Extracting, Capturing and Reusing Phosphorus from Cultivated Algae Systems (or other cellular biomass)

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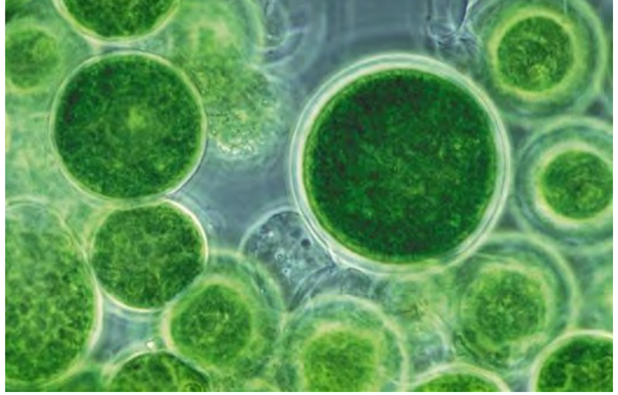
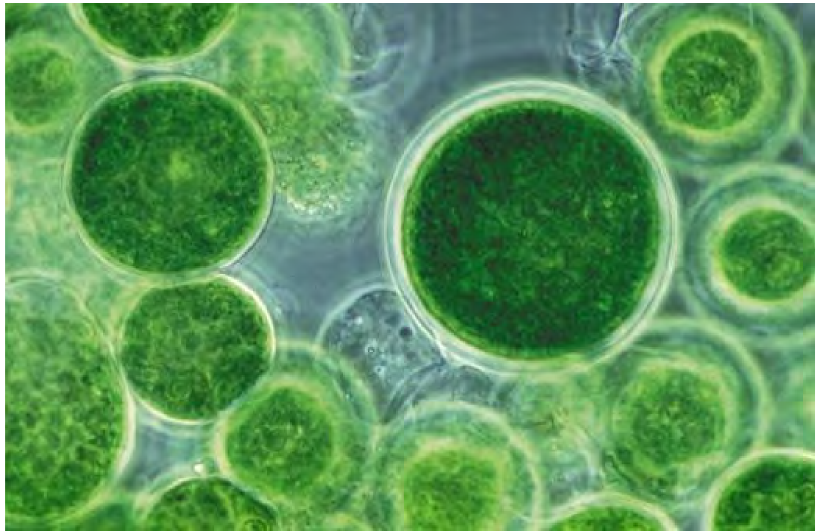
Outline



- Where is the P in biotechnology systems ?
- How do we recycling P in *Biorefineries* ?
  - Focus on smaller & more compact physical-chemical systems, rather than anaerobic digestors
  - Organic-P transformation to ortho-P
  - Capture & concentration of ortho-P to create mobile nutrient solutions
- Summary

Microbial Biofuels ?

In 2009, **32%** of all US corn went to ethanol, using 10% of all P fertilizer.



Engineered biorefineries with photosynthetic algae hold promise to be near P-neutral…

Advanced Algal Systems
(DOE Bioenergy Technologies Office (BETO))

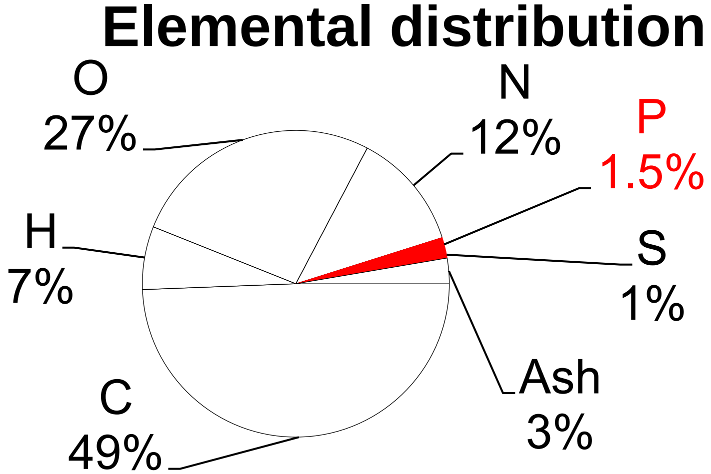
PRODUCTION

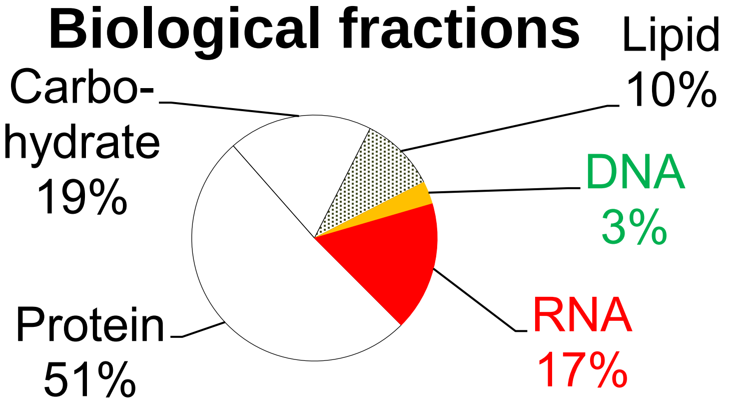
Algal production research and development (R&D) explores resource use and availability, algal biomass development and improvements, characterizing algal biomass components, and the ecology and engineering of cultivation systems.

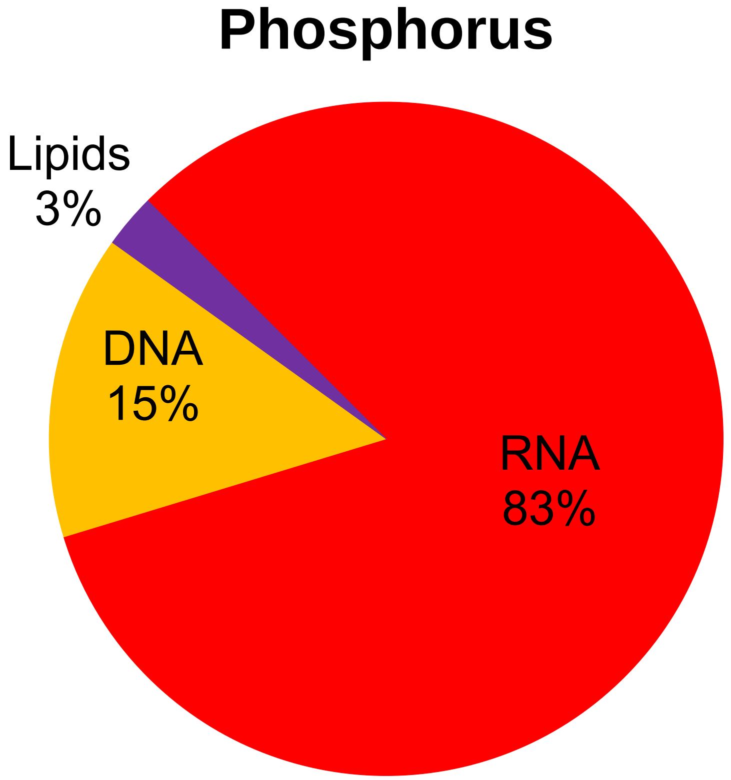
LOGISTICS

Algal logistics involve harvesting algae from the cultivation system and then dewatering and concentrating the harvested biomass so that it's suitable for preprocessing into a product that can then be refined and upgraded into a biofuel.

Biorefineries want to product & extract lipids (or produce short-chain fatty acids),
so where is the P in cells ?

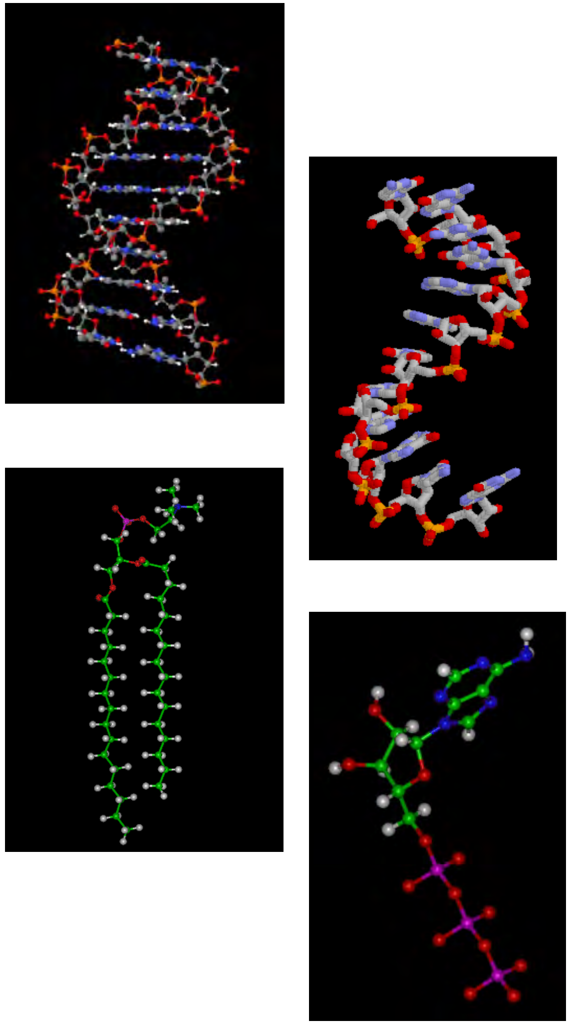






Synechocystis sp. PCC 6803

Molecular Composition



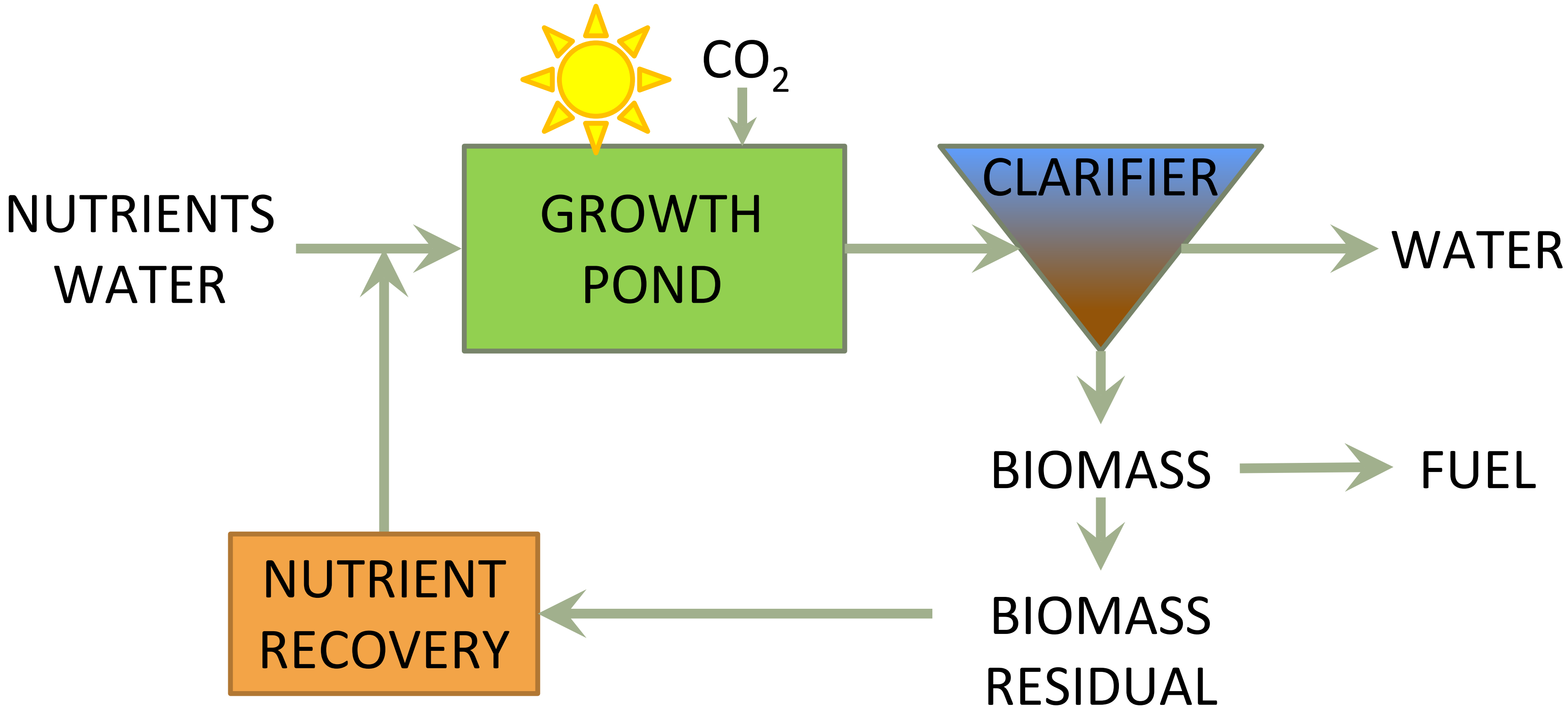
Structure	P Content	Biology
Deoxyribo Nucleic Acid	10% P	3% of cell
Ribo Nucleic Acid	10% P	17% of cell
Phospho-lipid	4% P	14% of lipids, which are 10% of cell
Adenisine Tri Phosphate	18% P	0% of cell

DNA
15%

RNA
83%

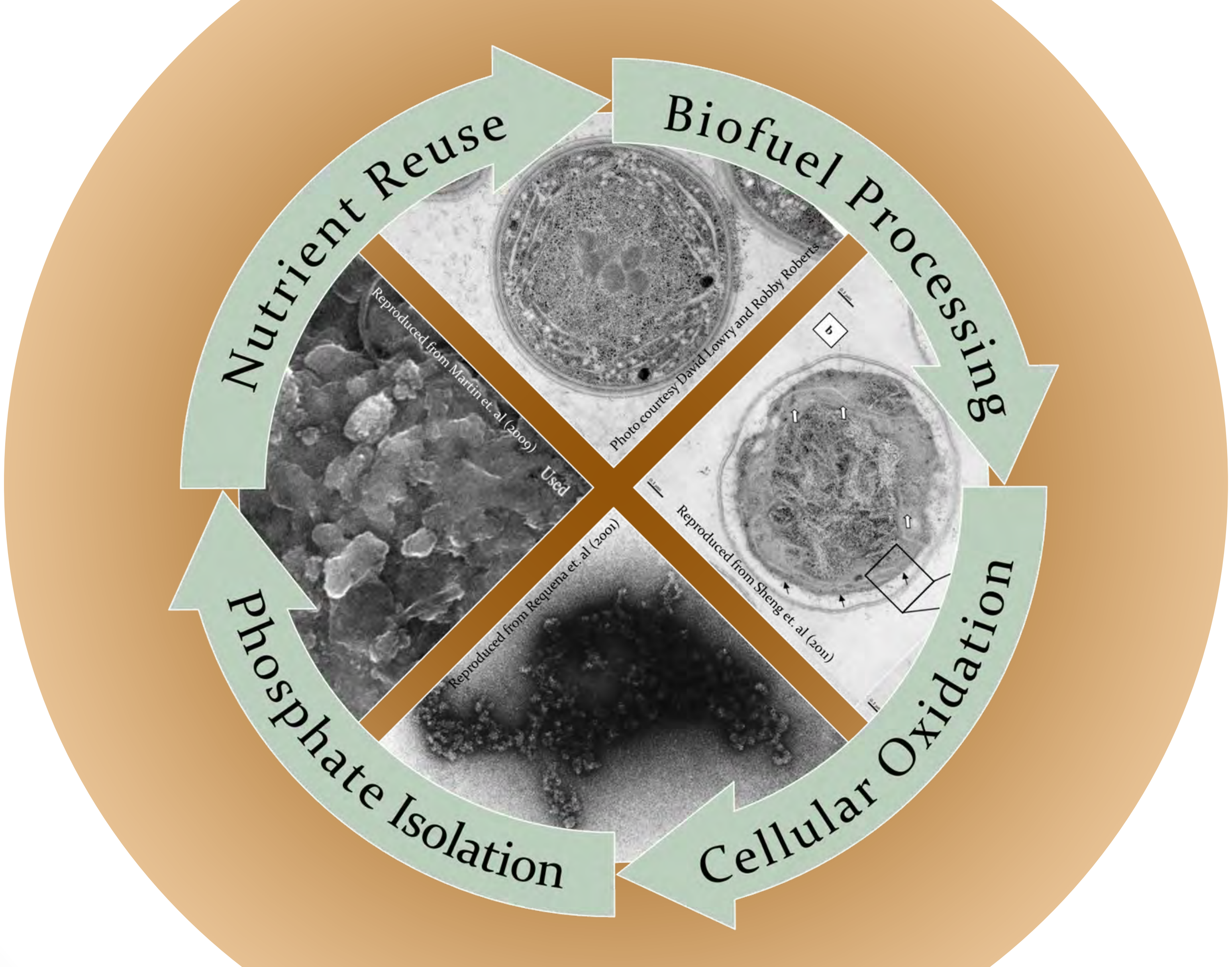
Lipid 2%

Closing the P-Loop in Biorefinery



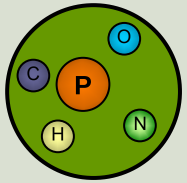
- Fertilizer nutrients & water contribute up to 50 % of biomass <u>production</u> cost
- > 50% cost reductions if CO_2, nutrients and water can be reused at low cost
- Nutrient costs are variable & account for 10-20% of <u>total biofuel</u> cost

Cycling Process



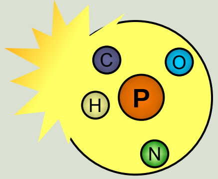
Nutrient Reuse

- Cyanobacterium *Synechocystis* sp. PCC6803 cultured in BG-11 with K_2HPO_4 in bench top photobioreactor



Biofuel Processing

- Centrifuge to rinse
- Freeze dry to dewater
- Folch lipid extraction
- Transesterification to extract fatty acids



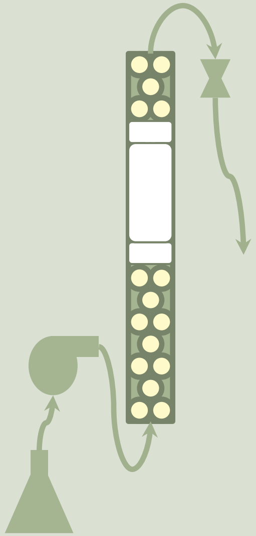
Total P Analysis

- Persulfate digestion
- ICP-OES

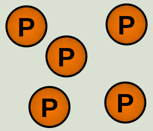
Ortho P Analysis

- Spectrophotometer

Phosphate Isolation

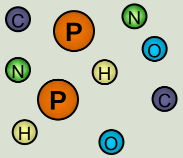


- Hybrid Anion Exchange vs. Strong Base Anion Exchange resins
- Treat 20 BV with 2 min EBCT in column mode
- Elute with 33 BV of 0.1N regenerant



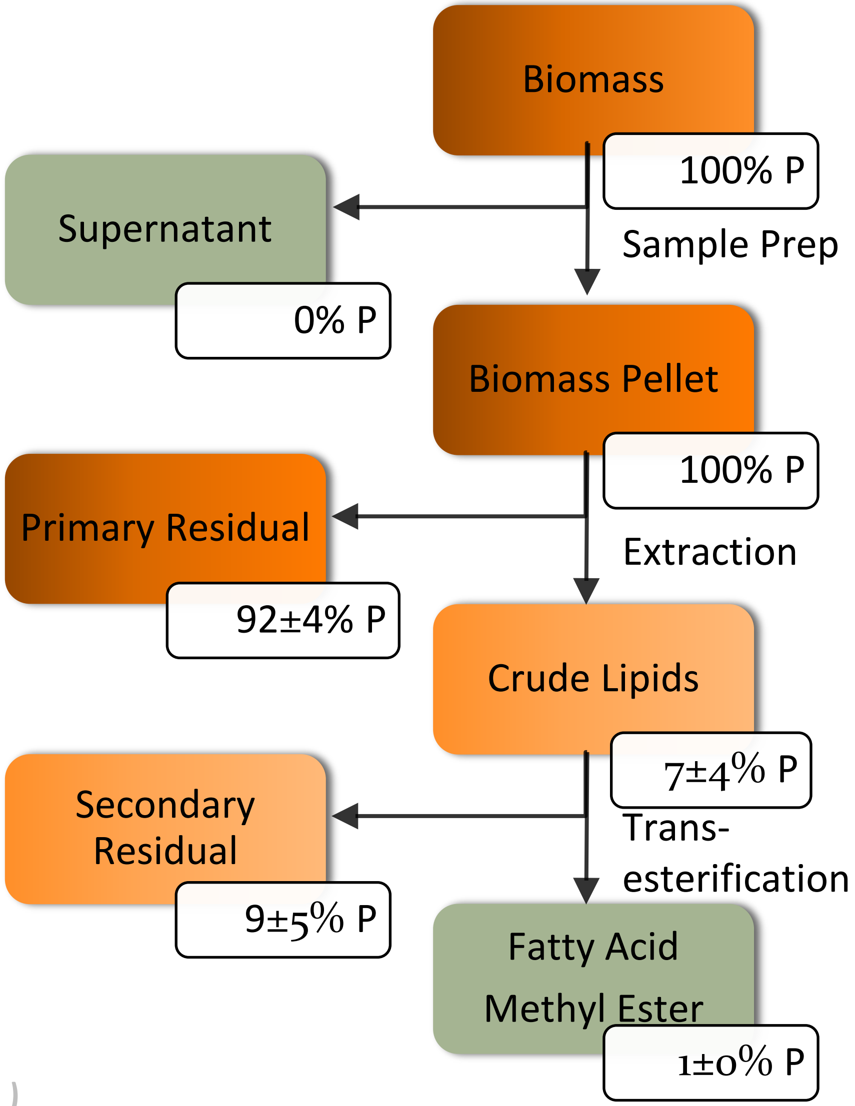
Cellular Oxidation

- Suspend in 30% hydrogen peroxide
- Microwave heat at 160°C for 10 minutes



P through Biofuel Processing

- *Synechocystis* is 1 wt% Phosphorus
- Primary Residual is 1.5% Phosphorus
- Majority Phosphorus found in primary residual



Gifford et al, Water Research (2015)

Oxidation Results

<u>Why microwave treatment:</u>

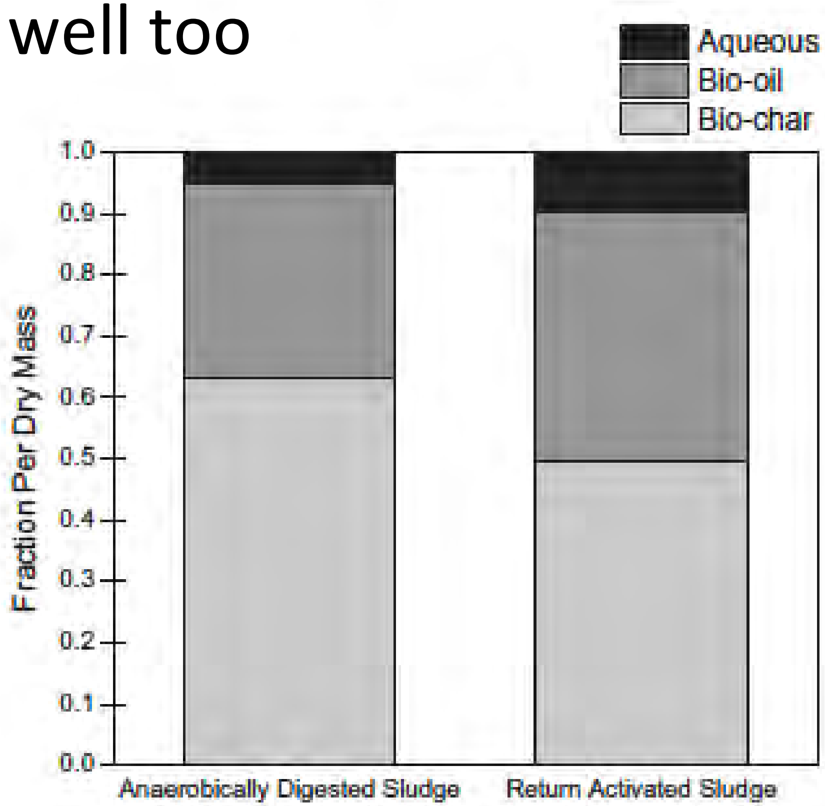
- Increases P-release from cells by >50%
- Decreases treatment time by >90% vs anaerobic digestin
- Mobile treatment & electrified systems

Step	Sample Description	Total P	Ortho P
Before Oxidation	complex solution	65%±10%	0.2%±0.0%
After Oxidation	complex solution	90%±12%	75%±12%

Other potential oxidation processes

- Microwave treatment
  - H_2O_2 not always required
  - KOH or NaOH works well too

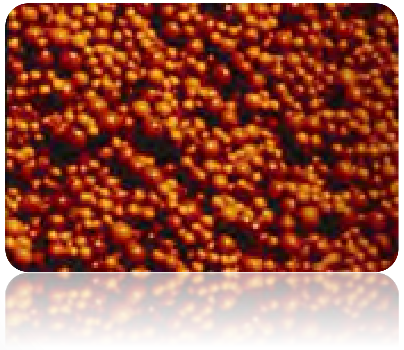
- Hydrothermal liquefaction

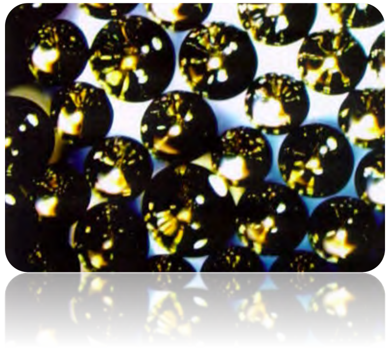


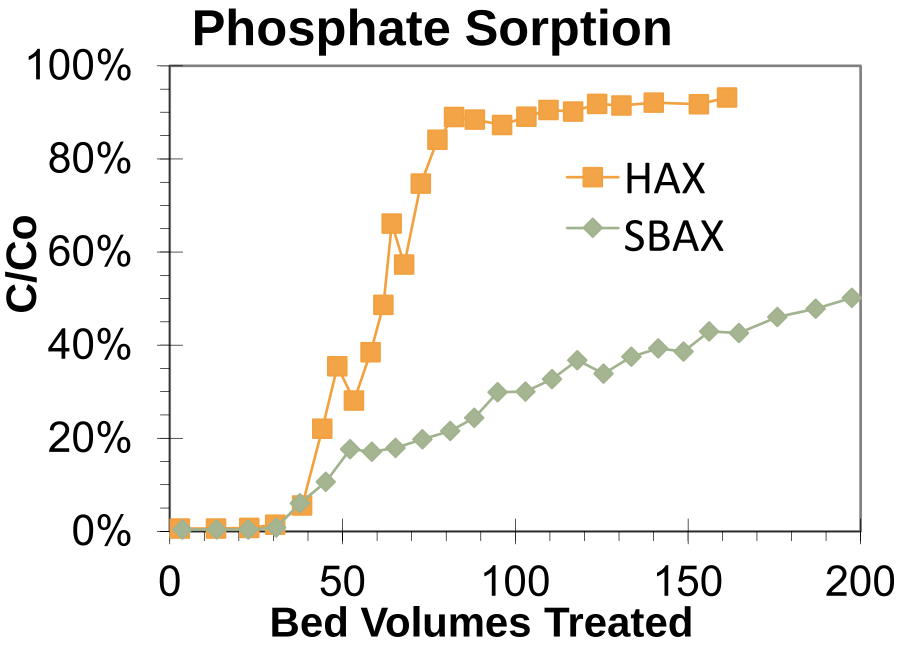
Mulchandani & Westerhoff / Bioresource Technology 215 (2016) 215–226

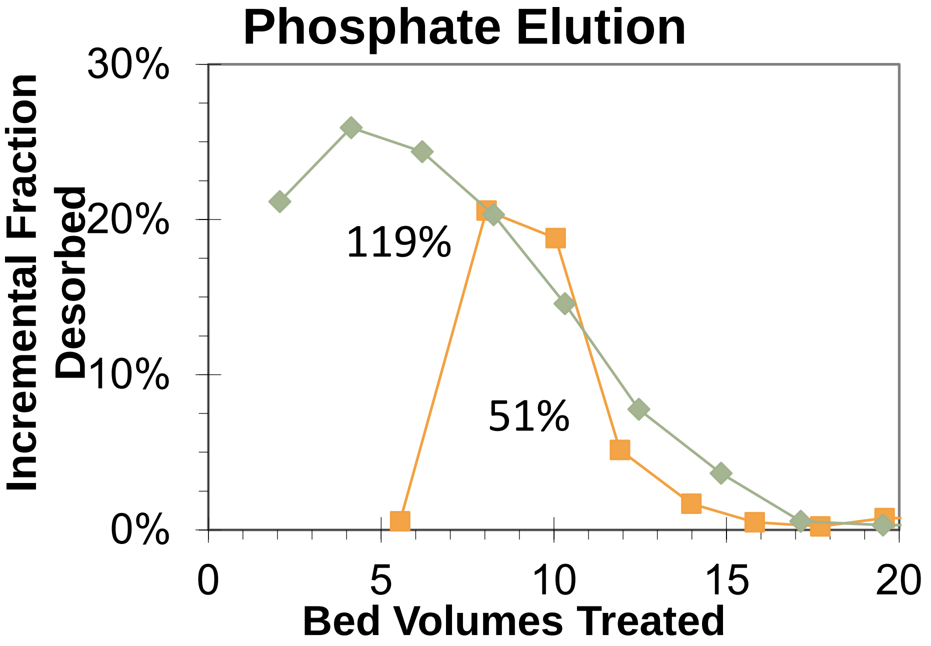
Capture & Release Paradox

- Hybrid Anion Exchange
  - Strong affinity for P
  - Doesn’t release
- Strong Base Anion Exchange
  - Slight affinity for P
  - Elutes well

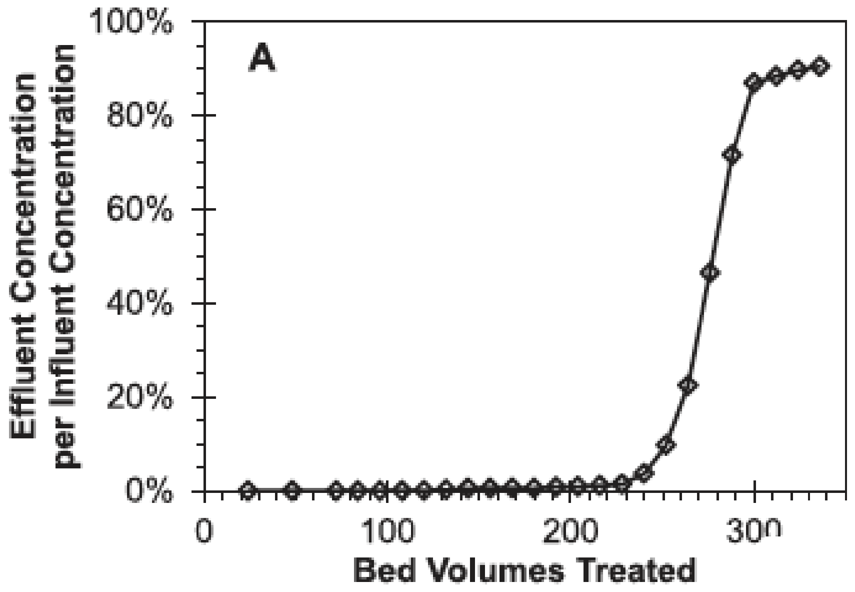






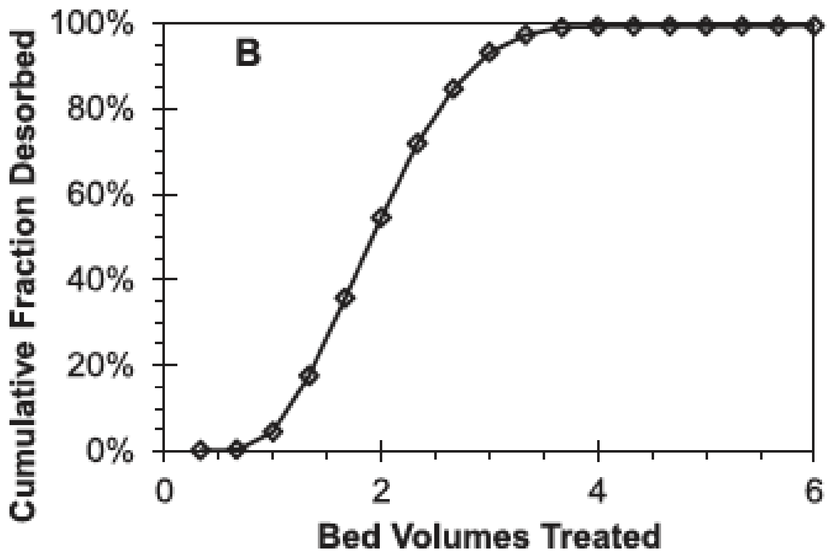


Improving SBAX Operation



Reduced loading rate
Longer Contact Time (EBCT)

Slower elution flowrate



Steeper/ Sharper
Breakthrough and
Elution curves are desirable

Algal Biorefinery *Net Phosphorus* Transformation & Recovery

Starting Biomass	Primary Residual	Oxidized Biomass	Recovered Nutrients
100 mg total P 0 mg ortho-PO_4^{-3}	93±2 mg total P 0 mg ortho-PO_4^{-3}	90±12 mg total P 75±6 mg ortho-PO_4^{-3}	54±9 mg total P 53±8 mg ortho-PO_4^{-3}

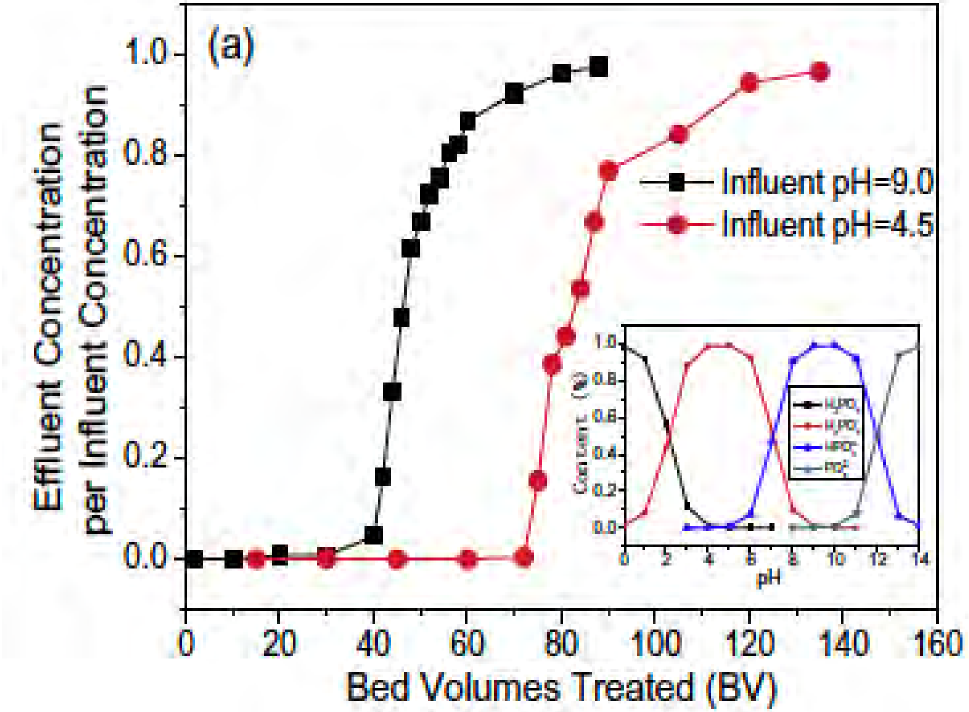
Microwave / H2O2 Efficient
Can be improved….??

Needs improvement…

How can we increase P-recovery?

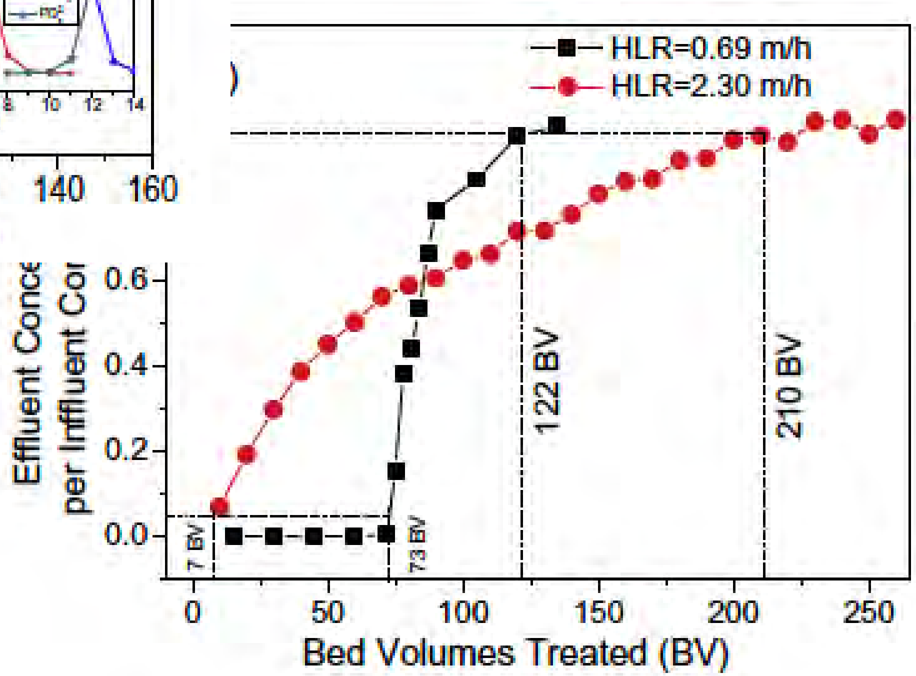
- Strong base ion exchange resin
- Optimize desorption flowrates to maximize P concentrations
- Compare NaCl, NaOH, KOH or KNO_3 regenerant solutions
- Experiments performed using Simulated & real anaerobic digestion liquid

Effect of pH on “Sorption” Step

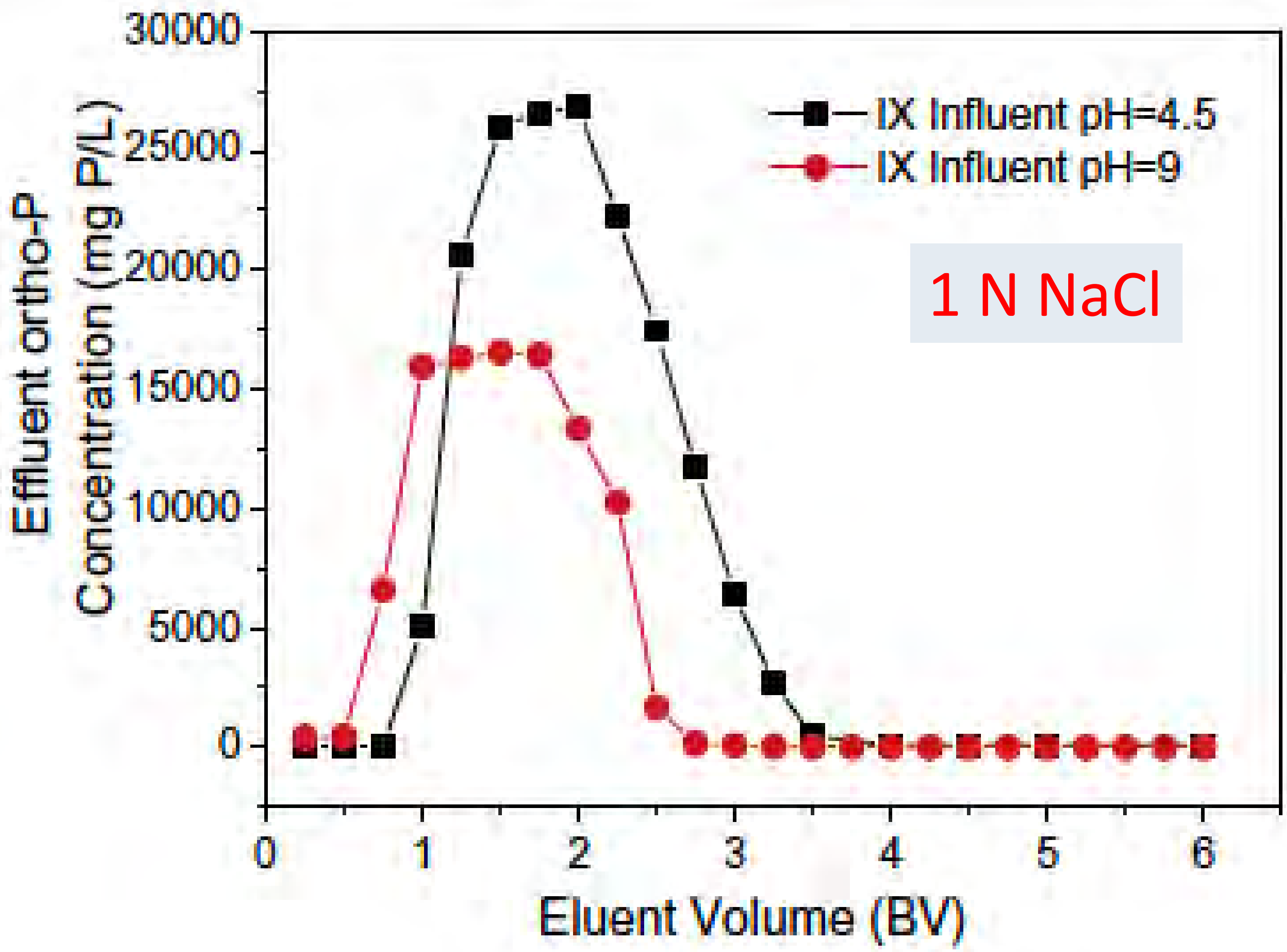


Better Sorption:

- Higher pH
- Slower loading rate



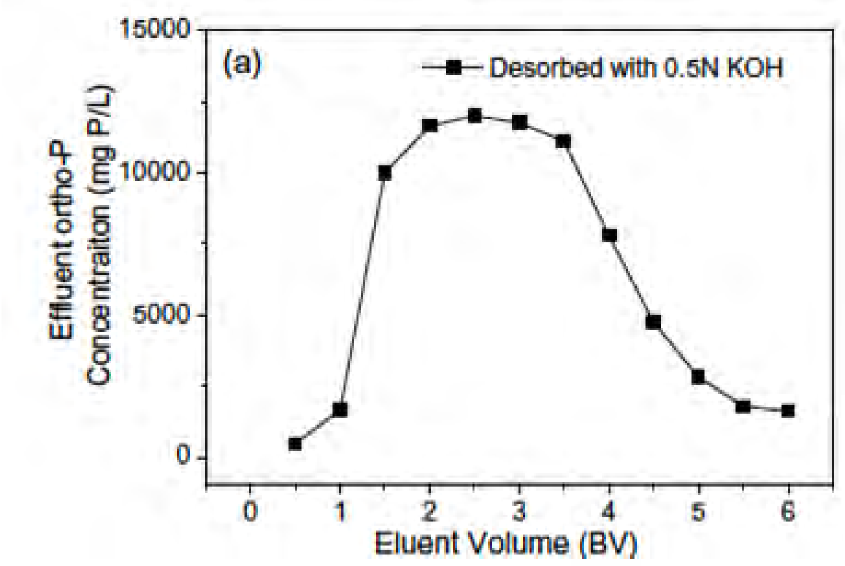
Desorption: Concentrates P by >100x



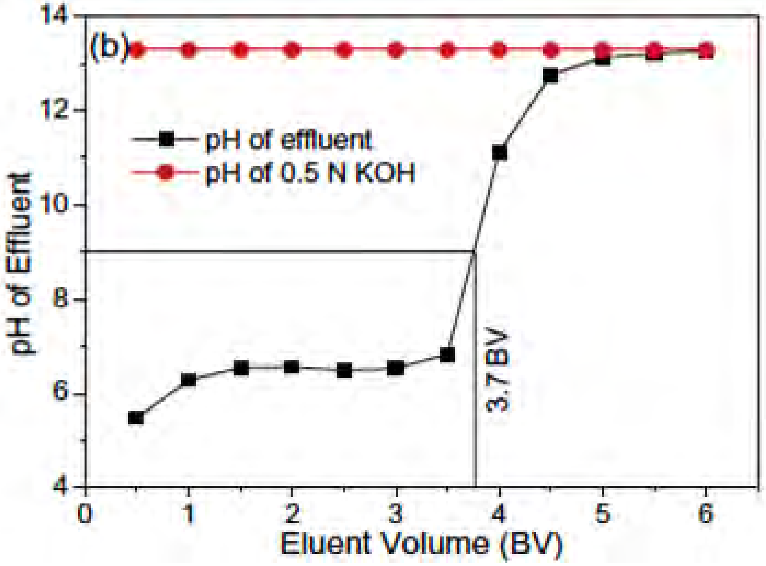
Creating useful products

Use K^+ instead of Na^+

& OH^- instead of Cl^-



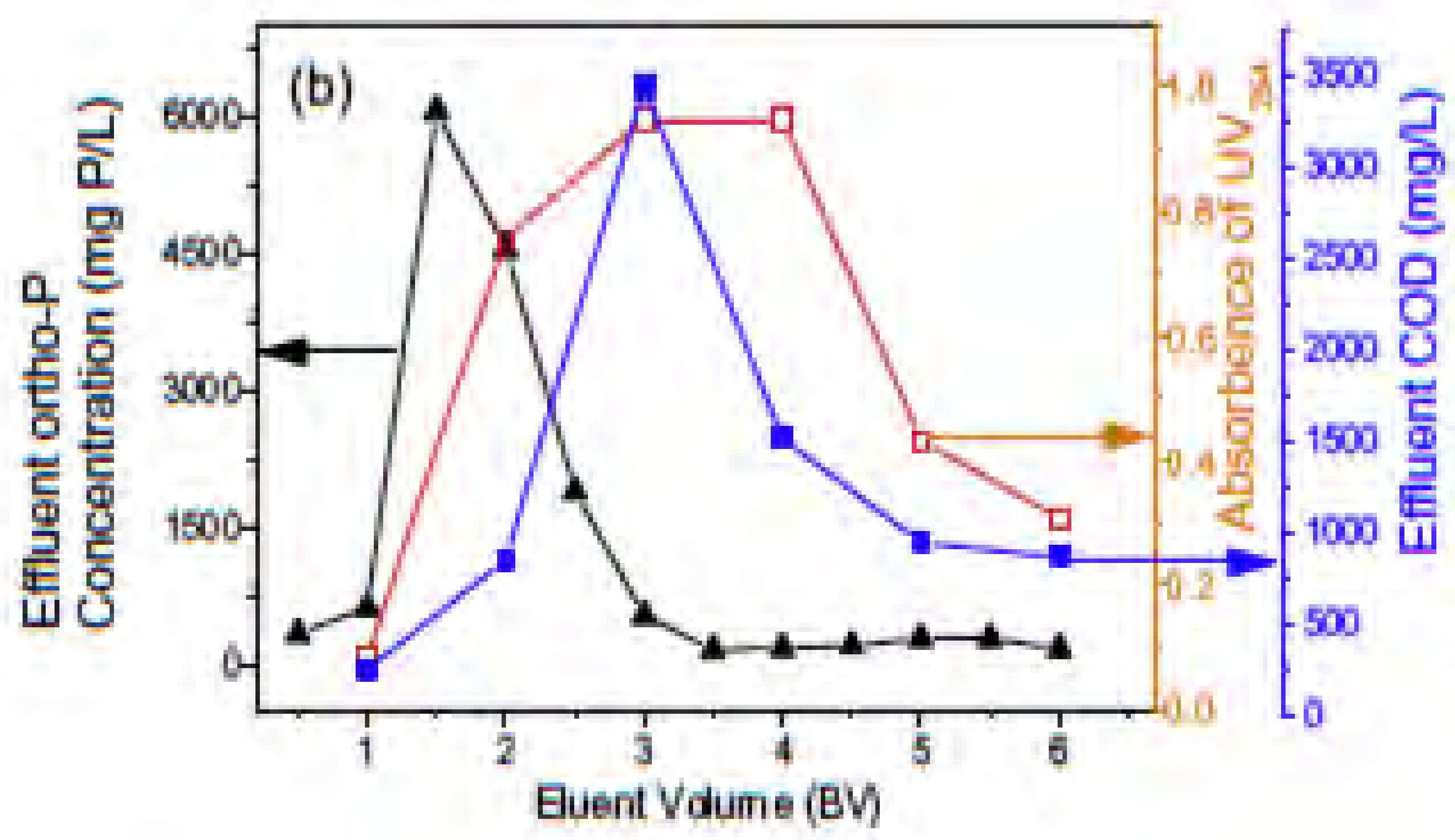
0.5 N KOH
Achieves efficient
Elution of ortho-P & can be
monitored by effluent pH
from IX column



Also demonstrated similar results using KNO_3 instead of KOH

Achieved: N/ortho-P/K mass ratio of 17:8:75

Optimizing elution can also separate inorganics from DOC



Loaded using oxidized RAS / Wastewater solids (0.5 N KOH)

Summary

- **Biorefineries can produce renewable fuels and be net-zero nutrient users !**
- Over 90% of the phosphorus is in RNA + DNA (not in lipids which are the fuels
- Electrified physical-chemical oxidation are available
  - Microwave
  - Hydrothermal liquification
  - Eliminates energy to “dry” cellular materials
- Capture and recovery technologies
  - Require optimization in flows
  - Requires optimization in chemical eluent composition (KOH, KNO_3) to create high-value added fertilizers as “by-products”

Acknowledgements

- **Mac Gifford, PhD**
  - USEPA/STAR
- **Jianyong (John) Liu**
  - Shanghai University
- **Anjali Mulchandani, PhD**
  - NSF GFRP
- **Algal biorefinery collaborator**
  - Bruce Rittmann, NAE (ASU)
  - Raveender Vannela

- Why not ------ **NSF / STEPS**

Overall Recovery

- Successfully recovered a 100mL volume of concentrated orthophosphate nutrient solution!

Starting Biomass	Primary Residual	After Oxidation	Resin Elution
100% P 0% orthoP	74% P 0% orthoP	90% P 75% orthoP	54% P 53% orthoP

- Operating cost for the MWs & NaOH process was found to be about 85–103 USD/t
- WAS management using
  - aerobic digestion: 64–120 USD / ton
  - Compositing/drying: 72–198 USD/ton
  - Incinerating, 99 USD/t,

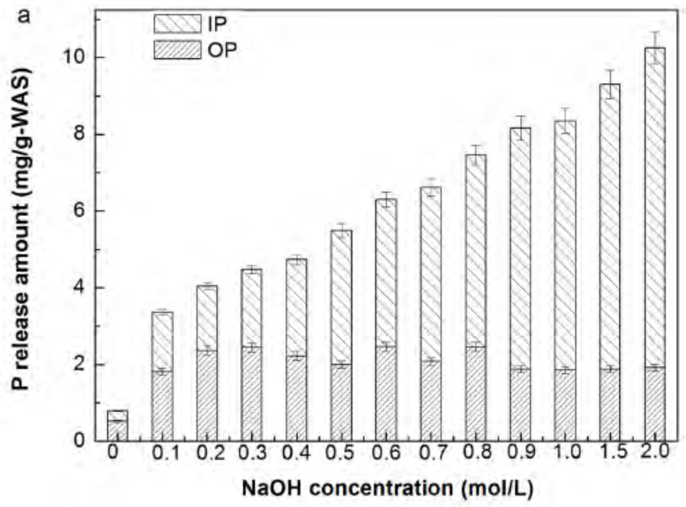


Table 2. P release proportion and OP/TP ratio under different treatments.

