generated **revenue globally**:
$9.0 billion from the recovery of N,
$2.3 billion from P,
$2.3 billion from P.

+

Energy, chemical consumption, sludge production
critical environmental benefits such as minimising eutrophication

POSSIBLE BUSINESS CASES

**https://circhubs.fi/tietopankki/puhdistamoliete/ *https://www.ymparisto.fi/fi-fi/kartat_ja_tilastot/

SOLUTION is

Combination of mature techniques

Adsorption → **New geopolymer adsorbent from low-cost sources: unique properties and steady quality**

+

Desorption → **adsorption-desorption cycles without reloading**

=

Concentration → **the max enrichment factor with min reagent use**

Air stripping
OR
Membrane separation

- **Independence from initial concentration**
- **pH already suits for this technologies**
- **Twice lower temperature could be used**
- **Minimize the dimensions of the setup**
- **Lower energy consumption**

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Design of the Treatment Process

Objects

- **Run-off waters and effluents**

Diluted solutions with complex matrix < 0.2 g N/L

1 stage

- **Nitrogen removal**
- Adsorption by new geopolymers

2 stage

- **Nitrogen preconcentration**
- Desorption with a regeneration solution

3 stage

- **Nitrogen recovery**
- Air-stripping or membrane technology for the regeneration solution purification

Stage 1: Design of cost-effective adsorbents

Cost-effective adsorbents

Source
- Abundant
- Low cost

Calcined clay
Pulp fibre sludges
BFS
Fly ash F

Process
- Easy to handle
- Fast removal
- High capacity

Granulated forms
Contact time

Waste management
- Easy to regenerate
- Minimal liquid waste discharge
- Secondary valuable product

Regeneration solution in the loop mode
Adsorbent recycling
Inorganic polymers: eco-friendly

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Geopolymers for ammonium concentration

Raw material for geopolymer preparation:

- paper mill sludge contained kaolinite as paper additive; **FS MKGP**
- calcined kaolinite (Luukkonen et all. 2016)

To recover clay and transform it to form needed, paper mill sludge was ignited, and the remaining kaolinite calcined at 750ºC.

- commercially available metakaolin (Aquaminerals Finland Oy); **MKGP**

To prepare reference geopolymer material, metakaolin was geopolymerized in accordance with standard procedure (Luukkonen et al. 2016).

Adsorbent	Capacity mg/g	Regeneration
MKGP	1,3	5M NaCl, pH 12
FS MKGP	3,7	5M NaCl, pH 12 + acetic acid
Zeolite (Spain)	2,2	5M NaCl, pH 12 + acetic acid
Zeolite (China)	1,3	5M NaCl, pH 12
Zeolite (Bulgaria)	3,7	5M NaCl, pH 12 + acetic acid

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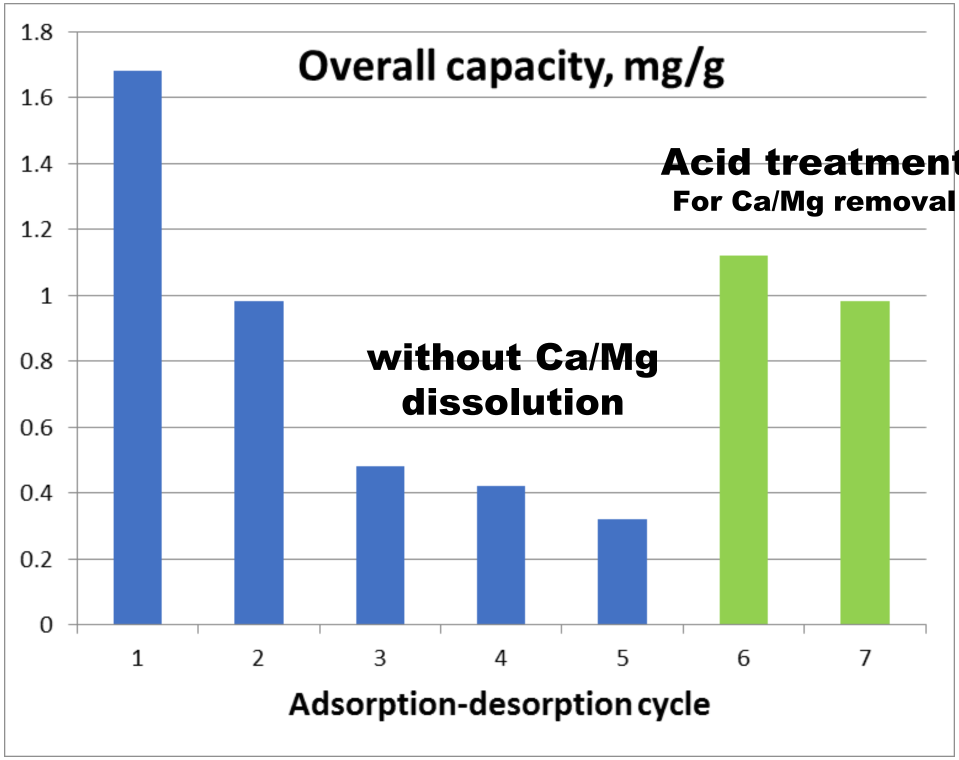
Regeneration study

