Evaluating historical releases from the Piney Point phosphogypsum facility in Tampa Bay Florida

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Sustainable Phosphorous Summit 2022

Anthropocene: Urban Phosphorous and Human Impacts

Background: Phosphogypsum in Florida

- Phosphogypsum (PG) precipitates as a byproduct during the creation of phosphoric acid for fertilizer production
  - 1 t phosphoric acid : 5 t phosphogypsum
    (Zielinski et al. 2011)
- Stored in repositories termed “Phosphogypsum stacks”
- Heavily concentrated in coastal area threatening aquatic critical zones (ACZs)
- 10^9 t of phosphogypsum stored in 24 stacks in Florida
  - 17 stacks located in the Tampa Bay area
    (Silva et al. 2022, Beck et al. 2022)
- Stacks become difficult to maintain over time

Piney Point Phosphogypsum Facility

WUSF Public Media

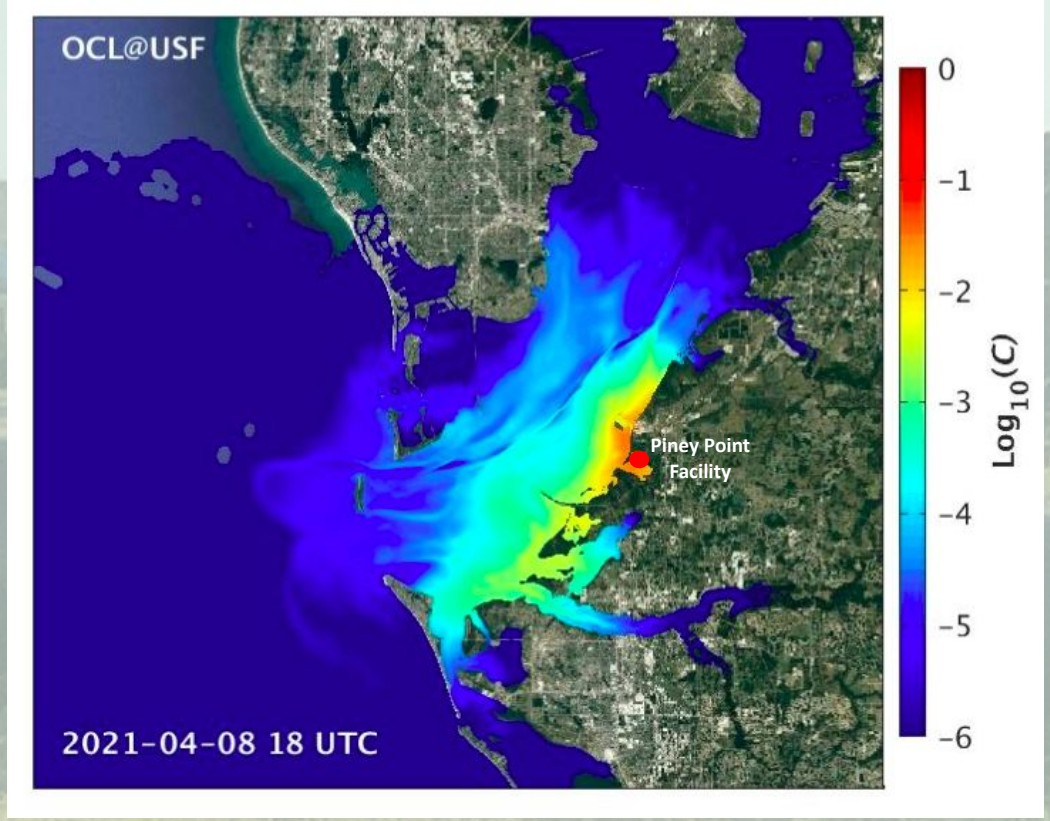
Anthro**PO_4**cene Impacts on Aquatic Critical Zones

Spills and releases of high-nutrient wastewater have become chronic stressors on nearshore environments