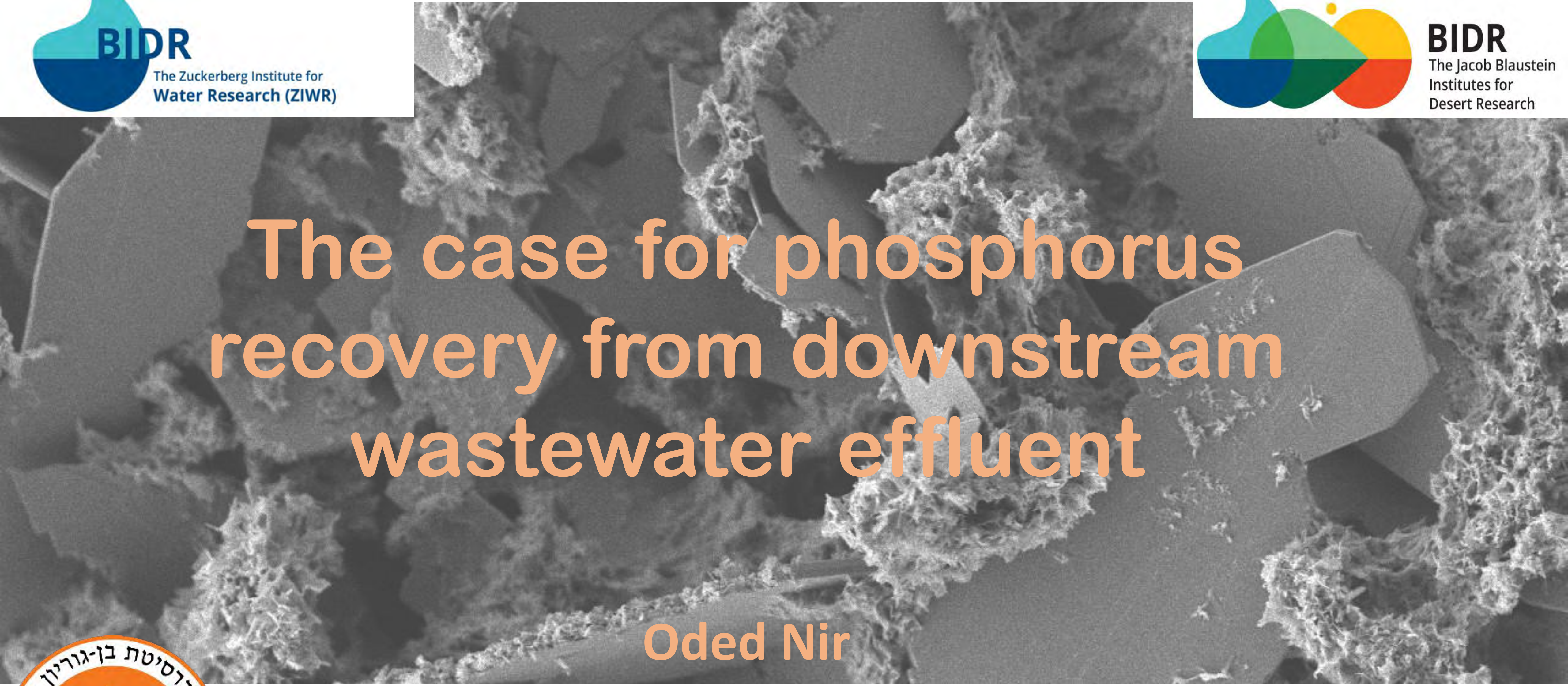
Treatment	P release amount (% total P in sludge)	OP/TP (%)
MWs (298 K)	2.05–2.25	45.74–47.06
MWs (323 K)	2.58–2.25	43.50–44.81
MWs (348 K)	2.97–3.49	35.89–41.95
NaOH	26.70	22.18
MWs (298 K)+NaOH	34.19–35.31	27.16–28.66
MWs (323 K)+NaOH	34.63–36.21	26.38–28.08
MWs (348 K)+NaOH	39.68–43.70	22.97–25.76

Alternate Methods

- Other Recovery Methods
  - Oxidation
    - Anaerobic Digestion
    - UV/Peroxide, Ozonation
  - Isolation
    - Precipitation as Struvite ($MgNH_4PO_4 \bullet 6H_2O$) or Apatite ($Ca_x(PO_4)_y(OH)_z$)
    - Adsorption

BIDR
The Zuckerberg Institute for
Water Research (ZIWR)

BIDR
The Jacob Blaustein
Institutes for
Desert Research



The case for phosphorus recovery from downstream wastewater effluent

Oded Nir

אוניברסיטת בן-גוריון בנגב
Ben-Gurion University of the Negev

BARD

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Binational Industrial Research
and Development Foundation

nirwaterlab.com

Nir Water Lab

One of the top three universities in Israel

20,000
Students

140,000
Alumni

930
Senior academic faculty, from a total of **6,700** staff members

30%
of students are enrolled in graduate degree programs

Campuses 3
- Beer-Sheva
- Sde Boker
- Eilat

אוניברסיטת בן-גוריון בנגב
Ben-Gurion University of the Negev

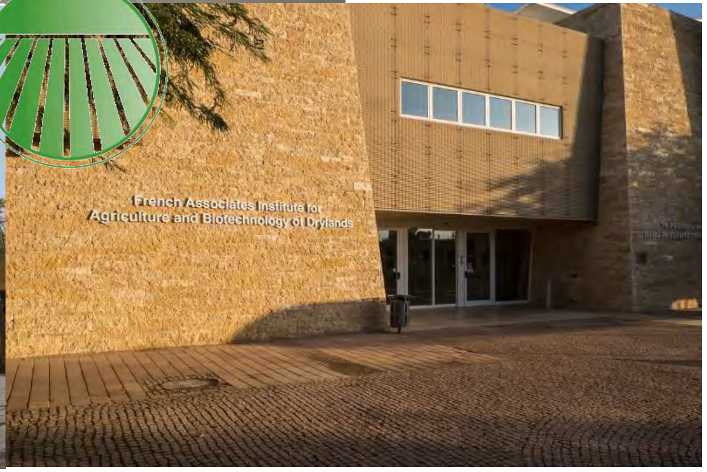
Main Campus at Beersheba

Sde Boqer Campus

Sde Boqer Campus

- Over 300 graduate students
- 50% international
- Program in English only

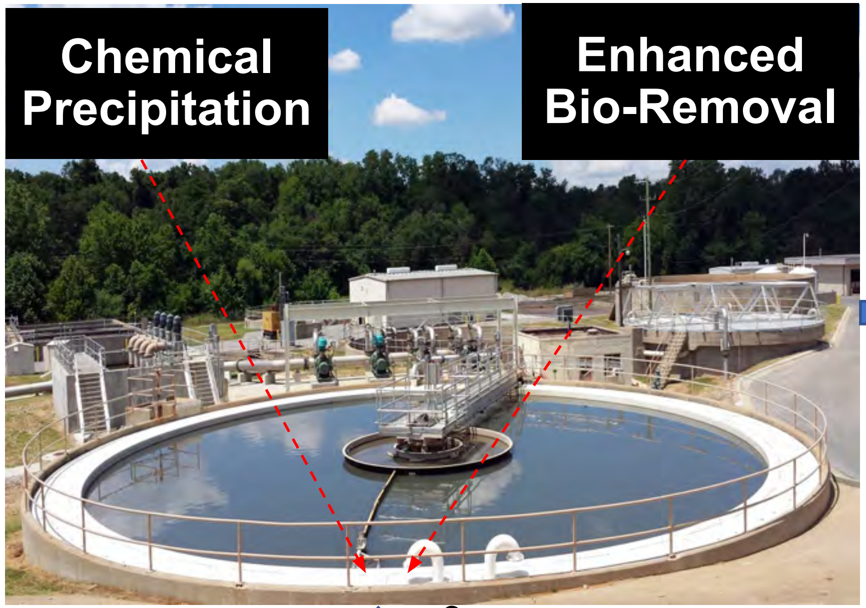
BIDR Institutes



The student village

Current strategies for P recovery

Urban Wastewater
(2~20 mg-P/l)



Effluent
(0.1~15 mg-P/l)

Sludge

Leading Strategies for P recovery

Direct application in agriculture

Acid leaching of raw/ incinerated sludge

Struvite ($MgNH_4PO_4$) induced crystallization

P recovery from sludge: Pros and Cons

Direct application in agriculture

- Cheap
- Simple to apply
- Organic matter

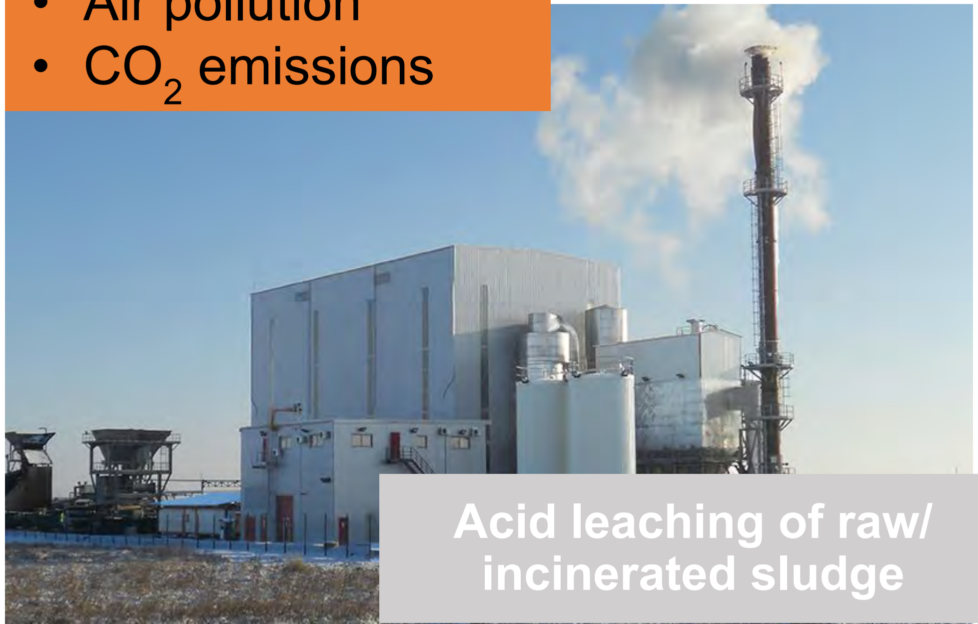
- Restricted by Regulation
- Sanitation, smell
- Pollution

- Most products have low market value
- are not suitable for fertigation and accurate modern agriculture
- Organic and inorganic contamination
- Nutrient release to the environment due to runoff or excess irrigation

Acid leaching of raw/ incinerated sludge

- High chemical consumption/cost
- Air pollution
- CO_2 emissions

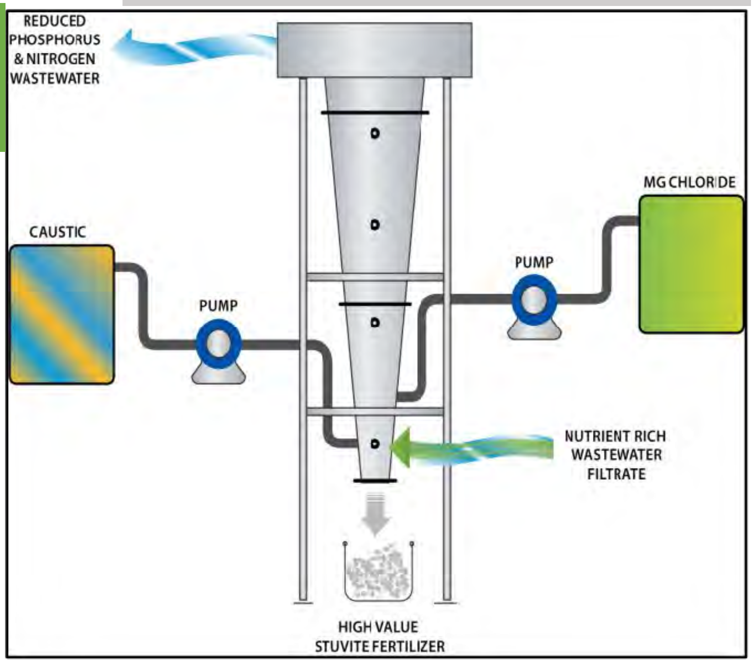
- No organic contamination



Struvite ($MgNH_4PO_4$) induced crystallization

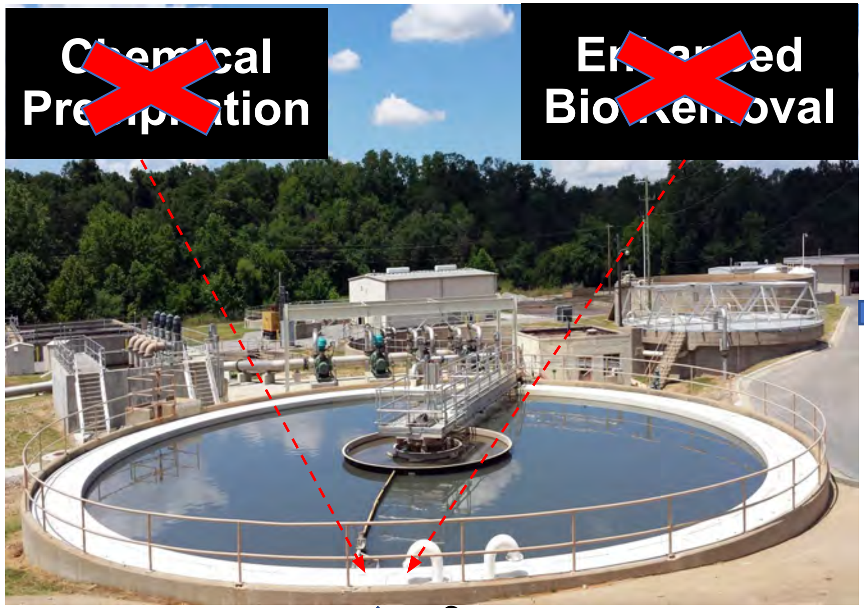
- Cleaner product
- Slow release

- High chemical consumption
- High cost
- Biological P removal is necessary
- Contamination
- Economics



Current practice and thinking

Urban Wastewater
(2~20 mg-P/l)



Effluent
(0.1~18 mg-P/l)

**P recovery
From effluent**

Sludge

**Complementary
Alternatives**

Main P recovery practices

Direct application in agriculture

Acid leaching of raw/ incinerated sludge

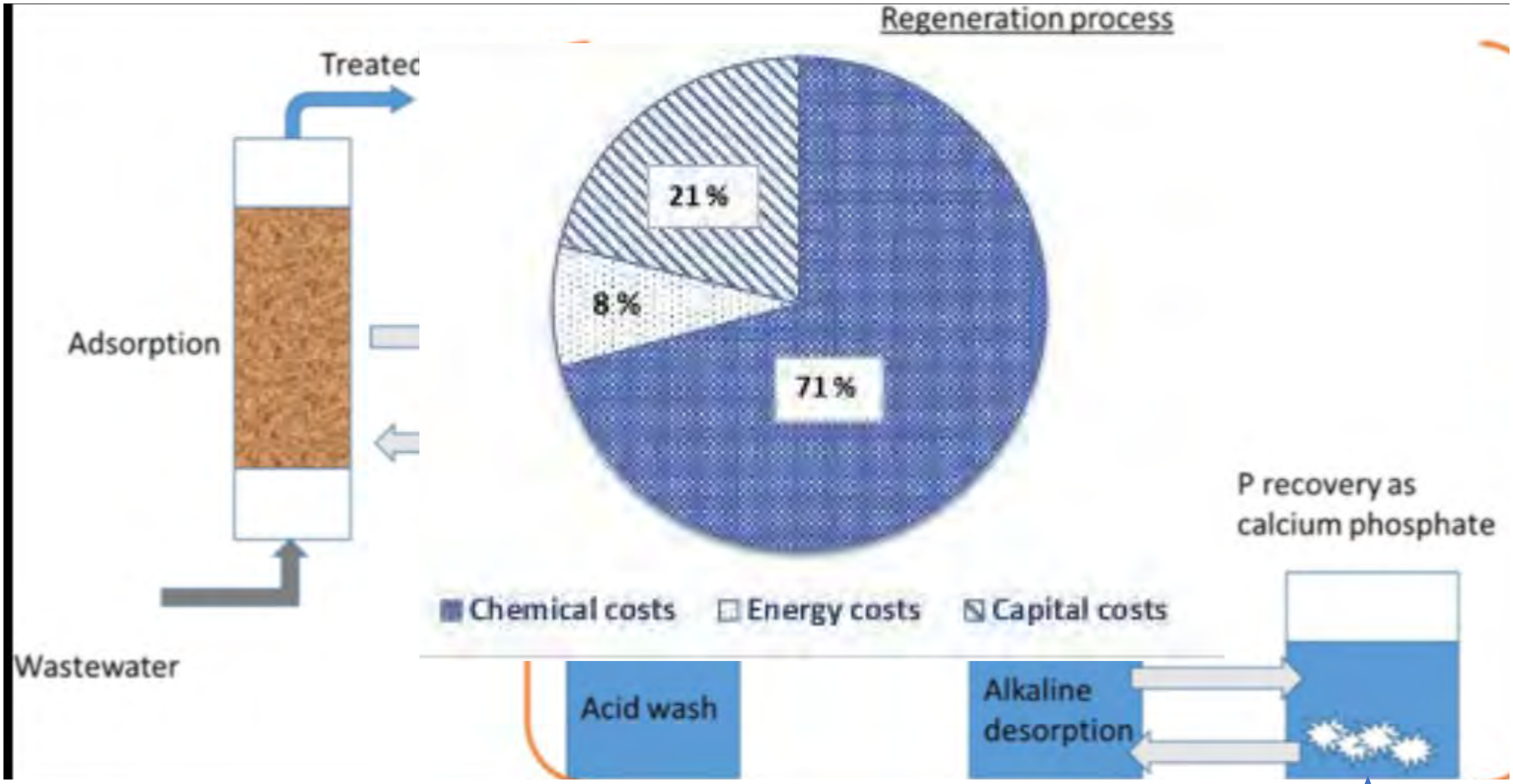
Struvite ($MgNH_4PO_4$) induced crystallization

Challenges

- Diluted source requires innovative technology
- R&D cost (piloting etc.) and initial investment

Opportunities

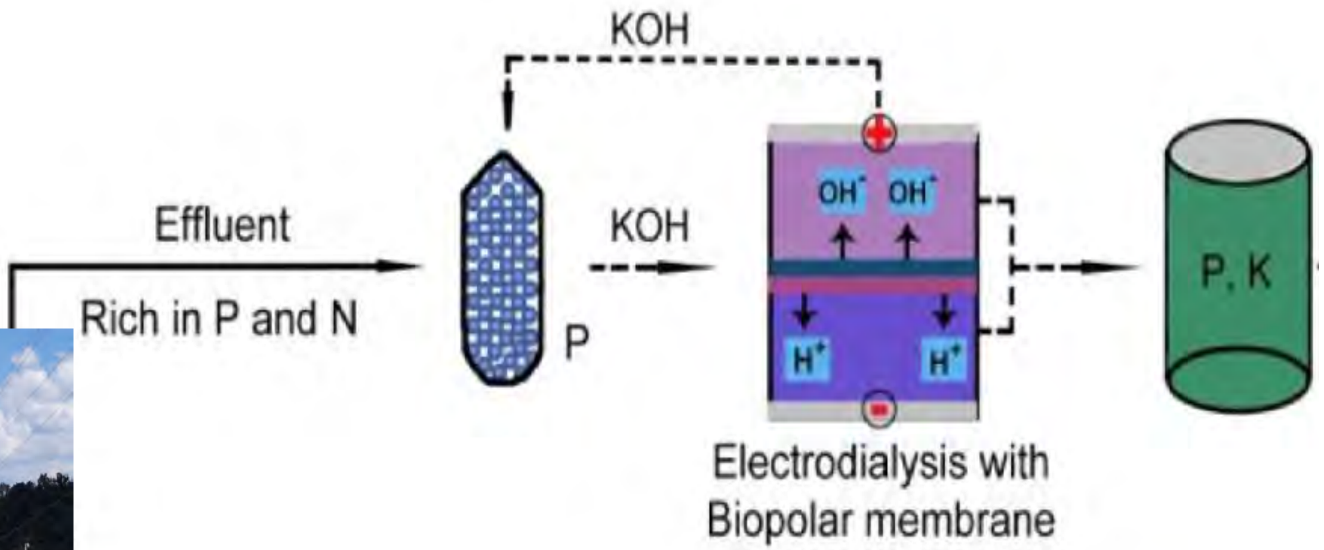
- Saving costs associated with upstream nutrient removal; i.e., aeration and chemicals addition
- Avoiding high P in the sludge – increasing P recovery yield
- Avoiding the need for P separation from high organic content in the sludge – cleaner product
- Minimizing both organic and inorganic contaminants associated with P
- Allowing flexibility in reusing the treated effluent for agriculture (switch on and off)
- Enabling routes to **high-value** products can offset costs
- Products compatible with accurate agriculture – enabling highly controlled fertilizer application to reduce leaching



Suresh Kumar et al. 2019 Water Research

Excess Acid addition – Iron sorbent dissolution ← High pH – clogging by CaP and iron dissolution ← $CaCl_2$ / $Ca(OH)_2$ addition

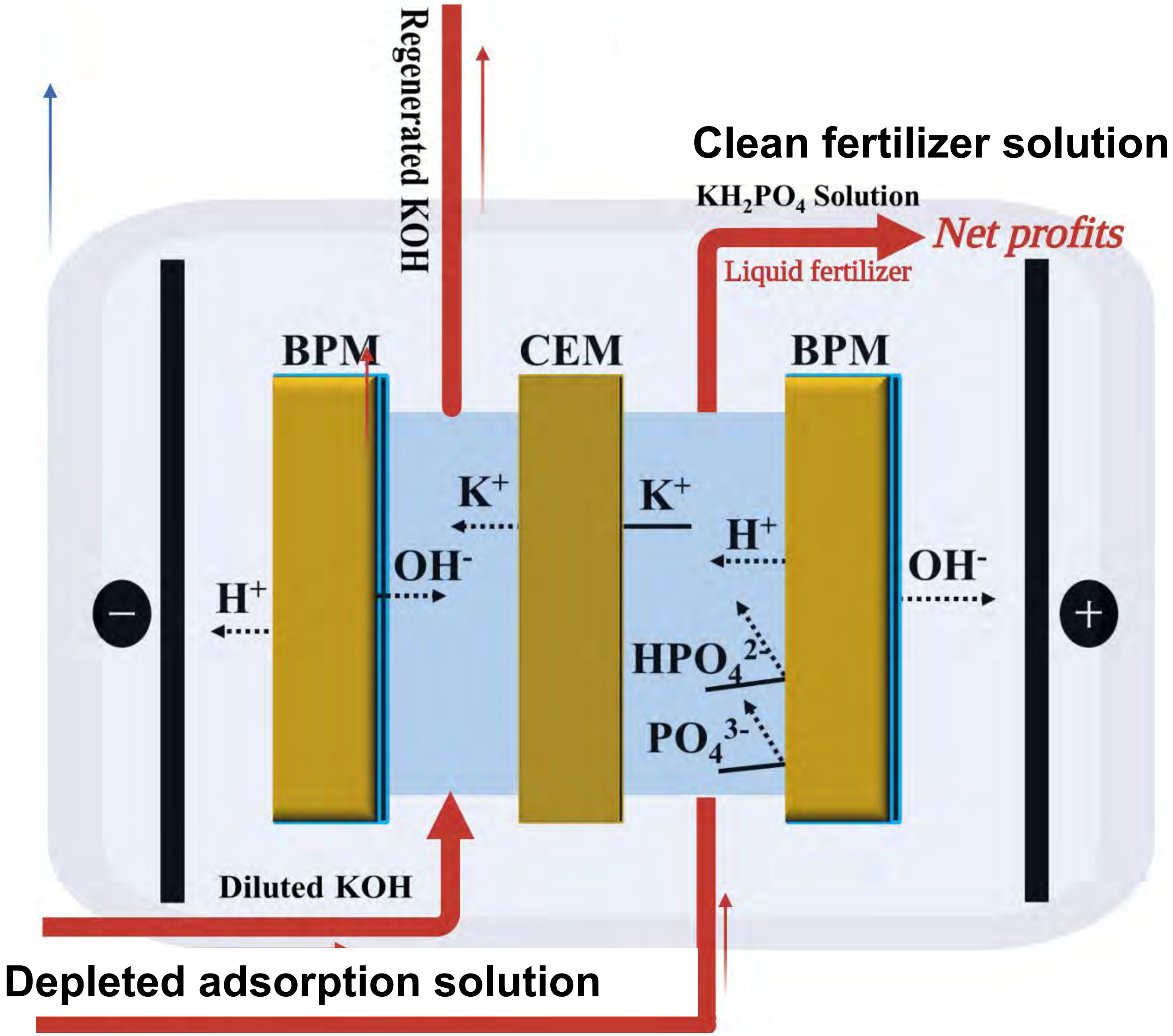
New concept including bipolar membrane electrodialysis



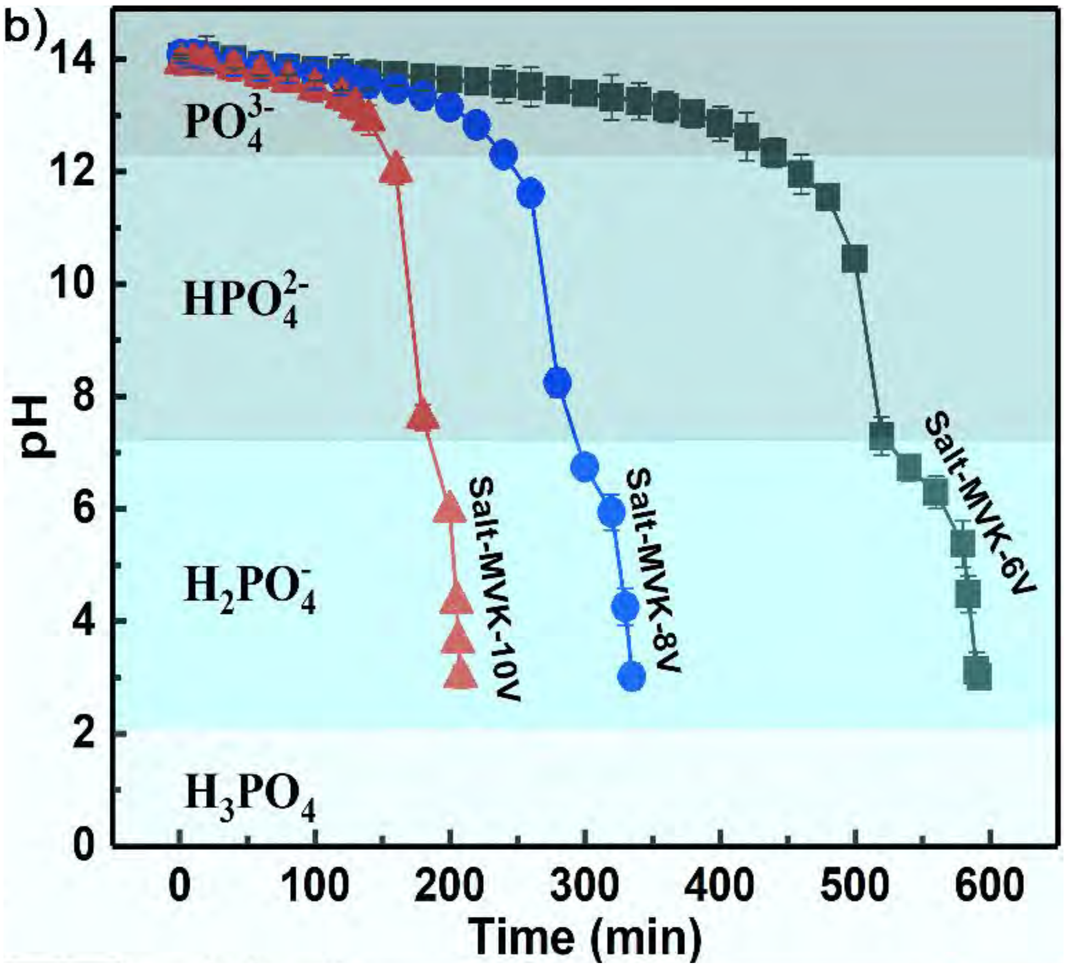
WWTP

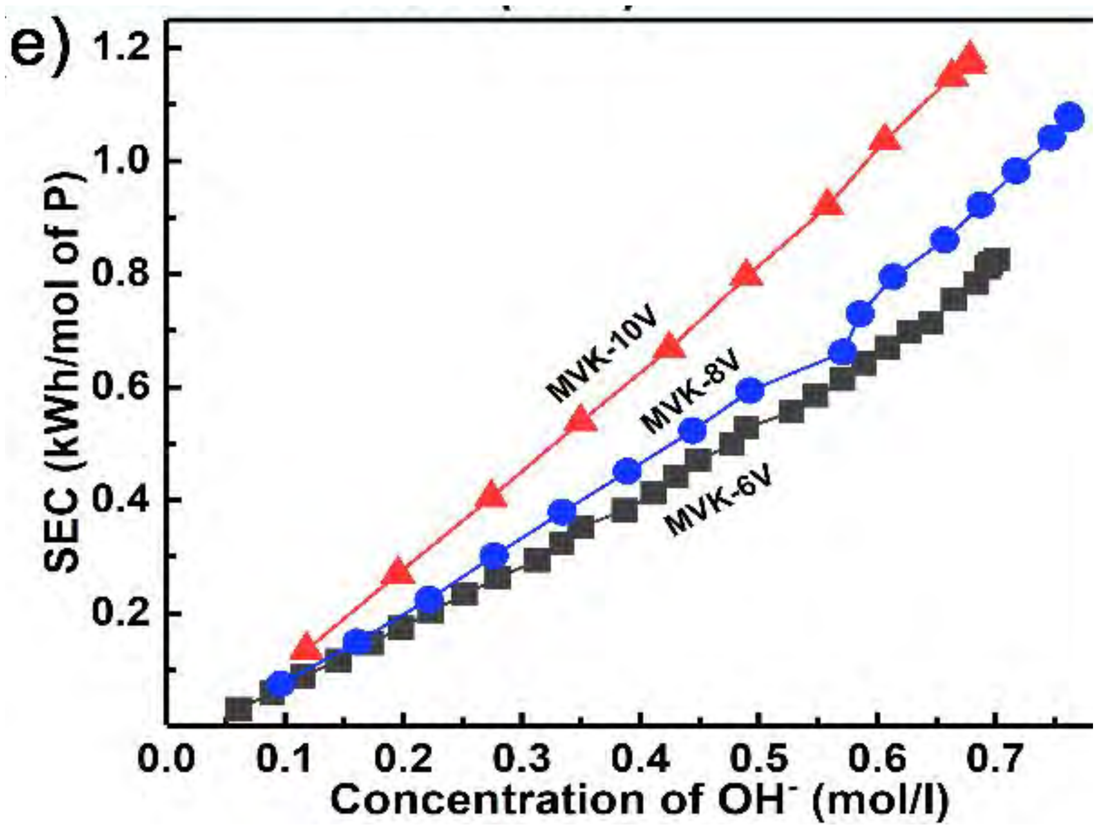
Ru Liu

BMED concept – P-K recovery



The process works! Effect of voltage

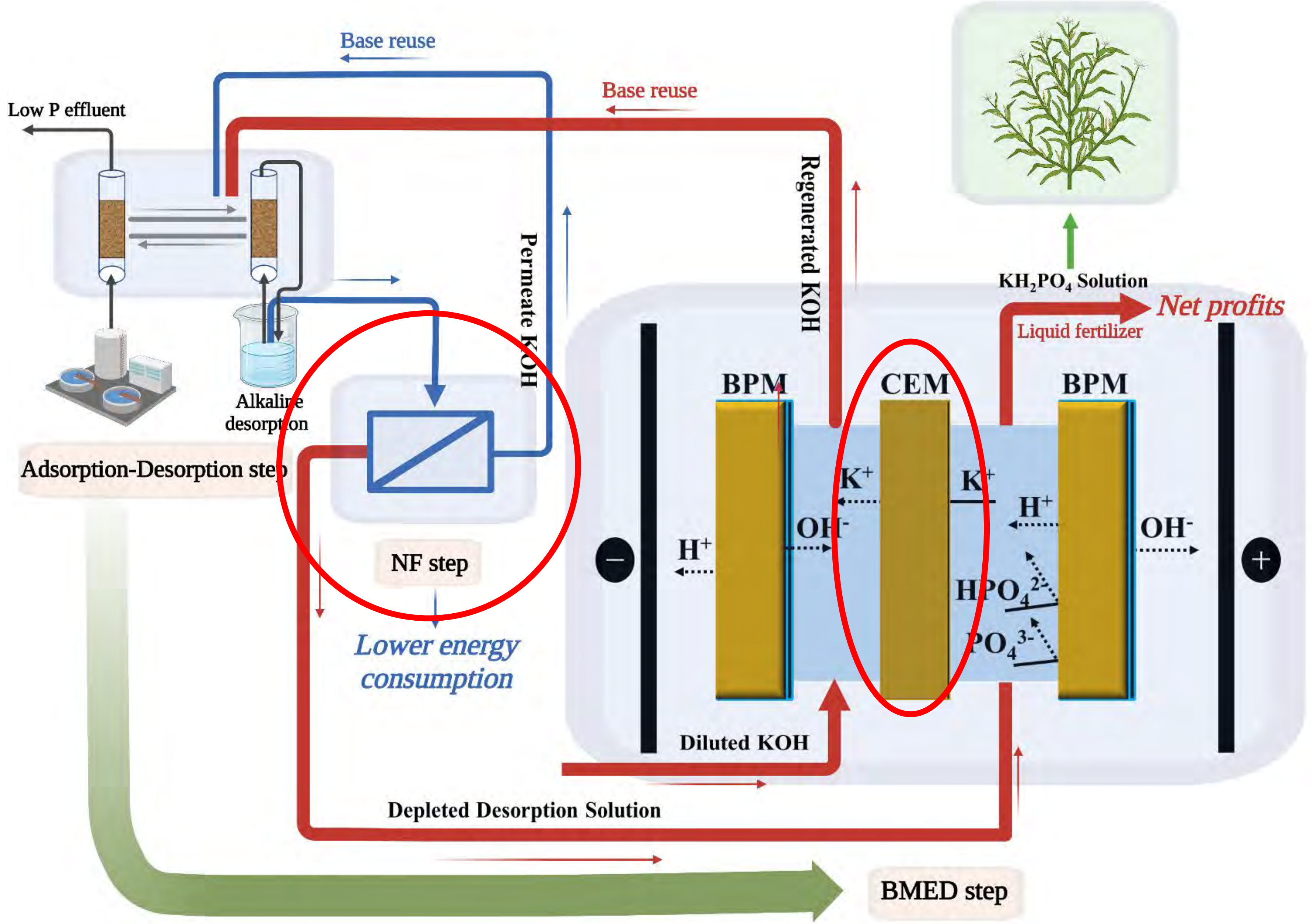




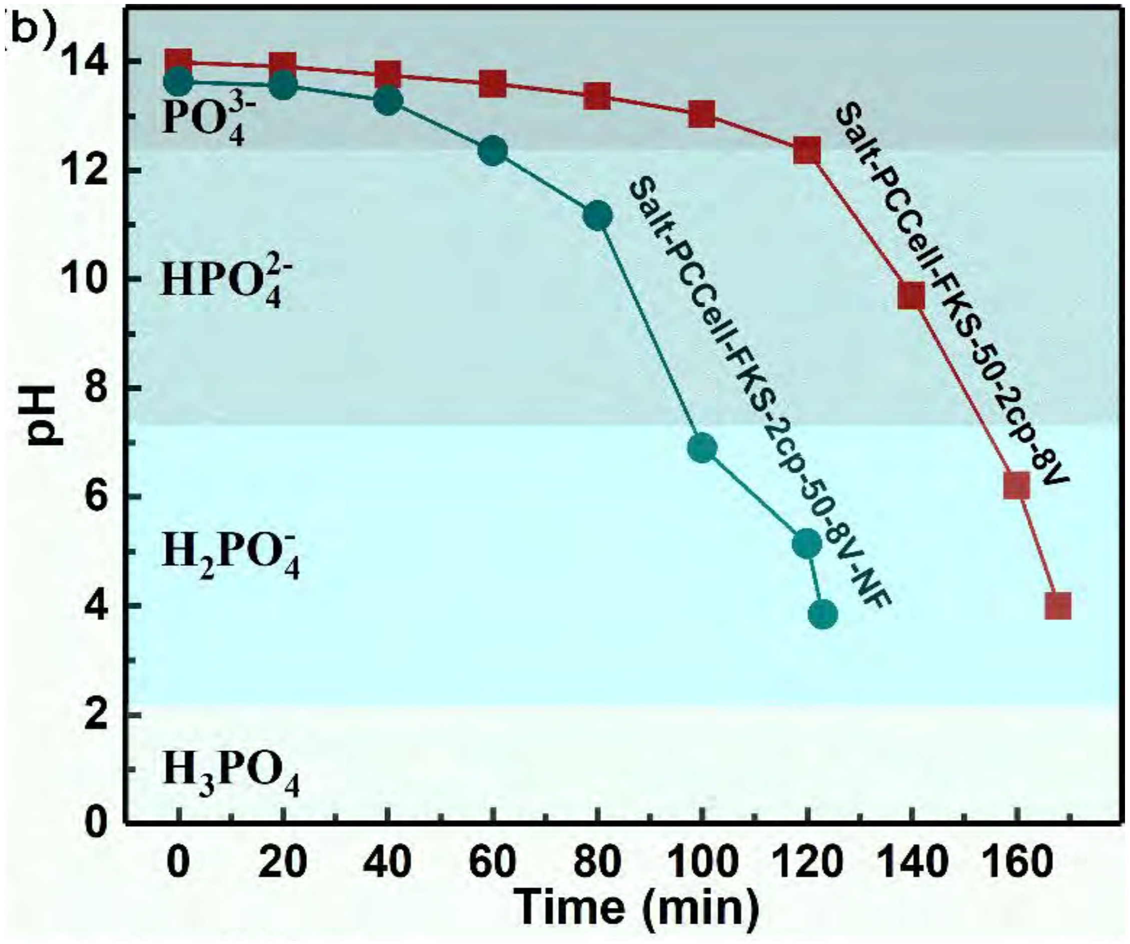
Commercial KH_2PO_4 700-900 \$/ton

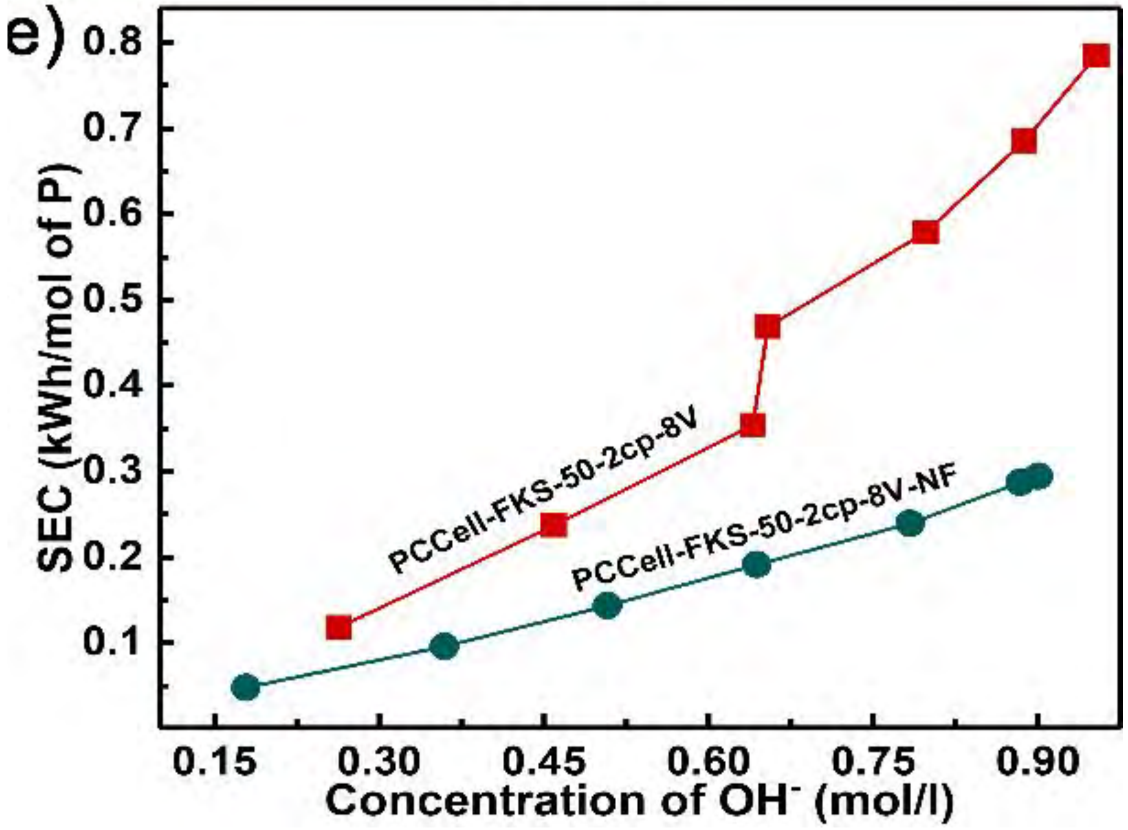
Lowest energy cost: ~615 \$/ton

Adding nanofiltration and replacing the CEM



Results – Effect of NF step



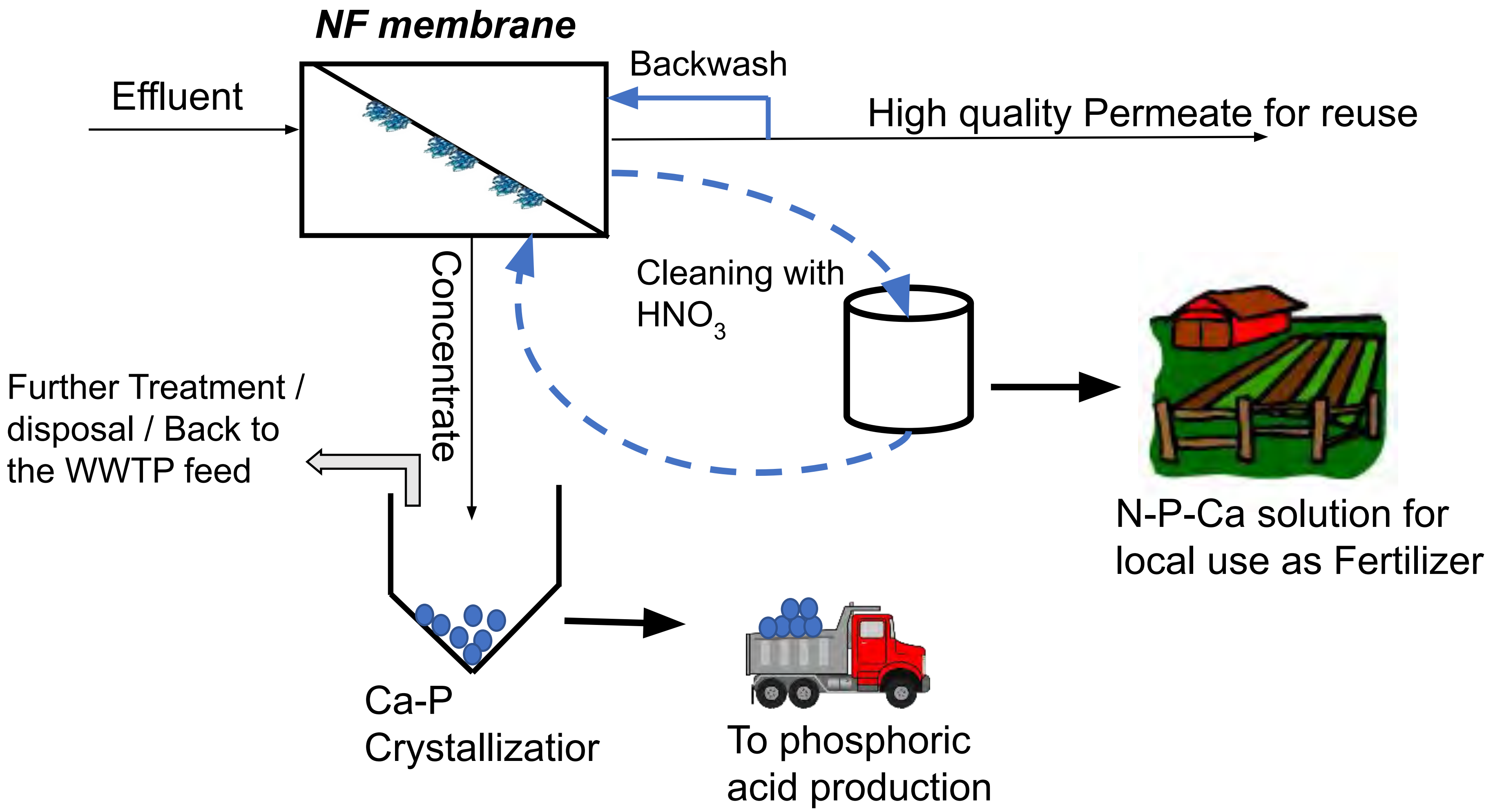


Commercial KH_2PO_4 700-900 $/ton

Lowest energy cost (including NF): ~150 $/ton

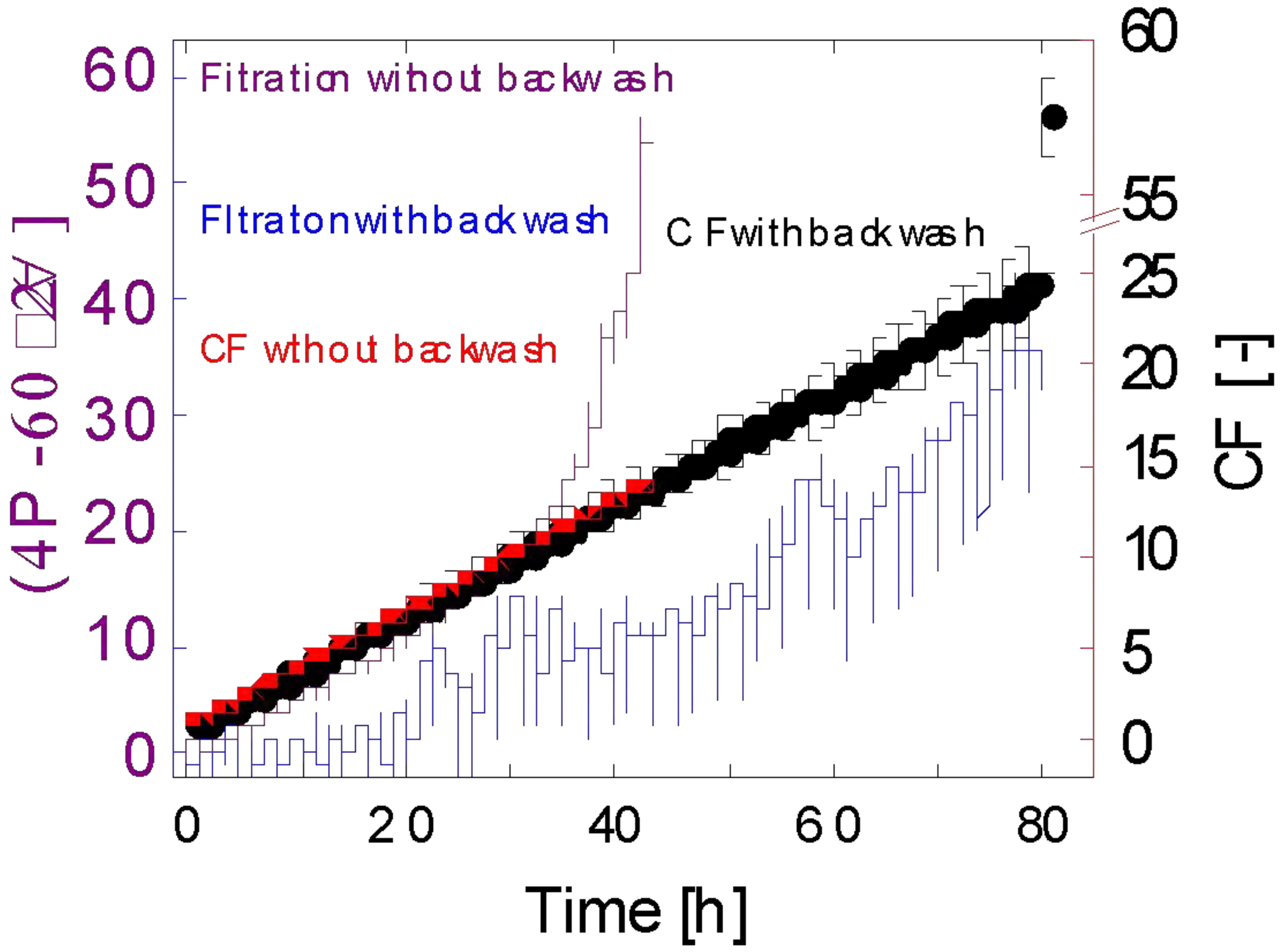
We are planning a small pilot

High Recovery NF Backwash and acid cleaning



Time/pressure-controlled backwash effectively controls fouling

- CF = 18 reached before ~ 40% increase in TMP
- Achieved very high recovery (98%) CF = 58
- Duplicates show that results are reproducible
- Backwash protocol was very effective



Take Home

- Embrace P recovery from the effluent going forward

- Investment in technology is needed

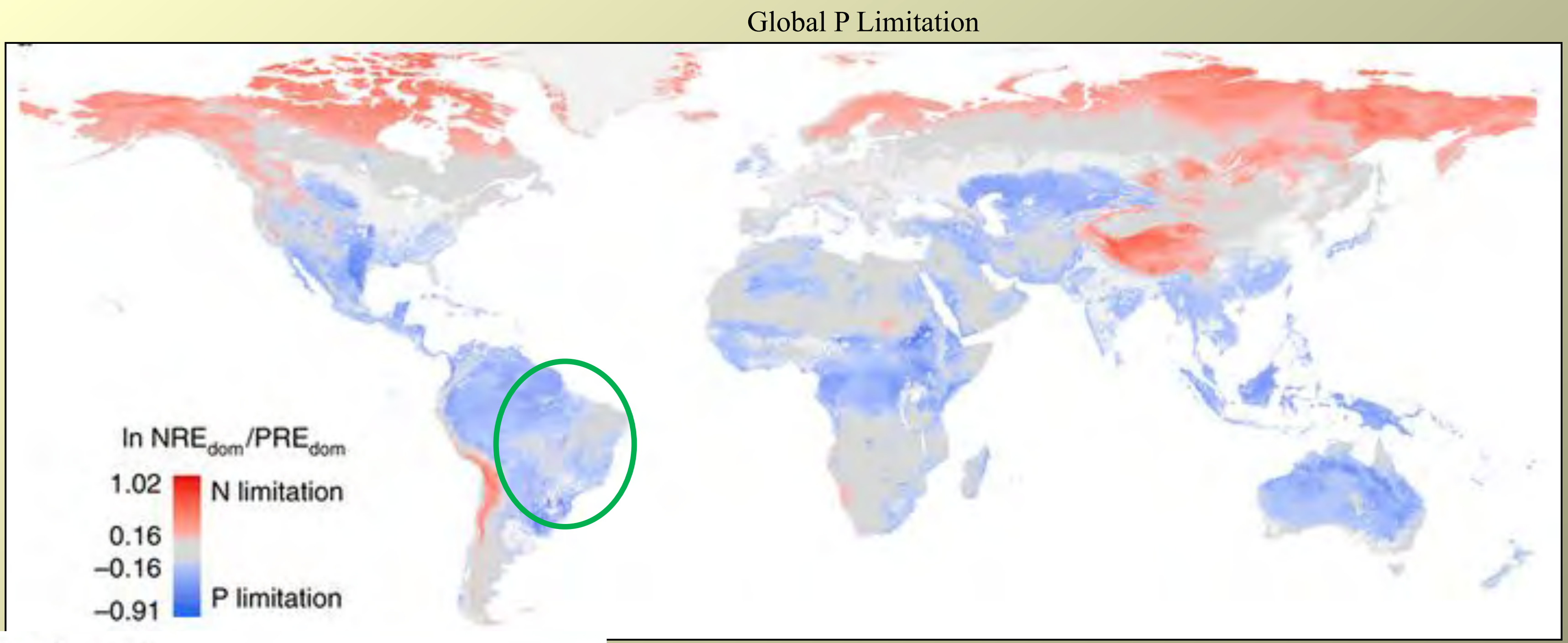
https://cowerc.northwestern.edu/

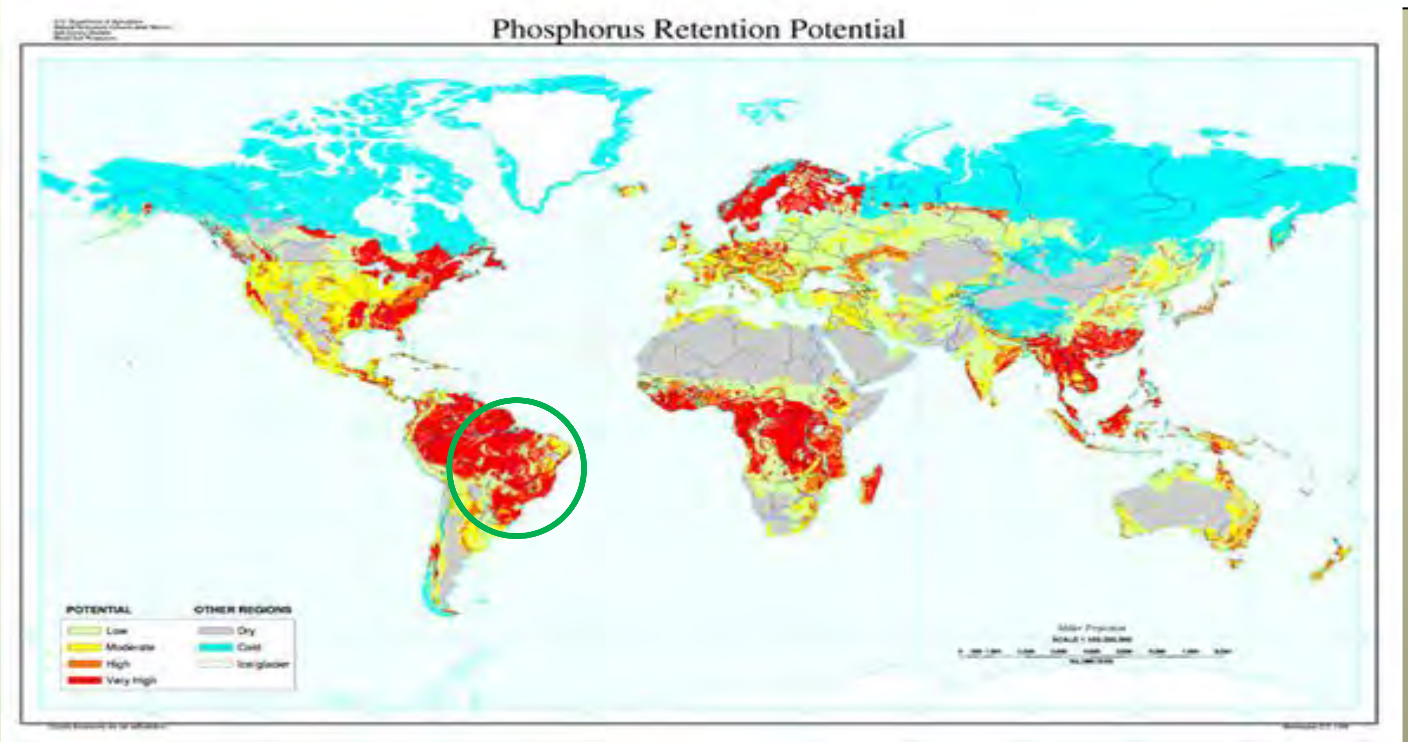
The use of phosphate organomineral associated with solubilizing microorganisms in corn cultivated in Brazil