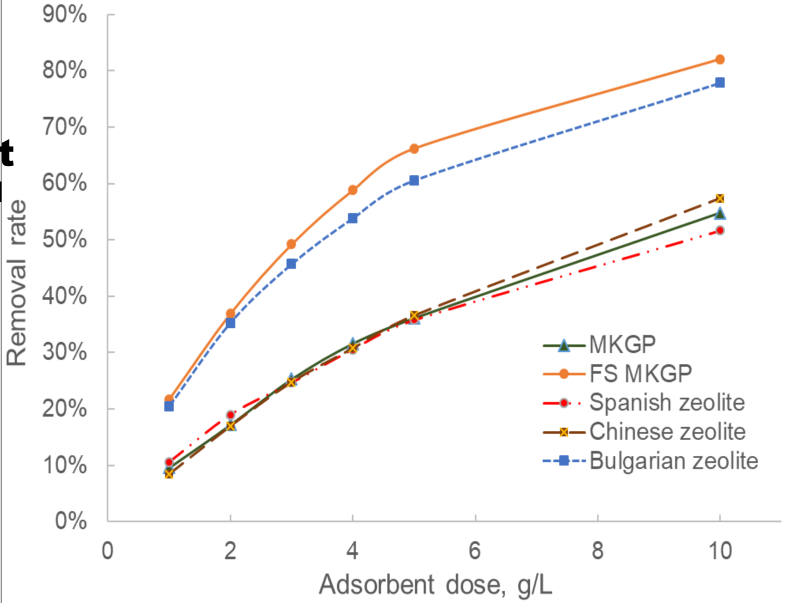
Sample Adsorbent	Run-off	Lake water	Mine water		WWTP effluents	
			Point 1	Point 2	Before	After
MKGP	68 %	64 %	44 %	45 %	54 %	52 %
FS MKGP	92 %	95 %	69 %	72 %	82 %	81 %
Spanish zeolite	61 %	58 %	32 %	38 %	51 %	56 %
Chinese zeolite	55 %	58 %	17 %	21 %	57 %	57 %
Bulgarian zeolite	87 %	84 %	52%	60%	77 %	78 %