- 2021 Piney Point emergency release event
  - 10 days of wastewater effluent release (March 30 – April 9)
  - **814 million liters of stack water discharged**
    - NH_3/NH_4^+, Ortho-P, Nitrate, Nitrite
    - ~186 metric tons of total nitrogen into Tampa Bay

  (Beck et al. 2022)
- Reactive hazardous elements and natural radionuclides remain bound to PG (Silva et al. 2022)
- Tampa Bay Coastal Ocean Model
  - Effluent plume prediction

  (University of South Florida College of Marine Science Ocean Circulation Lab)



Piney Point effluent Discharge Photo: L. Carnahan (UF IFAS)

Subsequent Events Following the Piney Point Discharge

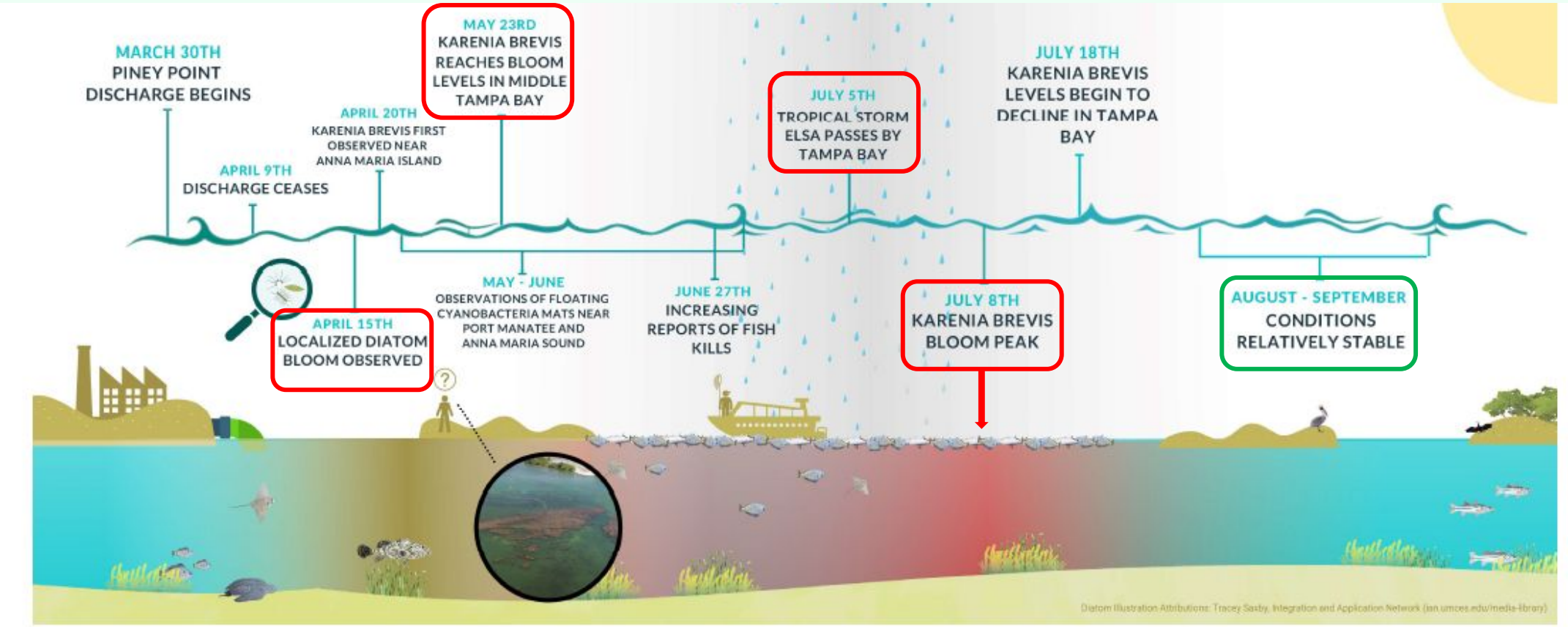


Figure 2: Graphical timeline of events in Tampa Bay from March 30th through September 2021 following the release from Piney Point. Inset image shows blooms of filamentous cyanobacteria (Dapis spp.).