Flávia Cristina dos Santos
Embrapa Maize and Sorghum

11-04-2022

Introduction





Brazilian soils:

Low available P

and

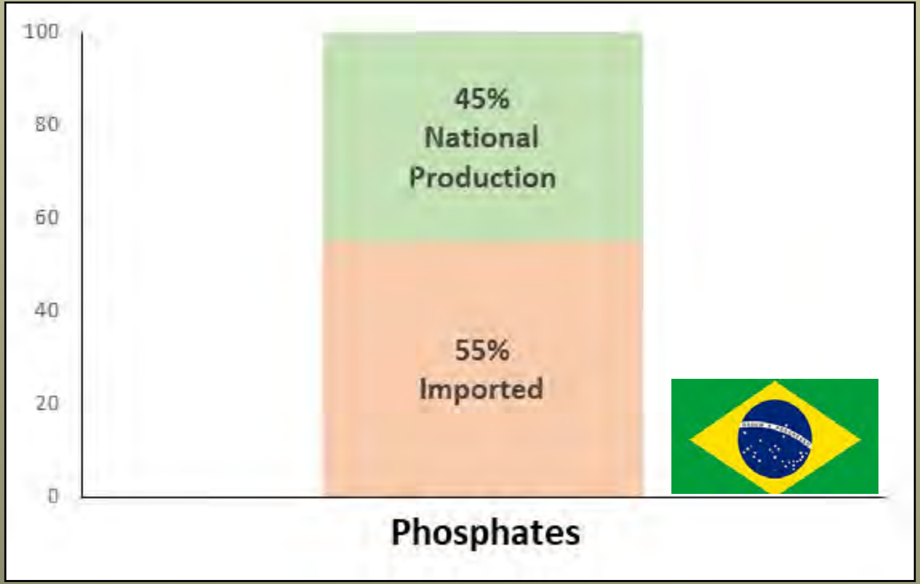
High retention potential

“It’s necessary to correct and fertilize the soils to produce more and better crops”

Brazilian reserves of phosphate rock

Top countries in phosphate fertilizer imports

#	165 Countries	Metric Tons
1	Brazil	3,266,441.61
2	India	2,912,240.36
3	United States	1,624,006.07

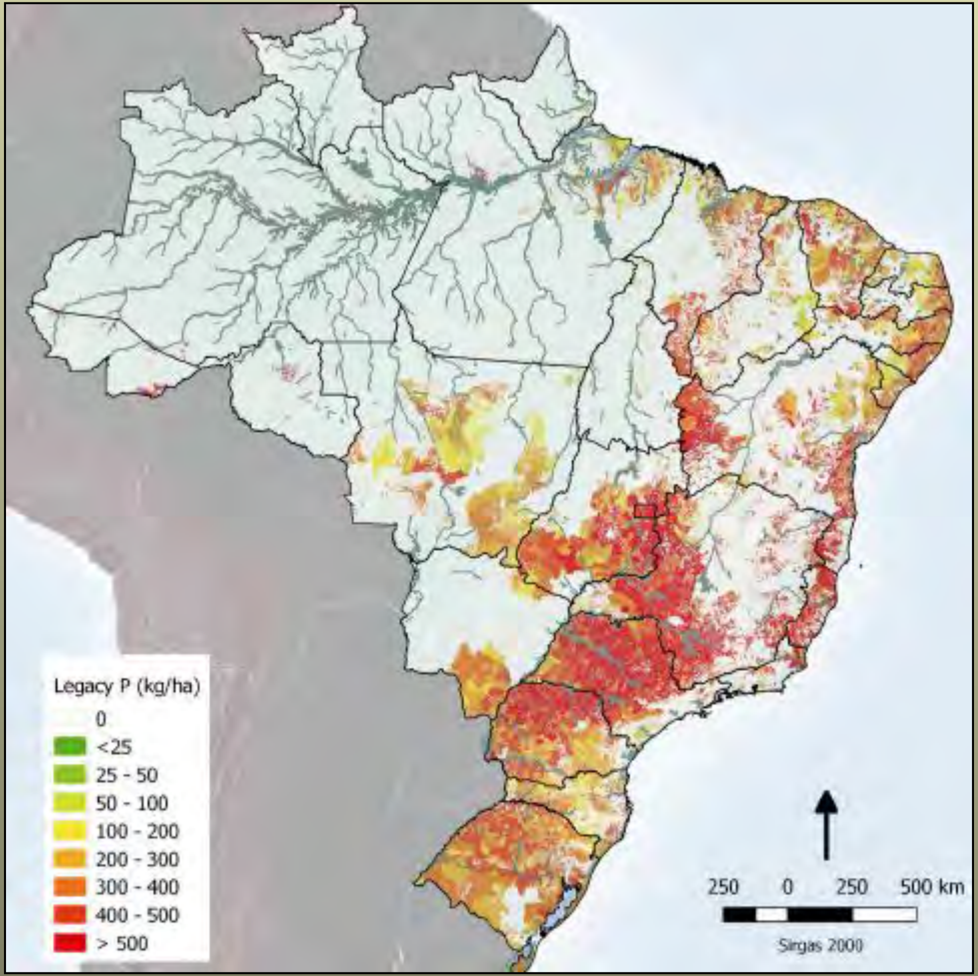


Sources: FAO, Sirgas

Brazil is a powerhouse agricultural producer

Brazil: in the top-5 producers of 34 commodities and is the largest net exporter in the world

Map of "soil legacy P" accumulated during cultivation and mineral fertilizer P addition in Brazilian croplands – 1960 to 2016



Source: Pavinato et al. (2020)

Demands

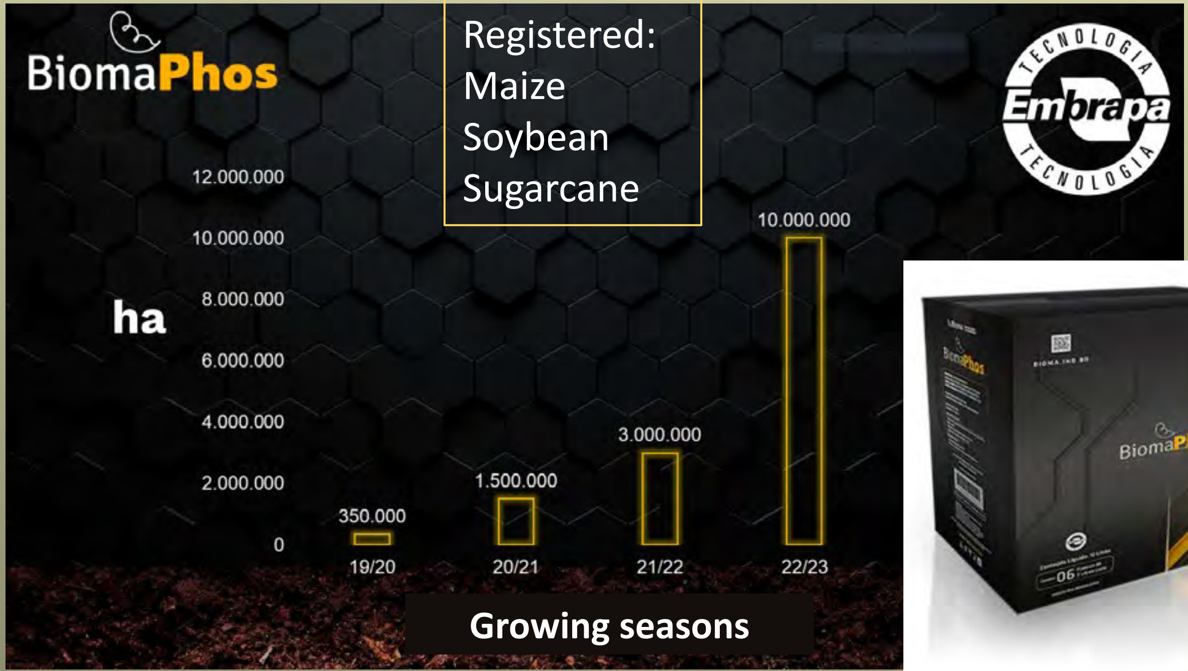
TO INCREASE YIELD GAINS AND NUTRIENT USE EFFICENCY

TO ADOPT MANAGEMENT PRATICES THAT INCREASE ORGANIC SOURCES OF NUTRIENTS, NUTRIENT CYCLING, BIOLOGICAL INPUTS AND LOW CARBON AGRICULTURE

Embrapa

BiomaPhos

Inoculant to increase phosphorus absorption with microrganisms that solubilize phosphates – Launched 2019



- B119 (*B. megaterium*)
- B2084 (*B. subtilis*)

Dra. Christiane Paiva

- **+ 660 kg ha^{-1} maize**
- **+ 240 kg ha^{-1} soybean**
- **+ 11 t ha^{-1} sugarcane**

New trials:

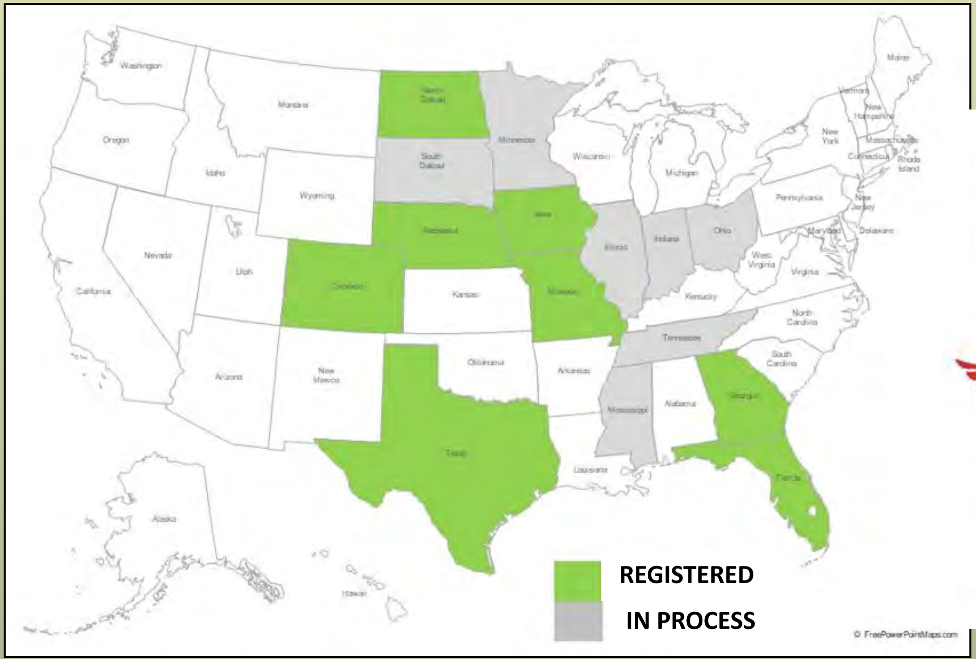
Sorghum, brachiaria, strawberry, garlic, tomato, carrot, rice, beans, coffee,

peanut, wheat, banana, mango, potato, cotton.

Embrapa

The spread of technology across borders

- Paraguay (2020)
- Bolivia (2022)
- USA (2022)



Embrapa

Simbiose

Bioma

CORTEVA agriscience

Source: Simbiose

Collection of multifunctional microorganisms at Embrapa Maize and Sorghum: a strategic component for partnerships.

Description Preservation

- Started in 1983

Collection 11,000 strains

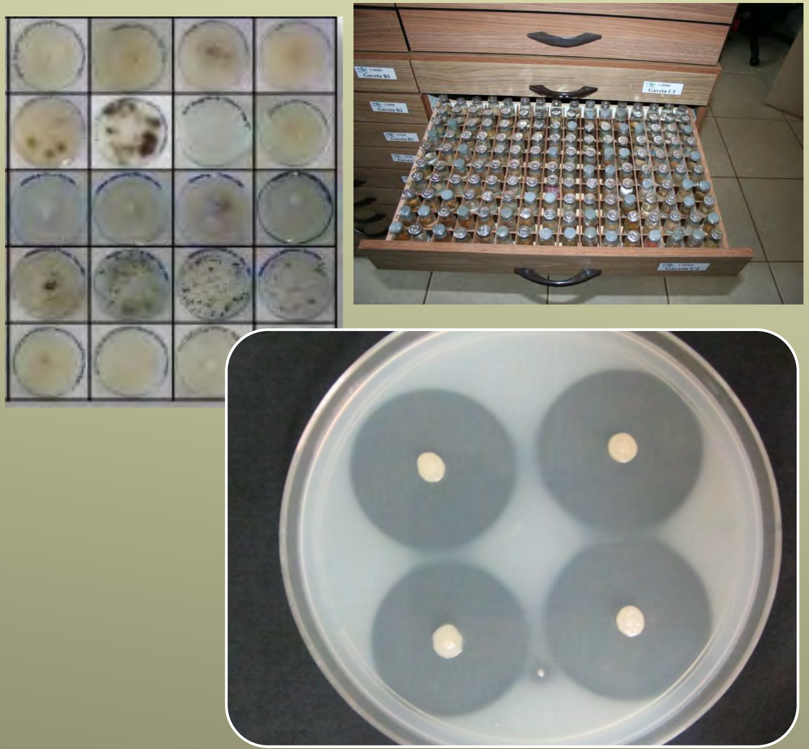
- Isolation and maintenance
- Characterization

Use Research, partnerships and products

- Biological Control
- Bioproducts
- Genes for GMO production

Research lines – other bioproducts

Selection of phosphorus solubilizing microorganisms (PSM)



Phosphorus fertilizers

C source, Nanotecnology

BIOFERTILIZER

Embrapa

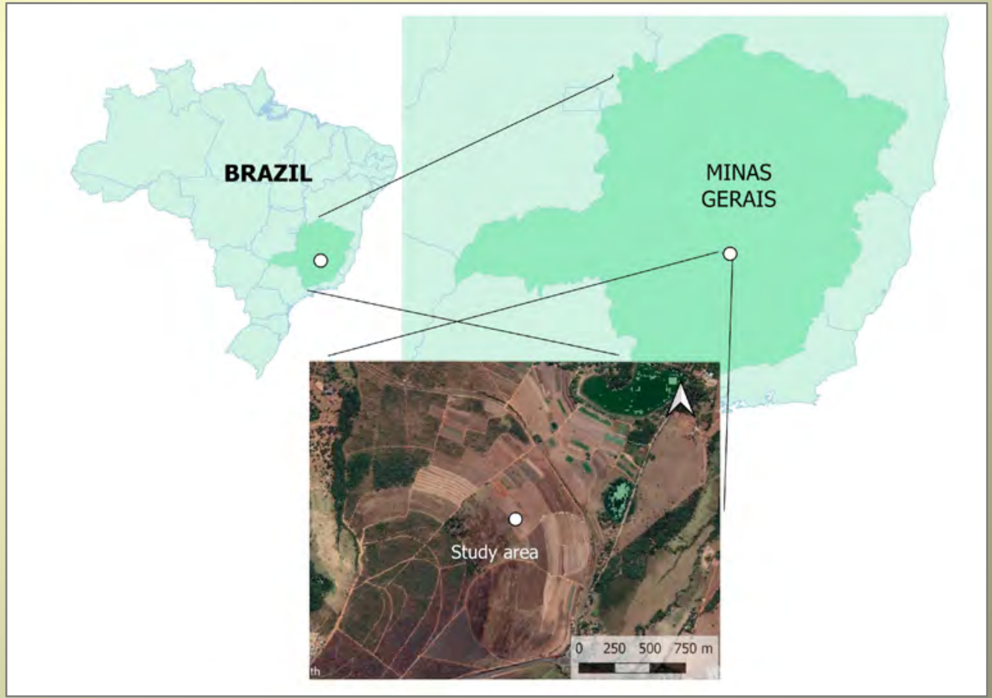
Objective: to evaluate the use of organomineral phosphate associated with PSM in corn

Materials and Methods

- Soil: Oxisol, clay heavy, initially available P (4.0 mg dm^{-3} M-1)
- Two consecutive harvests of corn (P30F53)
- 8 treatments
- Randomized blocks, 5 repetitions

Treat	Product	Dose P_2O_5	Strains
1	Control	0	
2	Org	60	B70+B116
3	Org	120	B70+B116
4	Org	180	B70+B116
5	TSP	60	
6	TSP	120	
7	TSP	180	
8	Org	180	

Org = organomineral = Chicken manure and bedding + Bayovar phosphate rock
TSP = triple superphosphate
B70 = *B. subitilis*
B116 = *B. thurigiensis*



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Materials and Methods

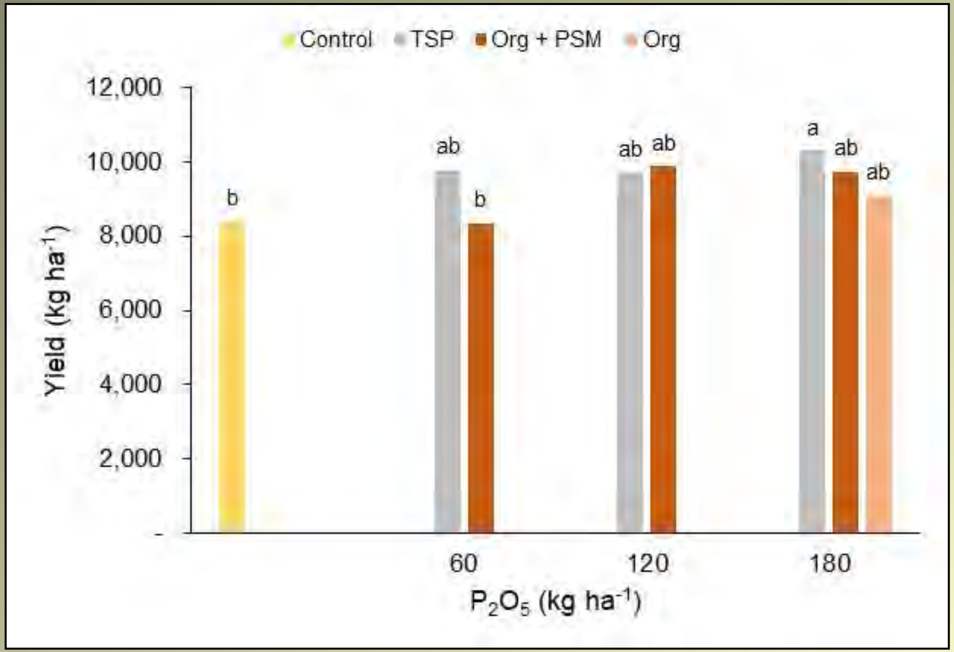
- Evaluations: Plant and soil characteristics

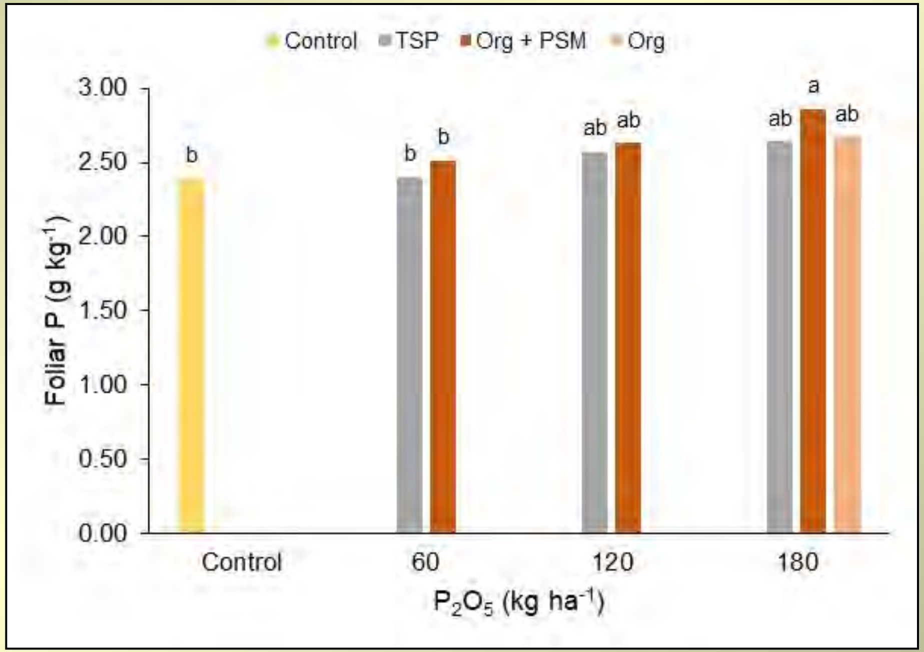
- Data analysis: ANOVA, means were compared by the Tukey test ($p \leq 0.05$) using R program, (www.R-program.org)

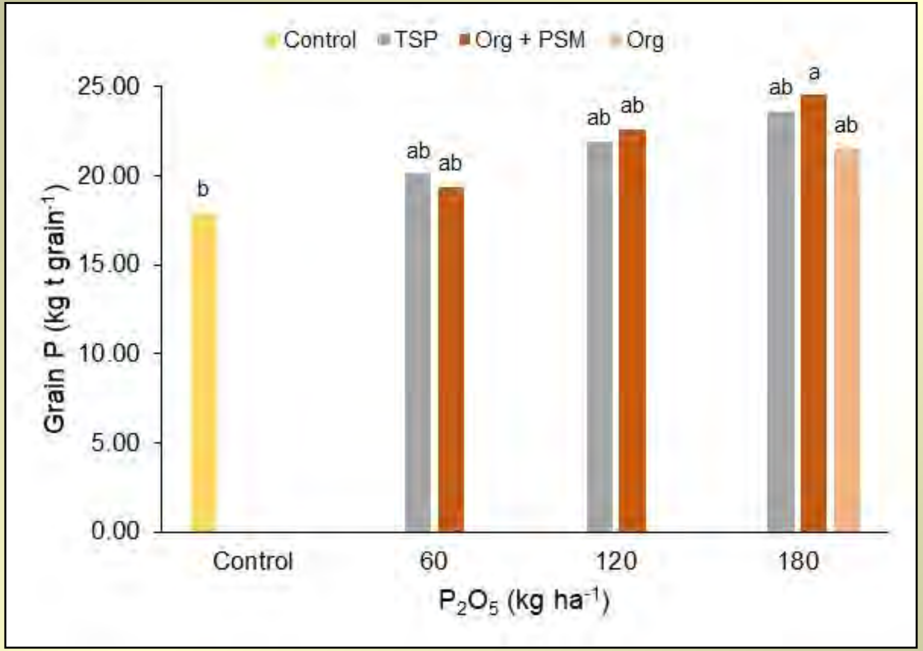
Planting

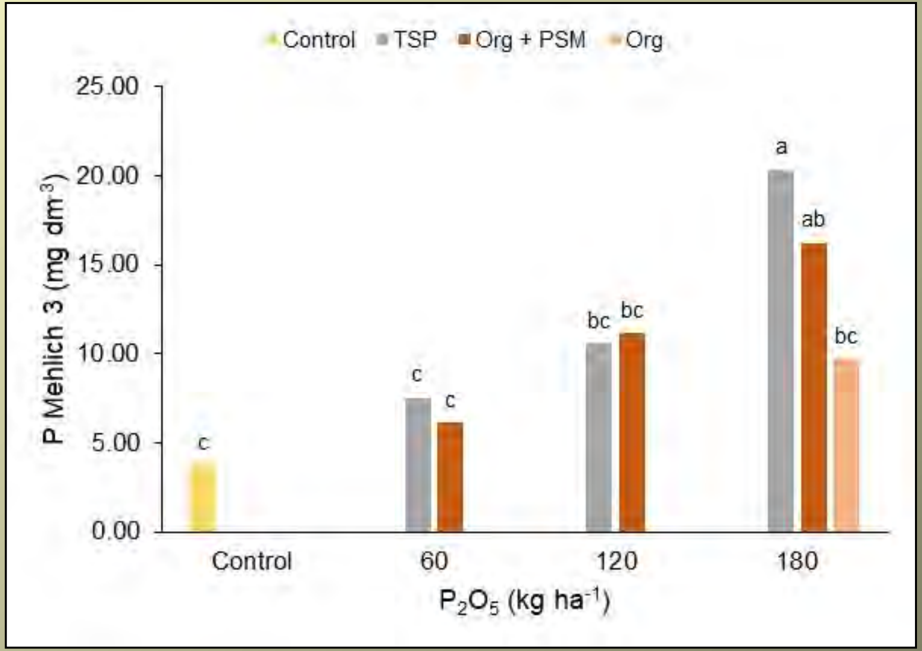
35 days after planting

Results and Discussion – Harvest 1









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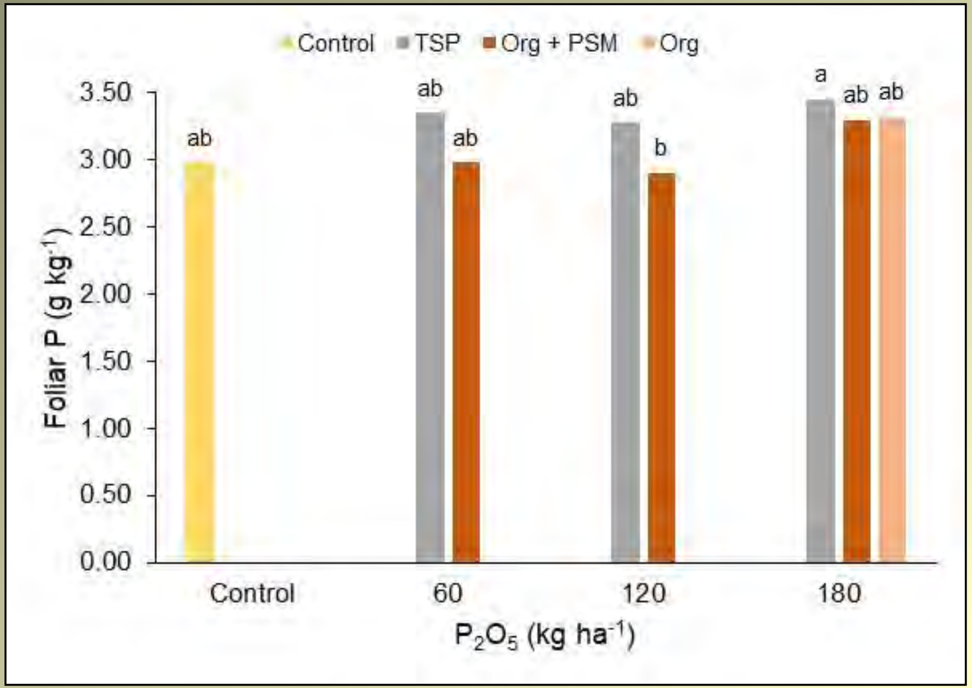
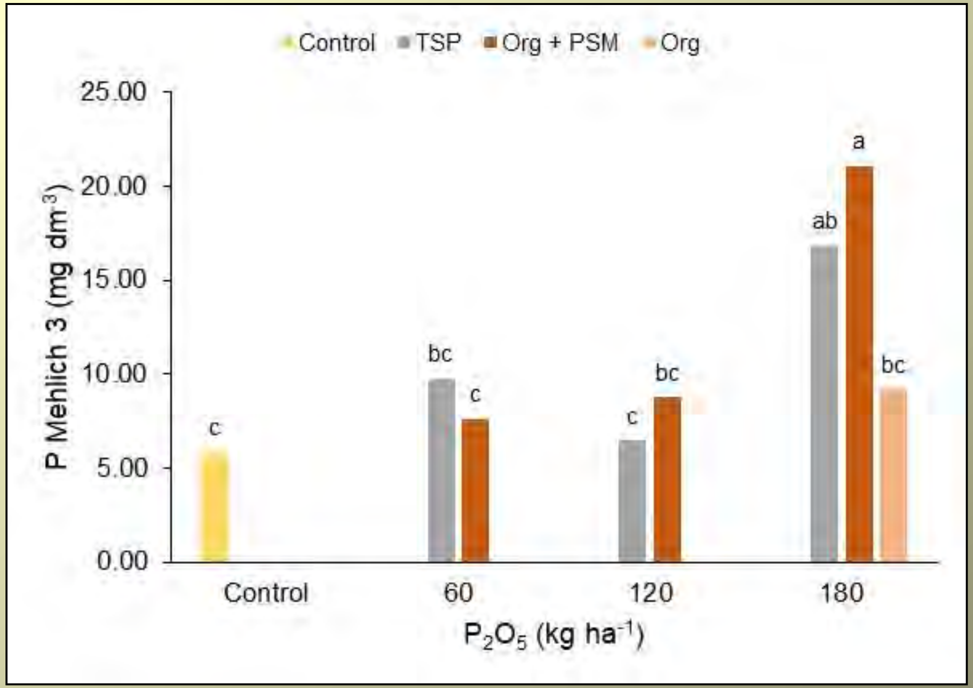
Results and Discussion – Harvest 2





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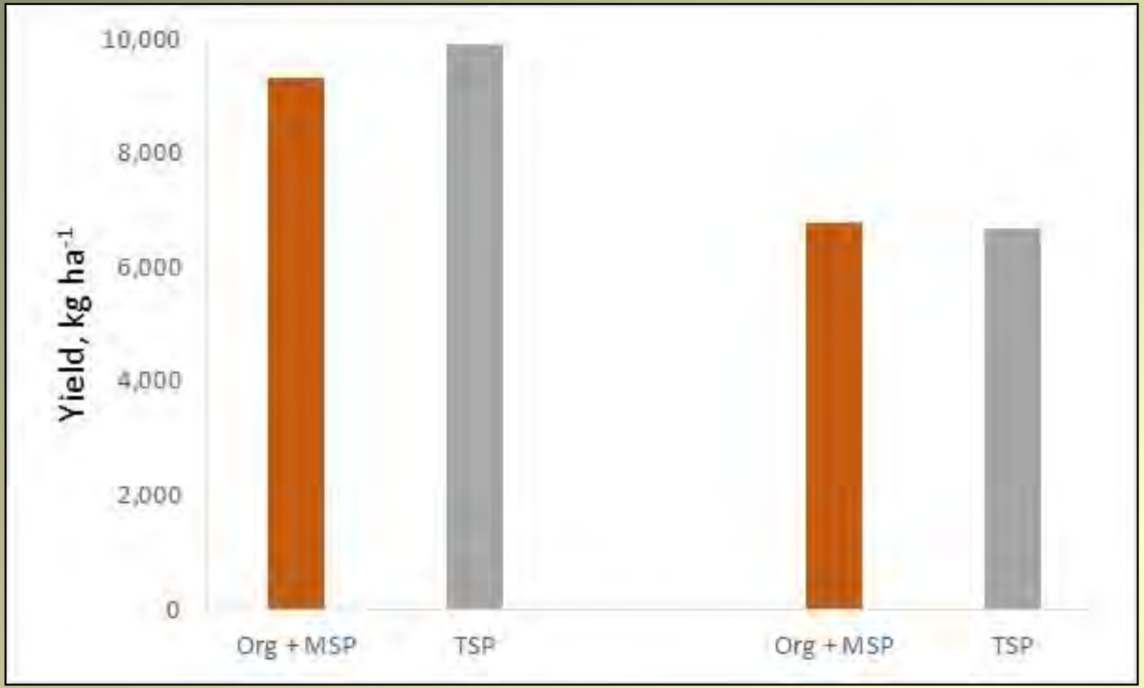
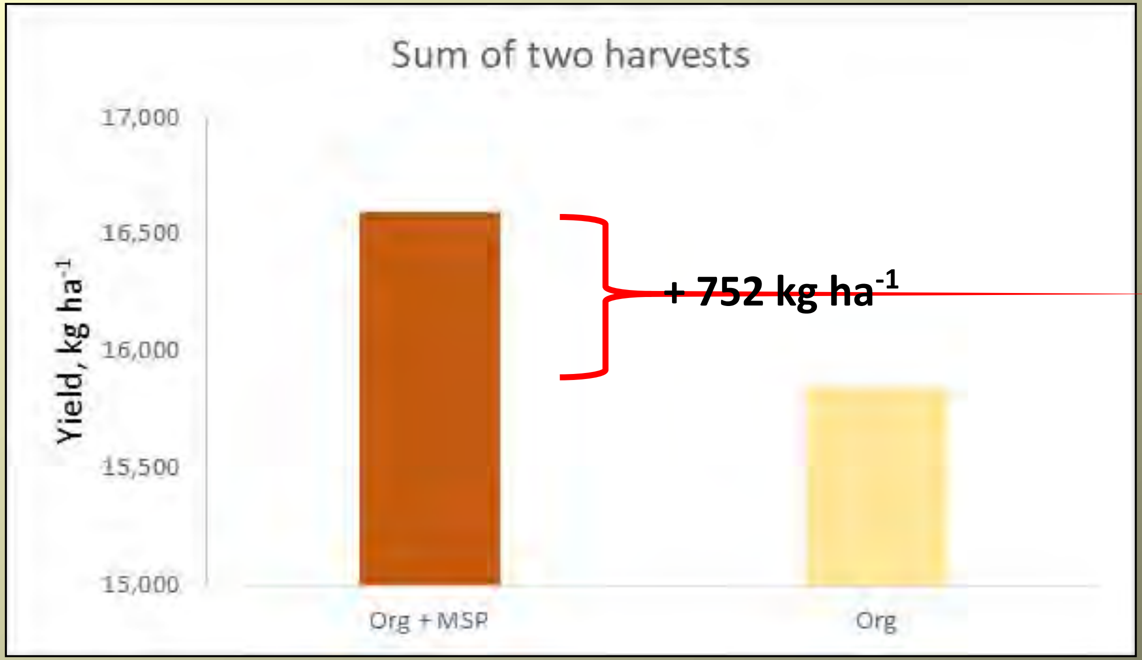
Results and Discussion – both harvests



Harvest 1 **Harvest 2**



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Other Results with PSM

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ISSN: 1996-0808
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http://www.academicjournals.org/AJMR
ACADEMIC JOURNALS
African Journal of Microbiology Research

Influence of phosphorus-solubilizing microorganisms and phosphate amendments on pearl millet growth and nutrient use efficiency in different soil types

Flávia Cristina dos Santos[1], Denise Pacheco dos Reis[2], Eliane Aparecida Gomes[1], Daniela de Azevedo Ladeira[2], Antônio Carlos de Oliveira[1], Izabelle Gonçalves Melo[2], Fabiane Ferreira de Souza[1], Bianca Braz Mattos[3], Cleide Nascimento Campos[1] and Christiane Abreu de Oliveira-Paiva[1]*

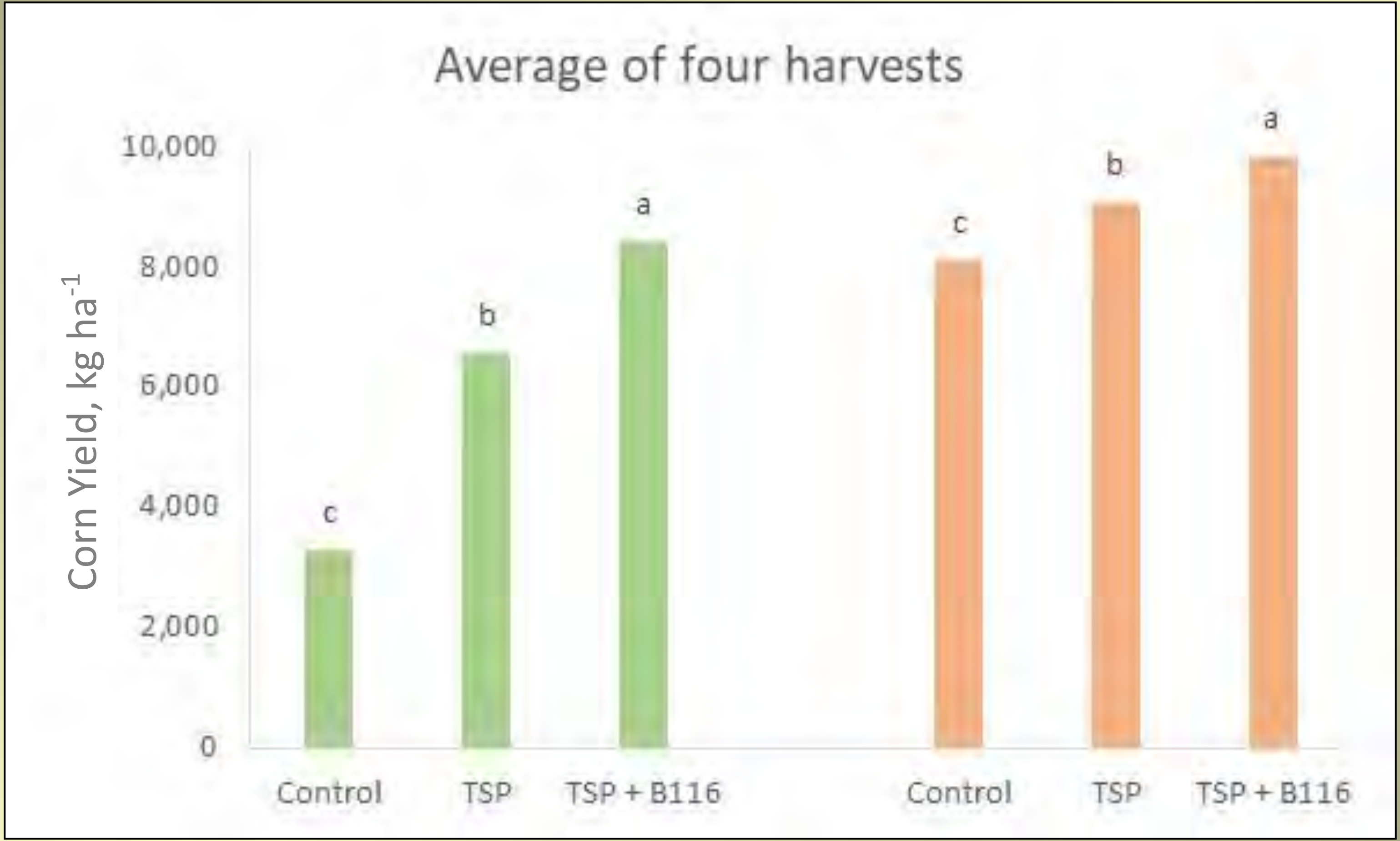
- Pearl Millet

Inoculation with PSM may increase pearl millet yield, enzyme activity and soil biological quality

Soil	Source	DM	ACI PHOS	ALK PHOS	β-GLUCOS
		g pot^{-1}	µg p-nitrophenol h^{-1}g^{-1} soil	µg p-nitrophenol h^{-1} g^{-1} soil	µg p-nitrophenol h^{-1} g^{-1} soil
Sandy	Test*	3.94^{f**}	126.99^{bc}	27.99^{e}	17.65^{c}
	Test +Inoc	4.61^{ef}	132.20^{abc}	55.80^{cd}	21.81^{bc}
	GO	8.20^{bcd}	158.56^{ab}	58.42^{cd}	25.89^{ab}
	GO +Inoc	12.64^{a}	187.69^{a}	79.92^{ab}	32.00^{a}
	BO	7.76^{cd}	158.04^{ab}	56.65^{cd}	23.47^{bc}
	BO +Inoc	10.93^{ab}	141.60^{abc}	98.02^{a}	27.99^{ab}
	Bayovar	7.94^{cd}	106.78^{bc}	38.03^{de}	21.80^{bc}
	Bayovar +Inoc	10.47^{abc}	143.72^{abc}	72.93^{bc}	24.03^{bc}
	TSP	8.03^{bcd}	94.40^{c}	29.68^{e}	22.91^{bc}
	TSP +Inoc	7.40^{de}	112.75^{bc}	45.14^{de}	23.43^{bc}
Clay	Test	2.33^{c}	409.56^{c}	275.67^{b}	43.97^{e}
	Test +Inoc	1.67^{c}	664.74^{b}	308.88^{b}	49.23^{de}
	GO	13.05^{ab}	715.11^{b}	321.22^{b}	69.54^{bcd}
	GO +Inoc	14.10^{ab}	1047.78^{a}	434.88^{a}	114.84^{a}
	BO	13.83^{ab}	681.26^{b}	294.08^{b}	70.98^{bcd}
	BO +Inoc	10.71^{b}	1024.74^{a}	444.25^{a}	90.81^{ab}
	Bayovar	13.92^{ab}	631.31^{b}	259.86^{b}	62.55^{cde}
	Bayovar +Inoc	13.85^{ab}	946.21^{a}	423.32^{a}	76.62^{bc}
	TSP	16.95^{ab}	564.07^{bc}	243.10^{b}	68.23^{bcde}
	TSP +Inoc	15.10^{ab}	655.63^{b}	330.07^{b}	78.01^{bc}

*Test: non-inoculated control; GO: granulated organomineral; BO: branned organomineral; Inoc.: inoculated; TSP: triple superphosphate

Application for registration of the *Bacillus thurigiensis* (B116 – PGPB/PSM) is being sent to Brazil's Ministry of Agriculture (2022)



MG, medium P

GO, high P

TSP + B116

+ Foliar P

+ Grain P

Source: Paiva et al. (2022) not published

Other Results with PSM

Contents lists available at ScienceDirect

Soil Biology and Biochemistry

journal homepage: www.elsevier.com/locate/soilbio

Phosphate solubilizing microorganisms isolated from rhizosphere of maize cultivated in an oxisol of the Brazilian Cerrado Biome

C.A. Oliveira[a], V.M.C. Alves[b], I.E. Marriel[b], E.A. Gomes[b], M.R. Scotti[a], N.P. Carneiro[b], C.T. Guimarães[b], R.E. Schaffert[b], N.M.H. Sá[a,*]

BRAZILIAN JOURNAL OF MICROBIOLOGY

http://www.bjmicrobiol.com.br

Environmental Microbiology

Endophytic Bacillus strains enhance pearl millet growth and nutrient uptake under low-P

Vitória Palhares Ribeiro[a], Ivanildo Evódio Marriel[b], Sylvia Morais de Sousa[b], Ubiraci Gomes de Paula Lana[b], Bianca Braz Mattos[c], Christiane Abreu de Oliveira[b,*], Eliane Aparecida Gomes[b,**]

available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/apsoil

Assessment of the mycorrhizal community in the rhizosphere of maize (*Zea mays* L.) genotypes contrasting for phosphorus efficiency in the acid savannas of Brazil using denaturing gradient gel electrophoresis (DGGE)

Christiane A. Oliveira[a,*], Nadja M.H. Sá[a], Eliane A. Gomes[b], Ivanildo E. Marriel[b], Maria R. Scotti[a], Claudia T. Guimarães[b], Robert E. Schaffert[b], Vera M.C. Alves[b]

[a] Federal University of Minas Gerais, Botany Department, PO box 486, 31270-901 Belo Horizonte, MG, Brazil
[b] Embrapa Maize and Sorghum, PO box 151, 35701-970 Sete Lagoas, MG, Brazil

Archives of Microbiology (2022) 204:143
https://doi.org/10.1007/s00203-022-02759-3

ORIGINAL PAPER

Co-inoculation with tropical strains of *Azospirillum* and *Bacillus* is more efficient than single inoculation for improving plant growth and nutrient uptake in maize

Vitória Palhares Ribeiro[1] · Eliane Aparecida Gomes[2] · Sylvia Morais de Sousa[1,2,3] · Ubiraci Gomes de Paula Lana[2,3] · Antonio Marcos Coelho[2] · Ivanildo Evódio Marriel[1,2,3] · Christiane Abreu de Oliveira-Paiva[2,3]

Minerals Engineering

Volume 128, November 2018, Pages 230-237

Nanocomposite of starch-phosphate rock bioactivated for environmentally-friendly fertilization

Rodrigo Klaic[a,b], Amanda S. Giroto[a,c], Gelton G.F. Guimarães[a], Fabio Plotegher[a,c], Caue Ribeiro[a,c], Teresa C. Zangirolami[b], Cristiane S. Farinas[a,b]

GMR

Maize endophytic bacteria as mineral phosphate solubilizers

C.S. de Abreu[1], J.E.F. Figueiredo[2], C.A. Oliveira[2], V.L. dos Santos[3], E.A. Gomes[2], V.P. Ribeiro[1], B.A. Barros[2], U.G.P. Lana[2] and I.E. Marriel[1,2]

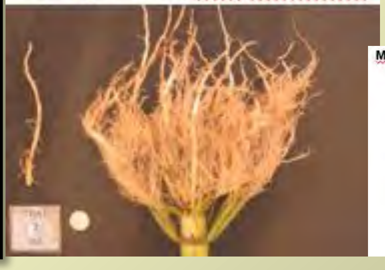
Journal of Plant Growth Regulation
https://doi.org/10.1007/s00344-020-10146-9

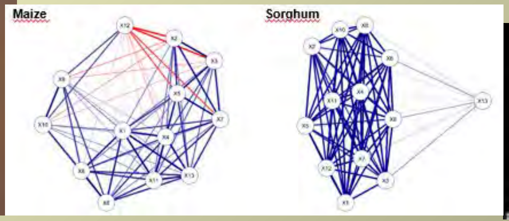
Tropical *Bacillus* Strains Inoculation Enhances Maize Root Surface Area, Dry Weight, Nutrient Uptake and Grain Yield

Sylvia Morais de Sousa[1,2,3] · Christiane Abreu de Oliveira[1,2] · Daniele Luiz Andrade[2] · Chainheny Gomes de Carvalho[2] · Vitória Palhares Ribeiro[3] · Maria Marta Pastina[1,3] · Ivanildo Evódio Marriel[1,2,3] · Ubiraci Gomes de Paula Lana[1,2] · Eliane Aparecida Gomes[1]

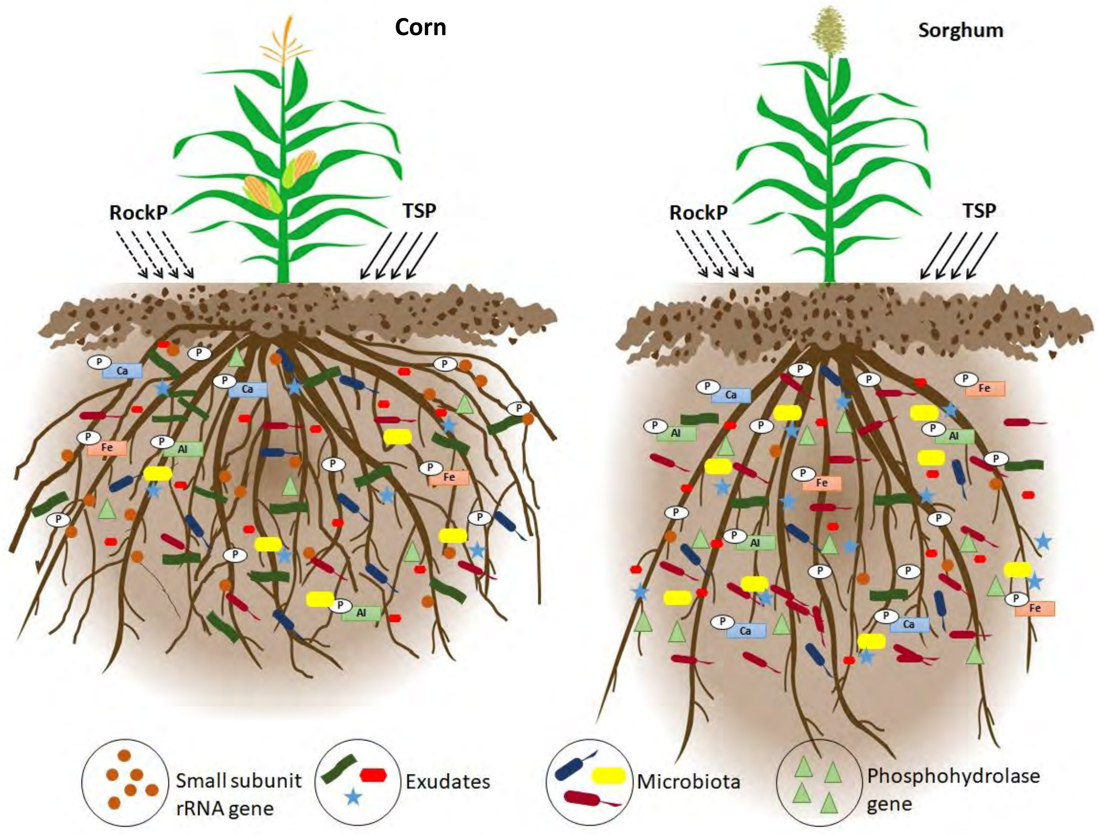
Bioactive Material with Microorganisms for Application as Coating Fertilizer Granules **Majaron *et al.*, Journal of Polymers and the Environment, 2022**

120 kg ha⁻¹ TSP, with inoculation





Conclusion



PSM (PGPB)

Root morphological changes
+
Siderophore production
+
Biofilm production
+
Organic acid exudation
+
Phosphatase secretion

Abundance and specie richness of microbial communities

+P+P+P+P+P+P

Higher yield

Response depends: Genotypes, microbial strains, P soil status and P source

Source: Adapted from Sylvia Tinoco

Researchers:
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Eliane Aparecida Gomes
Ivanildo E. Marriel
Sylvia M. S. Tinoco

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UFV
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UPIS
Graduação e Pós-Graduação

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Embrapa

TRIJUNÇÃO

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Bioavailability and Crop Uptake of Phosphorus from RhizoSorb®

Aaron Waltz, PhD.
Phospholutions, Inc.

Phosphorus Forum + Sustainable Phosphorus Summit

Raleigh, North Carolina, USA.