adsorbent dose
10 g/L

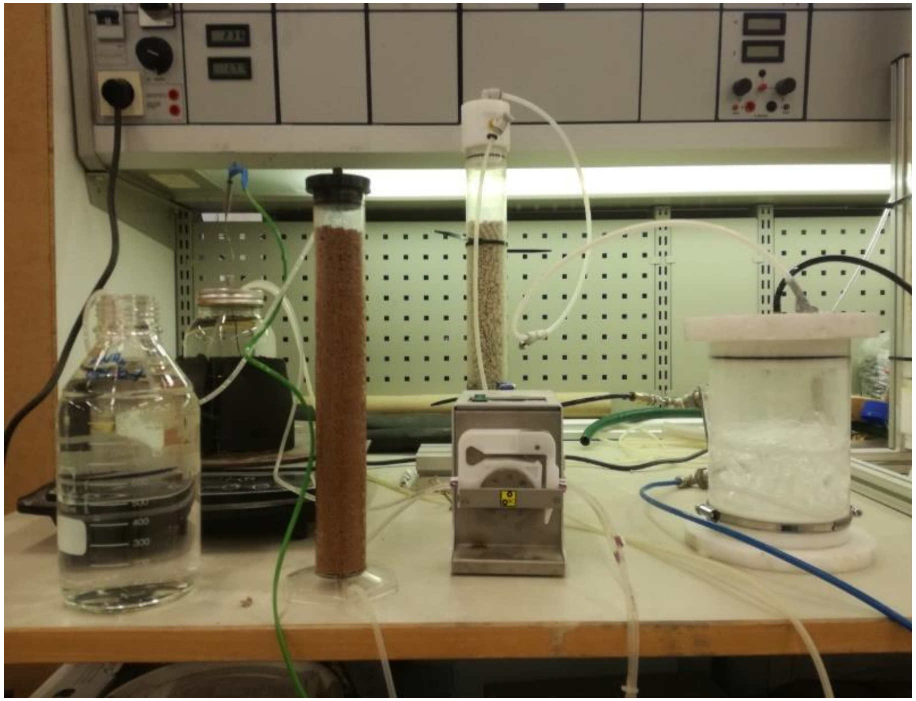
grain size
63-125 µm

contact time 3h





Lab-scale demonstrations and pilotings



Geopolymer adsorbents:

Adsorption-desorption cycles were piloted on local WWTP Kajaanin Vesi

Lab-scale setup for air-stripping evaluation:
adsorption and stripping cycles analysis
alkali and acid dosage
optimal temperature testing
liquid and air supply rates
hydraulic loading optimization

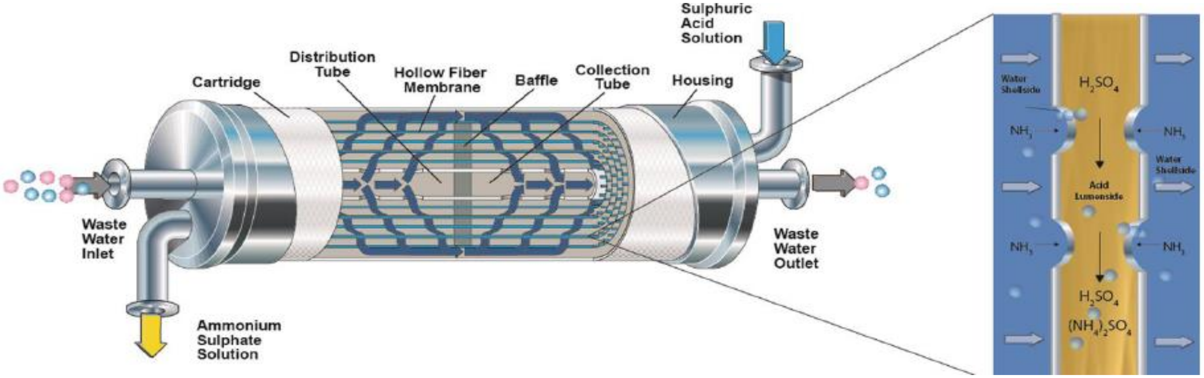
Results

Temperature 45±5⁰C was enough to reached conversion rate 91 %.

After the regeneration solution was purified, it was used over 5 times for desorption procedure.

Lab-scale demonstrations and pilotings

Transmembrane Chemical Absorption



Results

3M Liqui-Cel® membrane contactor **provided by manufacturer** for piloting on WWTP