Beck et al. 2022

Long-Term Monitoring

NSF RAPID GRANT

Photos: S. Anderson, P. Norby, A. Chappel

Assess the fate and transformation of nutrients as they move through the ecosystem

Evaluate *regime shifts* of primary producer communities

Biweekly sampling: April 2021-October 2022

Parameters collected:

- YSI EXO2 Sonde
  - Temperature, pH, Salinity, turbidity, DO, FDOM, Chl-a,
- Nutrients
  - TP, OrthoP, PP, TDP, SRP, DOP, TKN, NO_3, NH_4
- Primary producers
  - Phytoplankton, macroalgae, seagrass
- Stable isotopes
  - $\delta^{18}Op$, $\delta^{18}O_{H2O}$, $\delta^{13}C$, $\delta^{15}N$

Piney Point Historical Release Timeline

1966
- Piney Point facility opened

1970s
- Wastewater released into Bishop Harbor (volume unknown)

Fish kills observed

1997
- 204 million liters released into Bishop Harbor

Tropical Storm Gabrielle

2001
- Owners file Bankruptcy
- FDEP takes over
- 40 million liters released into Bishop Harbor

2003-2007
- Multiple emergency releases into Bishop Harbor
- Totaling over 4 billion liters

Hurricane Francis 2004

Fish kills and algal blooms observed

2011
- 640 million liters of wastewater and dredge material are released into Bishop Harbor and Piney Point Creek

Tropical Storm Elsa

2021
- 814 million liters released into Bishop Harbor and Piney Point Creek
- State of emergency declared

(Garrett et al. 2011, Florida Museum [Bausback, 2022], Tampa Bay Times [O'Donnell, 2021])
Photo: Piney Point NGS South Reservoir October 2021 (Chappel)

Is there evidence of phosphogypsum discharge events within the Tampa Bay sediment record?

Piney Point Creek

STUDY AREA

ArcGIS Online (Esri, DigitalGlobe, GeoEye, i-cubed, USDA FSA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community)