November 4, 2022

Global P use is **inefficient and unsustainable**

Inefficient Use

Less than **25%** of P fertilizer is taken up by the crop

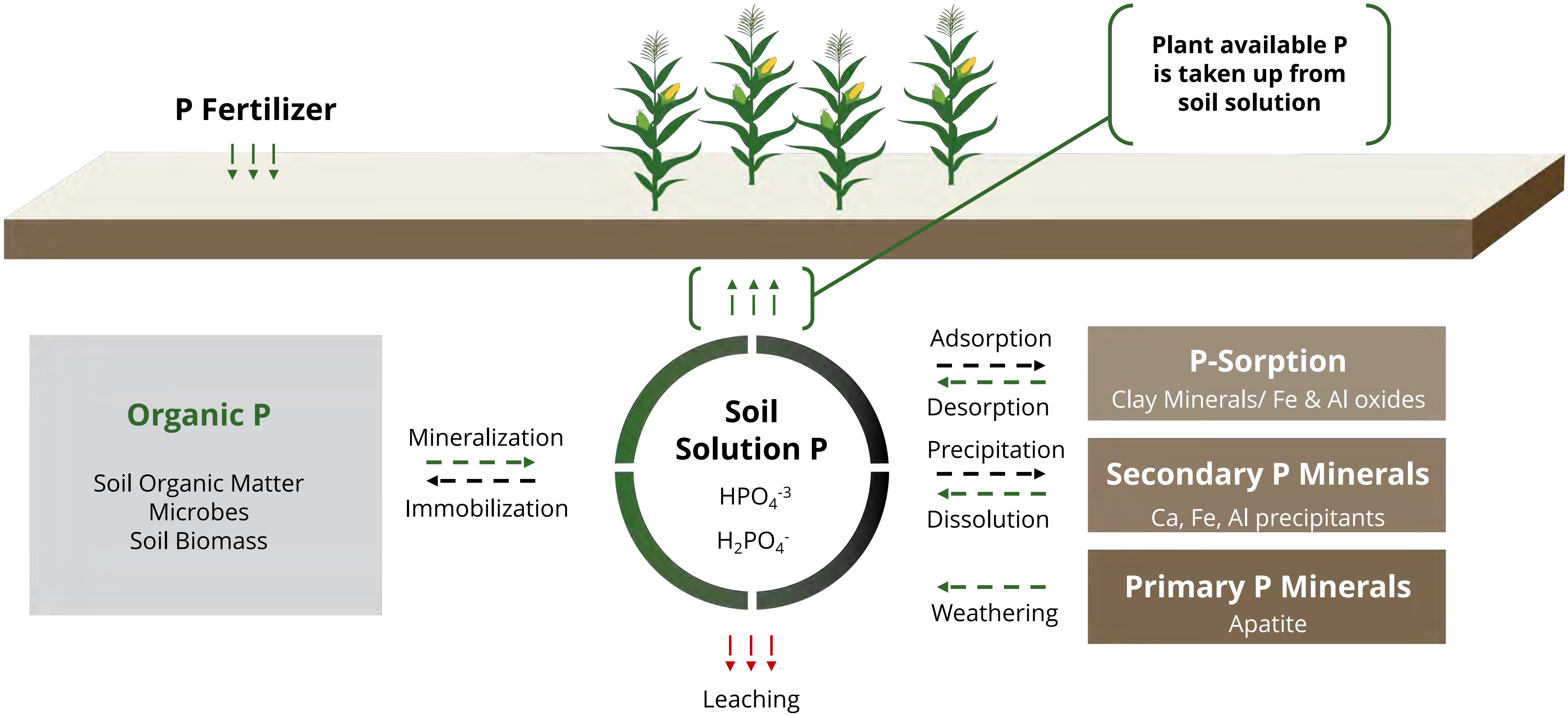
Global Impact

Phosphorus degrades 70% of freshwater worldwide contributing to climate change

Finite Resource

2nd largest nutrient used in food production; 90% of mined P is lost mine to fork

Phosphorus ties up in complex soil interactions



RhizoSorb® acts as a buffer to store and release P only when needed

High Soluble P

RhizoSorb® adsorbs excess P
storing for future release

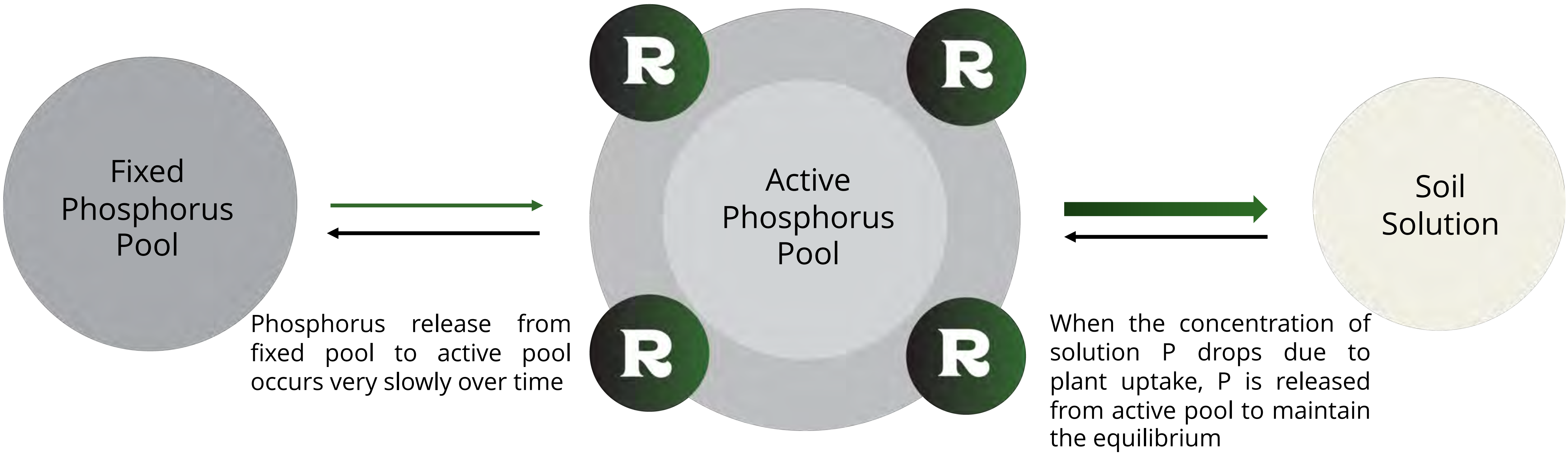
Low Soluble P

RhizoSorb® desorbs P
into soil solution for **plant uptake**

Product Attributes

- Increases uptake efficiency of applied P fertilizers by storing P in a more available form
- Acts as reservoir for phosphorus releasing fertilizer more consistent with plant needs
- Soil chemistry approach rather than biological; No shelf life issues; Agnostic of P source/crop
- Embedded into fertilizer granule for ease of scalability and application using standard practices

Mimicking natural soil chemistry – **Adsorption/Desorption of P**

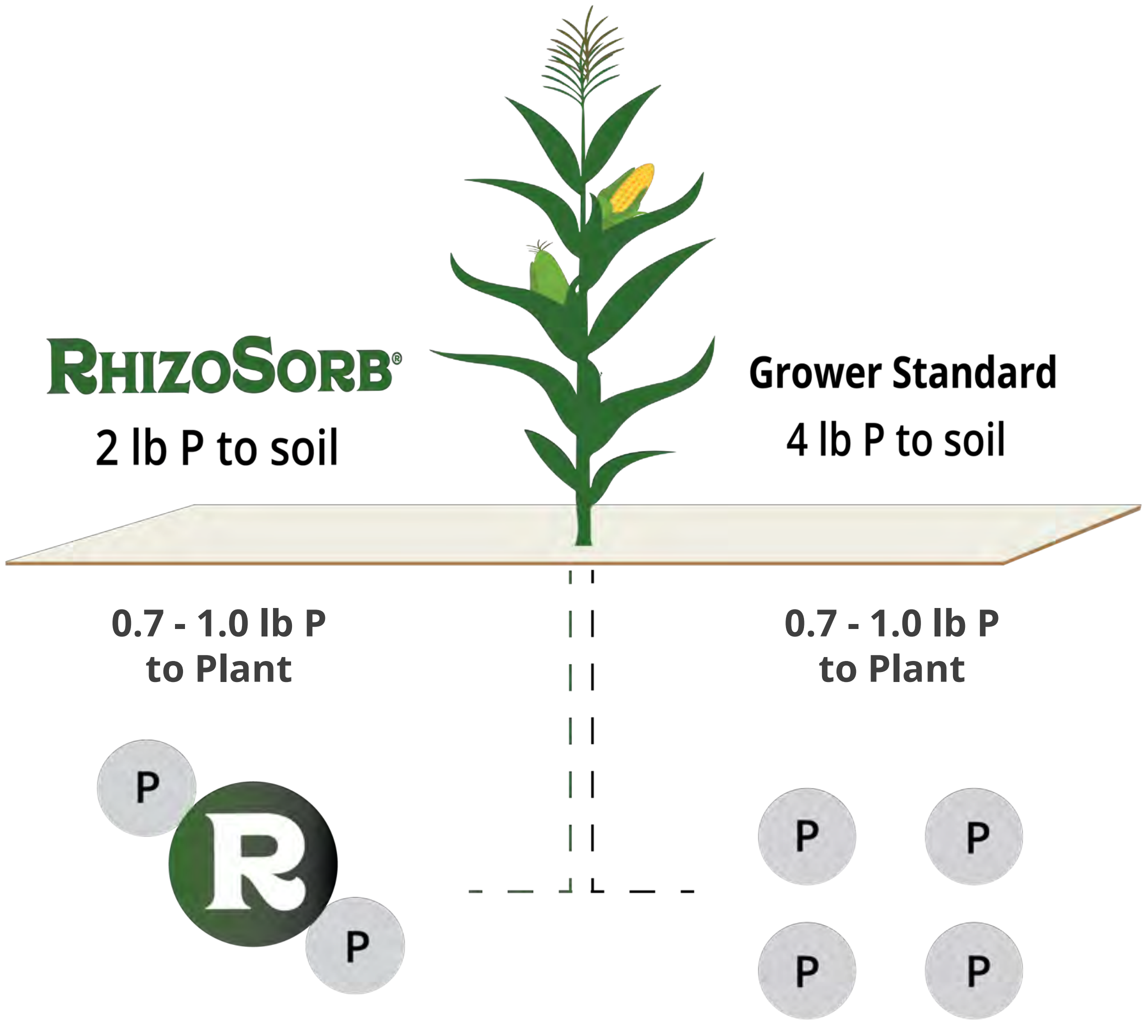


RhizoSorb® stores P in the active pool for greater accessibility throughout growing season

RhizoSorb® delivers phosphorus more efficiently

Applied vs. **Delivered**

- RhizoSorb® technology is incorporated into fertilizer granules to increase nutrient use efficiency
- Fertilizer with RhizoSorb® is twice as efficient as conventional
- Allows a grower to achieve equal or higher yield with half the fertilizer input



RhizoSorb® optimizes P efficiency

Producers

Higher efficiency products

Double mine operating life

Sustainability benefits

Channel

Higher value products

Stretch P over more acres

Reduce handling by 37%

Environment

Decrease nutrient pollution

Reduce greenhouse gas emissions

Improve soil health

Farmers

Reduce P use by 50%

Optimize input costs

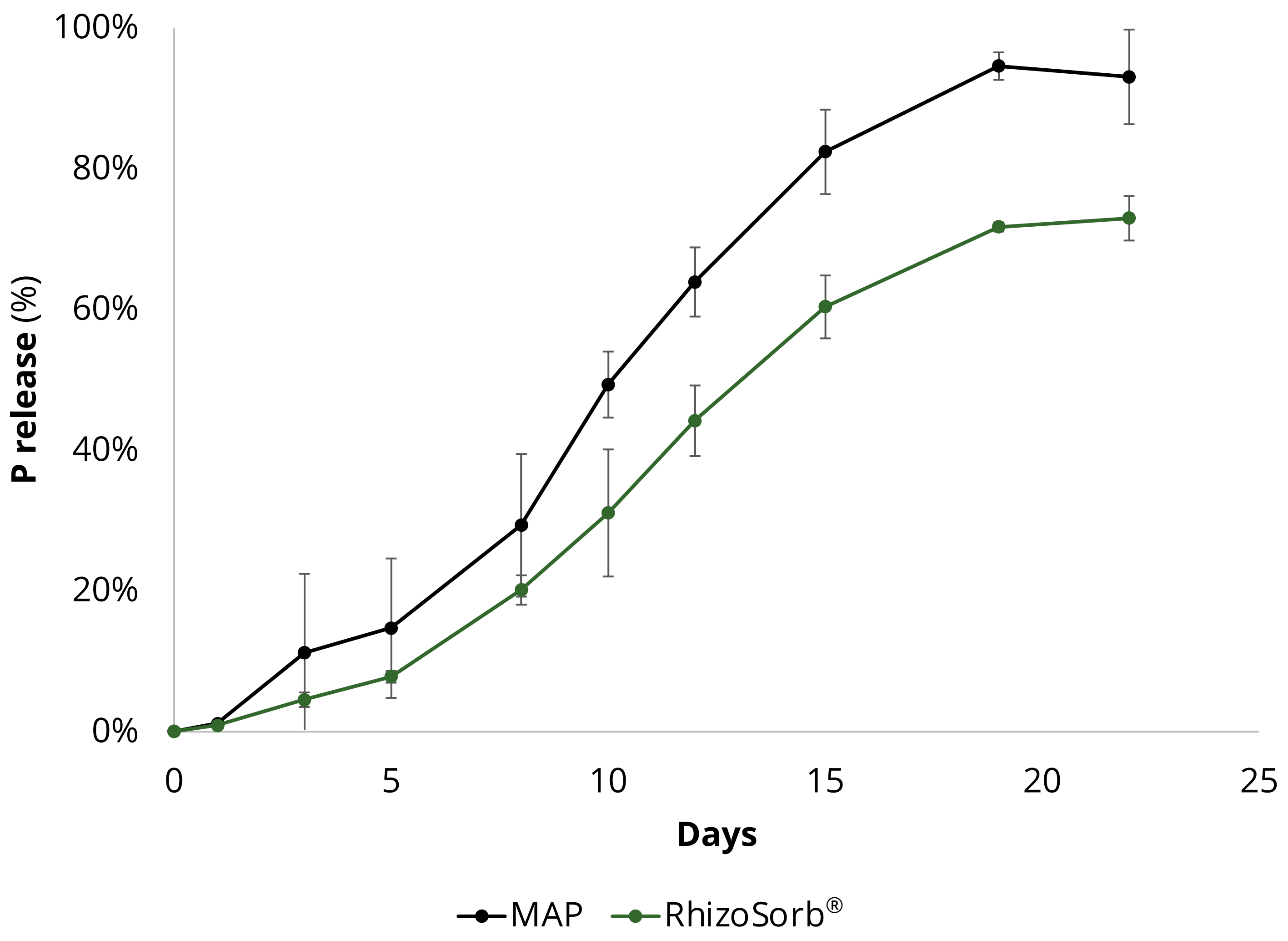
Higher grower ROI

Granule Phosphorus Release Profile Assay

- **Objective**: To quantitatively determine the release of phosphorus from granules (MAP vs RhizoSorb®) over time in a water-based environment.
- **Set up**: 2 treatments × 3 reps. Fertilizer granules (2-4 mm) with 0.1 g P_2O_5 were weighed into 50-ml centrifuge tubes and 40-ml DI water added.
- **Sampling**: 2-ml solutions collected on day 1, 3, 5 , 8, 10, 12, 15, 17, 19, 22.
- **Ortho-P determination**: Samples analyzed colorimetrically by the Murphy and Riley (1962) procedure using a SEAL AQ400 autoanalyzer, Method EPA-118-A Rev.5 (SEAL Analytical, 2004).

RhizoSorb® slow-P release

The proprietary composition of RhizoSorb® as a non-polymer coated fertilizer provides a more efficient slow P release when compared to conventional MAP fertilizer.

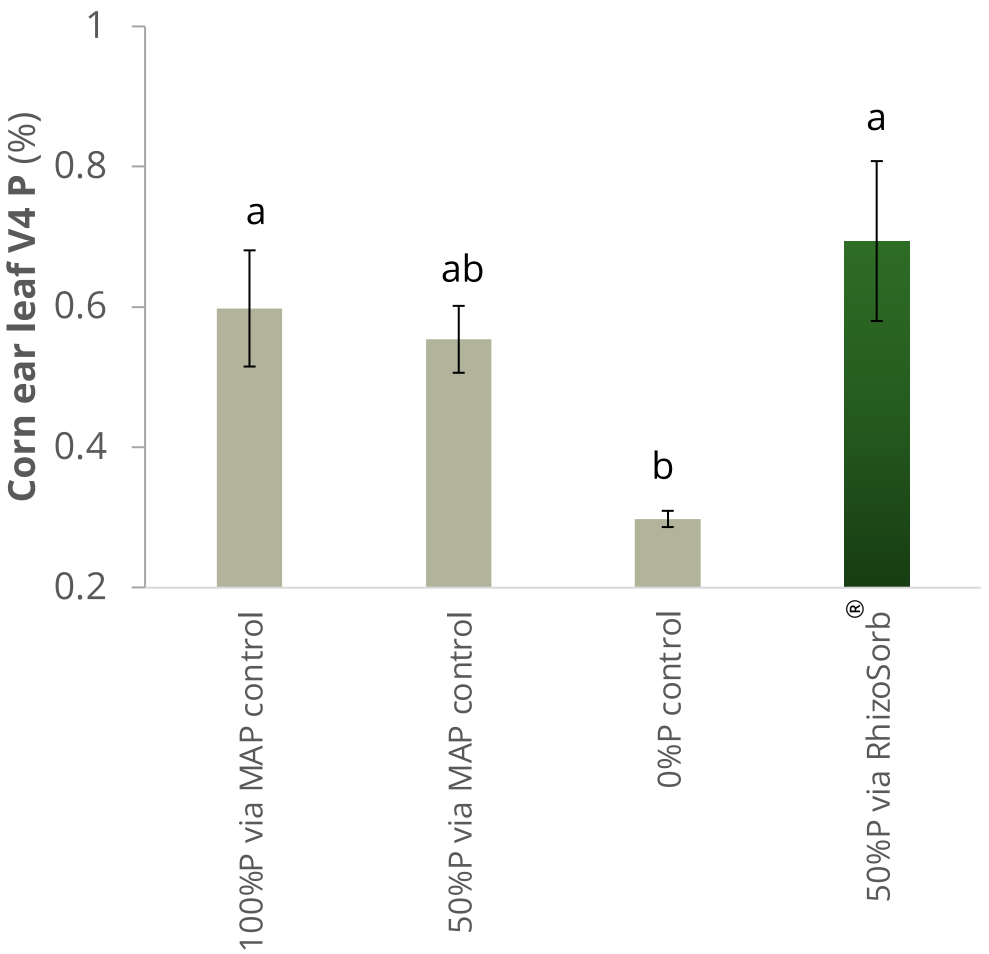


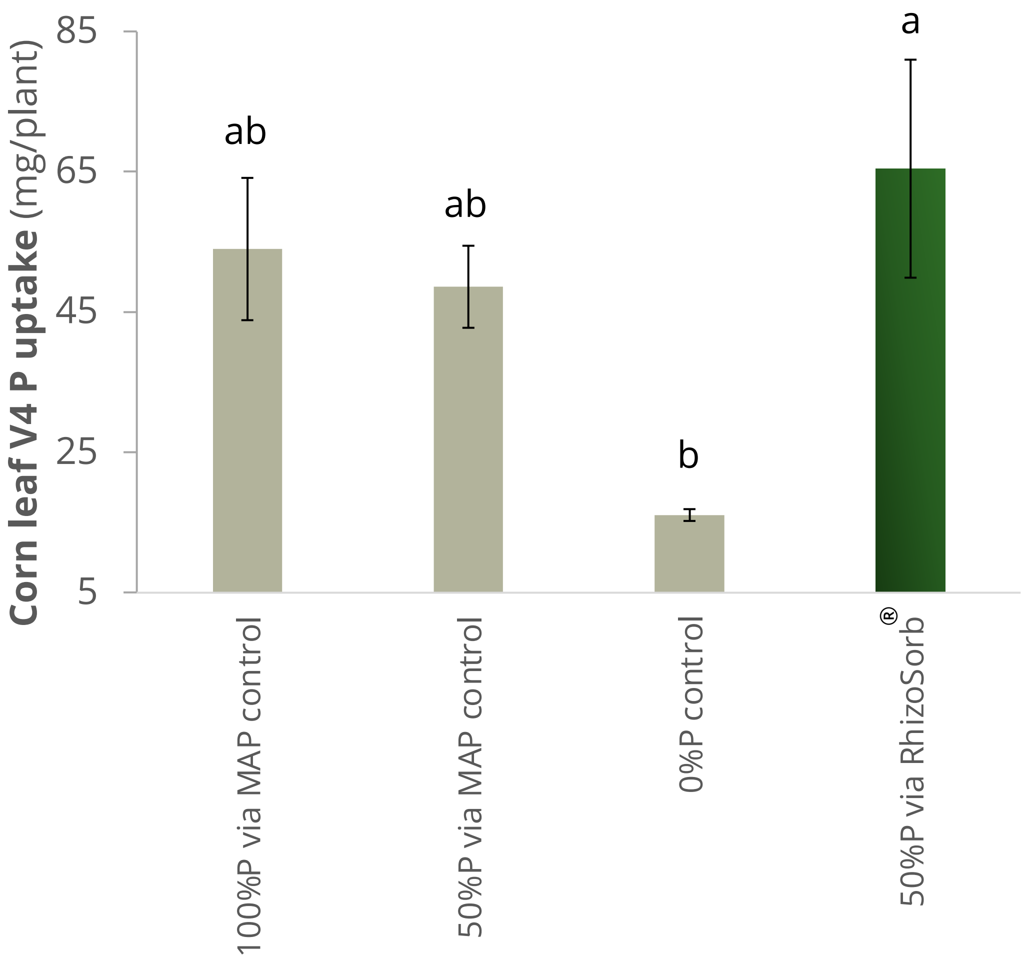
Greenhouse corn trial setup

Trt #	Treatment
1	100% P via MAP (control)
2	50% P via MAP (control)
4	0% P (control)
8	50% P via RhizoSorb

- **Objective**: To evaluate the phosphorus supply of a controlled-release RhizoSorb® fertilizer against conventional MAP
- **Design:** Completely Randomized Design
- **Replications**: 5
- **Pot size:** 10” pots
- **Media**: Sandy soil (average Soil test P = 19 ppm)
- **Application**: MAP (controls) and RhizoSorb (treatments) mixed thoroughly into top 6” soil prior to sowing
- **Tissue Sampling**: V4 corn growth stage
- **Leachate sampling:** Weekly

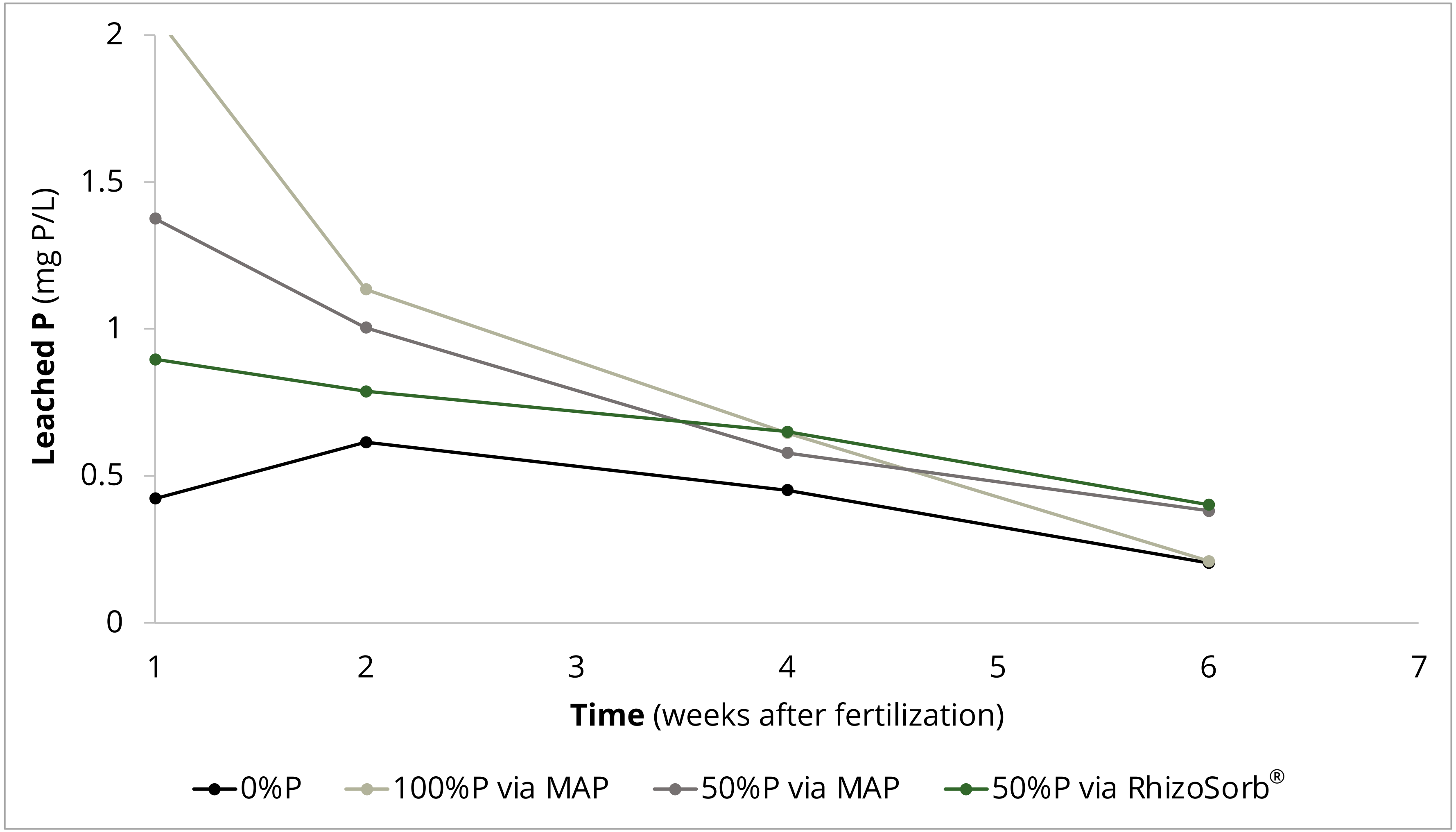
RhizoSorb®, maintains tissue P concentrations and uptake with 50% less P





Treatments with the same level are not significantly different (alpha = 0.1, $p < 0.01$)

Reduced P leachate from RhizoSorb® treatments immediately after application compared to MAP

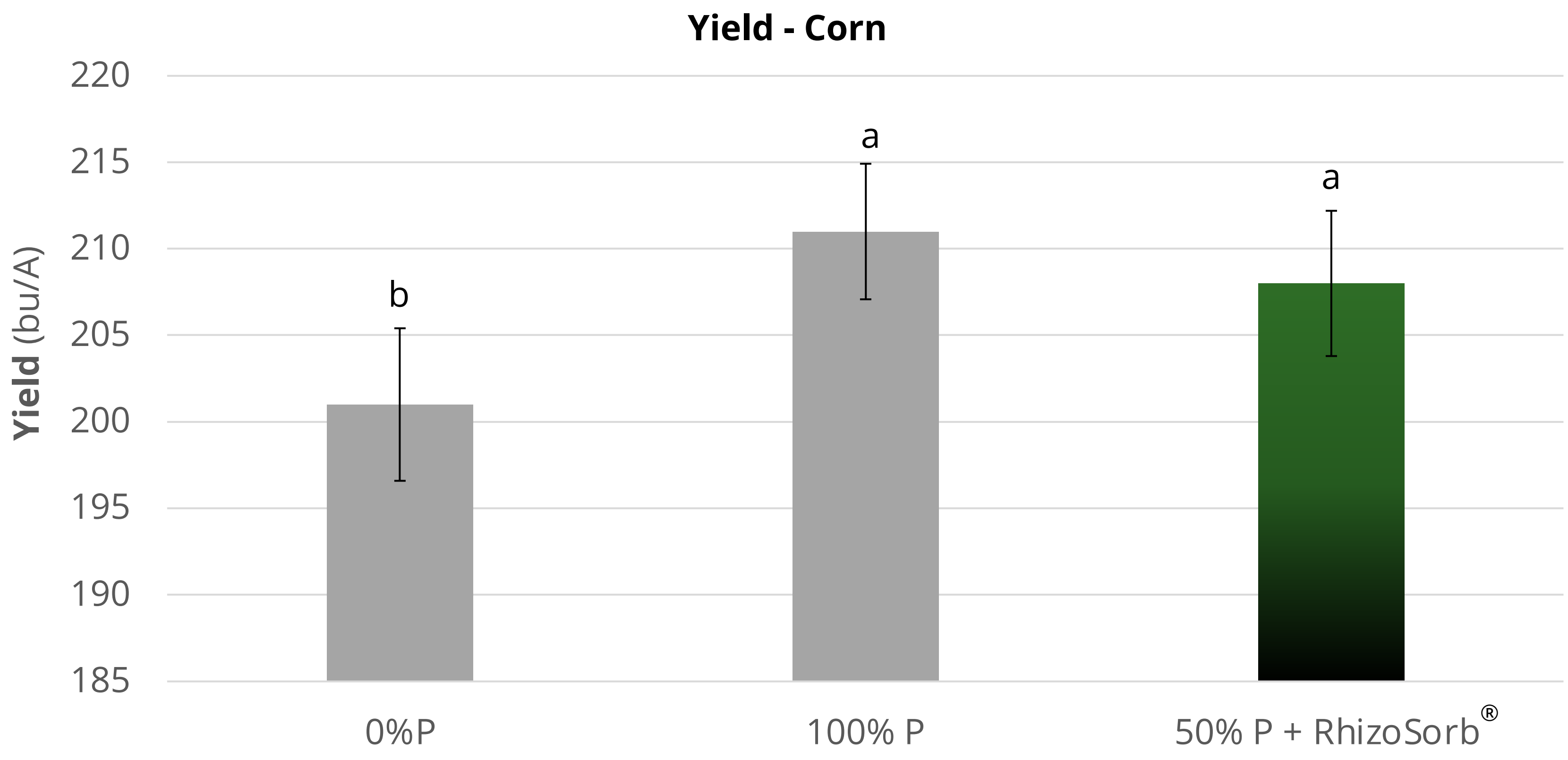


Small-plot replicated trials

- Crop: Corn and Soybean
- 6 reps x 12 treatments – RCBD
  - 0 and 100% P controls (MAP)
  - P levels at 50% of full P
  - RhizoSorb® at multiple levels (rate response)
- Soil sampling beginning of season for initial soil values
- Tissue sampling
  - R3 stage to evaluate effect of treatments on plant nutrient status
  - End of season grain sampling for plant nutrient status (selected trials) and yield

RhizoSorb® maintains yield with 50% less P

2021 Corn replicated small-plot trials

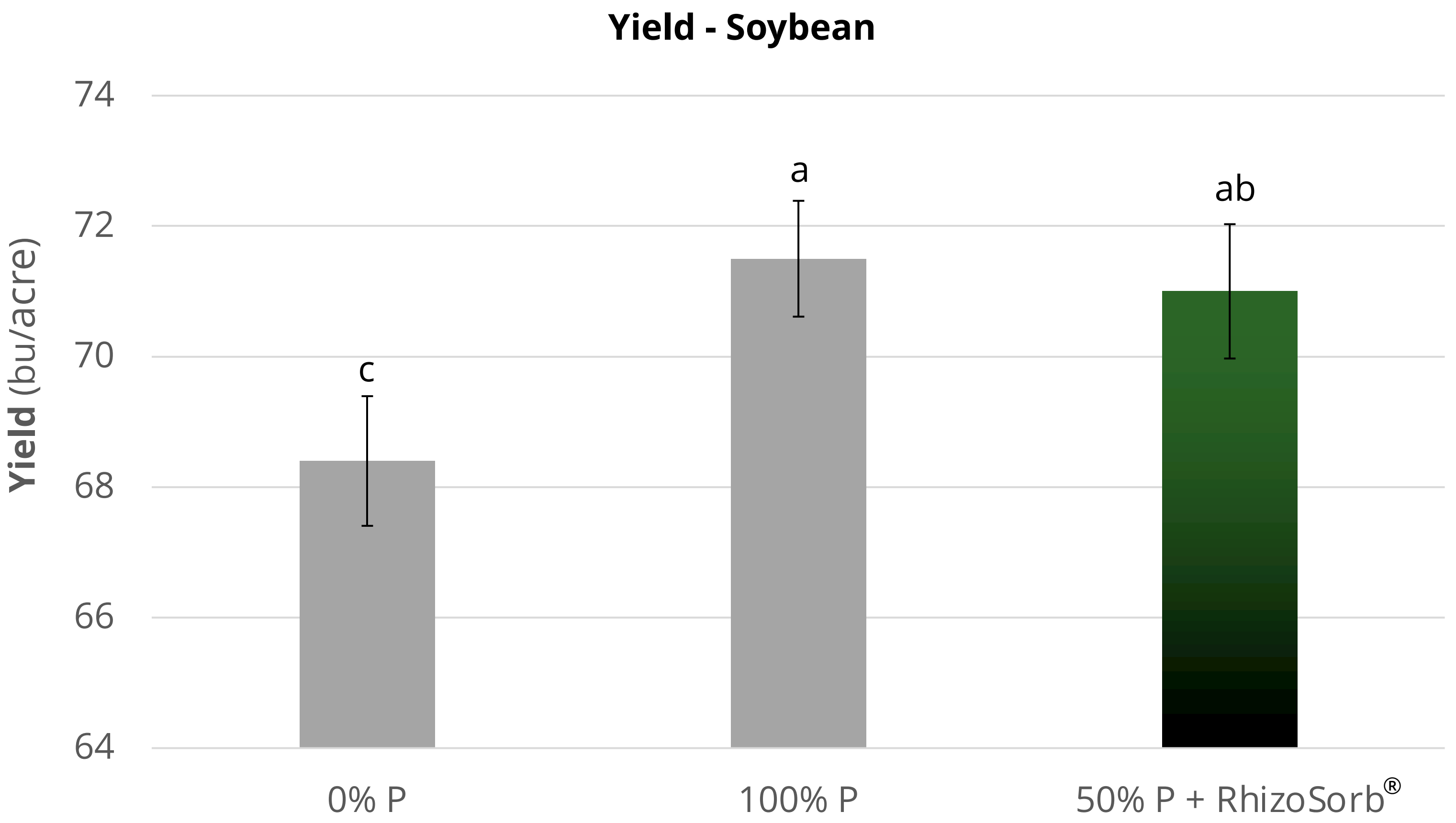


7 locations, 17 trials, 6 reps each treatment; n=714

Treatments with the same letter are not statistically different at a=0.05.

RhizoSorb® maintains yield with 50% less P

2021 Soybean replicated small-plot trials



7 locations, 17 trials, 6 reps each treatment; n=714

Treatments with the same letter are not statistically different at a=0.05.

Conclusion

Breakthrough Technology

RhizoSorb® is a novel, proprietary, slow-P release fertilizer with the potential to contribute to more sustainable crop production systems

Advanced Delivery

RhizoSorb® reduces soil P immobilization processes, and improves P bioavailability and recovery based on a chemical gradient driven by plant needs

Performance Milestones

Maintains crop P uptake and yield with 50% less phosphorus in both green house and field trials

Reduces the risk of fertilizer P loss in leachate/runoff immediately after application

Offers a sustainable alternative to conventional, high solubility fertilizers

Aaron Waltz, PhD.

Chief Technology Officer

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Applications of the oxygen isotope ratio of phosphate to identify phosphorus sources in agricultural areas

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Outline

Applications of the oxygen isotope ratio of phosphate to identify phosphorus sources in agricultural areas

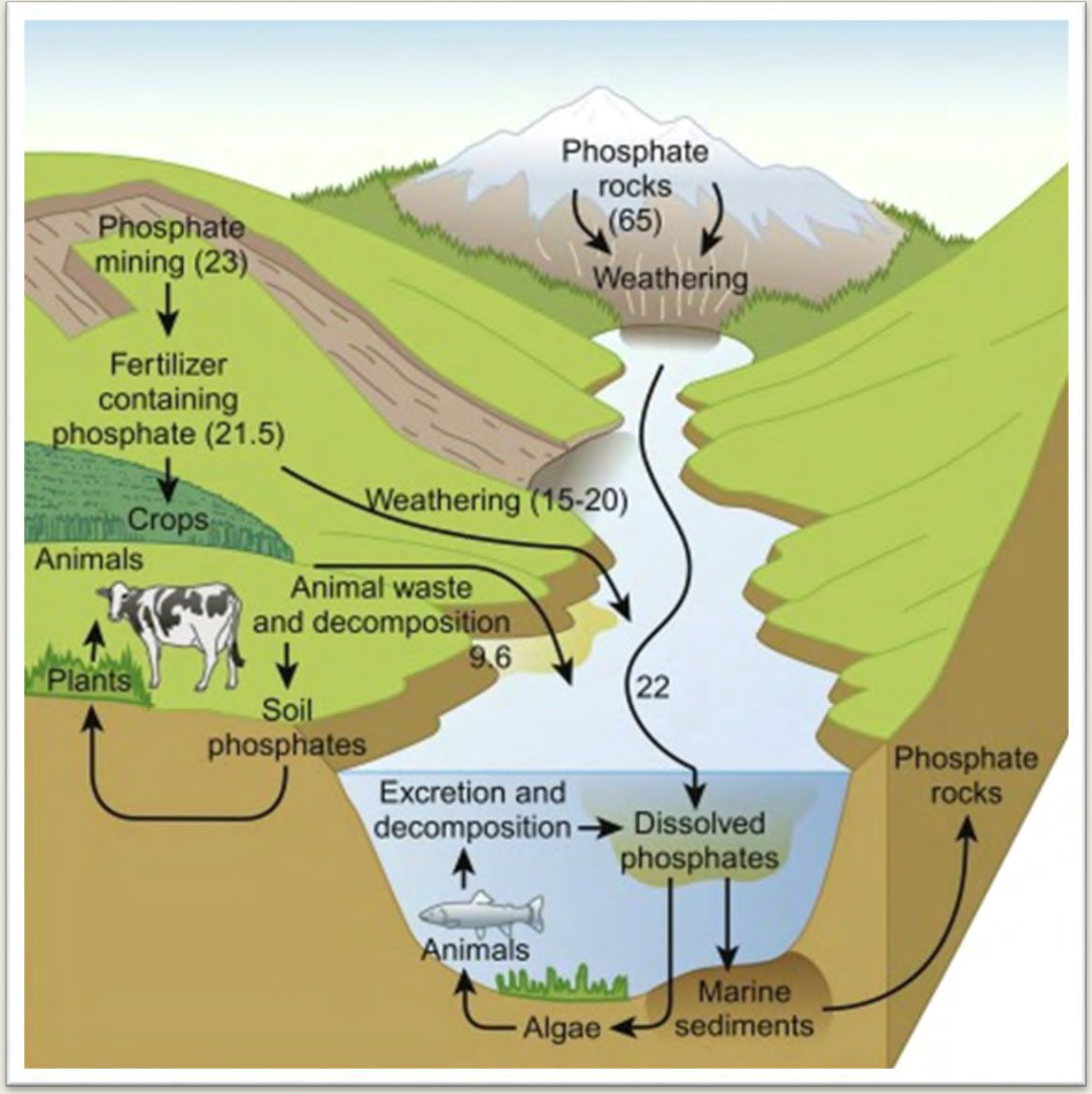
- Introduction
- Materials and Method
- Preliminary results in North Carolina
- Next steps

INTRODUCTION

BACKGROUND FOR OXYGEN ISOTOPE OF PHOSPHATE AND APPLICATIONS

Introduction

- Phosphorus is often a limiting nutrient in many environments.
- An excess of phosphorus can be problematic causing <u>eutrophication</u> and <u>algal blooms</u>.
- Identifying the **origin** of phosphorus (P) is essential to understand the **cycling** of nutrients.



(Schipanski and Bennett, 2021)

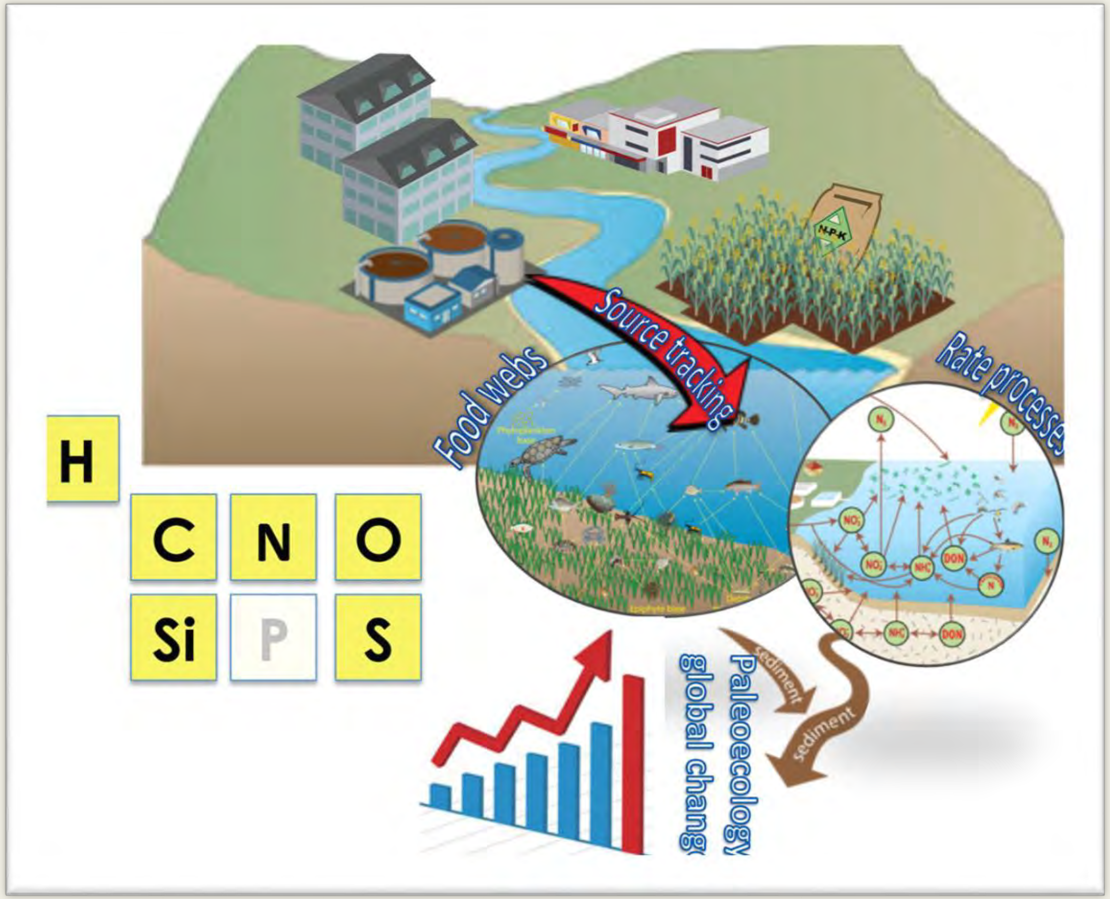
Introduction

Stable Isotopes

- **Stable isotope ratios** have been widely used to understand sources and processes for ions in various systems.
- Carbon (C), nitrogen (N), Hydrogen (H), and Oxygen (O) are commonly used.
- The relative abundance of heavy to light isotopes is indicated by the widely used **delta** notation.

$$\delta = \left(\frac{R_{sample} - R_{standard}}{R_{standard}}\right) \times 1000$$

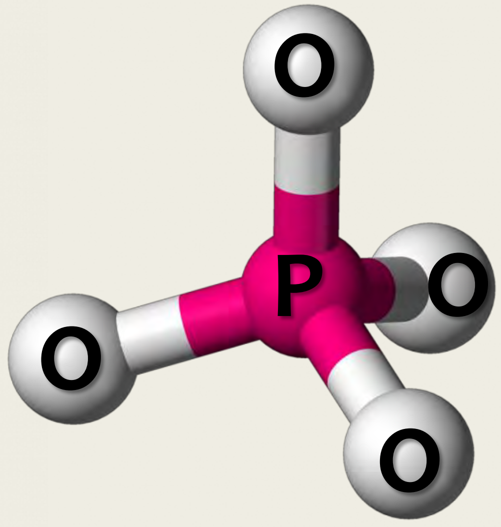
*R is the ratio of abundance of the heavy to light isotopes



(Glibert et al., 2018)

Introduction

- Because P has <u>only</u> one stable isotope (^{31}P), researchers have started to explore the behavior of O isotopes in phosphate (**$\delta^{18}O_{PO4}$**).
- The P–O bond is highly resistant to inorganic hydrolysis.



- A temperature-dependent equilibration with oxygen in ambient water (Longinelli and Nuti 1973)

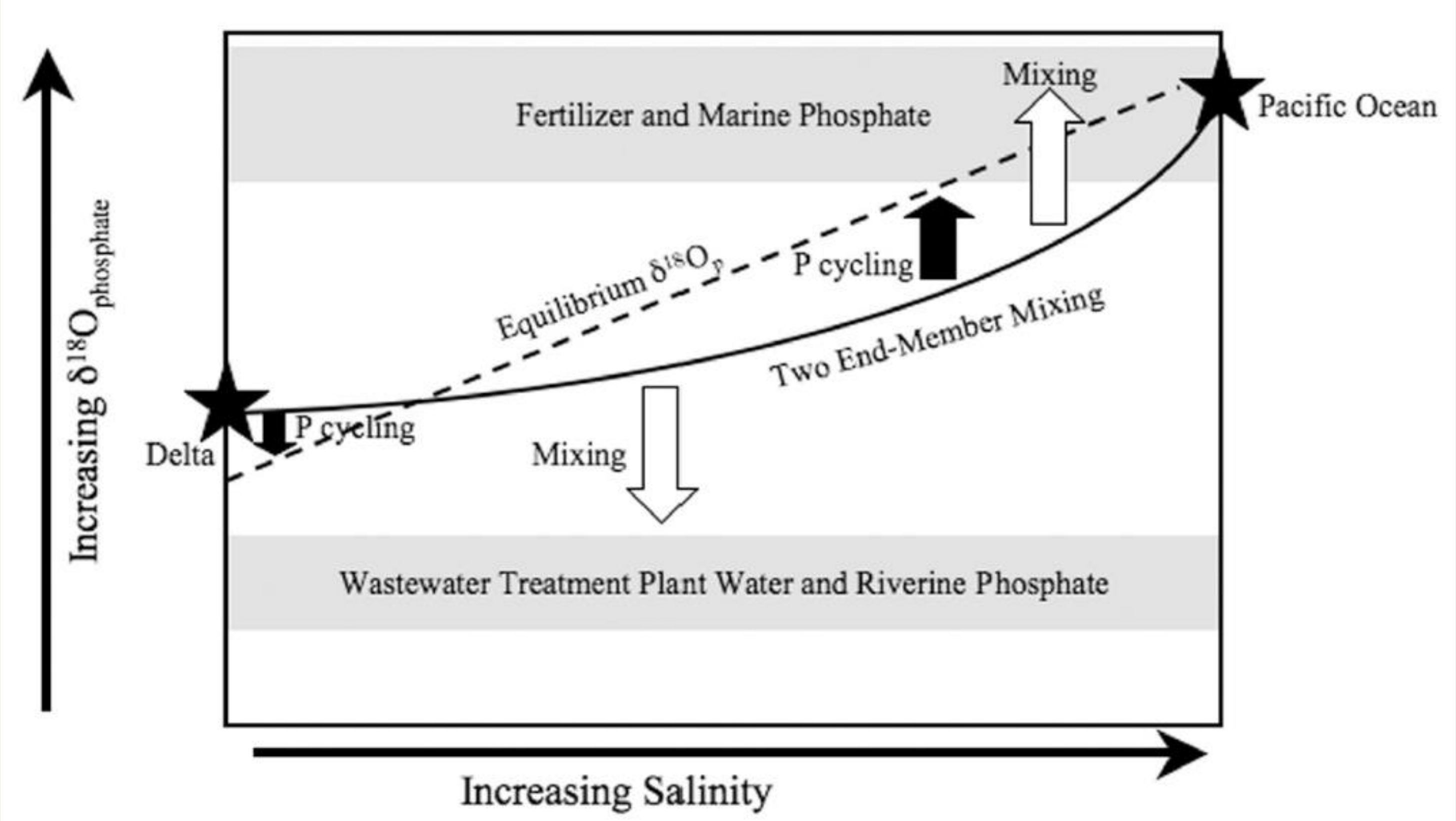
$$T\ (°C) = 111.4 - 4.3\ (\delta^{18}O_P - \delta^{18}O_w)$$

*where T is the water temperature and $\delta^{18}O_P$ and $\delta^{18}O_w$ are the oxygen isotopic composition of phosphate and water, respectively.