Receiving acids:
phosphoric or sulfuric

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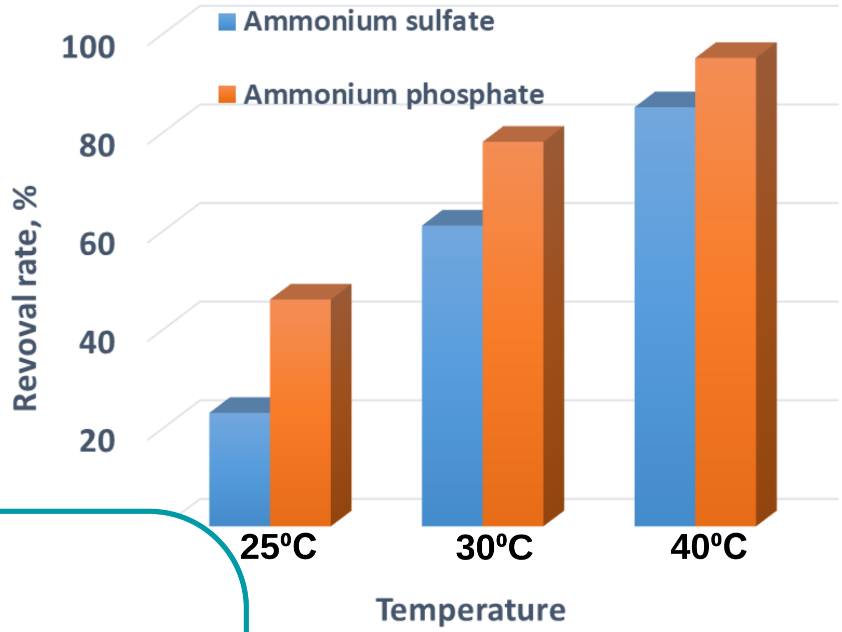
Recovery of ammoniacal nitrogen Transmembrane Chemical Absorption

Final product:
ammonium sulfate

ammonium
mono(di)phosphate



- **Optimized conditions:**
- 100 L/h shellside flow with pH ≥ 11
- 60L/h lumenside feed flow with pH ≤ 5,6
- working temperature - 40ºC.

- **Lumenside absorbtion liquid:**
- Sulfuric or phosphoric acids (tech.) up to 5%.

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Lab-scale demonstrations and pilotings

First piloting for
WaterPro
at Kajaani Vesi

- Prebooked for Karelia CBC piloting (SUSWAM, REMAC)

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Nutrient removal from run-off waters

What else could be beneficial?

Unique properties

- **Buoyancy**
- **High porosity**
- **Lightness but hardness**

Work co-funded by of Maa- ja vesitekniikan tuki (№ 13-8271-17).

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Lab-scale demonstrations and pilotings

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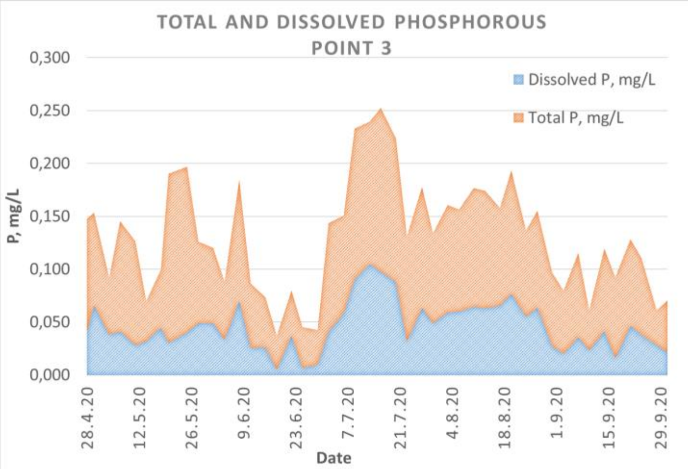