Photo: P. Norby

Downcore Analyses

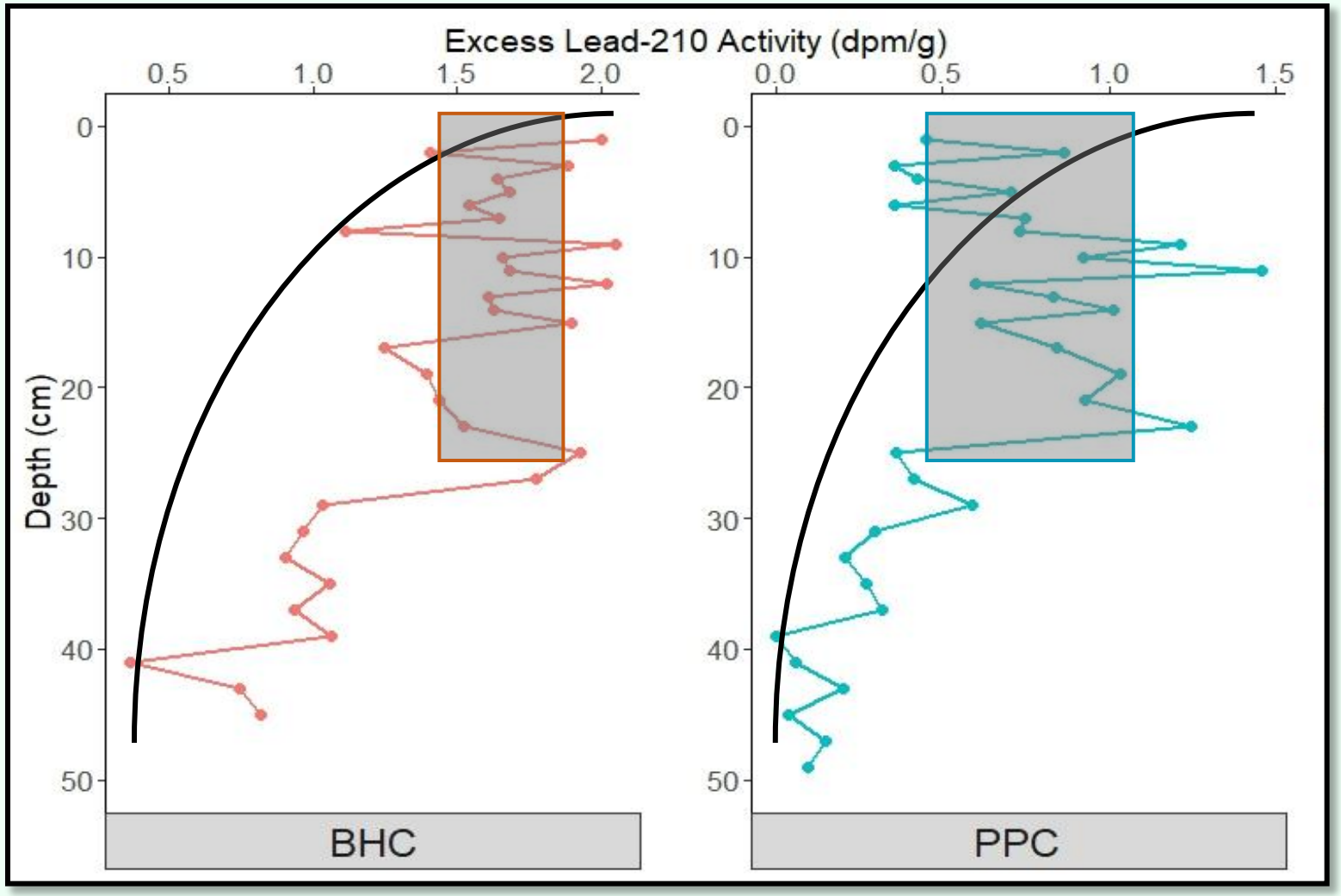
- Quantifying depositional history and phosphorus accumulation rates in Bay sediments

Collected February 2022

- Multi-stable isotopes
  - $\delta^{18}Op$, $\delta^{13}C$, $\delta^{15}N$
- Radioisotopes
  - PG is known for high radium levels
  - Excess^{210}Pb = Total^{210}Pb – Supported ^{210}Pb
  - ^{226}Ra = Supported ^{210}Pb
- Nutrients
  - Total phosphorous and nitrogen
  - Accumulation rates