Introduction

Examples of application of $\delta^{18}O_{PO4}$

- Phosphate oxygen isotope ratios as a tracer for sources and cycling of phosphate in North San Francisco Bay, California

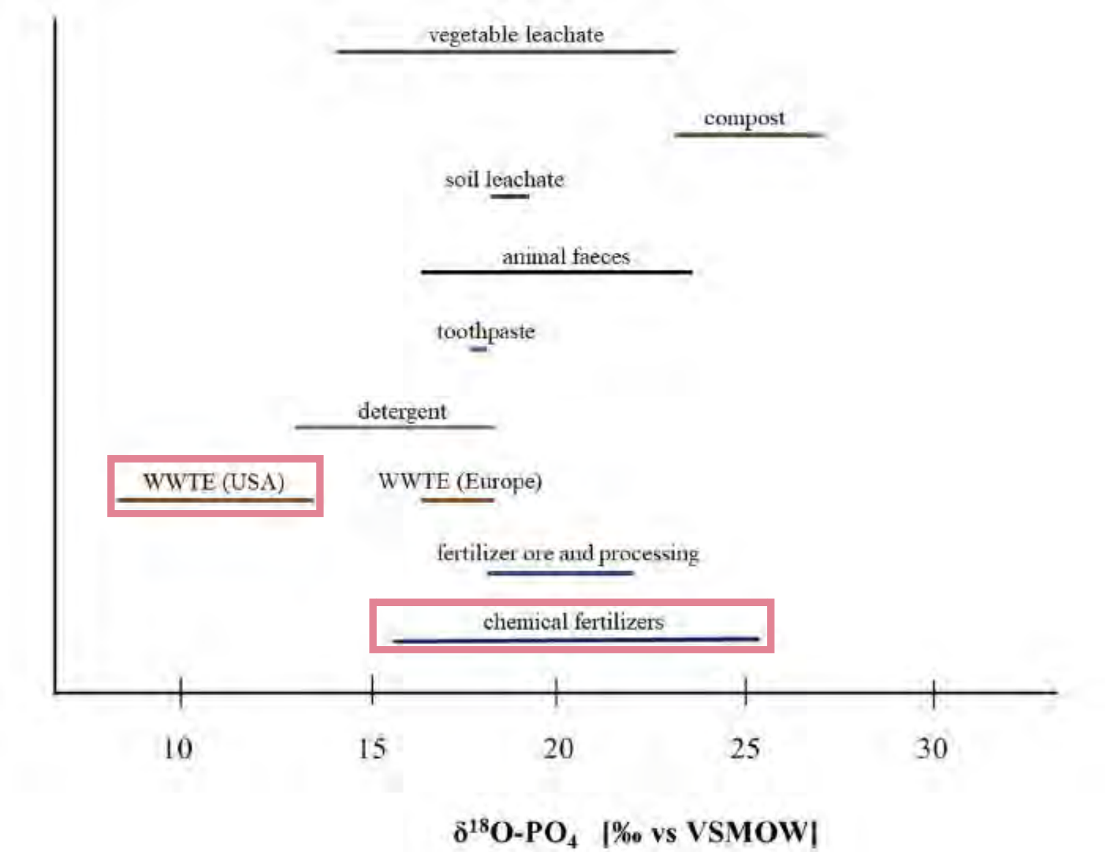


(McLaughlin et al., 2006)

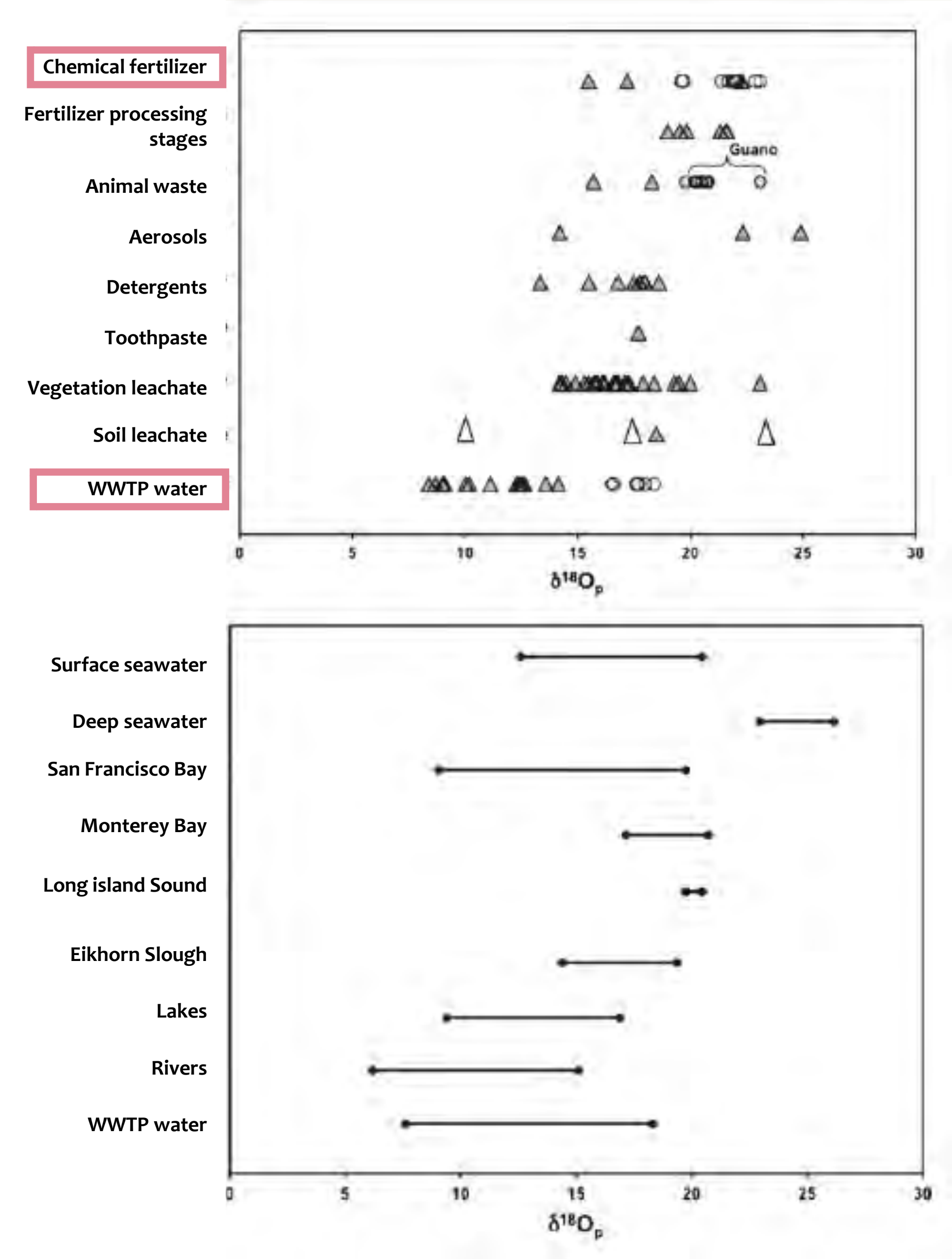
Introduction

Examples of application of $\delta^{18}O_{PO4}$

- The ranges for $\delta^{18}O_{PO4}$ values for potential phosphate sources in soil and aquatic systems



(Gebus-Czupyt and Wach, 2022)

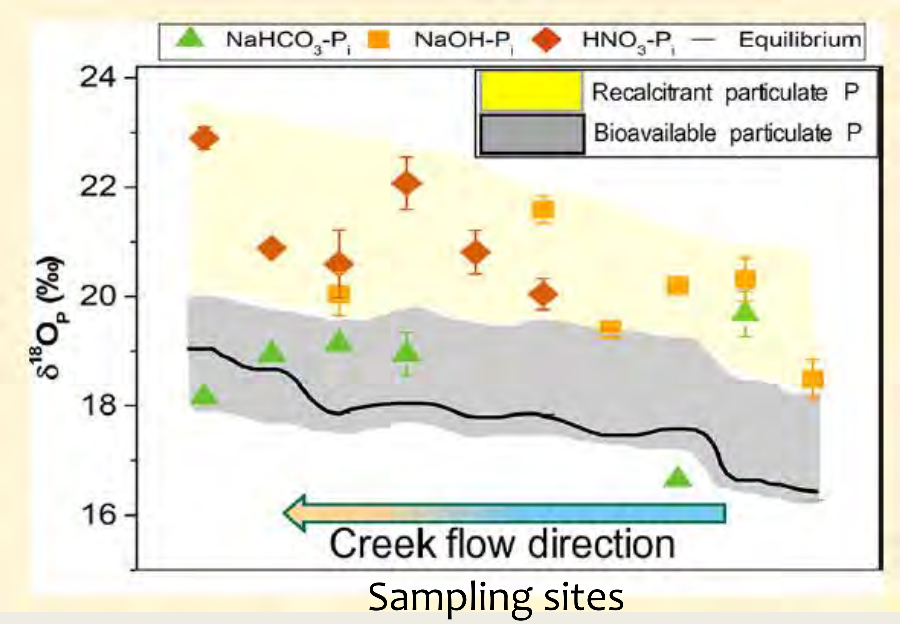


(Paytan and McLaughlin, 2011)

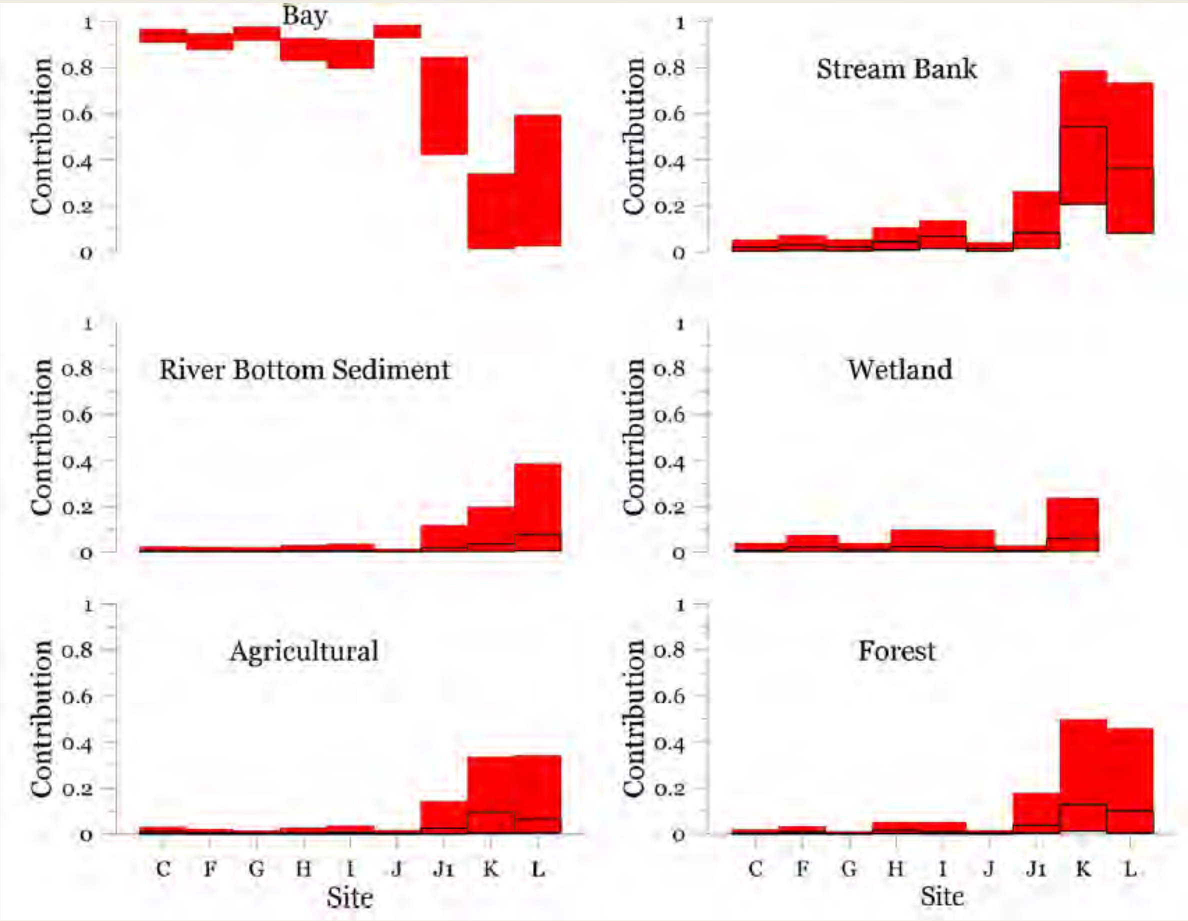
Introduction

Examples of application of $\delta^{18}O_{-PO_4}$

- Stable Isotopes and Bayesian Modeling Methods of Tracking Sources and Differentiating Bioavailable and Recalcitrant Phosphorus Pools in Suspended Particulate Matter



(Mingus et al., 2019)



(Mingus et al., 2019)

MATERIALS AND METHODS

IN AGRICULTURAL AREA, NC

This study

Applications of the oxygen isotope ratio of phosphate to identify phosphorus sources in agricultural areas

- **Purpose**: to determine seasonal changes in the source of P and the contributions of each primary source between pre/post-fertilization in agricultural areas

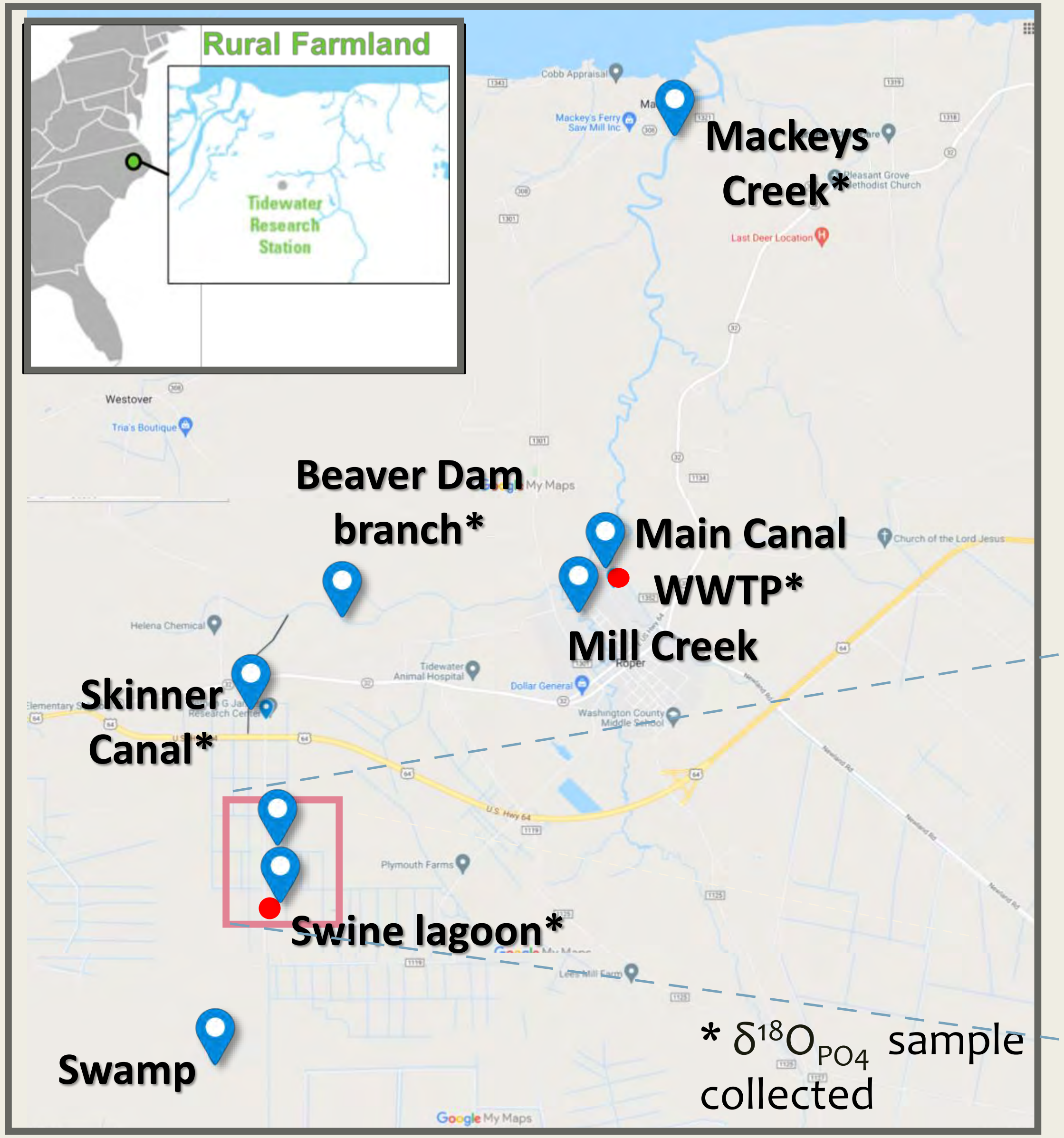
Tidewater Research Station (NC)

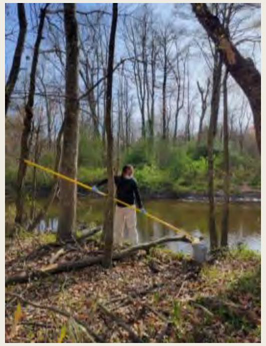
(https://steps-center.org/steps-news/)

- **Study site**: Tidewater Research Station, Plymouth, NC and surrounding area

- **Sampling campaign**:
  Jan 19th 2022 (preliminary)
  Mar 22nd 2022 (pre-fertilization)
  Jun 29th 2022 (post-fertilization)

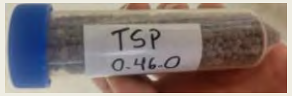
Study site



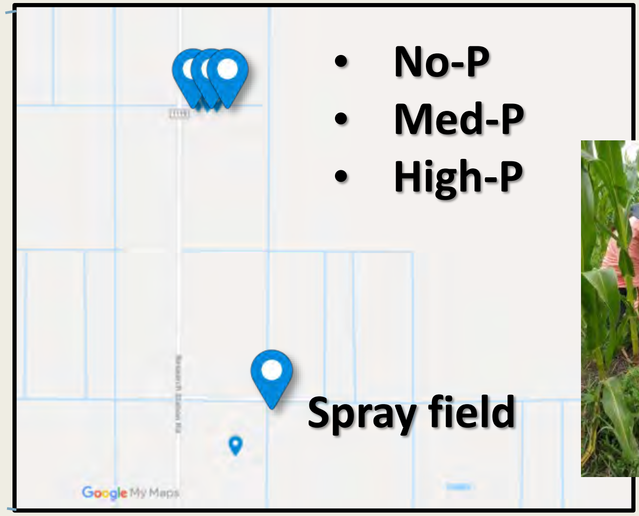


Water sampling

- Potential endmembers:
  - Swine lagoon liquid
  - Treated wastewater effluent (Roper WWTP)
  - Fertilizer



Soil/Plant sampling

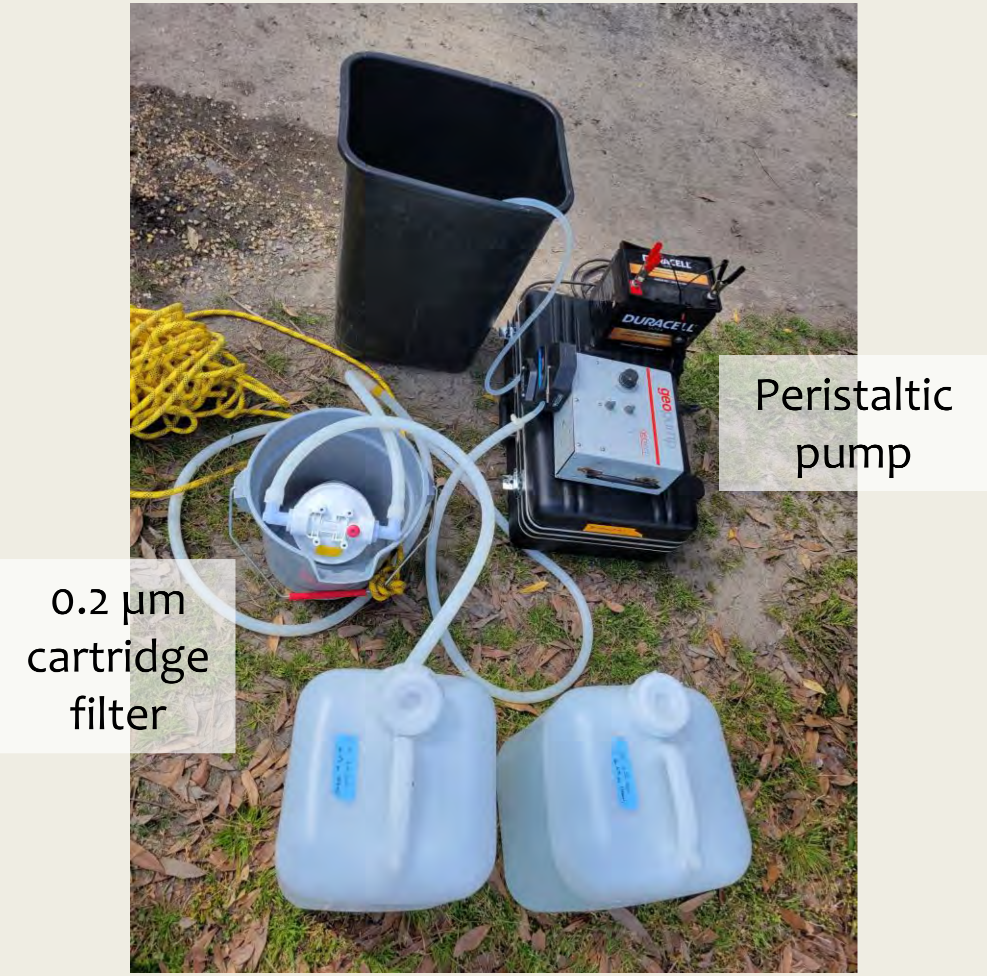


Materials and Methods (Water sample)

- Sample collection

  - Target to dissolved orthophosphate (P_i)

  - Filtration using a <u>0.2µm filter</u> (dissolved P)
  - Sample volume required from a few liters to more than 200L to sample a minimum of **15 µmol of P_i.**
  - Collect a parallel water sample for measurement $\delta^{18}O$ of water ($\delta^{18}O_w$)



Materials and Methods (Water sample)

- Magnesium-induced coprecipitation procedure (**MagIC method**) (Karl and Tien, 1992)

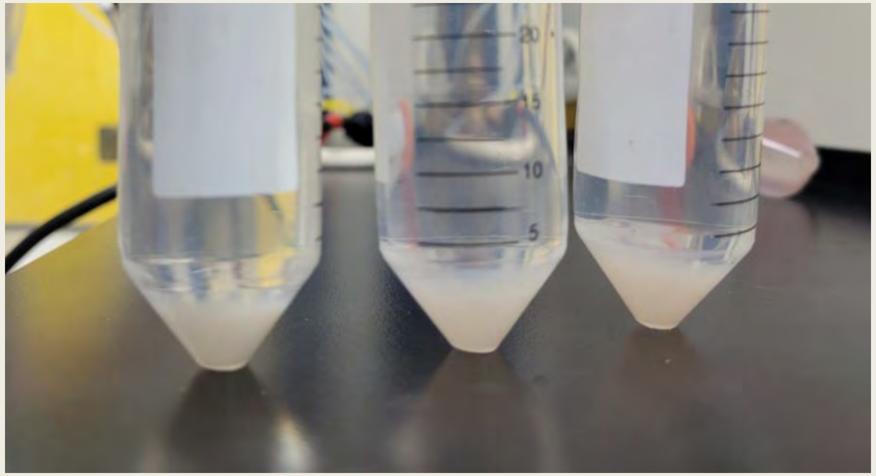
- MagIC procedure can quantitatively remove dissolve P_i by absorption onto $Mg(OH)_2$ (brucite).

  - Add **Mg**$(NO_3)_2$ to achieve 50-100 mM $[Mg^{2+}]$

  - Add Na**OH** (1M) to raise the pH

  => **$Mg(OH)_2$ (brucite)** will precipitate.

  - Centrifuge to get only pellets and check if there's P in the supernatant



- Dissolve the pellets by adding HNO_3 (1M)

✓ The additional MagIC process may be necessary for high organic materials.

Materials and Methods (Soil sample)

- Sample collection
  - For soil/fertilizer sample
    - Collected and freeze-dried (oven-dried)

- Sample extraction
  - Hedley extraction (Hedley et al., 1982; Tissen et al., 1984)
  - **P extraction from soil** (Tamburini et al., 2010 and 2018)
  - Sequential extraction from marine sediments (Ruttenberg et al., 2009)

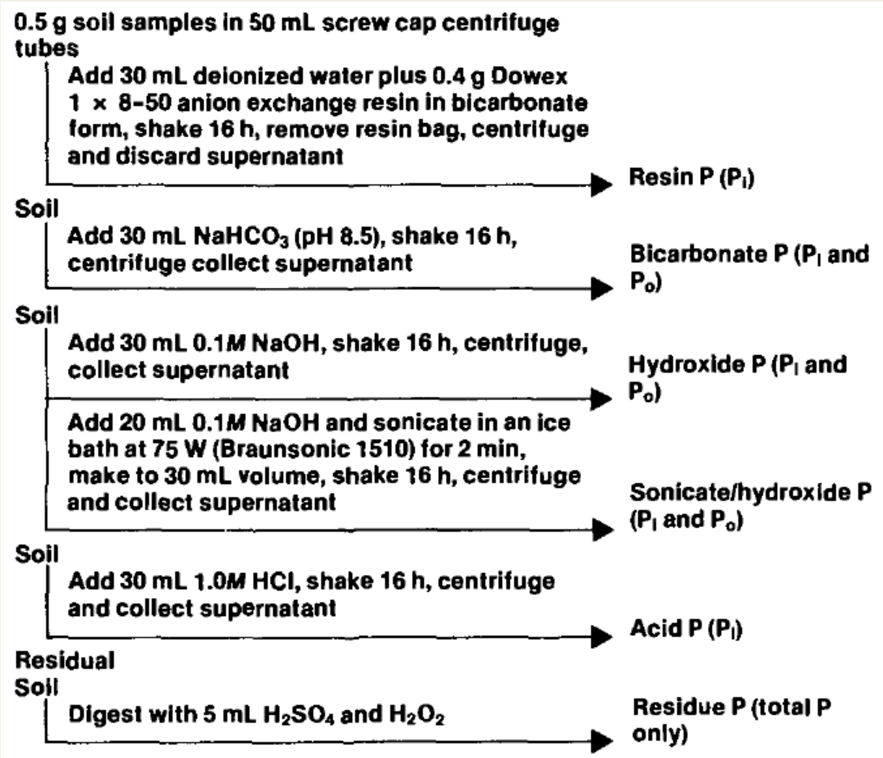


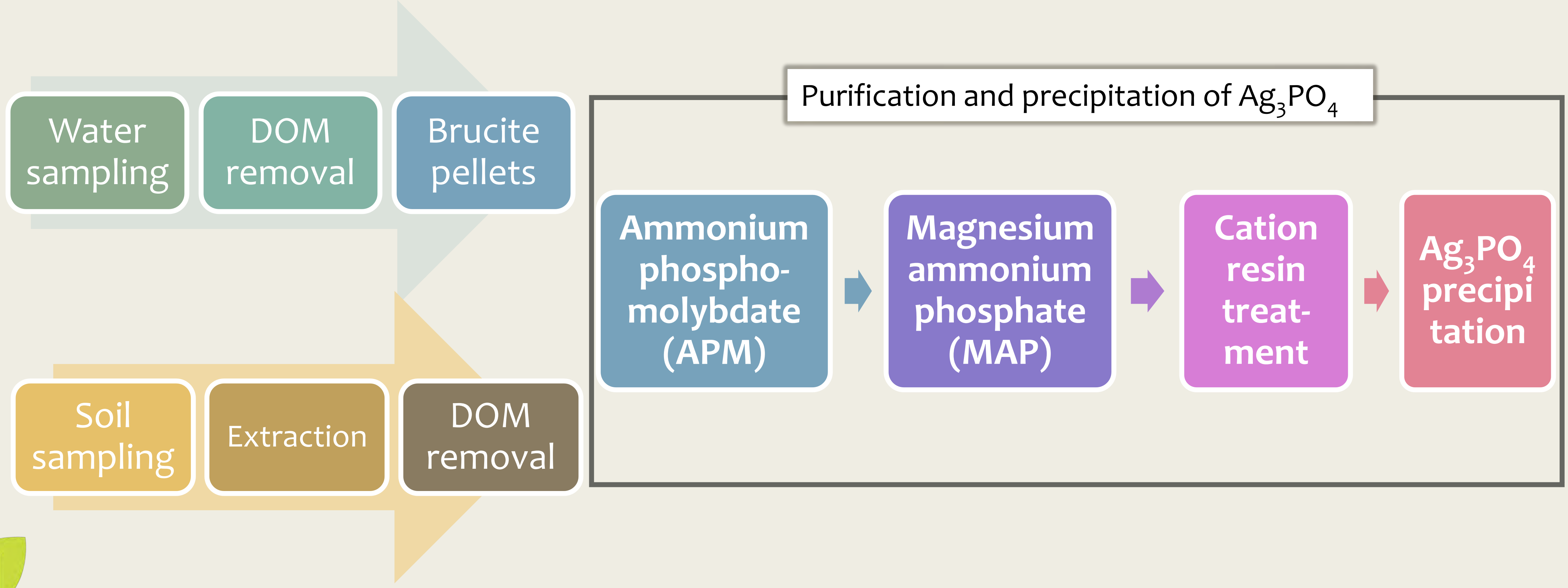
Fig. 1—Sequential extraction procedure for soil phosphorus.

(Tissen et al., 1984)

- DOM removal
  - using DAX-8 resin to trap organic compounds (Tamburini et al., 2010)

Materials and Methods

- Overview for the precipitation of Ag_3PO_4 (Jaisi and Blake (2010, 2014))



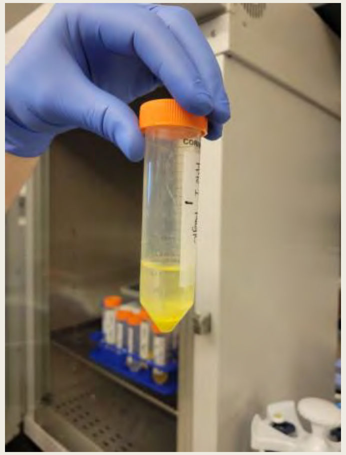
Materials and Methods

❑ Ammonium phospho-molybdate (APM)

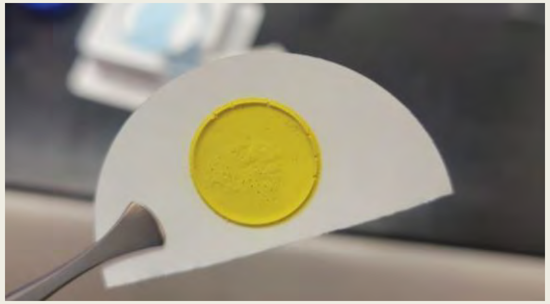
Precipitate at low pH => it remove ions and contaminants that are soluble at acidic condition.

- Add ammonium nitrate (NH_4NO_3)
- Add ammonium molybdate reagent

*Heat samples and reagent to increase the speed of the reaction



=> $(NH_4)_3PMo_{12}O_{40}$(APM) will precipitate (bright yellow)



- filter APM precipitates using a 0.1 µm filter

- dissolve precipitate using NH_4-citrate solution.

Materials and Methods

❑ Magnesium ammonium phosphate (MAP)

Precipitate at high pH => it remove ions and contaminants that are soluble at basic condition.

- Add Mg reagent
- Add 1:1 NH_4OH

$\Rightarrow$ $Mg(NH_4)_3PO_4$ (MAP) will precipitate (white)

- filter MAP precipitates using a 0.1 µm filter

- dissolve precipitate using 2M HNO_3

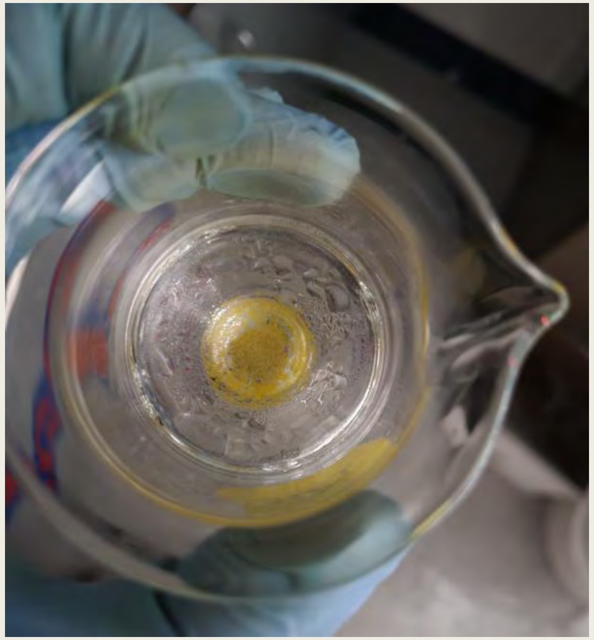
Materials and Methods

- **Cation resin exchange**

To remove cations (e.g., Mg, Na, and NH_4^+)

- Set up cation resin column
- Pass phosphate solution and collect in a glass beaker
- Evaporate the excess water in the water bath

Materials and Methods



❑ **Silver phosphate precipitation**

- Add silver amine solution
- Add 1:1 NH_4OH

*do this in a dark place (light-sensitive!!)

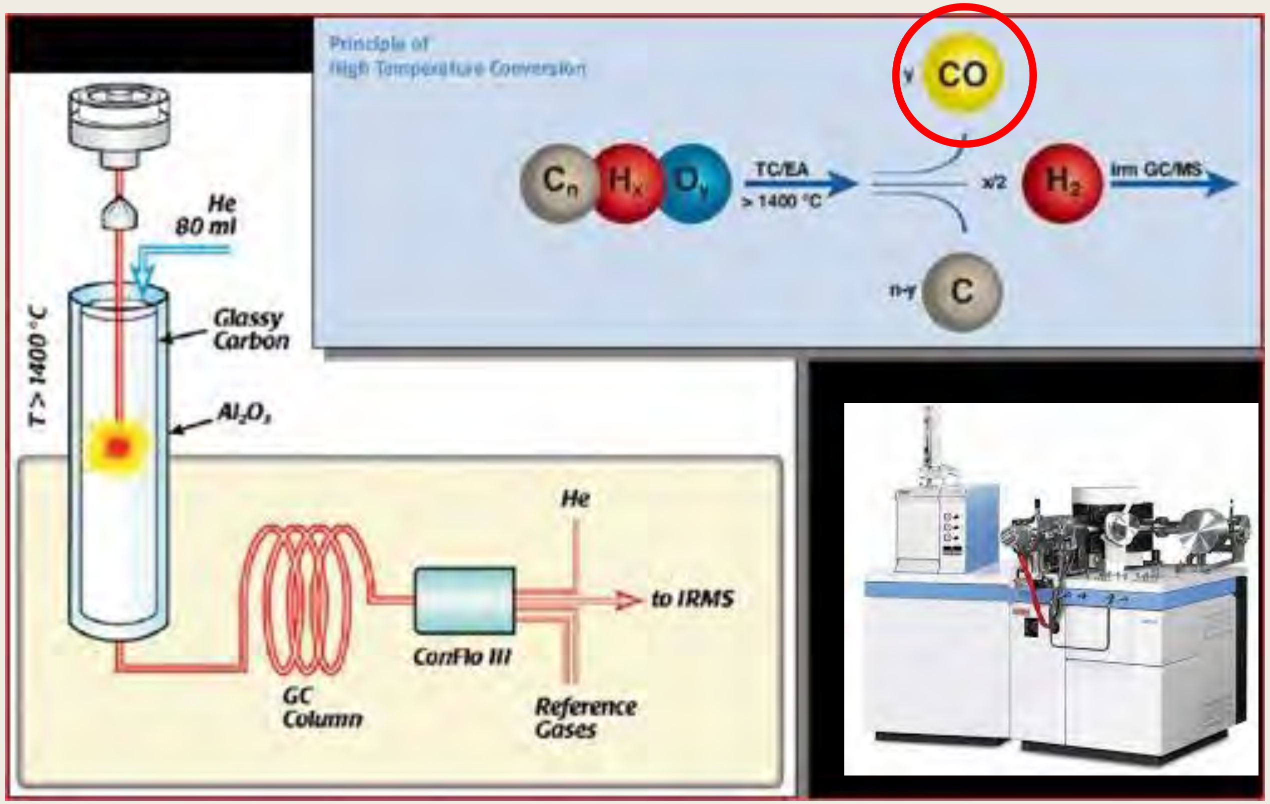
$\Rightarrow$ Ag_3PO_4 will precipitate (yellow-green)

- filter Ag_3PO_4 precipitates using 0.1 μm filter
- dry at 110°C in the oven overnight
- pack in the silver capsule for TC/EA-IRMS

Materials and Methods

❑ Analytical equipment:

Thermal conversion/elemental analyzer isotope ratio mass spectrometry (TC/EA –IRMS)



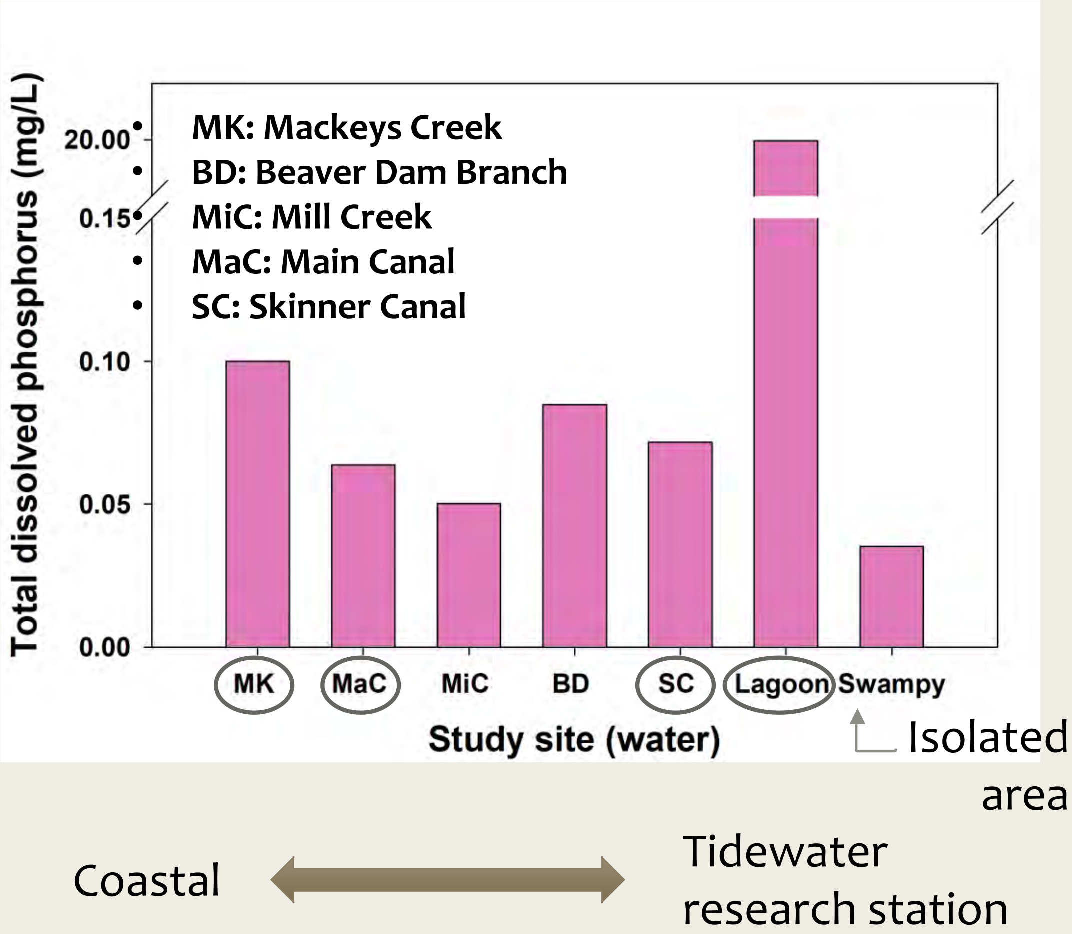
TC/EA –IRMS

PRELIMINARY RESULTS AND PLAN

IN AGRICULTURAL AREA, NC

Preliminary result and plan

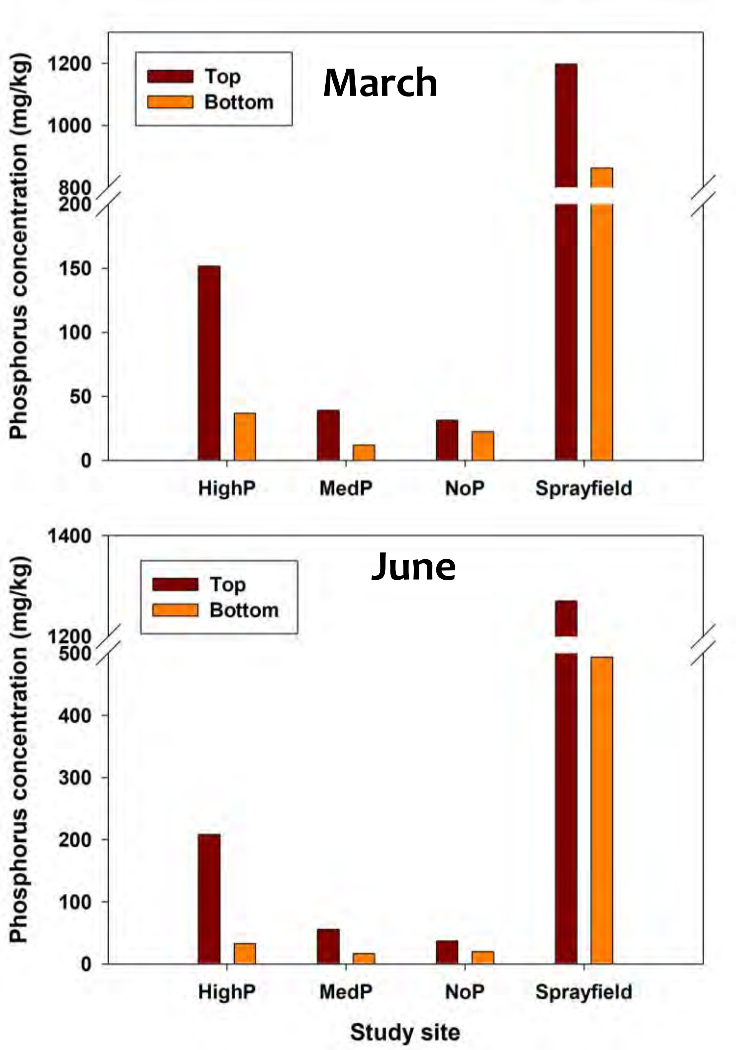
❖ Phosphorus data for water samples in March (Pre-fertilization)



- The concentrations of nutrients (total phosphorus, total dissolved phosphorus, nitrate, ammonium, and total Kjeldahl nitrogen) and organic matter were measured for water.
- It seems that there are more than two sources in this area.
- $\delta^{18}O_{PO4}$ values along with nutrients in water will be applied to identify the P sources and their contributions in each site.

Preliminary result and plan

❖ Phosphorus data from soil

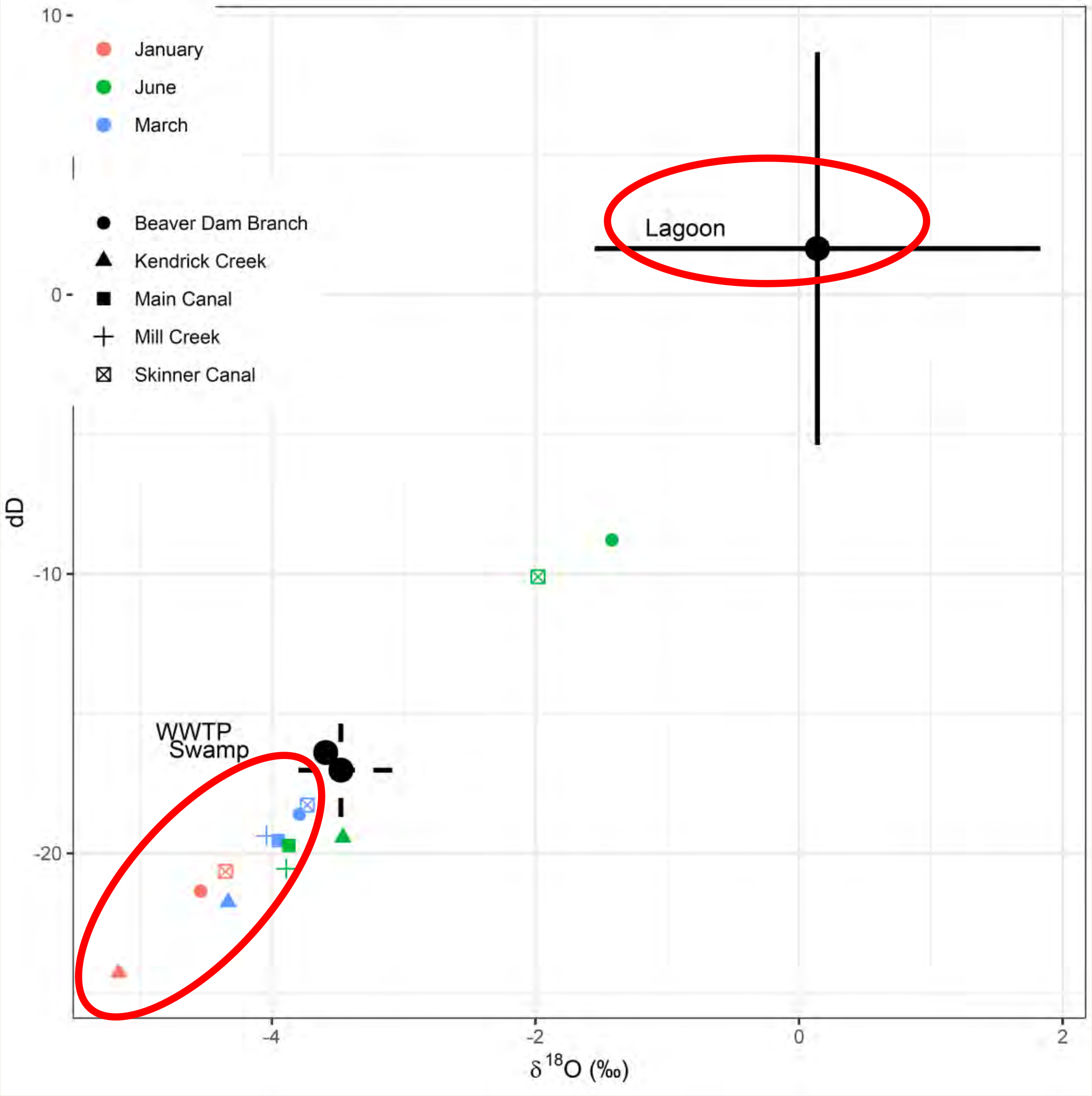


- Phosphorus fertilization long-term trial field (soil from 0-6 inch and 6-12 inch depth and plant) (from Luke Gatiboni)
  - High P fertilization
  - Mid P fertilization
  - No P fertilization
- Spray field where lagoon liquid is sprayed as fertilizer (soil from 0-6 inch and 6-12 inch depth and plant)
- High P concentration was observed in the sprayfield.
- $\delta^{18}O_{PO4}$ values in soil and plant will be applied to determine P cycling in soil and plant system and P transport from land to watershed area.

Preliminary result and plan

❖ Multiple stable isotopes

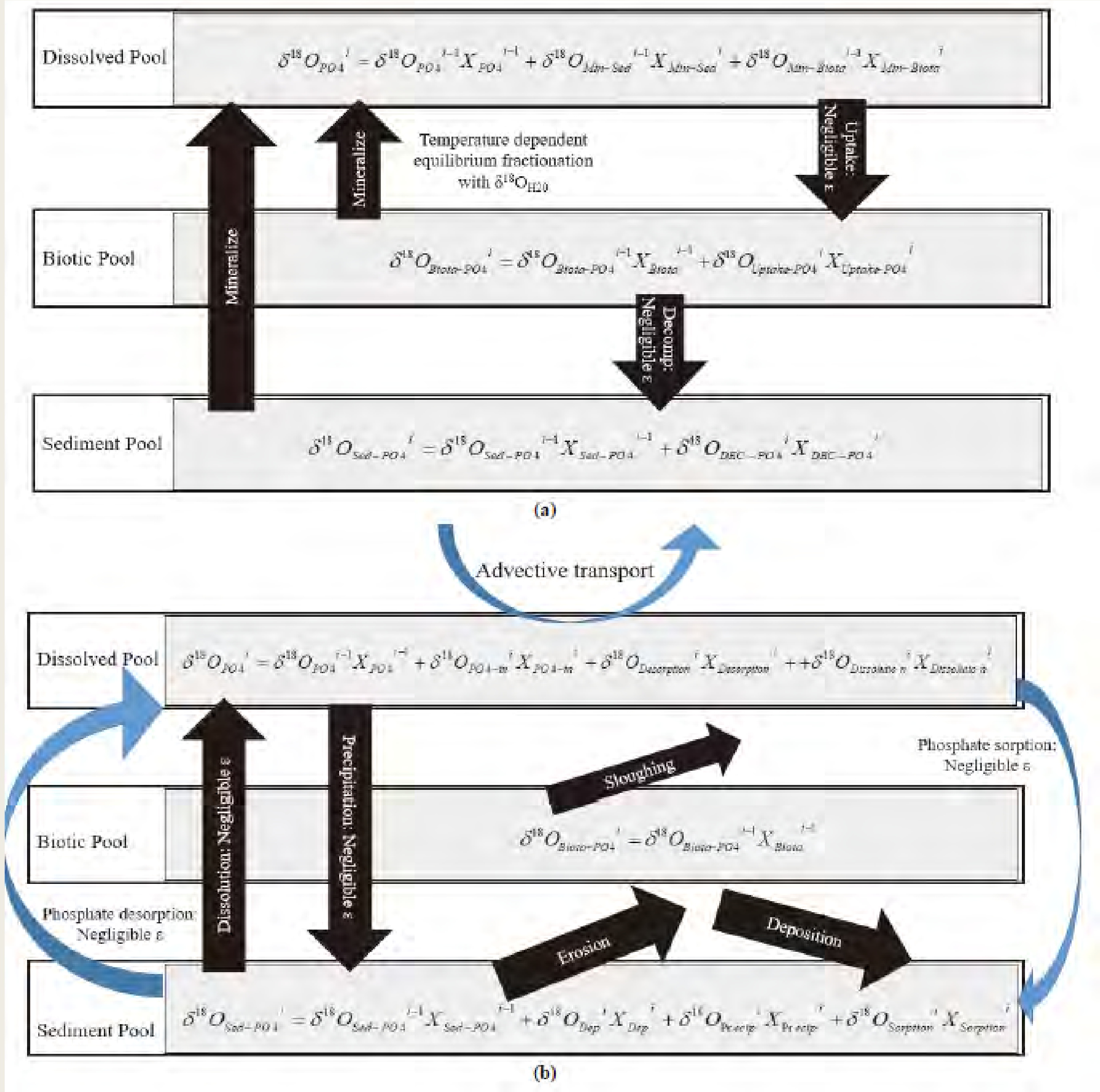
- The stable isotope values of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) of particulate organic matter, as well as deuterium (δD) and oxygen ($\delta^{18}O$) isotopes of water were also collected.
- Multiple stable isotopes may be useful to discriminate the source of P in complex systems, especially if there are overlapping signatures in $\delta^{18}O_{PO4}$
- A multiple-stable isotope framework could be used to assist with model calibration.



NEXT STEP

Next step

- Analyzing $\delta^{18}O_{PO4}$ samples
- Linking up isotope data with modeling for simulating P flows (hydrologic fluxes) and cycling mechanisms
- Advancing model for evaluation of P sources and fluxes and developing P flow diagrams



(Jensen et al., 2018)

Acknowledgments

- Deb Jaisi and Spencer Moller at University of Delaware
- Tamburini Federica at ETH Zurich
- Andrea Watzinger at University of Natural Resources and Life Sciences, Vienna
- Jason Curtis at University of Florida
- Luke Gatiboni at North Carolina State University
- Amanda Chappel at University of Florida
- Fausto Rodriguez, Raven McLaurin, and Smitom Swapna Borah at North Carolina State University

THANK YOU!

Enrichment of Groundwater Chemical Composition Data for Convergence Informatics

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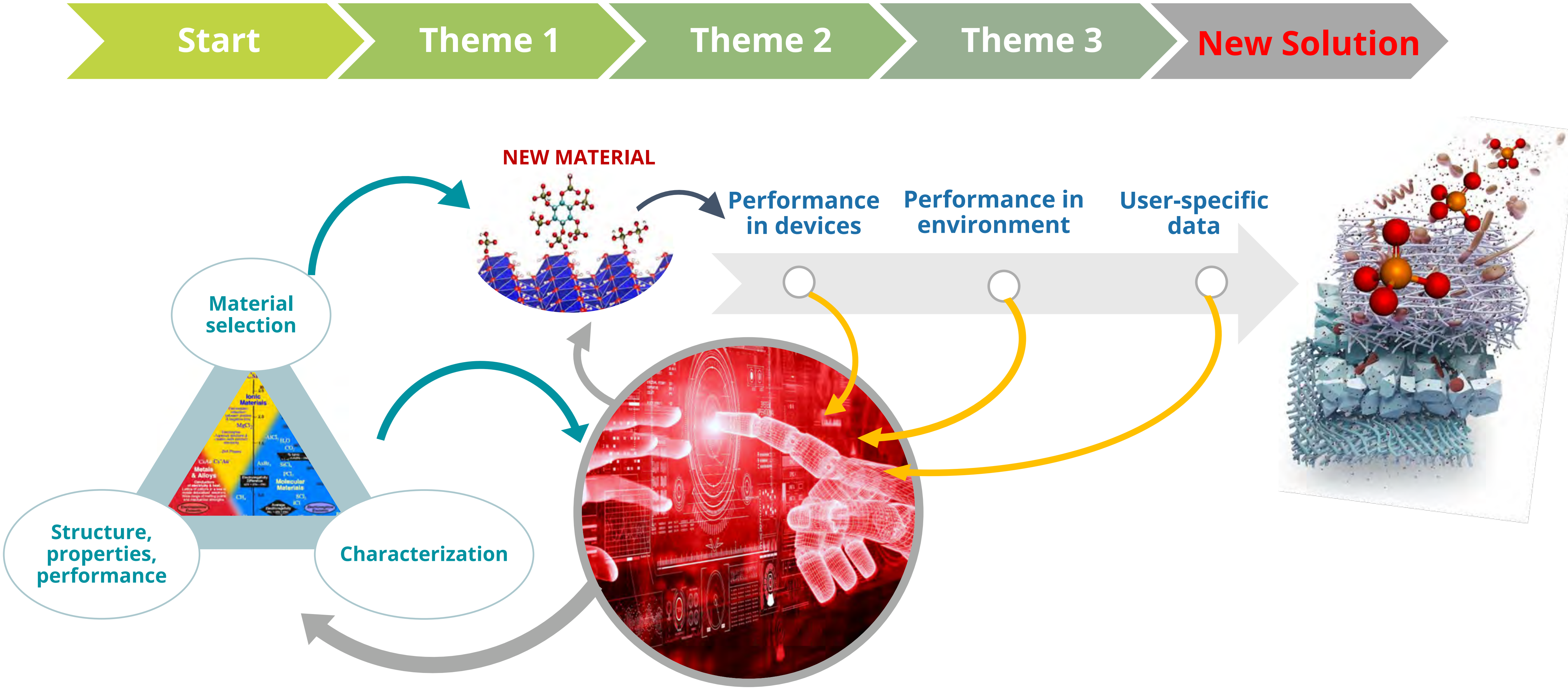
***Postdoctoral Researcher at Yingling lab,**
Materials Science and Engineering, NC State

Sustainable Phosphorus Summit
11/04/22

NC STATE

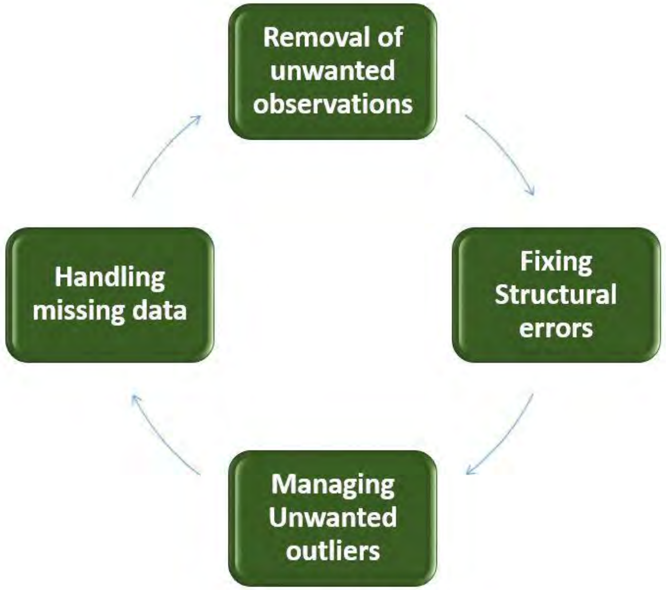
Convergence Informatics



Convergence Research enabled by Artificial Intelligence

Possible issues with your data

1. The data may be of **unknown structure** that may need to be altered, modified
2. The data may contain **outliers or errors** that may need to be removed or replaced
3. The data can be simply **noisy**
4. There may be the values/datapoint simply **missed** by any reason



- Data cleaning is the process of removing irrelevant data, errors, and inconsistencies that could skew your results.
- The data cleaning process includes removing empty cells or rows, removing blank spaces, correcting misspelled words, or reformatting things like dates, addresses, and phone numbers, so they are all consistent.