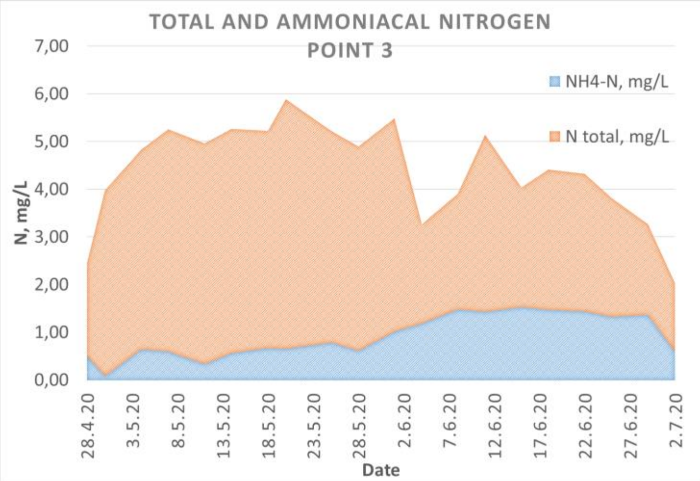

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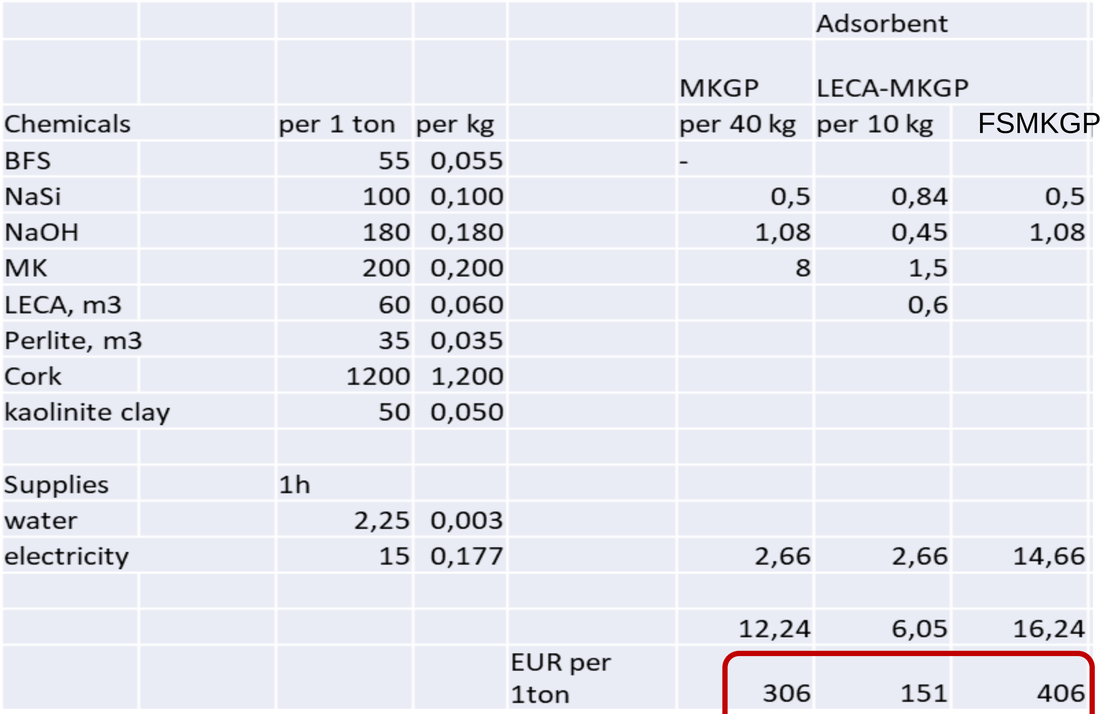
Lab-scale demonstrations and pilotings

After 10 weeks of piloting

Total P less than 0,03 mg P/L
PO_4-P less than 0,01 mg P/L ⬇ ~**60%**

Total N less than 1 mg N/L
NH_4-N less than 0,05 mg N/L ⬇ ~**80%**



						Adsorbent	
					MKGP	LECA-MKGP	
Chemicals		per 1 ton	per kg		per 40 kg	per 10 kg	FSMKGP
BFS		55	0,055		-		
NaSi		100	0,100		0,5	0,84	0,5
NaOH		180	0,180		1,08	0,45	1,08
MK		200	0,200		8	1,5	
LECA, m3		60	0,060			0,6	
Perlite, m3		35	0,035				
Cork		1200	1,200				
kaolinite clay		50	0,050				
Supplies		1h					
water		2,25	0,003				
electricity		15	0,177		2,66	2,66	14,66
					12,24	6,05	16,24
				EUR per 1ton	306	151	406

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Thank You for your attention!

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