Orig.dataset

Row	Par1	Par2	Par3
1	Val	Val	?
2	Val	?	Val
3	Val	Val	Val
4	Val	?	Val

Solution - **Data imputation**

Imputation is the process of replacing missing values with substitutional data using various methods.

Typically, is considered as a preprocessing step

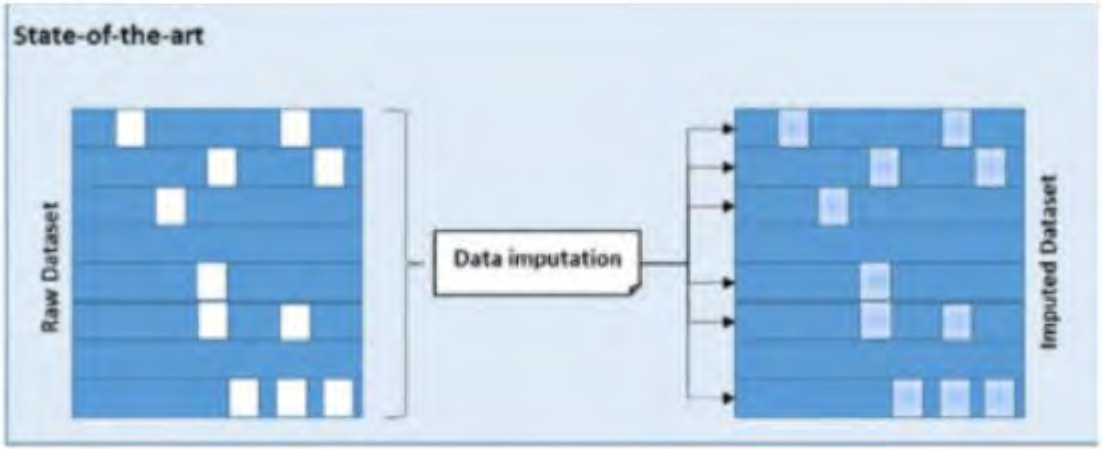
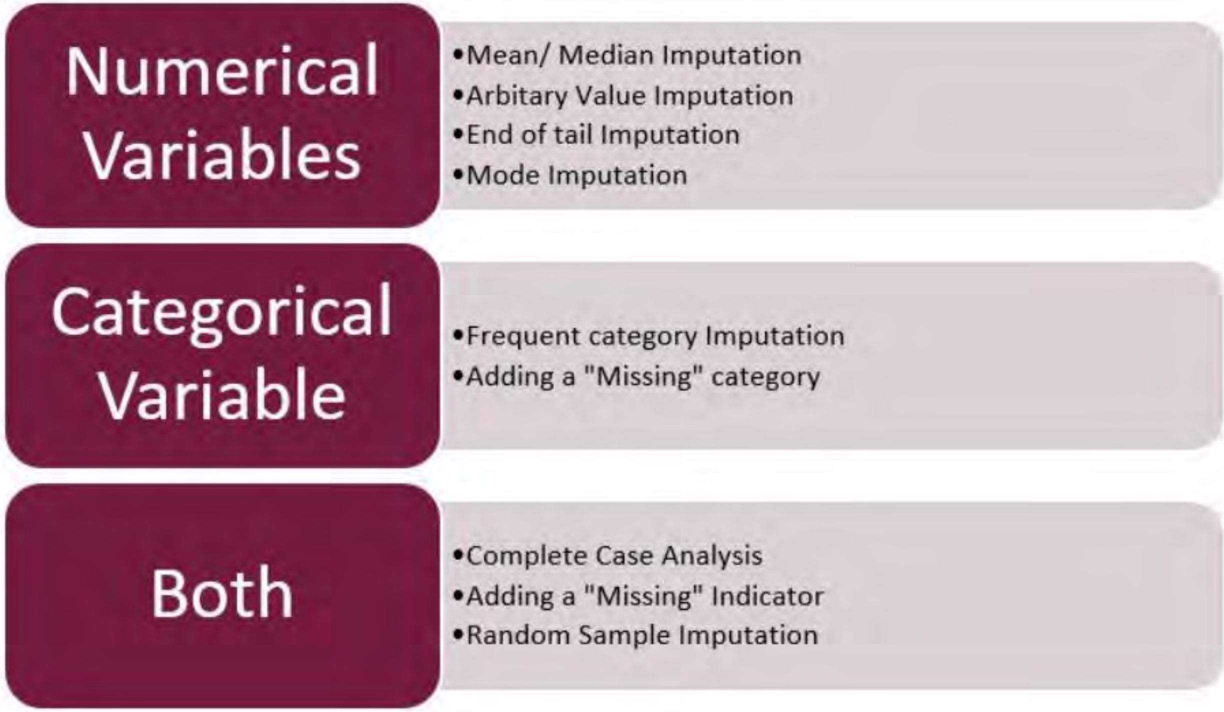


Figure 1: Data imputation, taken from DBSCAN



Origin: AnalyticsVidia

Data imputation methods

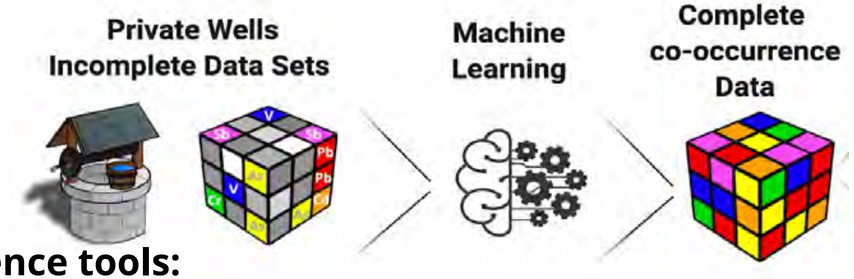
Method	Description	Pros	Cons
Listwise deletion	• Get rid of all the rows where at least one column is missing	• Easy and straightforward	• Most rows get deleted • Biases the outcome of predictions (Ginkel2020, Rubin1996)
Central value imputation	• Fill up the missing rows with mean/median of available values on each column	• Keeps the central values of the distribution unchanged	• Yields highly overconfident results in subsequent analyses
Single value imputation	• Train a linear/K-NN/RF/SVM/kriging regression to predict the missing values from all other available values. • Fill one missing column first, then iterate for all others missing columns, repeat many times.	• Use of information already present in the dataset • Incorporation of aleatoric uncertainty (due to randomness)	• Analysis models don't know the difference between the observed values and the imputed values. • Overconfident predictions. (Buuren2018)
Multiple imputations	• Do single value imputation multiple (*m*) times (Honaker2011) $\bar{q} = \frac{1}{m}\sum_{j=1}^{m} q_j.$ $SE(q)^2 = \frac{1}{m}\sum_{j=1}^{m} SE(q_j)^2 + S_q^2(1+1/m).$	• Incorporation of epistemic uncertainty (due to missing information)	• Later analyses must be done over all imputed datasets, then pooled together. • We will need ANN when the dataset is so large as ours (Lall and Robinson 2021) • Can be *really* slow if not trained with GPUs

Practical situation: research project

NC STATE UNIVERSITY

Arizona State University

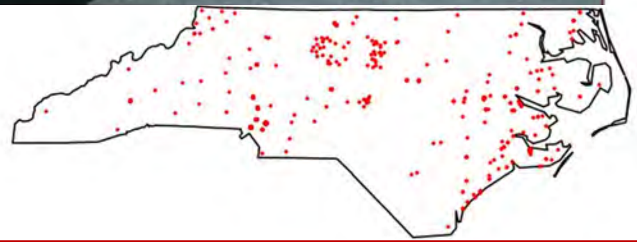
GOAL: Use machine learning tools to predict phosphorus distribution and chemical concentrations in groundwater



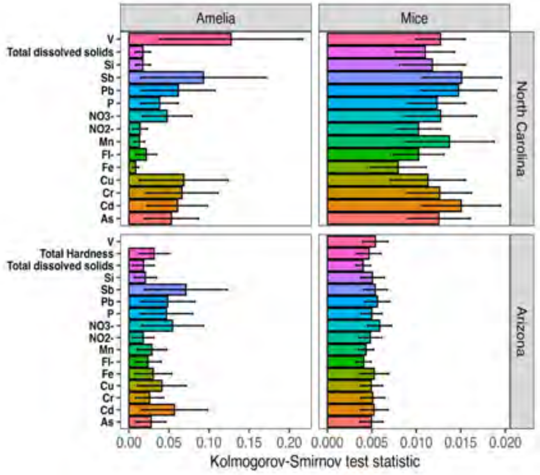
MACHINE LEARNING for COMPLETE WATER QUALITY

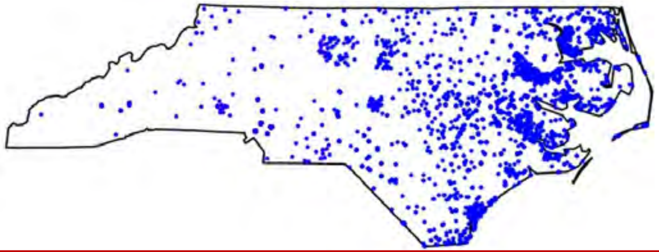
Artificial Intelligence tools:

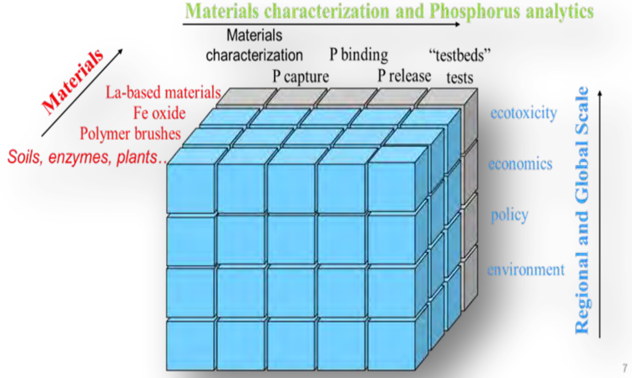
Traditional groundwater data collection



Data imputation







Fill missing data

1. Dataset analysis

<u>Preliminary analysis</u>:

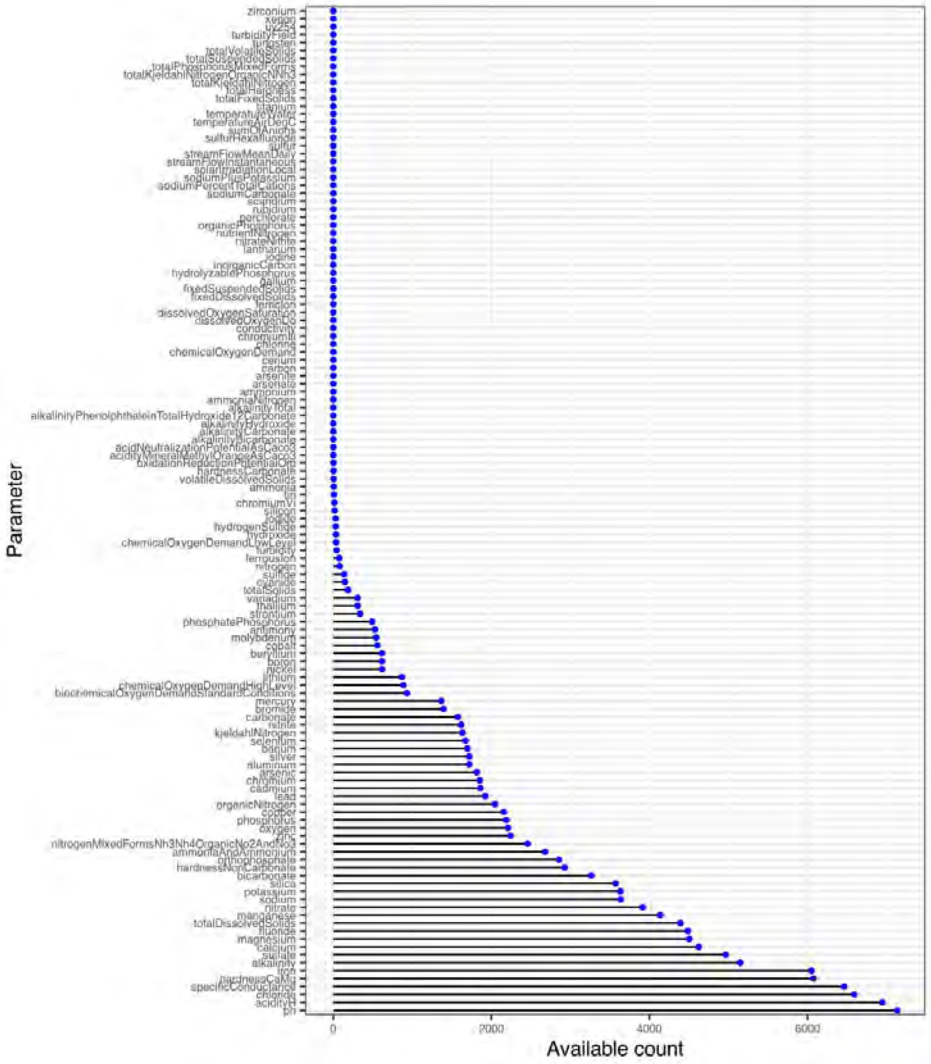
- Worked with the smaller chunk of data
- Picked AZ and NC data as a sampler
- Performed the visualization of the dataset
- <u>Identified possible directions of data wrangling</u>

	date	latitude	longitude	sampleid	monitoringloca	TestTime	ph	iron	calcium	magnesiu	fluoride	TDS	nitrate	ma
2	8/29/2012	33.8466333	-77.9659972	USGS-335048077575801_2012-08-	USGS-335048077575801	16:16	7.10000001	136	186000	276000	0.071427444	4940.009112	94.28571078	850
3	8/23/2000	33.8779526	-78.0044336	USGS-335140078001701_2000-08-	USGS-335140078001701	7:26	6.65000001	270	96000	30000	0.33000001	556.3338683	44.39285715	71.
4	12/19/2012	33.86129167	-77.9938972	USGS-335141077593801_2012-12-	USGS-335141077593801	16:15	7.10000001	6.20000001	75200	14500	0.37000001	243.5004488	257.9285714	
5	12/19/2012	33.8621	-77.9939444	USGS-335144077593801_2012-12-	USGS-335144077593801	7:23	7.40000001	2450	91300	20800	0.28000001	312.0002765	84.57142858	
6	4/10/1975	33.94140278	-78.19895	USGS-335229078115402_1975-04-	USGS-335229078115402	16:17	9.10000001	25.00000001	140000	90000	0.40000001	6250.01156	210.0601279	
7	4/28/1980	33.94140278	-78.19895	USGS-335229078115402_1980-04-	USGS-335229078115402	7:22	6.60000001	1900	240000	94000	0.50000001	7966.674011	132.92858	
8	8/1/2000	33.88495	-78.5083528	USGS-335306078303001_2000-08-	USGS-335306078303001	16:15	7.00000001	145	74000	4300	0.05000001	179.6668344	1592.142857	43.
9	8/1/2000	33.8856083	-78.5296472	USGS-335308078314701_2000-08-	USGS-335308078314701	7:27	7.30000001	1500	91000	3300	0.05000001	157.6668661	44.39285715	50.
10	5/3/1960	33.8890611	-78.5664	USGS-335320078340001_1960-05-	USGS-335320078340001	16:50	7.90000001	200	22000	22000	0.10000001	115.66678	1.00E-08	
11	4/10/1975	33.89286667	-78.5892611	USGS-335334078352101_1975-04-	USGS-335334078352101	7:24	8.70000001	25.00000001	15000	24000	0.50000001	3175.005875	110.7142875	25.
12	1/28/1988	33.89286667	-78.5892611	USGS-335334078352101_1988-01-	USGS-335334078352101	16:16	9.00000001	160	3500	21350	1.11000001	4340.003989	110.7142984	20.
13	5/12/1975	33.89305556	-78.5890278	USGS-335334078352102_1975-05-	USGS-335334078352102	7:45	9.30000001	25.00000001	2200	1700	2.80000001	740.0013668	695.6426649	25.
14	5/16/1973	33.89286667	-78.5892611	USGS-335334078352103_1973-05-	USGS-335334078352103	16:05	8.40000001	1300	5500	3600	2.766484791	740.0013668	94.2857112	25.
15	5/24/1973	33.89286667	-78.5892611	USGS-335334078352104_1973-05-	USGS-335334078352104	6:04	8.40000001	200	7800	6600	0.8030156	850.0015708	304.9738081	40.
16	4/10/1975	33.89286667	-78.5892611	USGS-335334078352105_1975-04-	USGS-335334078352105	16:18	9.60000001	270.4248574	9836.289143	2055.569264	0.689496351	8510.991013	88.53571108	9.9
17	1/28/1988	33.89286667	-78.5892611	USGS-335334078352105_1988-01-	USGS-335334078352105	7:34	9.50000001	190	5100	9995	0.305955903	2883.335935	110.7142873	20.
18	8/31/2010	33.89277778	-78.5891667	USGS-335334078352106_2010-08-	USGS-335334078352106	12:22	7.749779459	321.7388922	43099.30338	10079.76611	0.405598595	426.3758111	221.4297971	60.
19	9/15/2011	33.89277778	-78.5891667	USGS-335334078352106_2011-09-	USGS-335334078352106	7:21	6.501444818	230.9798744	59258.01989	10465.16374	0.092114587	188.0872495	26.74219963	19.
20	9/12/2012	33.89277778	-78.5891667	USGS-335334078352106_2012-09-	USGS-335334078352106	16:14	5.40000001	4574.412138	16906.80925	2757.134759	0.401465654	175.6312335	78.66044789	54.
21	9/11/2013	33.89277778	-78.5891667	USGS-335334078352106_2013-09-	USGS-335334078352106	7:19	5.20000001	686.7261167	9592.003208	3371.502045	0.091790346	89.66675918	22.14285739	194
22	9/12/2014	33.89305556	-78.5886111	USGS-335335078351901_2014-09-	USGS-335335078351901	16:20	7.20000001	600.1991597	32917.0823	2048.942167	0.053747988	94.15554135	44.37030567	37.
23	9/10/2015	33.89305556	-78.5886111	USGS-335335078351901_2015-09-	USGS-335335078351901	7:23	7.10000001	3021.972232	13992.74645	782.0737965	0.047273381	83.66675087	44.39285771	252
24	9/12/2016	33.89305556	-78.5886111	USGS-335335078351901_2016-09-	USGS-335335078351901	17:43	6.90000001	70364.62929	31949.82247	1802.899653	0.081014048	59.66672672	110.559511	59.
25	9/20/2017	33.89305556	-78.5886111	USGS-335335078351901_2017-09-	USGS-335335078351901	7:25	7.00000001	108264.1999	67616.68483	6847.723854	0.051770194	244.8468271	0.142630984	408
26	9/5/2018	33.89305556	-78.5886111	USGS-335335078351901_2018-09-	USGS-335335078351901	7:20	6.30000001	49.82898418	117771.4481	23567.33018	0.095819071	209.4062301	265.7142982	49.
27	4/24/2019	33.89305556	-78.5886111	USGS-335335078351901_2019-04-	USGS-335335078351901	12:04	6.00000001	12908.53193	39998.81018	2404.42632	0.052327958	90.33341897	1.00E-08	27.
28	9/24/2019	33.89305556	-78.5886111	USGS-335335078351901_2019-09-	USGS-335335078351901	7:22	5.70000001	111.3510233	40098.48026	5305.287722	1.00E-08	36.00000643	81345.18617	109

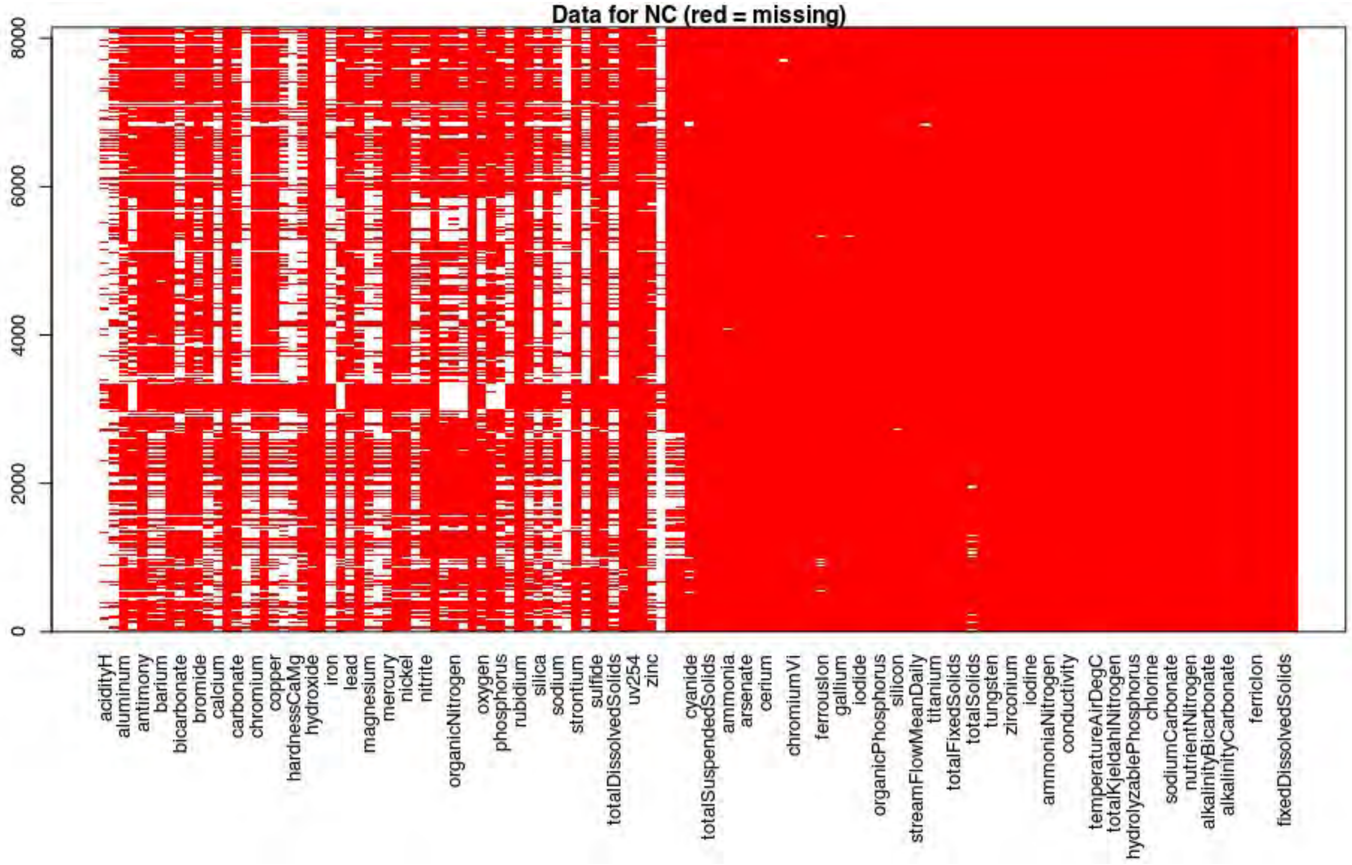
NC_AMELIA

Dataset structure

NC data - Available datapoints



Missing datapoints "heatmap"



Data Matrix: data wrangling steps

Matrix with gaps
Data not provided

Fingerprint	As	Fe	V	pH
1	10		56	6
2	5	24		7
3	4	30		7.2
4		4	2	7
5	2.5			6.2
6	6	2		7.1
7	1			6
8		3		5
9	14	10	4	3
10	2	1		
count	8	7	3	9
percent	80%	70%	30%	90%

Matrix of ≥70% parameter cutoff

Fingerprint	As	Fe	pH
2	5	24	7
3	4	30	7.2
6	6	2	7.1
9	14	10	3
count	8	7	9
percent	80%	70%	90%

Full matrix of ≥ 70% parameter cutoff

Fingerprint	As	Fe	pH
2	5	24	7
3	4	30	7.2
6	6	2	7.1
9	14	10	3
count	4	4	4
percent	100%	100%	100%

Our approach: Multiple Imputations

Method	Description	Pros	Cons
Listwise deletion	• Get rid of all the rows where at least one column is missing	• Easy and straightforward	• Most rows get deleted • Biases the outcome of predictions (Ginkel2020, Rubin1996)
Central value imputation	• Fill up the missing rows with mean/median of available values on each column	• Keeps the central values of the distribution unchanged	• Yields highly overconfident results in subsequent analyses
Single value imputation	• Train a linear/K-NN/RF/SVM/kriging regression to predict the missing values from all other available values. • Fill one missing column first, then iterate for all others missing columns, repeat many times.	• Use of information already present in the dataset • Incorporation of aleatoric uncertainty (due to randomness)	• Analysis models don't know the difference between the observed values and the imputed values. • Overconfident predictions. (Buuren2018)
Multiple imputations	• Do single value imputation multiple (*m*) times (Honaker2011) $\bar{q} = \frac{1}{m}\sum_{j=1}^{m} q_j.$ $SE(q)^2 = \frac{1}{m}\sum_{j=1}^{m} SE(q_j)^2 + S_q^2(1 + 1/m).$	• Incorporation of epistemic uncertainty (due to missing information)	• Later analyses must be done over all imputed datasets, then pooled together. • We will need ANN when the dataset is so large as ours (Lall and Robinson 2021) • Can be *really* slow if not trained with GPUs

2. Data imputation

The approach:

- Complete the dataset by adding missing values using various data imputation methods
- Verify the accuracy of data imputation process
- Compare data imputation methods performance

Used methods:

Amelia:

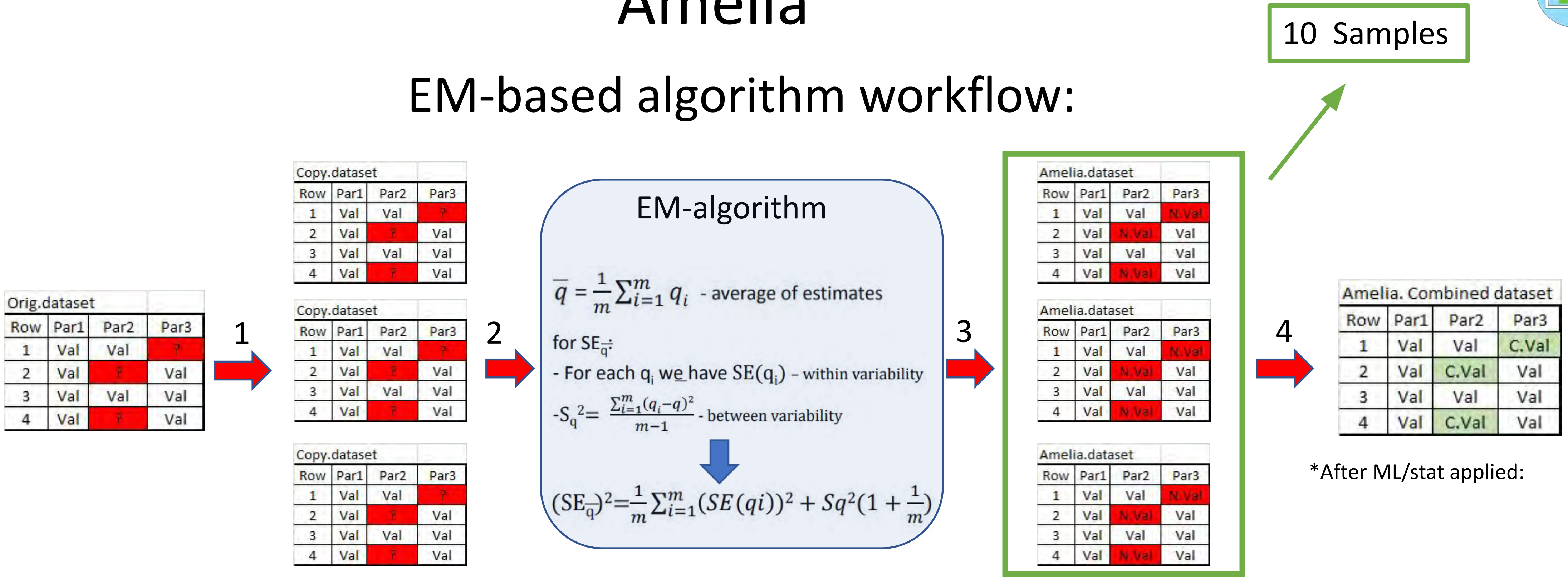
- GPR-based algorithm
- (+) multiple imputations at high speed
- (+) consistent
- (-) may underperform on big datasets
- (-) data-prep demanding (normal distribution)

MICE:

- Chained equation (CE) algorithm
- (+) consistency, accuracy
- (+) well-known and developed
- (-) slower

Amelia

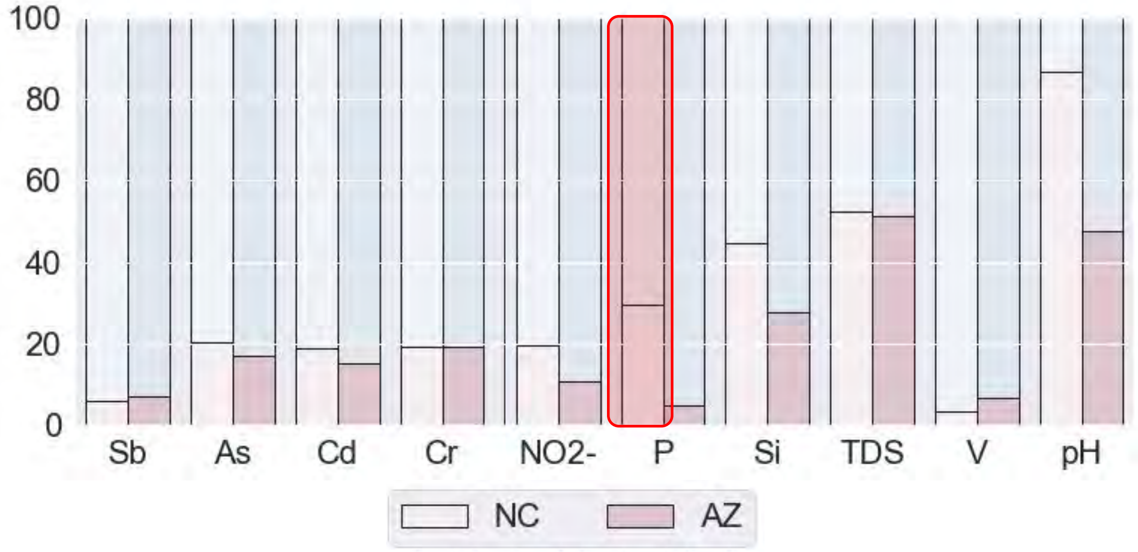
EM-based algorithm workflow:



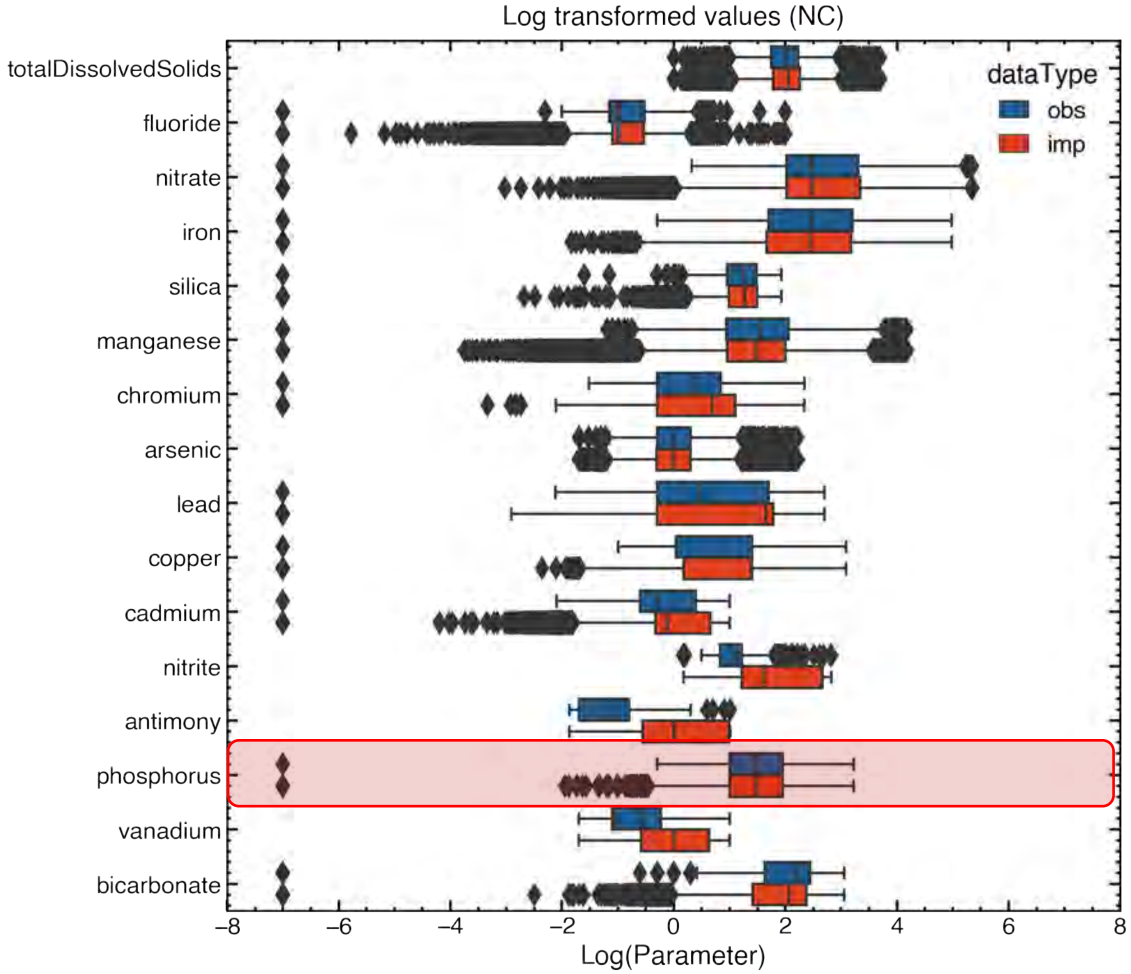
- 1. Creating multiple identical datasets with missing (?) values: bootstrapping
- 2 and 3. Method uses expectation–maximization (EM) algorithm to create parametric matrix with value predictions by alternating expectation (E) and maximization (M) steps until convergence. Predicted values (N.Val) are inserted into bootstrapped datasets.
- 4. Proper statistical analysis model to be applied onto generated datasets.
- *Optional: After statistical analysis, combined final dataset may be assembled.

Amelia – Data Imputation

Raw dataset

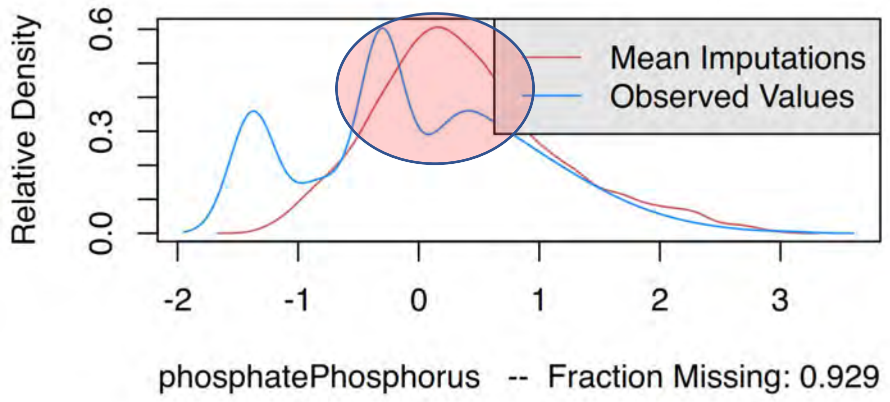


Amelia

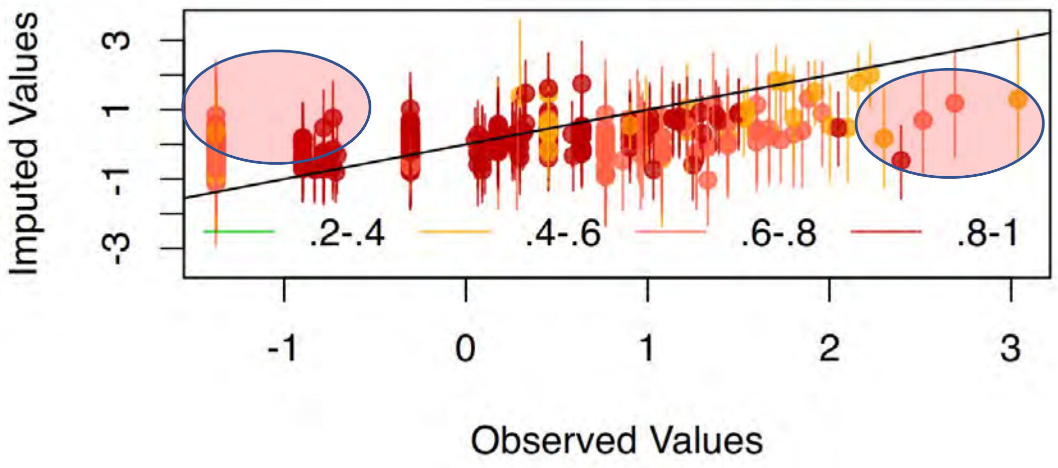


3. Validation of results

NC: Observed + Imputed (P)



NC: Observed vs Imputed (P)



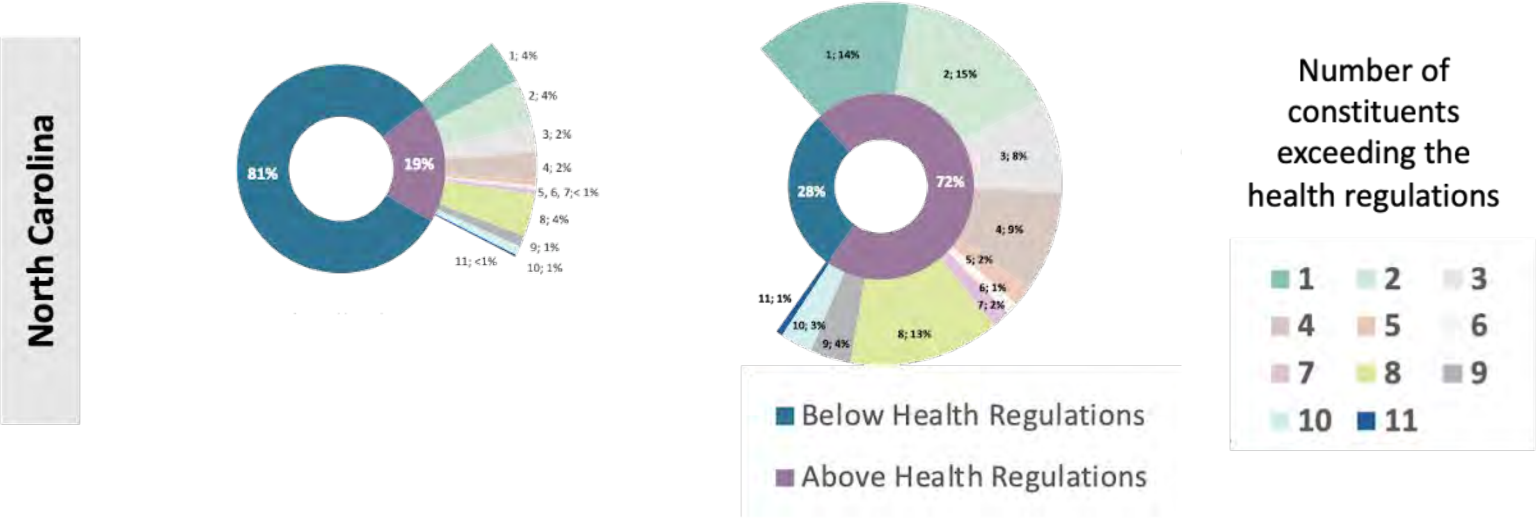
Outcome:

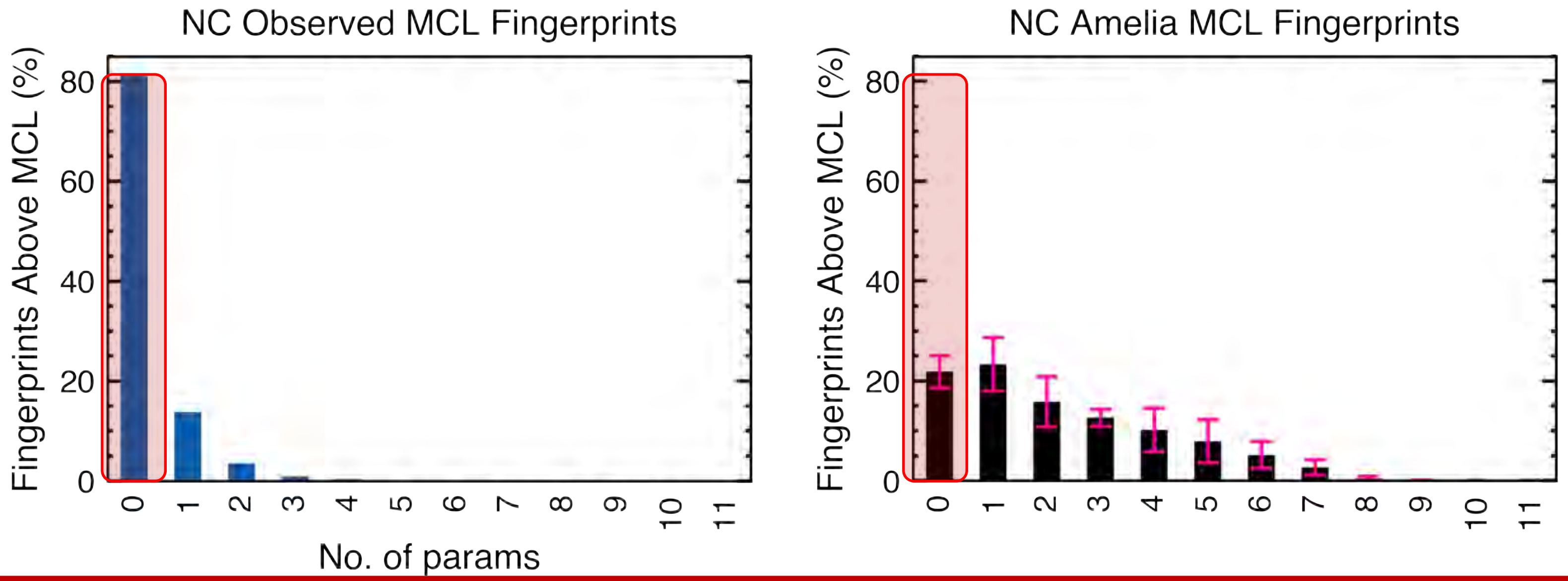
- Moderate accuracy in prediction
- Imputed data requires further validation
- Other correlated parameters to be involved in the analysis

Further analysis of the outcomes

MCL:

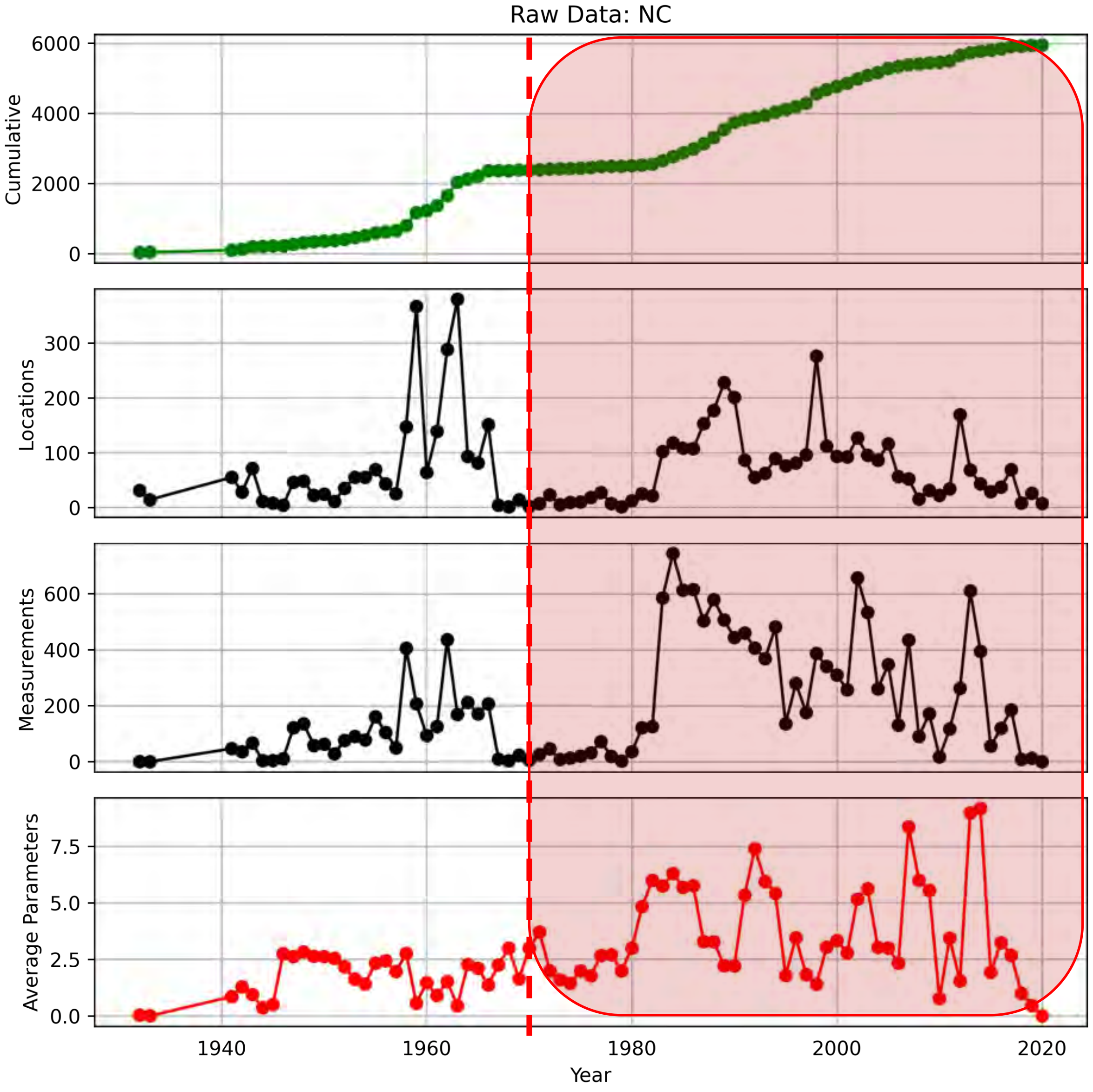
- Maximum Contaminant Levels (MCLs) represents the highest acceptable level of contaminants in drinking water

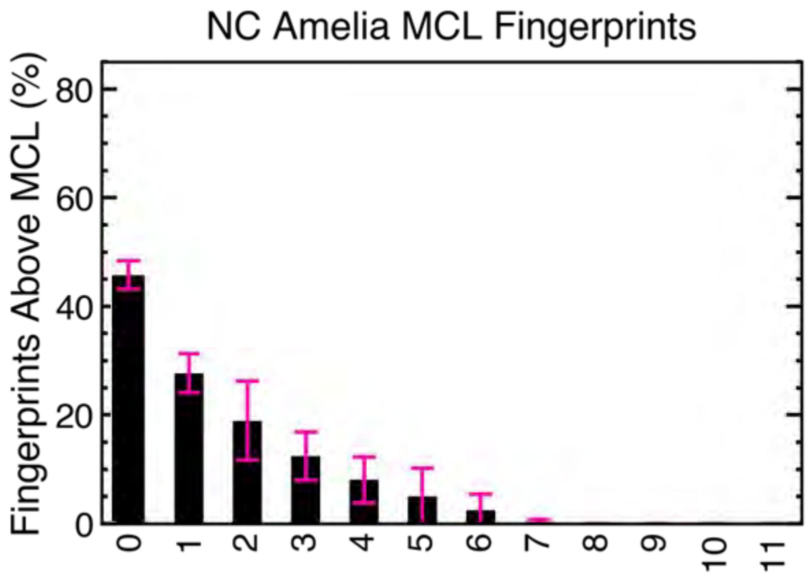




Possible issues?

Solution: more data analysis





Outcome:

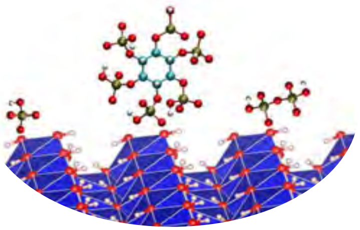
- Smart multi-stage data wrangling is the key for improved accuracy
- Sometimes sacrificing the data is unavoidable
- You must know your data & what you are looking for.

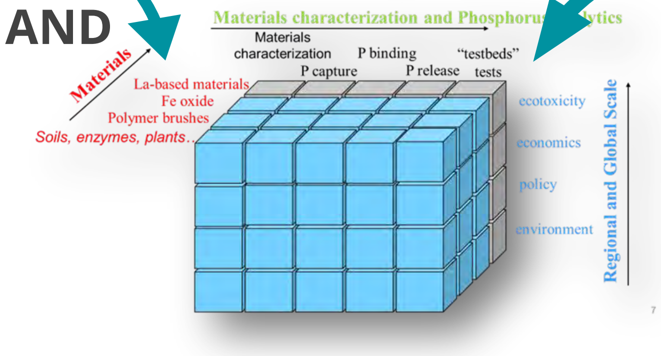
Next steps for STEPS

Designing Materials for Phosphate Removal from Water

Theme 1

MATERIAL SYNTHESIS AND CHARACTERIZATION





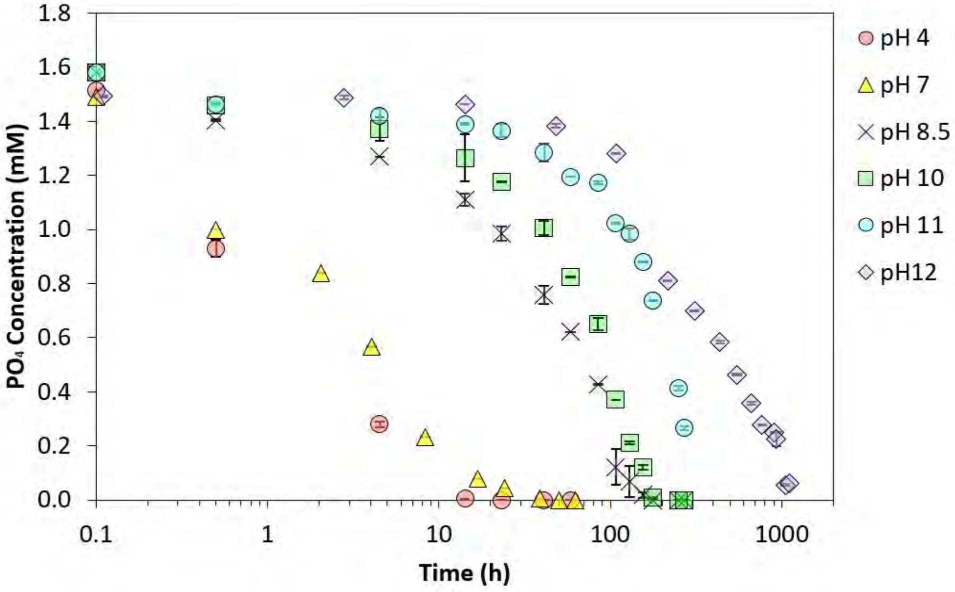
Theme 2 & Theme 3

APPLICATION CONSIDERATION

Metal cation (e.g., Lanthanum, Iron)-containing materials can remove phosphate under diverse environmental conditions

Eco-toxicological risks and environmental conditions: (1) **Acidity of water** and (2) **Phosphorus concentration**

Solution pH-dependent PO_4 removal kinetics



Acidity of water (pH) varies with downstream distance, depth

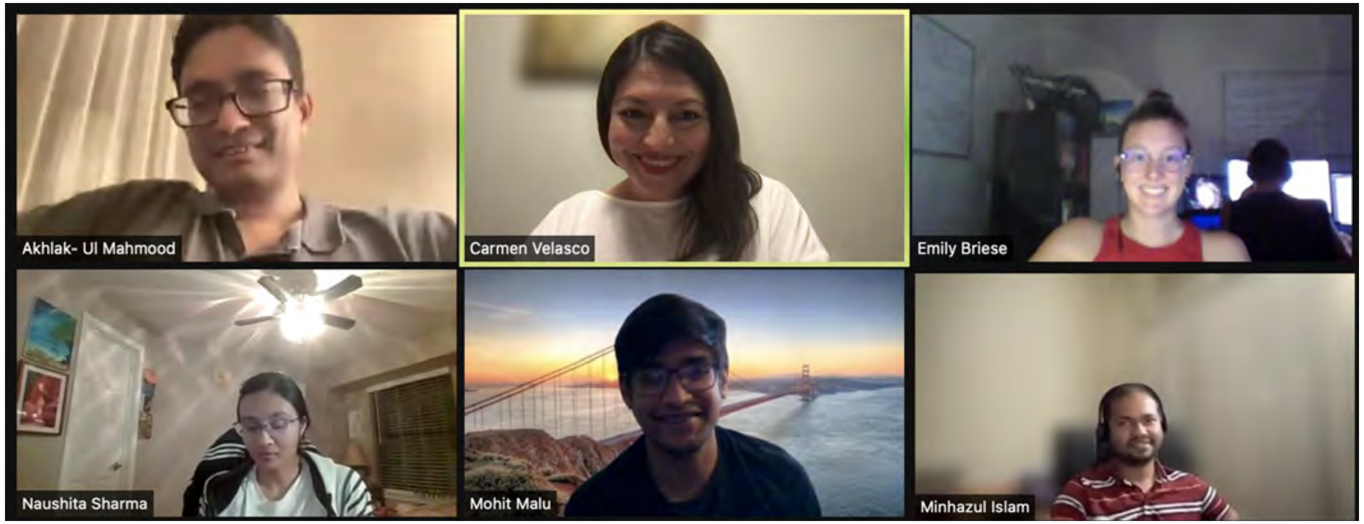
Phosphorus concentration NC:

Acknowledgements

Y. Yingling

P. Westerhoff

A. Spanias



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Akhlak Mahmood

Arizona State University

Westerhoff Research Group:

Carmen Velasco, Minhazul Islam, Emily Briese

Spanias Research Group:

Mohit Malu

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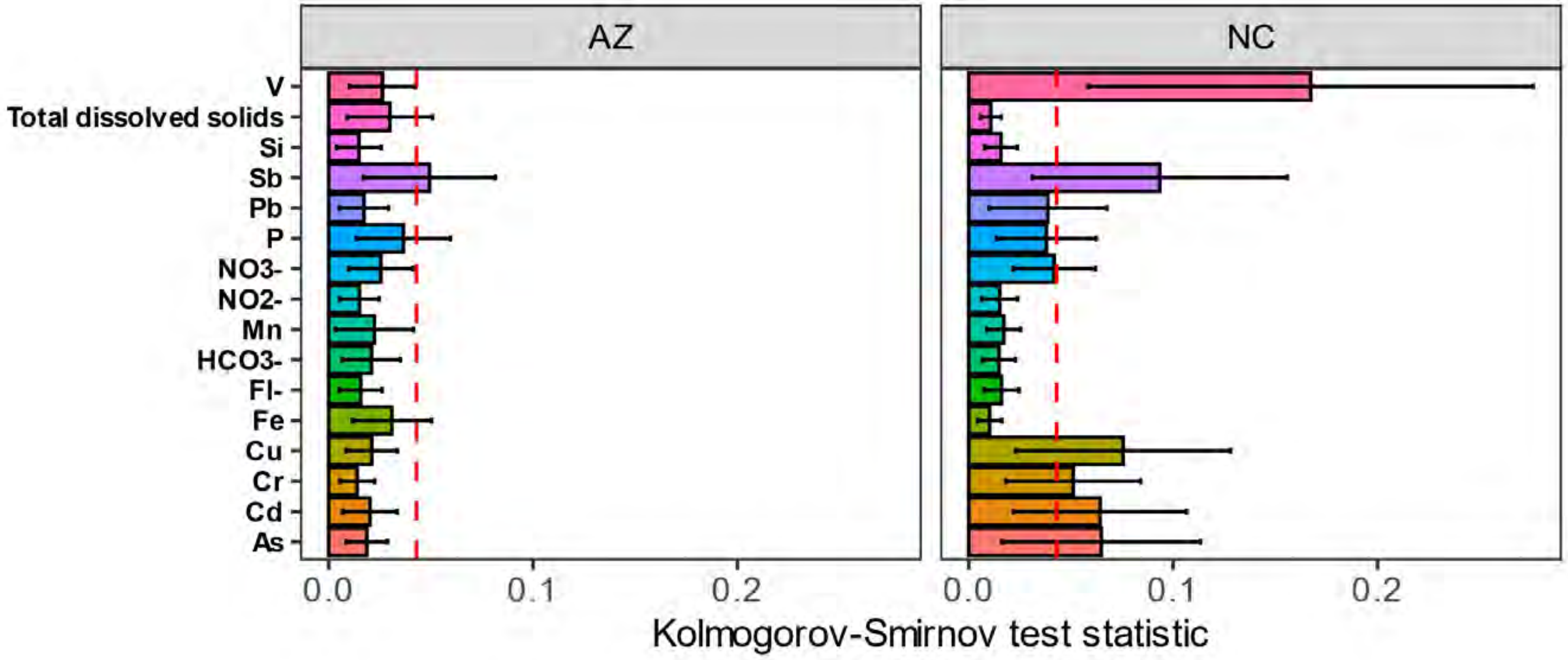
Backup Slides

Amelia Confidence – KS test



Performing analysis on the imputed datasets

Observed dataset

	Col 1	Col 2	…	Col P
Row 1	✓		✓	✓
Row 2		✓	✓	
…	✓			✓
Row R		✓	✓	

	Col 1	Col 2	…	Col P
Row 1	✓	✓	✓	✓
Row 2	✓	✓	✓	✓
…	✓	✓	✓	✓
Row R	✓	✓	✓	✓

	Col 1	Col 2	…	Col P
Row 1	✓	✓	✓	✓
Row 2	✓	✓	✓	✓
…	✓	✓	✓	✓
Row R	✓	✓	✓	✓

	Col 1	Col 2	…	Col P
Row 1	✓	✓	✓	✓
Row 2	✓	✓	✓	✓
…	✓	✓	✓	✓
Row R	✓	✓	✓	✓

Correlation as an example:

$c_1 = corr(col\ 1, col\ 2)$ from dataset 1

$c_2 = corr(col\ 2, col\ 2)$ from dataset 2

$c_3 = corr(col\ 1, col\ 2)$ from dataset 3

$$\bar{c} = \frac{c_1 + c_2 + c_3}{3}$$

Uncertainty of the prediction:

m = number of imputations = 3

$$\text{var}(c) = \underbrace{\frac{1}{m}\sum_{j=1}^{m} var(c_j)}_{\text{randomness}} + \underbrace{S_{\bar{c}}^2 (1 + {}^1/_m)}_{\text{missingness}}$$

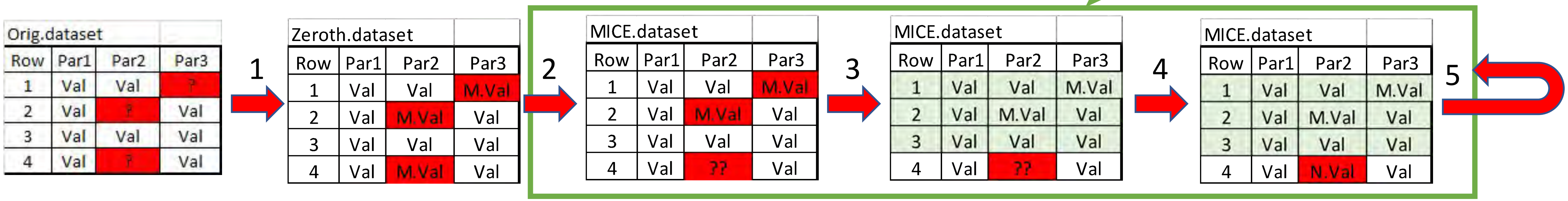
where,

$$S_{\bar{c}}^2 = \frac{1}{m-1}\sum_{j=1}^{m}(c_j - \bar{c})^2$$

MICE

10 Samples

CE algorithm workflow:



- 1. Impute all missing values using mean calculation (M.Val).
- 2. Set back one of the predicted values to “missing” (??).
- 3. Create feature matrix (non-missing values), apply regression model, use missing value row as a test data.
- 4. Replace missing value with predicted value (N.Val)
- 5. Repeat steps 2-4 for each missing value (M.Val) from step 1, updating the dataset with corresponding (N.Val)s and creating new corresponding feature matrices.
- 6. Repeat steps 2 through 5 for a number of cycles (10) with the imputation being updated at each cycle.
- *Optional (7). After statistical analysis of a all datasets, final dataset may be assembled.

Investigating Froth Flotation Effects on Biosolids and Phosphorus Separation

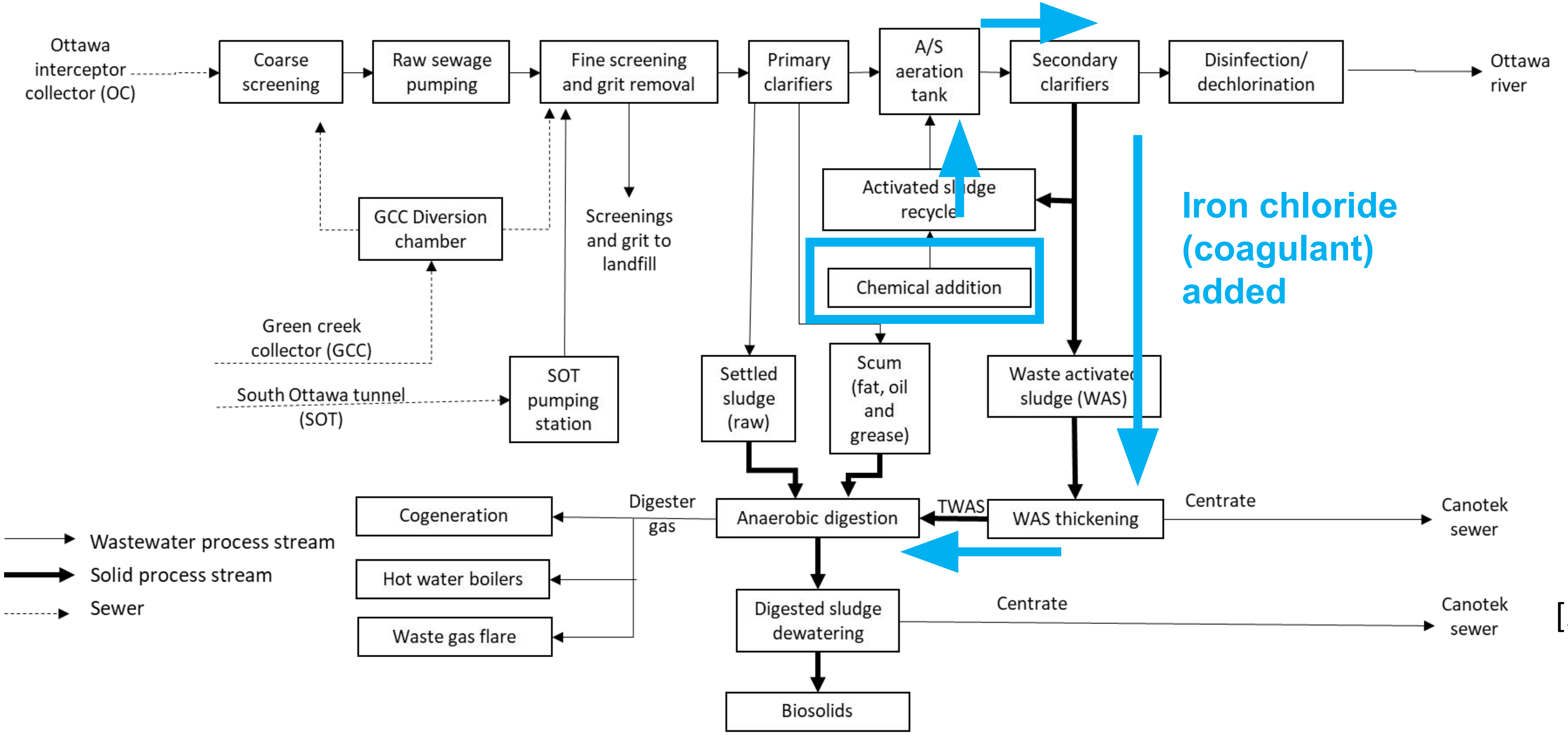
Bailee Johnson, Department of Mining and Materials Engineering
Supervisor: Dr. Sidney Omelon
Co-Supervisor: Prof. Kristian Waters, Prof. Dominic Frigon

McGill

Robert O. Pickard Environmental Center (ROPEC) Municipal Wastewater Treatment Plant (WWTP) for Ottawa, Ontario, Canada

[1]

ROPEC Block Flow Diagram



[2]

What are biosolids?

- Solids that remain after anaerobic digestion.
- Solids that are combination of organic material, anaerobic bacteria, and inorganic solids.
- Inorganic solids include iron phosphate from the upstream addition of ferric chloride to reduce the dissolved phosphate concentration to meet emission guidelines.
- Include a small concentration of heavy metals (e.g., chromium, cadmium)
- Applied to farms that produce crops that are not for human consumption.

[3]

ROPEC Biosolids:

- 30±2% solids
- 30±1 mg P/dry g
- 33±1 mg Fe/dry g

Can We Use Biosolids for P-Fertilizer?

- Organic carbon and nitrogen are useful
- Incinerated sewage sludge contains [9]:
  - high iron concentrations due to iron chloride additions during treatment
  - heavy metals from sewer
- Ash total P concentration is ~6% P, but its plant availability and P-concentration are lower than P-fertilizer.

Iron chloride added as flocculant/coagulant and P-concentration reducer in wastewater treatment:

$$FeCl_3 \rightarrow Fe^{3+} + 3Cl^-$$
$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$
$$FeCl_3 + XPO_4^{3-} \rightarrow \boldsymbol{Fe(OH)_3 \cdot XPO_4^-}$$

Grades of Incinerated Sewage Sludge [EasyMining, 2022]

Element	P	Fe
Concentration (%)	6 – 12	5 – 10

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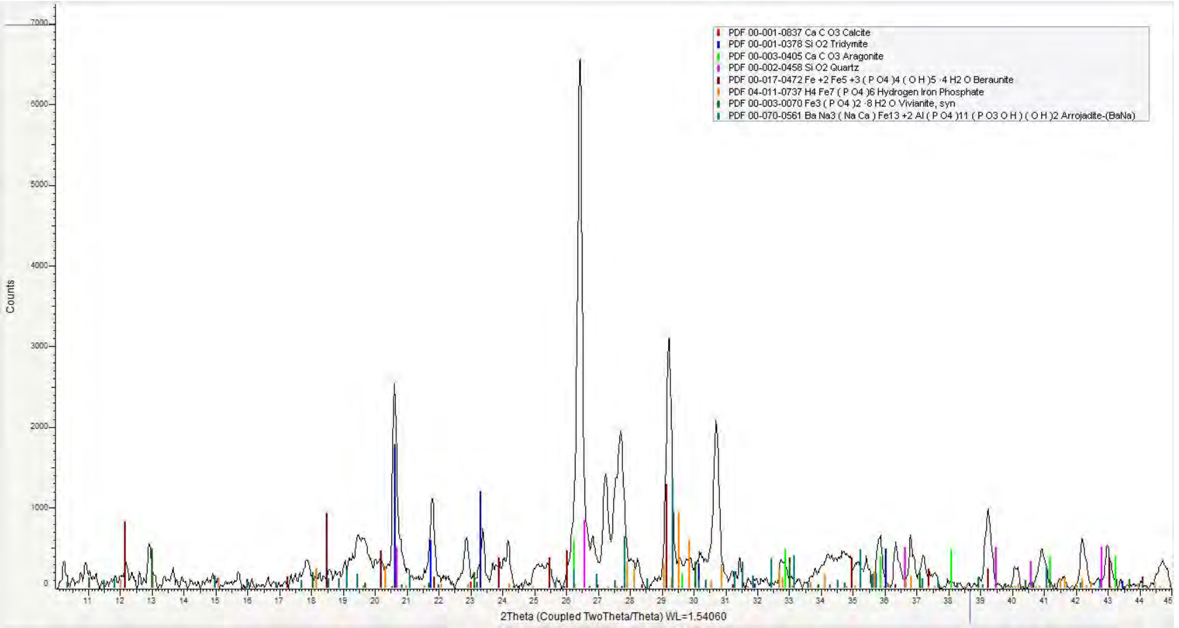
Inorganic Crystalline Biosolids Components



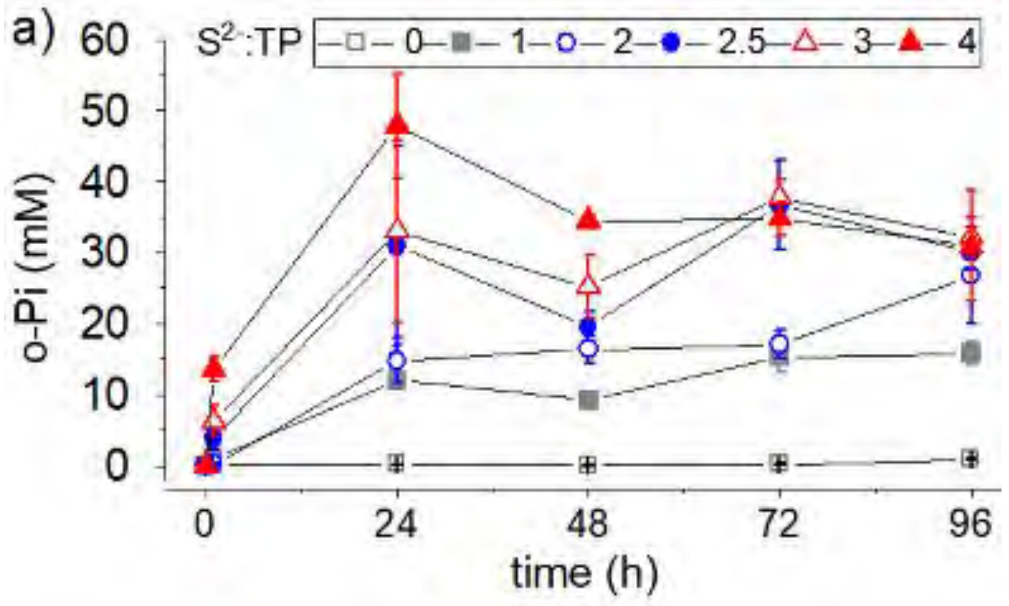
A (potential) XRD lineup of crystalline materials in biosolids:

- vivianite ($Fe_3(\mathbf{P}O_4)_2 \cdot 8H_2O$
- hydrogen iron phosphate ($Fe_7(H\mathbf{P}O_4)_4(\mathbf{P}O_4)_3$)
- beraunite ($Fe(II)Fe(III)_5(\mathbf{P}O_4)_4.(OH)_5 \cdot 4(H_2O)$)
- arrojadite ($(K,Na)_4(Ca,Mn)(II))_4Fe(II))_{10}Al(\mathbf{P}O_4)_{12}(OH,F)_2$
- calcite ($CaCO_3$)
- quartz (SiO_2)

Sulphide Ions Displace P from Iron Phosphate

Sulphide ions at different S/TP ratios (0, 1, 2, 2.5, 3, 4) can displace phosphate from the iron phosphate in biosolids (Bluteau, 2019).

$$Fe_x(PO_4)_{y\,(s)} + z\,HS^- \rightarrow Fe_xS_{z\,(s)} + y\,HPO_4^{2-}$$



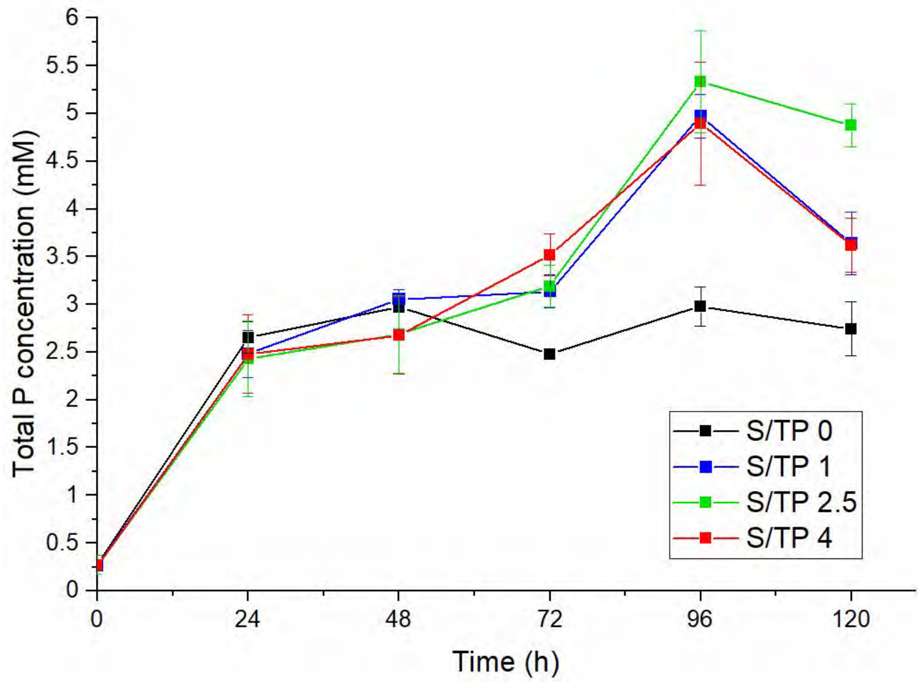
The chemical mechanism works, but sodium sulphide as a process input carries too many practical risks.

Incubating Elemental S with Biosolids Increased Dissolved Total P

$$S^0{}_{(s)} + microbes\ in\ biosolids \rightarrow S^{2-}_{(aq)}$$

$$Fe_x(PO_4)_{y\,(s)} + Z\ HS^- \rightarrow\ Fe_xS_{z\,(s)} +\ HPO_4^{2-}$$

Dissolved $total\ P\ versus\ time$



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Incubating Elemental S with Biosolids Increased Dissolved Total P

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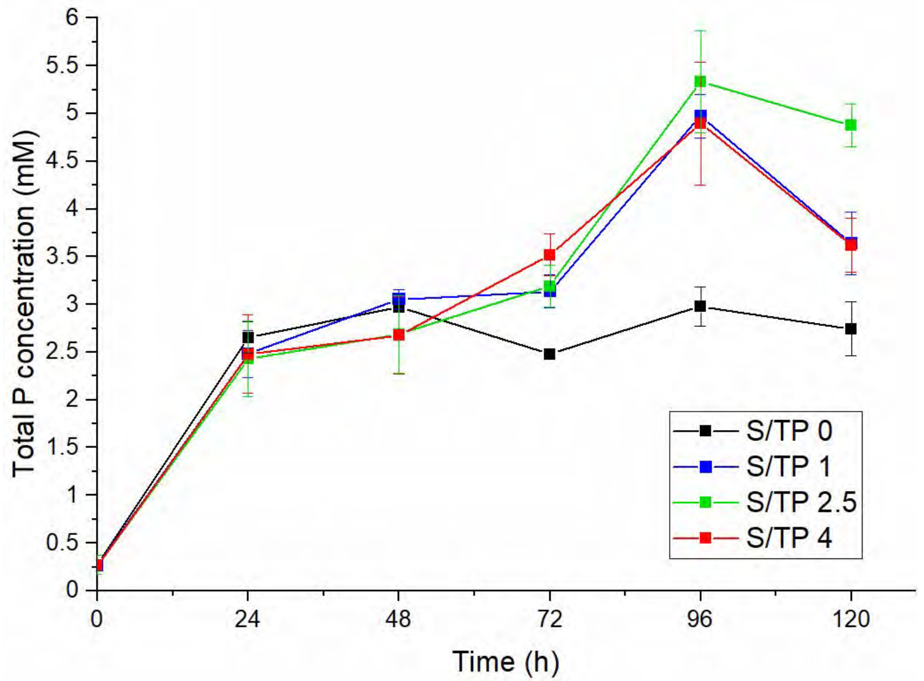
$$Fe_x(PO_4)_{y\,(s)} + Z\ HS^- \rightarrow Fe_xS_{z\,(s)} + HPO_4^{2-}$$

Dissolved *total P versus time*



Goal 1: Could this dissolved o-Pi be taken up by phototrophic bacteria if the S-treatment occurred with light (IR/heat lamp)

Incubating Elemental S with Biosolids Increased Dissolved Total P

$$S^0{}_{(s)} + microbes\ in\ biosolids \rightarrow S^{2-}_{(aq)}$$

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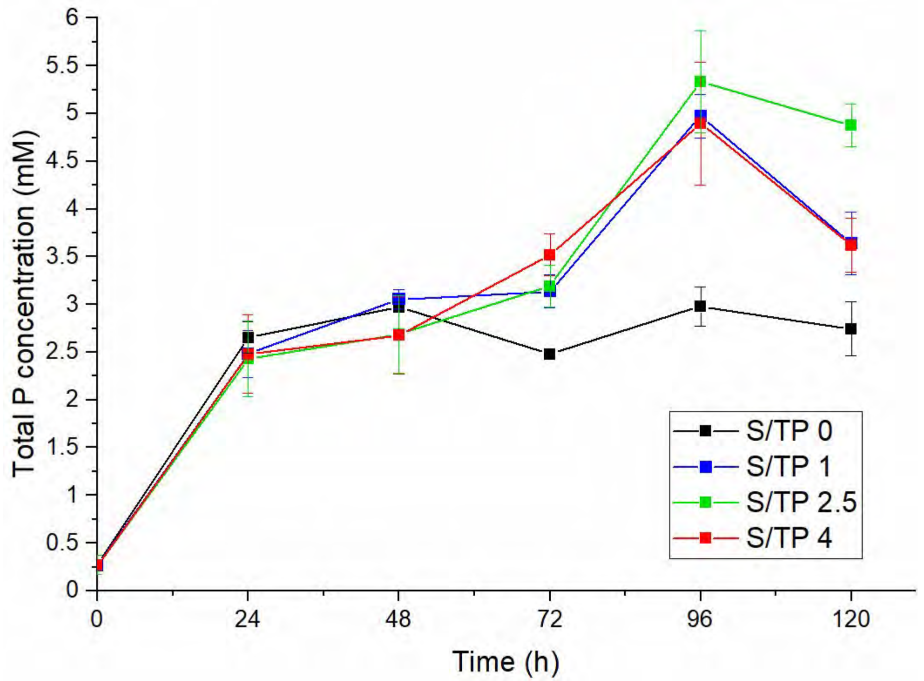
Dissolved *total P versus time*



Goal 1: Could this dissolved o-Pi be taken up by phototrophic (light-energized) bacteria if the S-treatment occurred with light (IR/heat lamp)

Goal 2: Could the organic and possibly P-enriched microbes be separated from the more dense, and less desirable (ex: sand, heavy metal-containing solids) components of biosolids by flotation?

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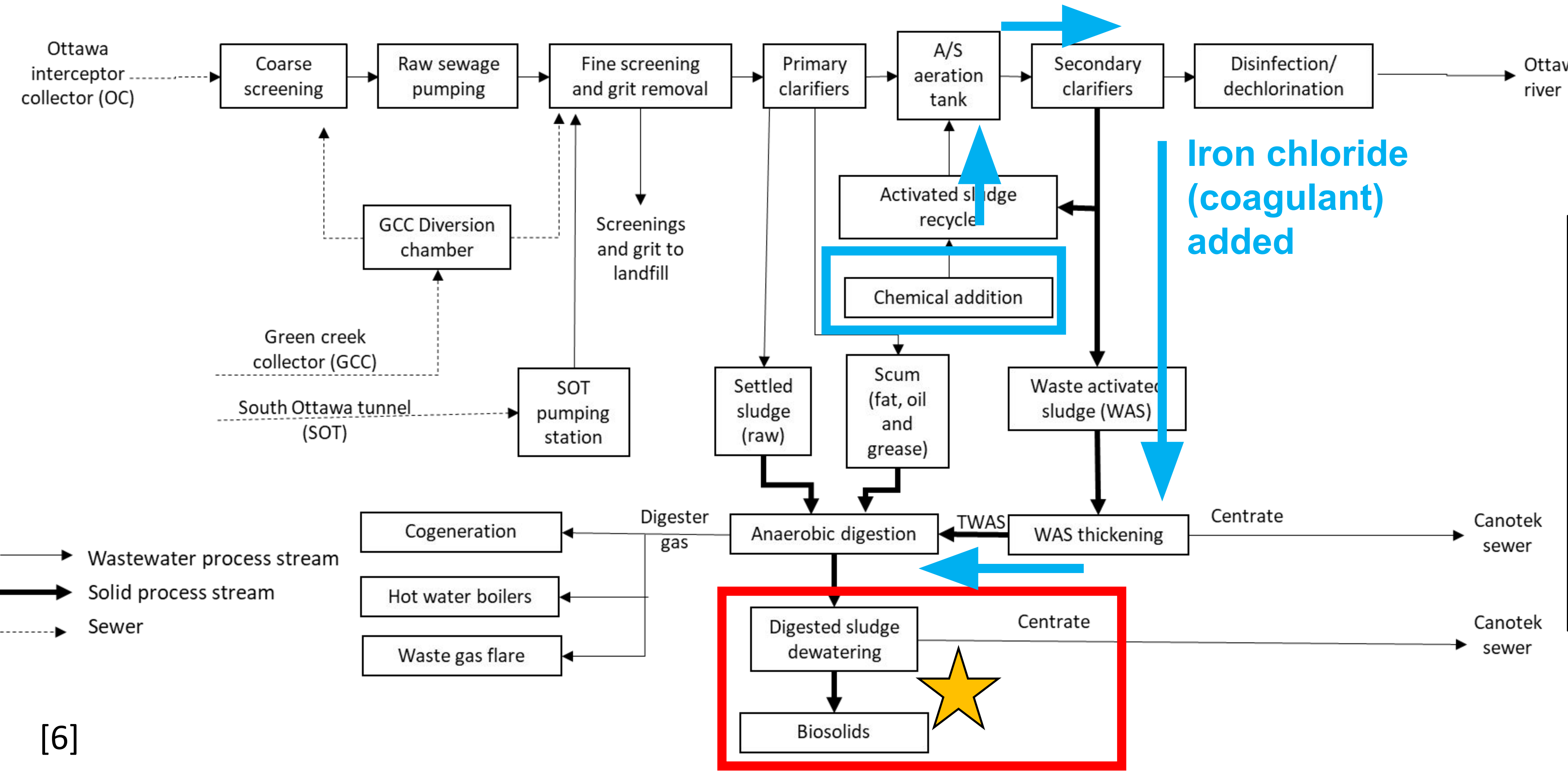
Why Try Flotation with Biosolids?

- “To tackle these challenges [of fertilizer quality and valorization] **different options for solid removal and biomass harvesting** (*e.g.*, sedimentation, flocculation, centrifugation, filtration or membrane reactors) **must be further tested**.” – Capson-Tojo et. al. (2020),
- “…microalgal species [can] have buoyancy (due to regulation of gas vacuoles)…**some studies suggest the possibility of bio flotation** whereby the photosynthetically generated oxygen would be utilized.” – Moheimani (2016)

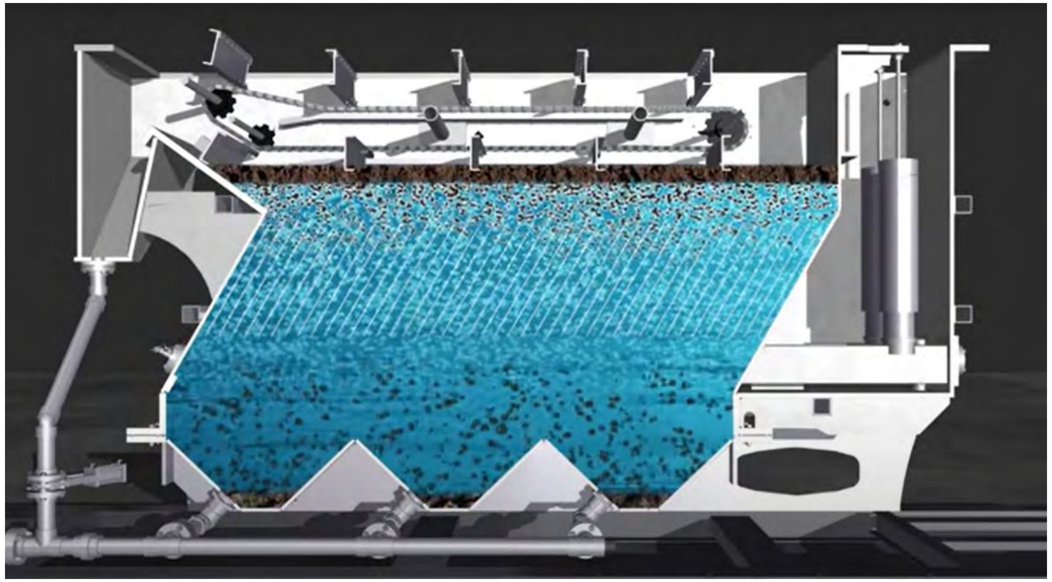
Project Objectives: Selective P-Enriched Biosolids Separation with Flotation



Represents where flotation could be applied. S added prior to flotation to enrich P in biomass and displace phosphate from iron phosphates.

[6]

What Is Flotation in Wastewater Treatment?



[4]

- Dissolved air flotation (DAF) is industry standard in wastewater treatment plants (WWTPs)
- Gravity driven, does not remove particles selectively
- Serves primarily to clarify (clear) water – but is not very effective

What Is Flotation in Mineral Processing?

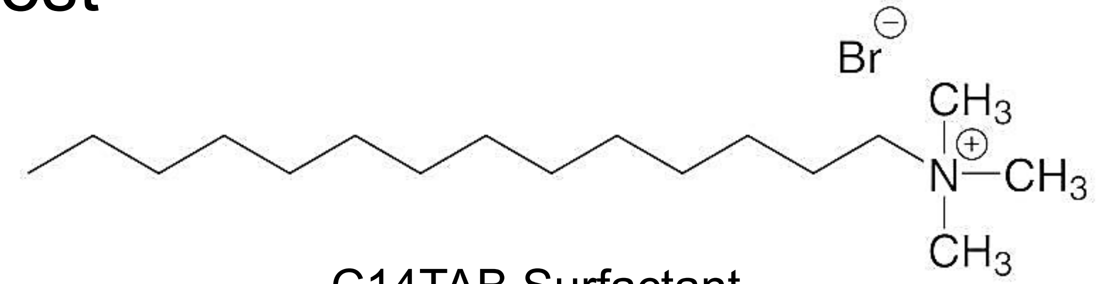
[5]

What Is Flotation in Mineral Processing?

- Froth flotation is industry standard technology in many metallurgical plants to separate finely ground minerals based on differences in their surface chemistry

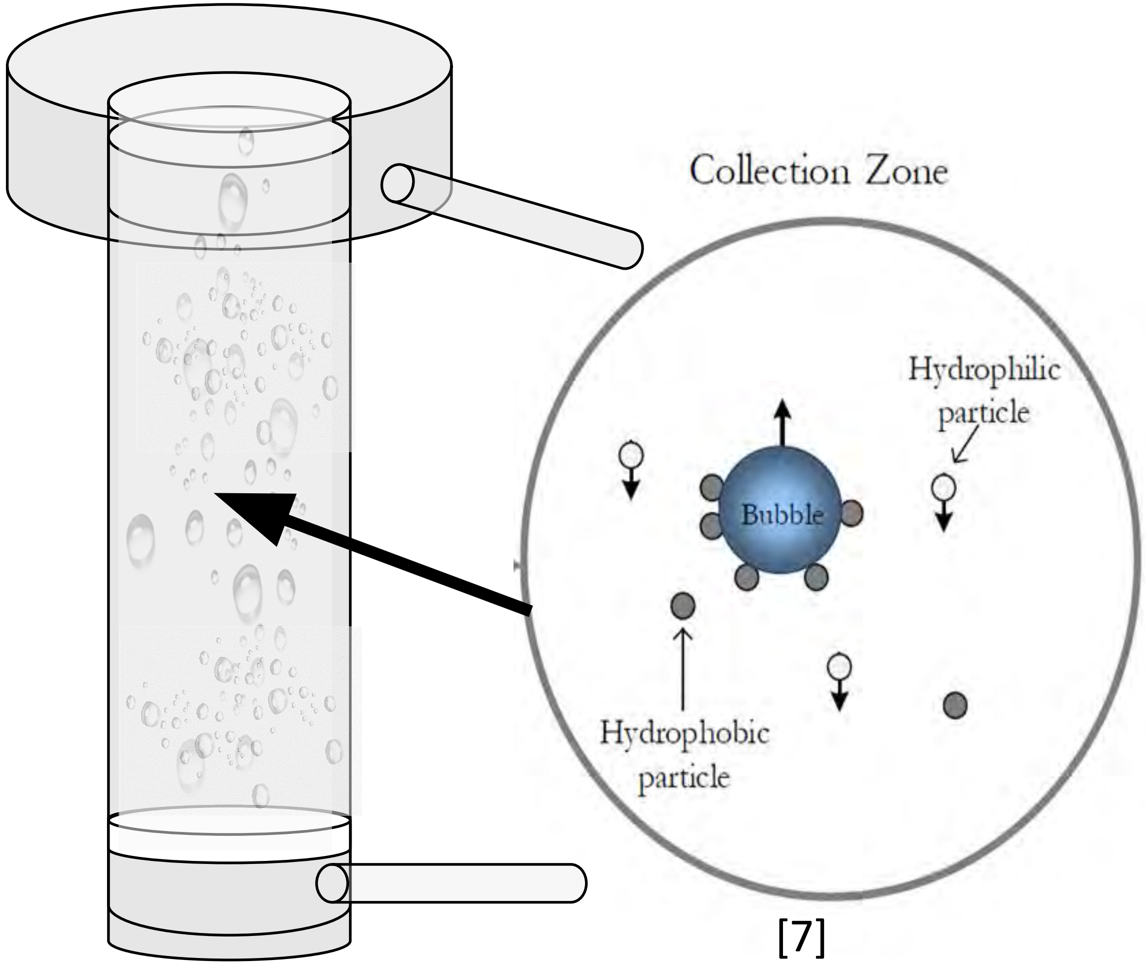
- Collectors (surfactants) are added to alter mineral surface hydrophobicity for selective capture of minerals of interest

[6]

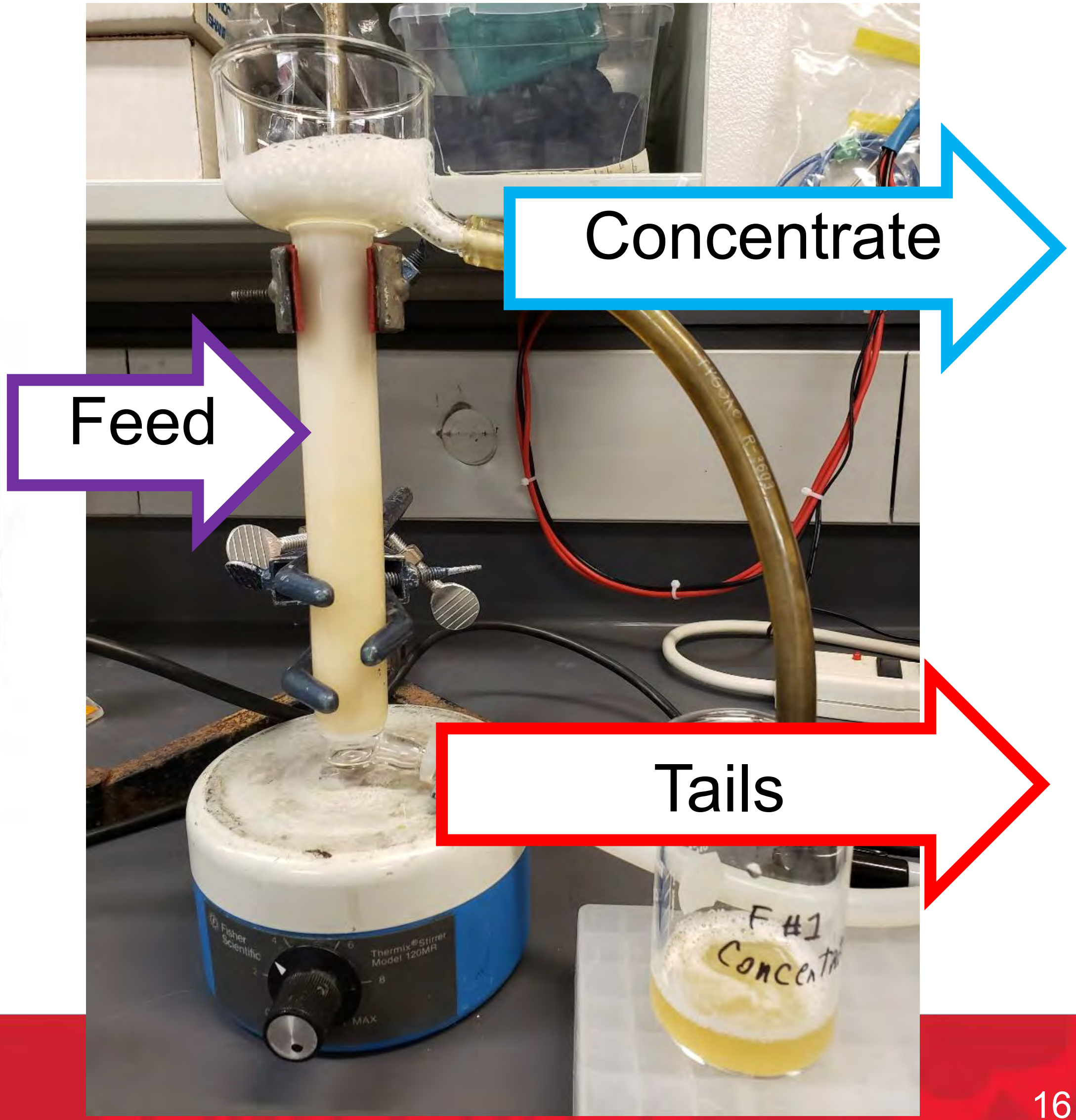


C14TAB Surfactant

Mineral Processing Flotation at the Lab Scale (Microflotation)

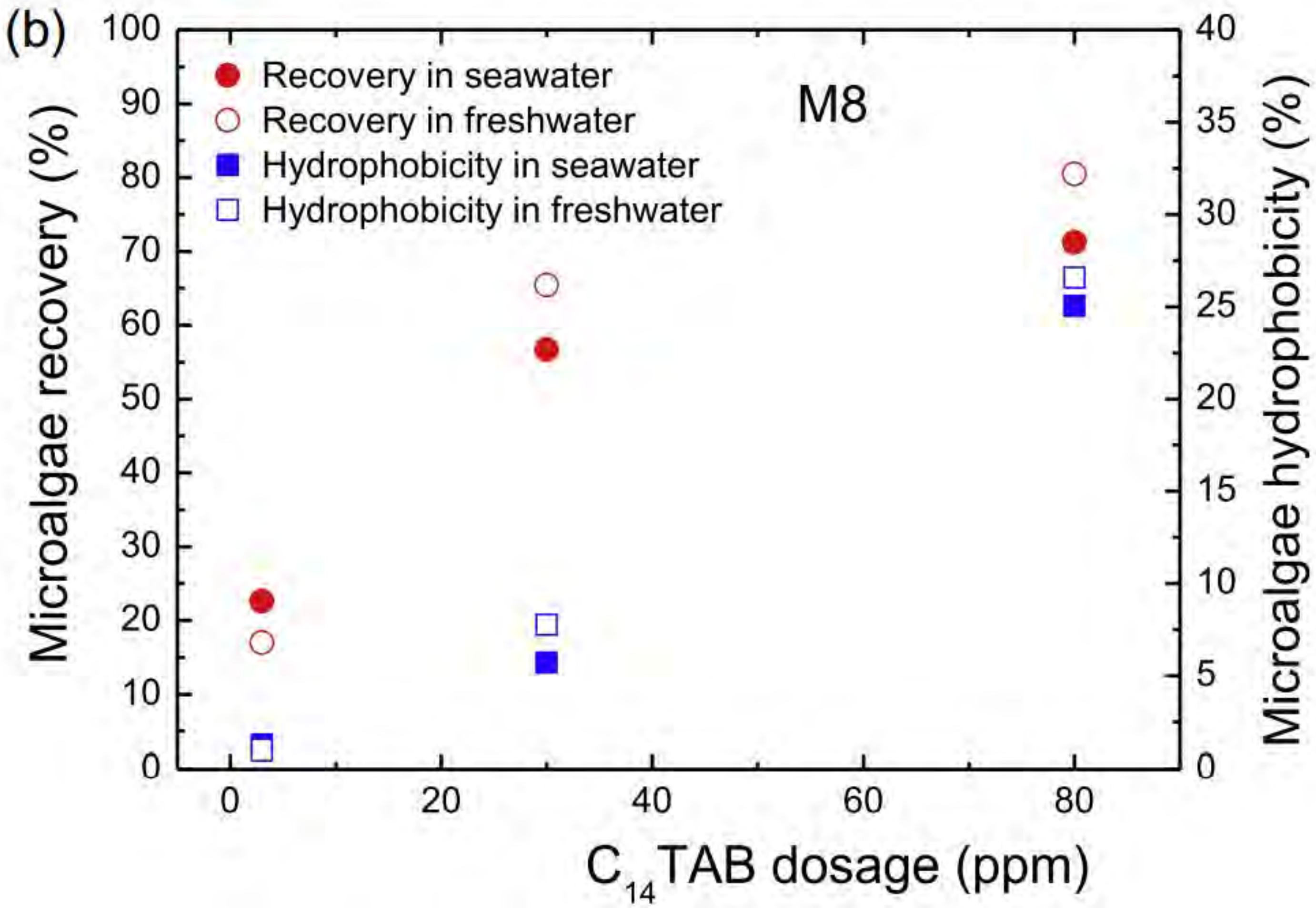


[7]



Evidence of Biological Flotation Successes

- Flotation performed on both marine and freshwater microalgae shows **inherent hydrophobicity within microalgae** [Garg 2012]



[8]

Project Guiding Questions

Confirmation P-Chemistry Question:

Can iron phosphate be dissolved by elemental sulphur addition?

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Can dissolved o-Pi be taken up by phototrophic anaerobic bacteria?

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Project Guiding Questions

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Can iron phosphate be dissolved by elemental sulphur addition?

Primary P-Chemistry Question:

Can dissolved o-Pi be taken up by phototrophic anaerobic bacteria?

Primary Flotation Question:

Can hydrophobic flotation be used as a mechanism to selectively concentrate P-enriched biosolids?

These questions will be asked simultaneously through the use of Design of Experiments (DoE).

What is Design of Experiments (DoE)?

- Experimental design to explore importance of and interactions between factors while minimizing number of experiments required
- Fractional Factorial Design (FFD) used in this study to screen conditions and create models that predict the experimental results

Available Factorial Designs (with Resolution)

	Factors													
Runs	2	3	4	5	6	7	8	9	10	11	12	13	14	15
4	Full	III												
8		Full	IV	III	III	III								
16			Full	V	IV	IV	IV	III	III	III	III	III	III	III
32				Full	VI	IV	IV	IV	IV	IV	IV	IV	IV	IV
64					Full	VII	V	IV	IV	IV	IV	IV	IV	IV
128						Full	VIII	VI	V	V	IV	IV	IV	IV

Available Resolution III Plackett-Burman Designs

Factors	Runs	Factors	Runs	Factors	Runs
2-7	12,20,24,28,...,48	20-23	24,28,32,36,...,48	36-39	40,44,48
8-11	12,20,24,28,...,48	24-27	28,32,36,40,44,48	40-43	44,48
12-15	20,24,28,36,...,48	28-31	32,36,40,44,48	44-47	48
16-19	20,24,28,32,...,48	32-35	36,40,44,48		

Microflotation DoE Factors

	Minimum	Center	Maximum
Sulphur Treatment (S/TP (mol))	0	0.5	1
Light Exposure	No	-	Yes
pH	5	7	9
Polymer Addition (g/kg)	0	12	24
Collector Addition (ppm)	0	60	120
Test Conditioning Time (min)	10	20	30

Microflotation DoE Responses

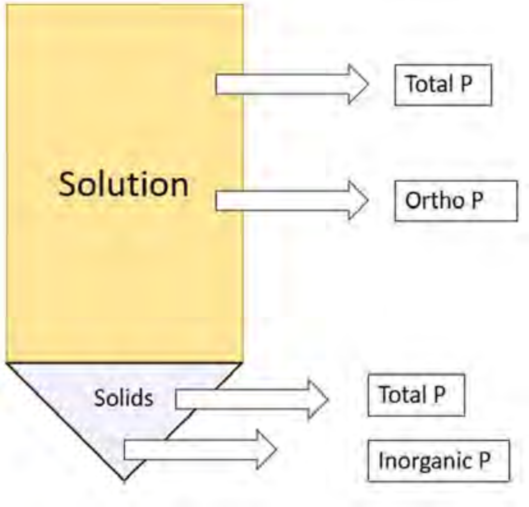
- Each test underwent the following analyses:

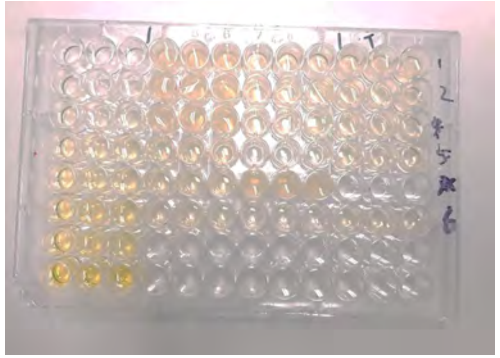
Analysis Type	Wet Mixed Sample	Supernatant Only	Dry Solids Only
Hexane Hydrophobicity Test	✓		
Supernatant Total P (mg/dry g)		✓	
Dry Mass (g)			✓
Solids Total P (mg/dry g)			✓
MP-AES (ppm cation concentration)			✓

Experimental Method

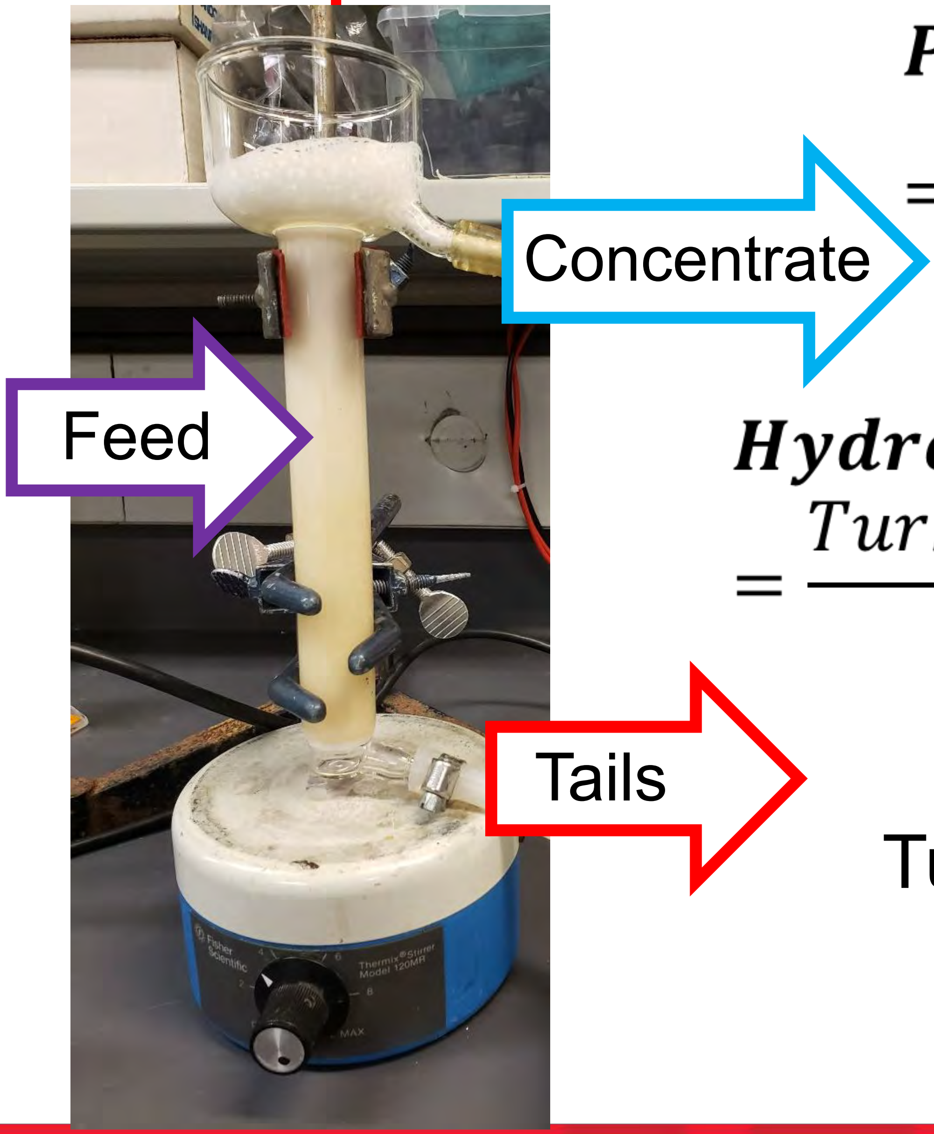
Biosolid Prep (S, light) → **Micro-float** → **Centrifuge & Dry Samples** → **Sample Digestion** → **P Measurement**







Experimental Method: Calculations



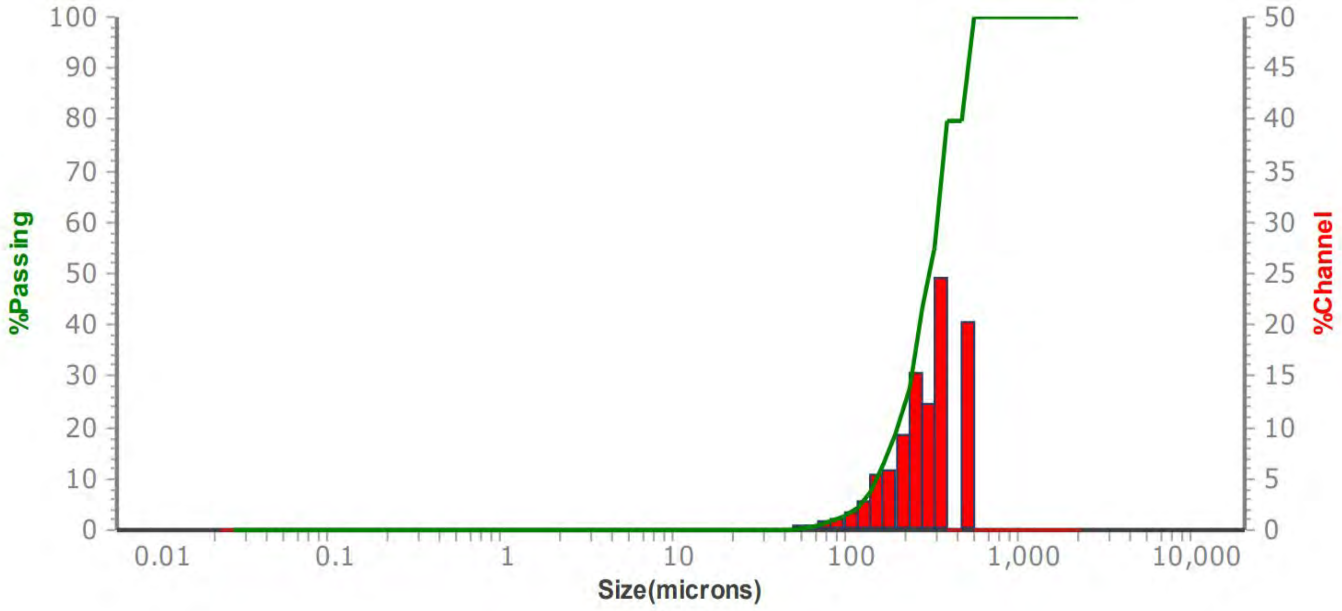
$$P\ Recovery = \frac{(Mass\ of\ Concentrate)(Conc.\ of\ P\ in\ Conc.)}{(Mass\ of\ Feed)(Conc.\ of\ P\ in\ Feed)}$$

$$Hydrophobicity = \frac{Turbidity\ in\ Water\ - Turbidity\ in\ Hexane}{Turbidity\ in\ Water} \times 100\%$$

Turbidity = OD600

Initial Results: Biosolids Microfloat Feed Characterization

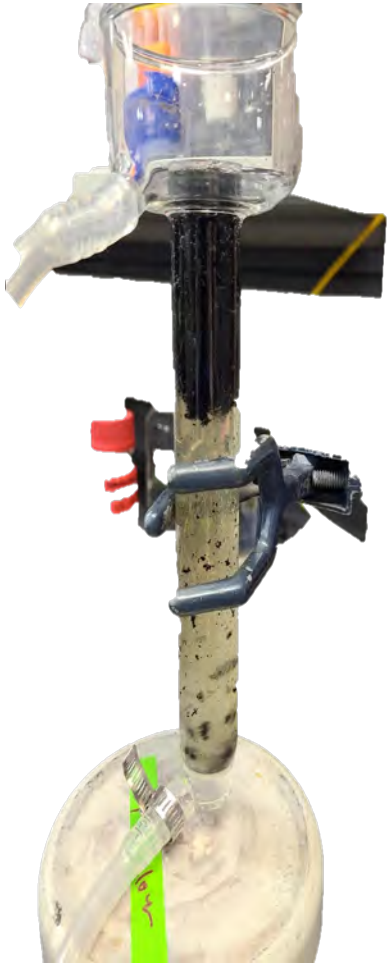
Dynamic Light Scattering of As-Received Biosolids



P80 Biosolids: 420 μm

- Received biosolids are ~30% solids
- Biosolids are diluted to 10% solids for sulphur addition and light incubation
- Flotation feed diluted to 1% solids

Initial Microflotation Results: Visual Observation

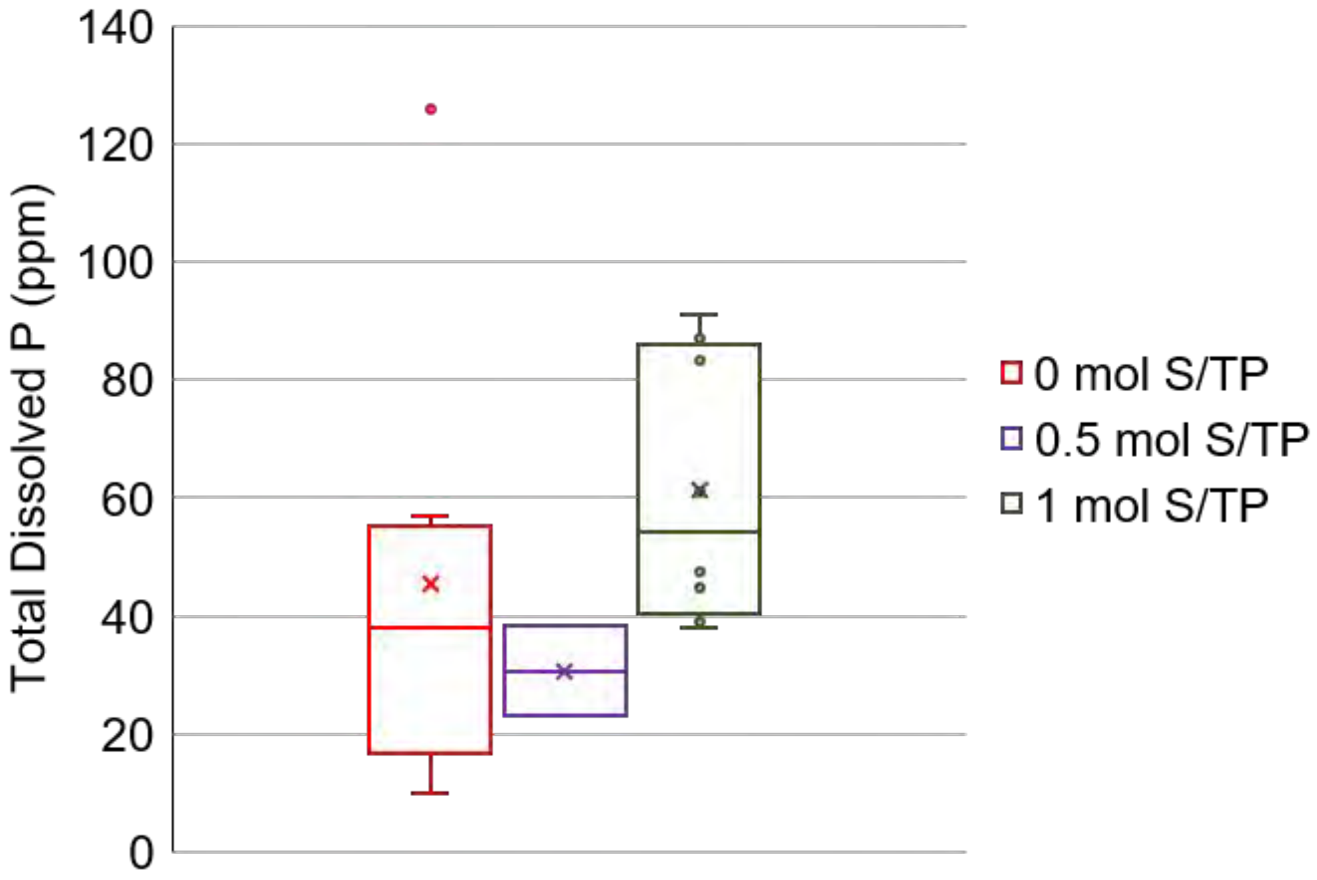


Quantitative Results

	Feed Total P Concentration* (ppm)	Con Total P Concentration* (ppm)	Upgrade Ratio (Con/Feed)	Total P Recovery in Concentrate (%)
Minimum	144	29	0.2	3.0
Mean	267	718	2.7	43
Maximum	546	2629	8.6	95

*combined liquid and solid portion reported

Dissolved TP in Feed vs. S Treatment

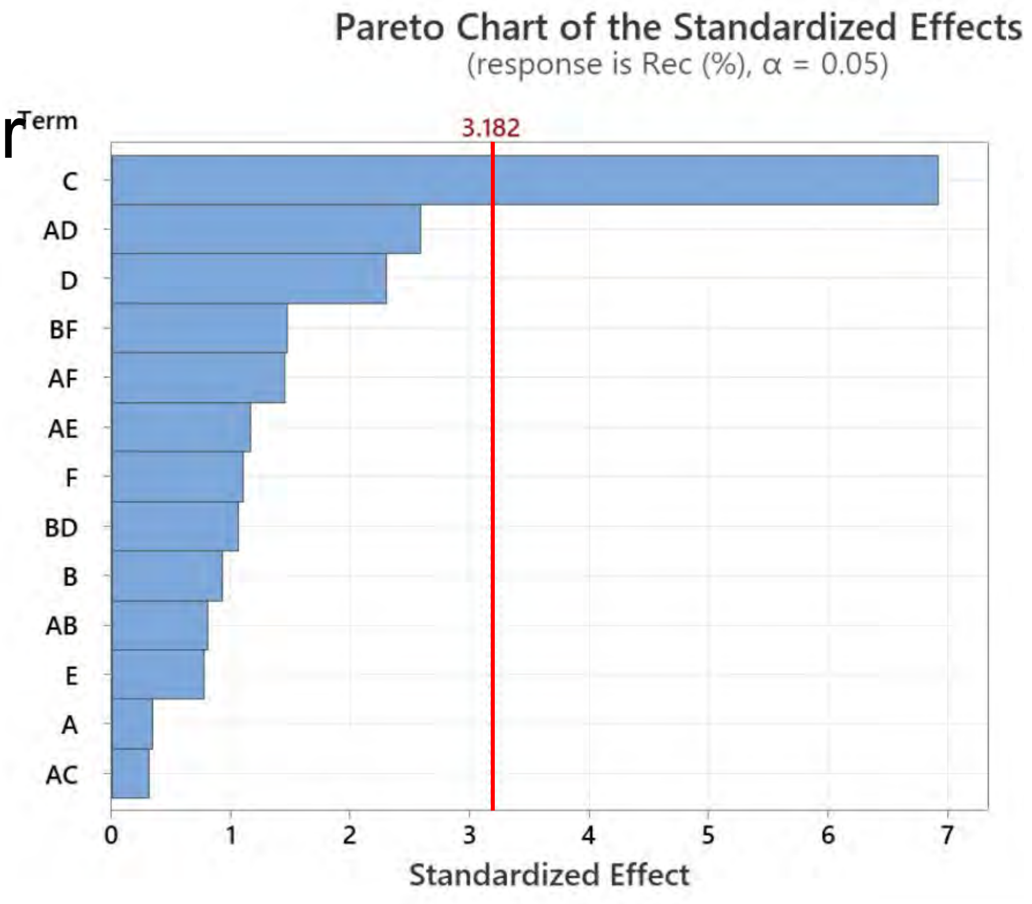


- Increased elemental S addition showed a trend of increasing total P in feed solution, but not statistically significant

Factors for Increasing Total P in Concentrate

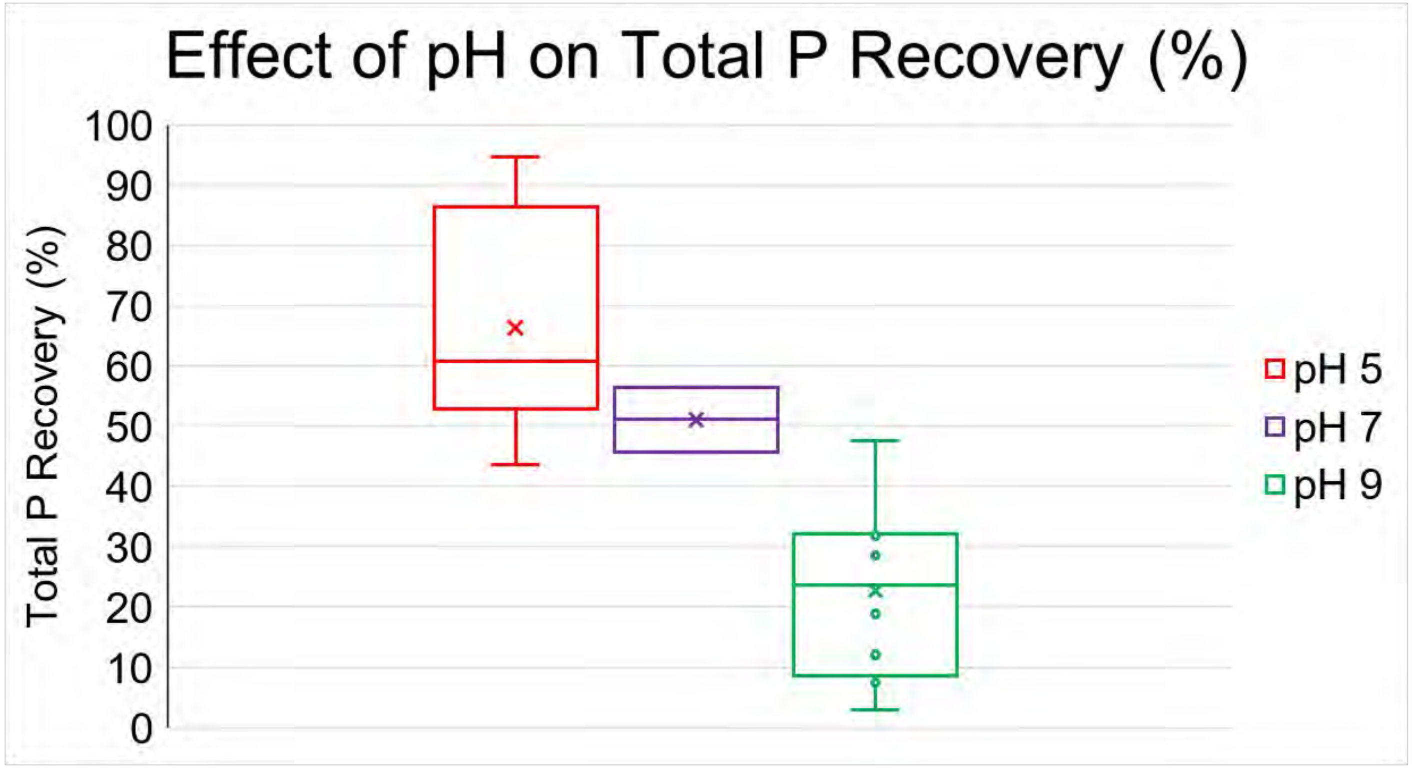
- pH is the most important factor

Factor	Name
A	Sulphur Treatment
B	Light Exposure
C	pH
D	Polymer Addition
E	Collector Addition
F	Test Conditioning Time



Factors for Increasing Total P in Concentrate

- pH is the most important factor
- Flocculant more effective and iron phosphates less stable at lower pH values



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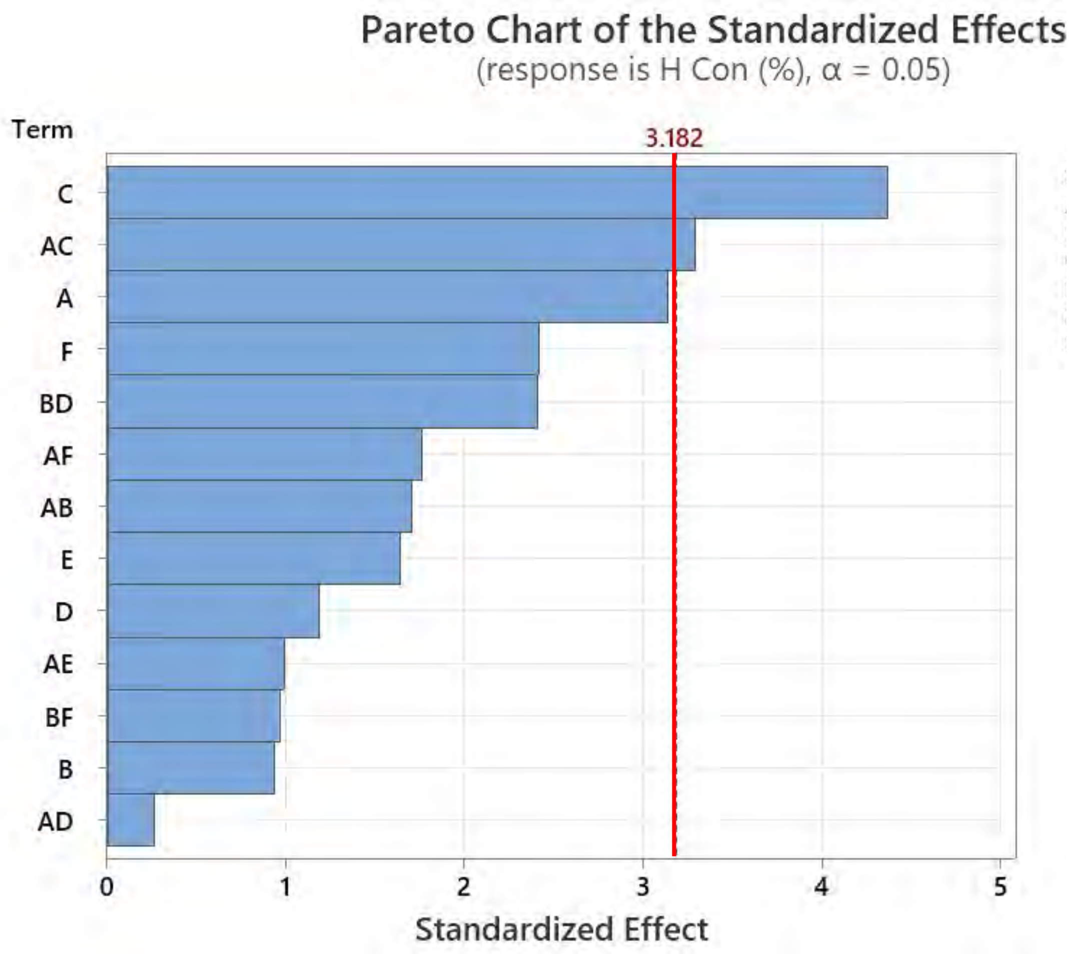
Factors for Increasing Hydrophobicity to Concentrate

- pH, sulphur treatment are the two factors most important factors to increase concentrate hydrophobicity

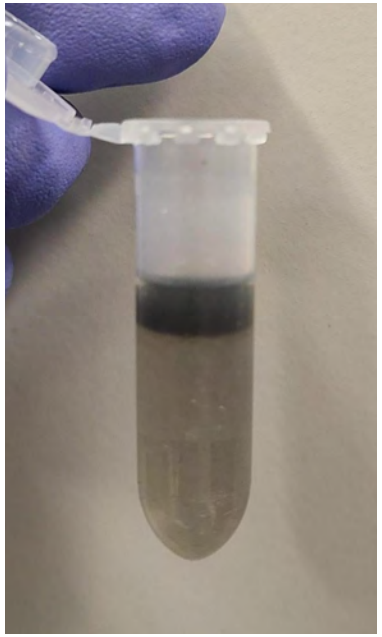
Factor	Name
A	Sulphur Treatment
B	Light Exposure
C	pH
D	Polymer Addition
E	Collector Addition
F	Test Conditioning Time

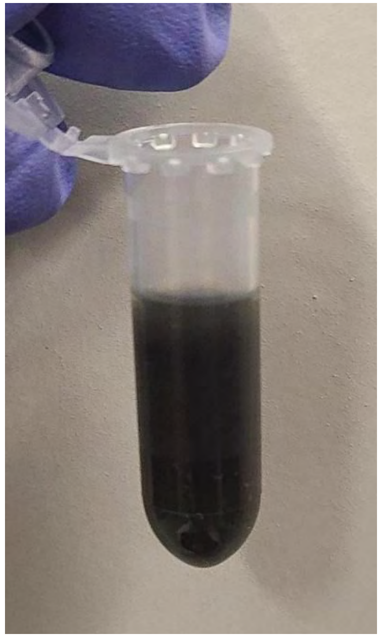


Caveat to Hydrophobicity Values

- Hydrophobicity test did not work for flocculated sample
- Concentrate has hydrophobic conditions when measurable

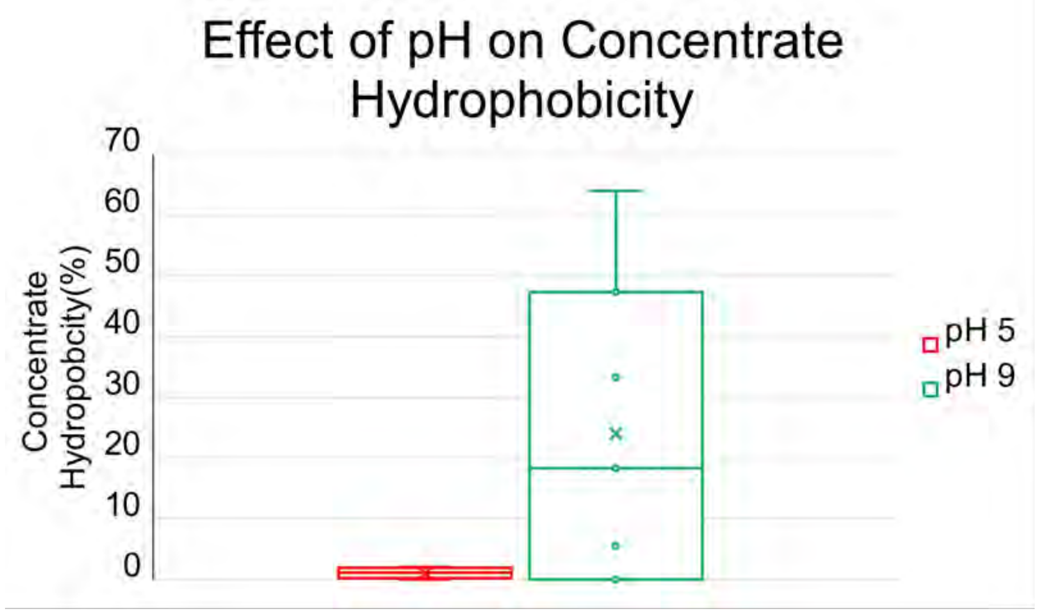

Flocculated Sample

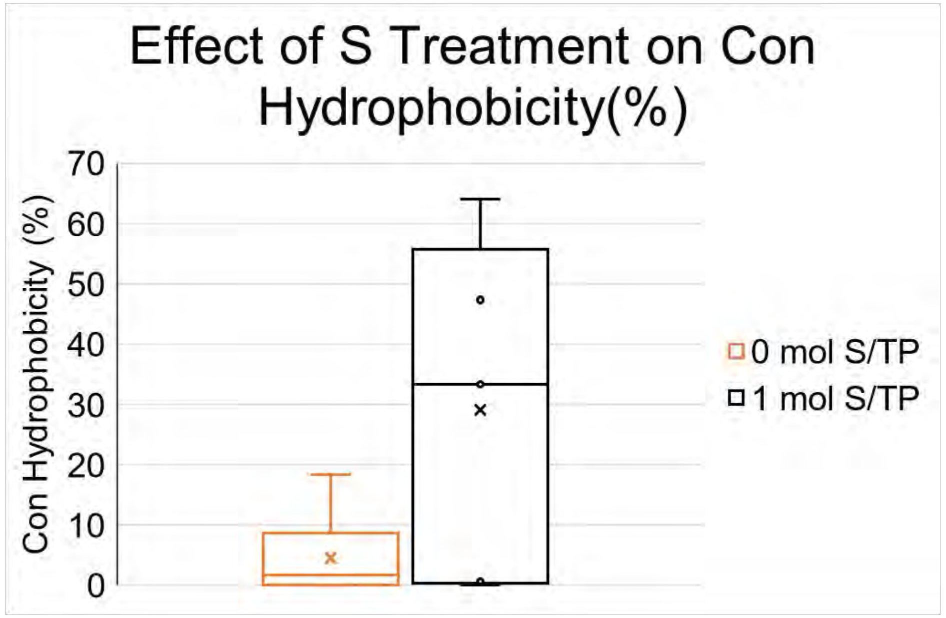

High Hydrophobicity Sample


Low Hydrophobicity Sample

Factors for Increasing Hydrophobicity to Concentrate

- pH, sulphur treatment are the two factors most important to increasing hydrophobicity





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8. Conclusions

- Total dissolved P showed a trend of increasing with elemental S addition due to iron phosphate dissolution, but not statistically significant
- pH is the most important factor for increasing total P in micro flotation, the rest of the factors had limited effect
- Hydrophobicity technique from literature does not work on flocculated samples and new method must be evaluated
    - Concentrates without floc addition did show some hydrophobicity
- 15/18 conditions showed P upgrade in concentrate vs feed sample

9. Future Work

- Complete a second DoE using Center Composite Design that is informed by the results of this Fractional Factorial DoE.
- Use carbon dioxide gas as an anaerobic flotation gas for biosolids to test if gas chemistry affects recovery.
- Incubate the biosolids with other wavelengths to encourage growth of purple phototrophic bacteria. (Hülsen, 2022)

Acknowledgements

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NSERC CRSNG

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Thank you for your attention!

Citations

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Image Sources

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2. Ottawa municipal WWTP (Image provided by ROPEC)
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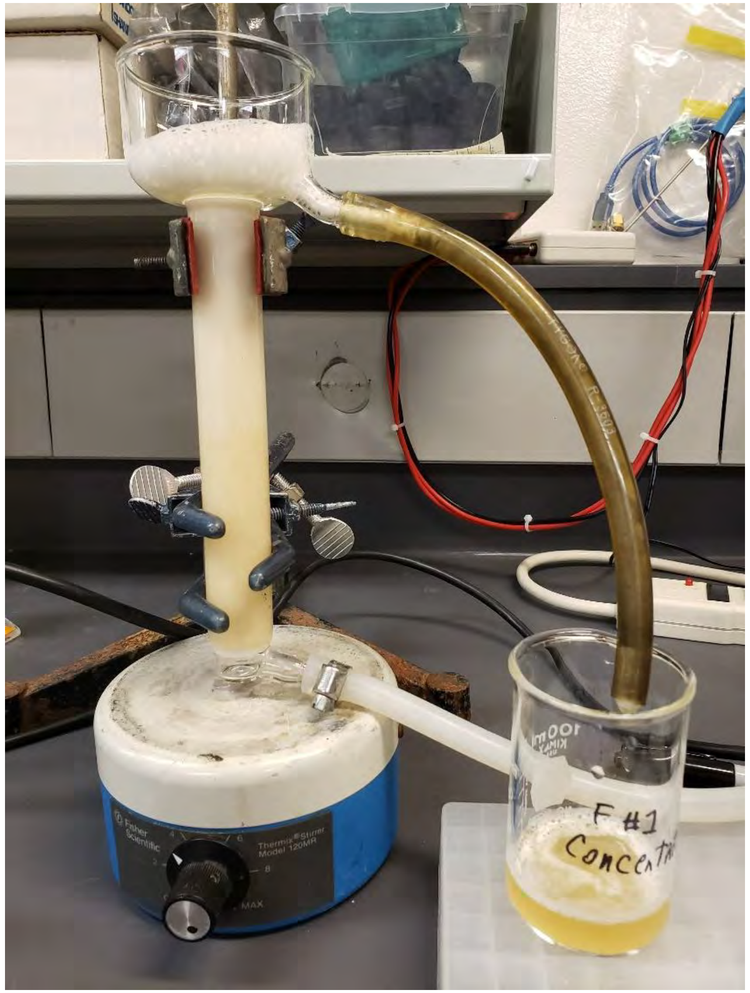
Backup Slides

Initial Microflotation Results: Visual Observation

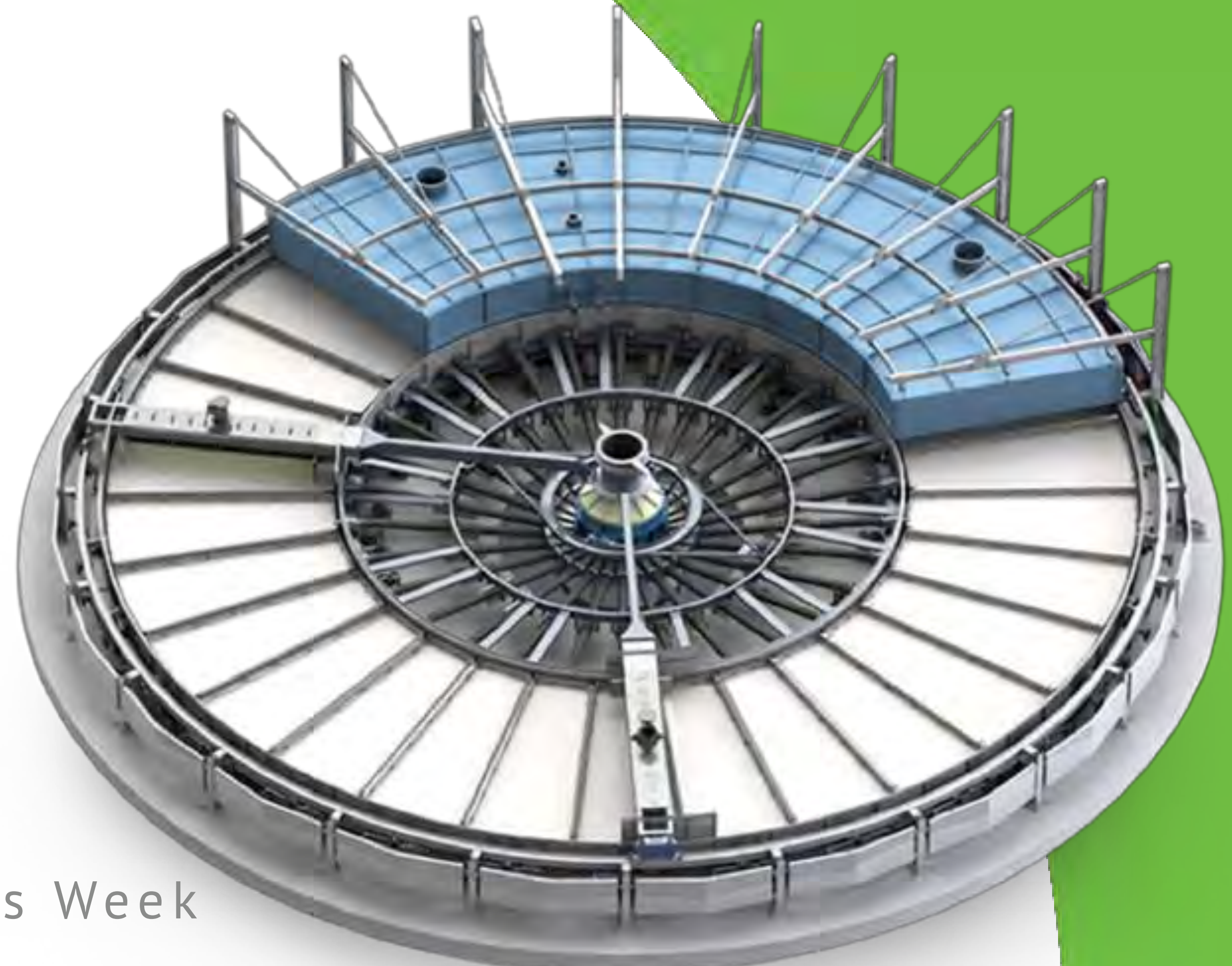


Concentrate

Tailings

- Microflotation of P-rich microbes was tested with aerobically grown *S. cerevisiae* (brewer's yeast) in YPD media.
- Yeast in its growth medium, flocculated with iron chloride and aluminum sulphate, has a very stable froth
- Concentrate and tailings can be visually distinct so continued on to biosolids

Prayon's Vision and Technologies for phosphate circular economy



04/11/2022 | Phosphorus Week

OUR MISSION

Enriching daily life...
through phosphorus chemistry

Prayon Group – Key Figures

TOTAL EMPLOYMENT WORLDWIDE

1,200

PRAYON **GROUP** JOBS *

* *according to equity method*

GROUP TURNOVER

900 millions euros*

* *according to equity method*

RESEARCH & DEVELOPMENT *

10,753 MILLIONS

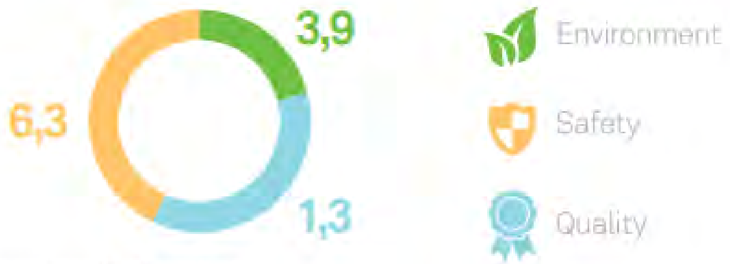
* *in euros for Prayon S.A.*

3 R&D CENTERS

—

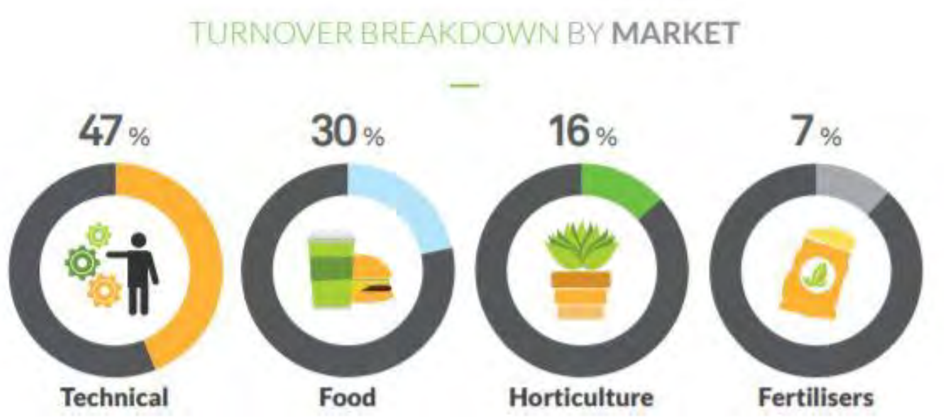
Engis & Puurs (Belgium) and Varna (Technophos, Bulgaria)

INVESTMENT BREAKDOWN
ENVIRONMENT | SAFETY | QUALITY *



* *in thousand euros for Prayon Group*

Prayon Group – Our products



Prayon Group

Prayon Technologies (PRT)

PRT: Licensing division of Prayon

More than References **130**

In over Different countries **30**

More than Validated phosphate rocks **65**

More than Processes **20**

Fertilizer grade Phosphoric Acid

- Dihydrate (**DH**)
- Hemihydrate (**HH**)
- DH Attack / HH Filtration (**DA-HF**)
- Central-Prayon Process (**CPP**)
- Hemi – Dihydrate (**HH-DH**)

Sustainability

- Low-grade rock – **Ecophos**
- Low-grade rock – **GetMore**
- Spent acids
- Secondary P-sources - **PELP**

Gas Treatment

- Fluorine Recovery
- Gas Scrubbing

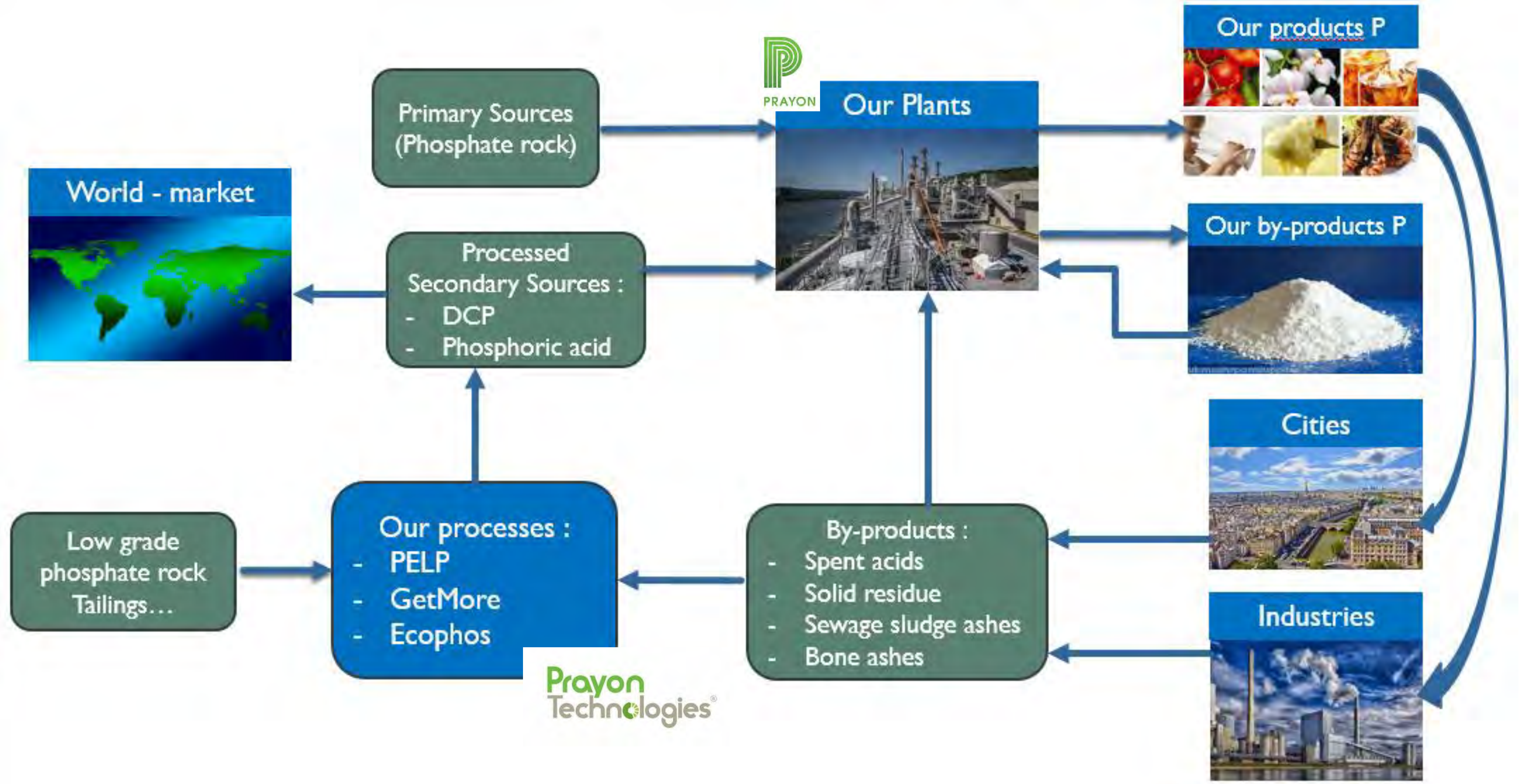
Feed grade DCP/MCP

- DCP – **Ecophos**
- DCP – **GetMoreP**
- MCP Process

Purification Technologies

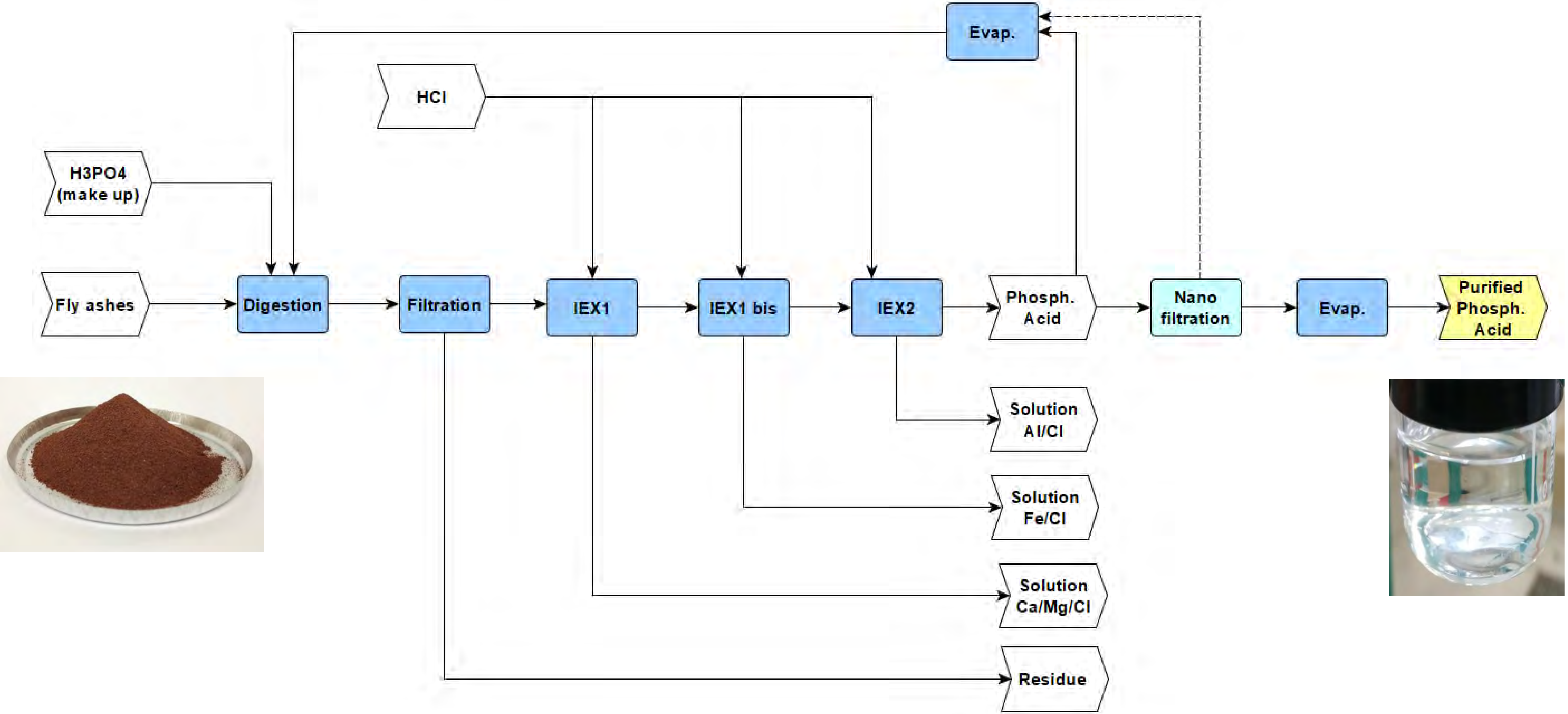
- PUMA - Membrane Filtration
- Desulfation
- Heavy Metals (**As, Cd…**) removal

Our Vision for Circular Economy



ONE PRAYON

Prayon Ecophos Loop Process (PELP)



Prayon Ecophos Loop Process (PELP)

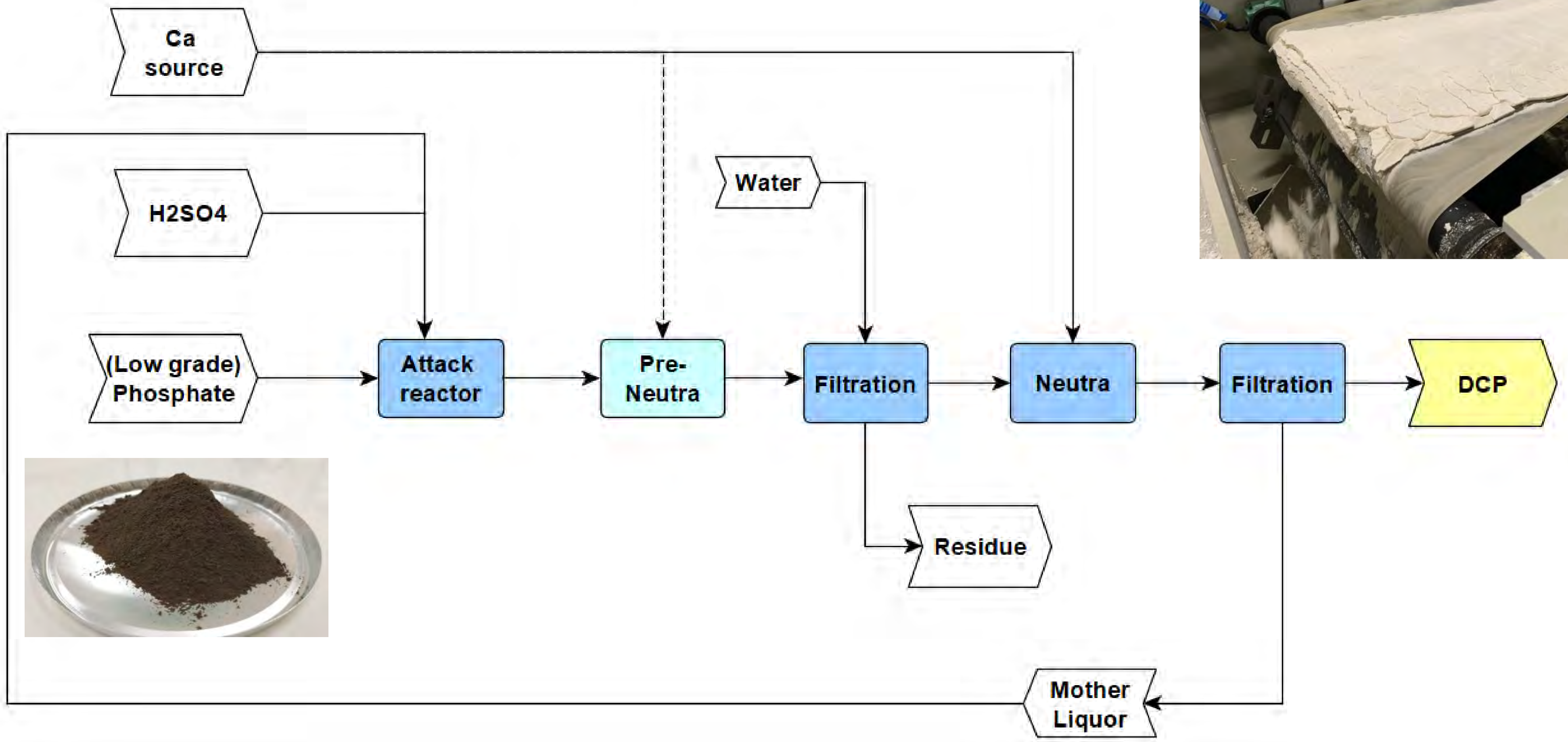
- Global yield
  - 96-98% recovery of P from fly ash
- Purification efficiency and acid quality:
  - Adapted for technical applications
  - Can be off-taken and distributed by Prayon

	TYPICAL ASH composition		PURIFIED PA composition		Removal efficiency	
Element	**Content**	**Unit**	**Content**	**Unit**	**Value**	**Unit**
P	11,2	%	26,5	%	-	%
Ca	10,2	%	*15,8*	*ppm*	>99,9	%
Mg	2,25	%	*< 5*	*ppm*	>99,9	%
Al	3,45	%	*121*	*ppm*	99,8	%
Fe	10,6	%	*18,5*	*ppm*	>99,9	%
Na	0,6	%	*136*	*ppm*	99	%
K	1,72	%	*< 5*	*ppm*	>99,9	%
As	*90,1*	*ppm*	*< 1*	*ppm*	>95	%
Cd	*6,21*	*ppm*	*< 2*	*ppm*	>86	%
Pb	*319*	*ppm*	*< 2*	*ppm*	>99,7	%
Ba	*973*	*ppm*	*< 2*	*ppm*	>99,9	%
Cr	*109*	*ppm*	*15,9*	*ppm*	93,8	%
Si	13,5	%	*150*	*ppm*	>99,9	%
SO_4	0,9	%	0,49	*%*	76,9	%

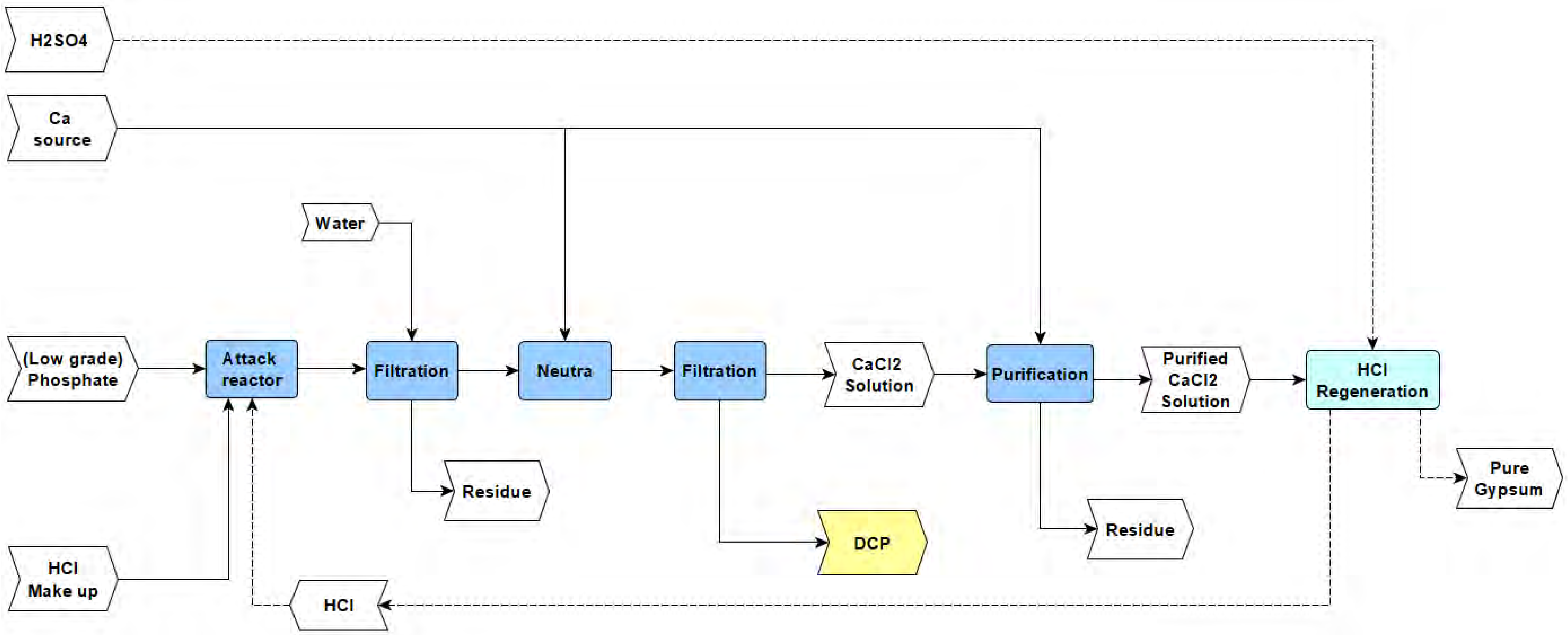
Prayon's Vision and Technologies for phosphate related circular economy

ONE PRAYON

GetMore Process (DCP)



Ecophos process (DCP)



GetMore and Ecophos DCP processes

- ✓ Use of low- to high- grade P-sources, including wastes from industry
- ✓ Use of standard quality or spent H_2SO_4 and HCl
- ✓ High quality DCP product up to 41% P_2O_5
- ✓ Low level of impurities in the DCP (Al, Fe, Mg, F, heavy metals…)
- ✓ Capacity flexible from 30,000 tons per year of DCP
- ✓ By-product (residue) for agronomical use
- ✓ High quality gypsum : plaster and plasterboards
- ✓ High recovery efficiency compared to standard beneficiation plant (up to 90%)

⇒ Two qualities of DCP can be reached:

- ✓ Feed grade
- ✓ “Super rock” (for the production of phosphoric acid)

Our pilot and semi-industrial facilities

ONE PRAYON

Conclusion

Prayon is paving the way of circular economy in the phosphates world…

- ✓ …as a **phosphate producer**: giving the opportunity to use secondary phosphate sources in our production plants
- ✓ …as a **technology supplier**: developping processes to bring the highest added value to secondary phosphate sources
- ✓ …as a **commercial partner**: helping to find the best valorization to products derived from secondary phosphate sources.

ONE PRAYON

Thank you for your attention

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https://www.prayon.com/en/