Preliminary Downcore Data

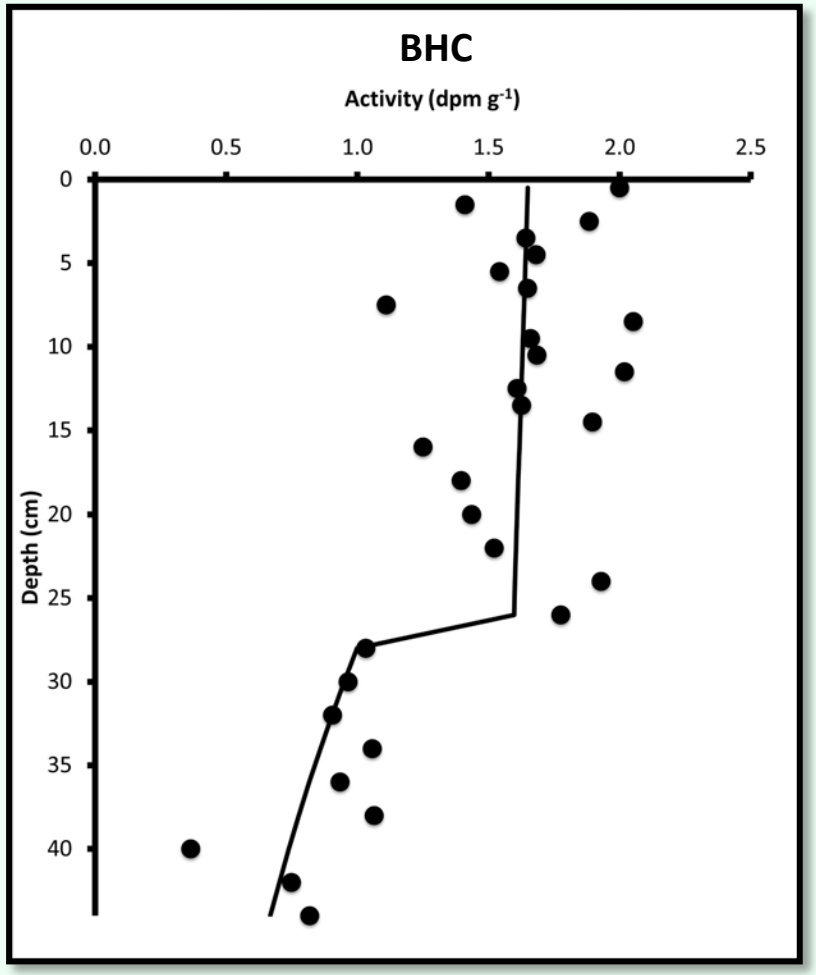
Excess ^{210}Pb Activity



- Not a classic decay curve seen in "undisturbed" systems
- **Variable Decay Curve**
- Sedimentation [inputs/outputs] vary over time
- Upper portion of cores [top ~25 cm] show either bioturbation or a **"dump"** of material into the system

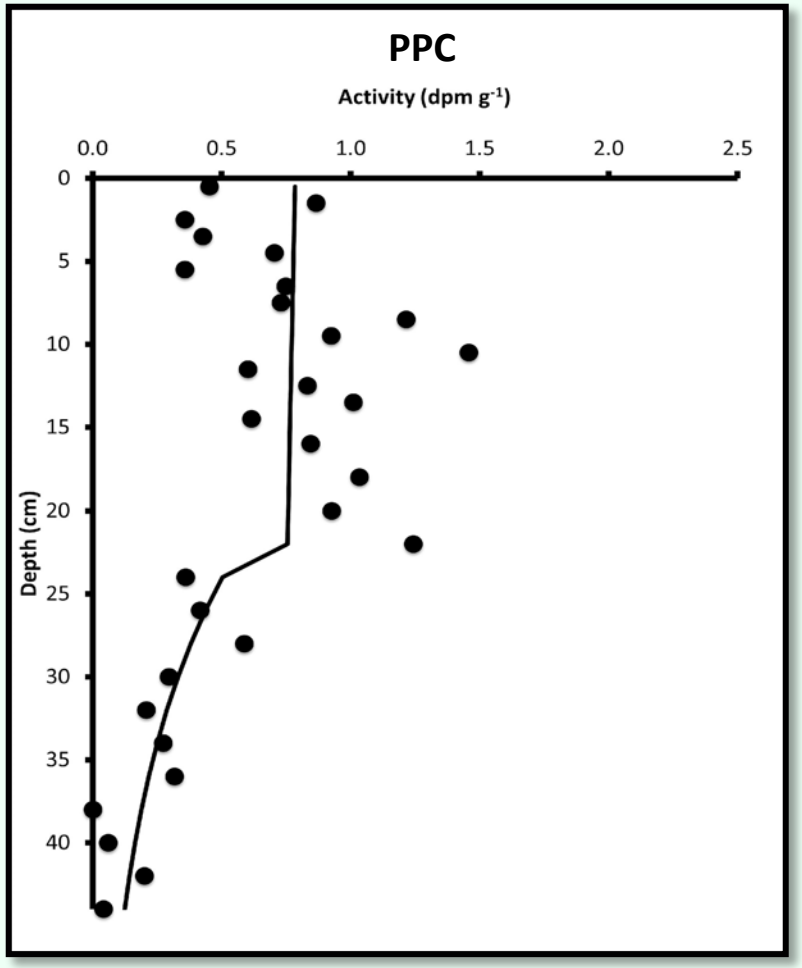
Preliminary Downcore Data

Biodiffusive Mixing Model



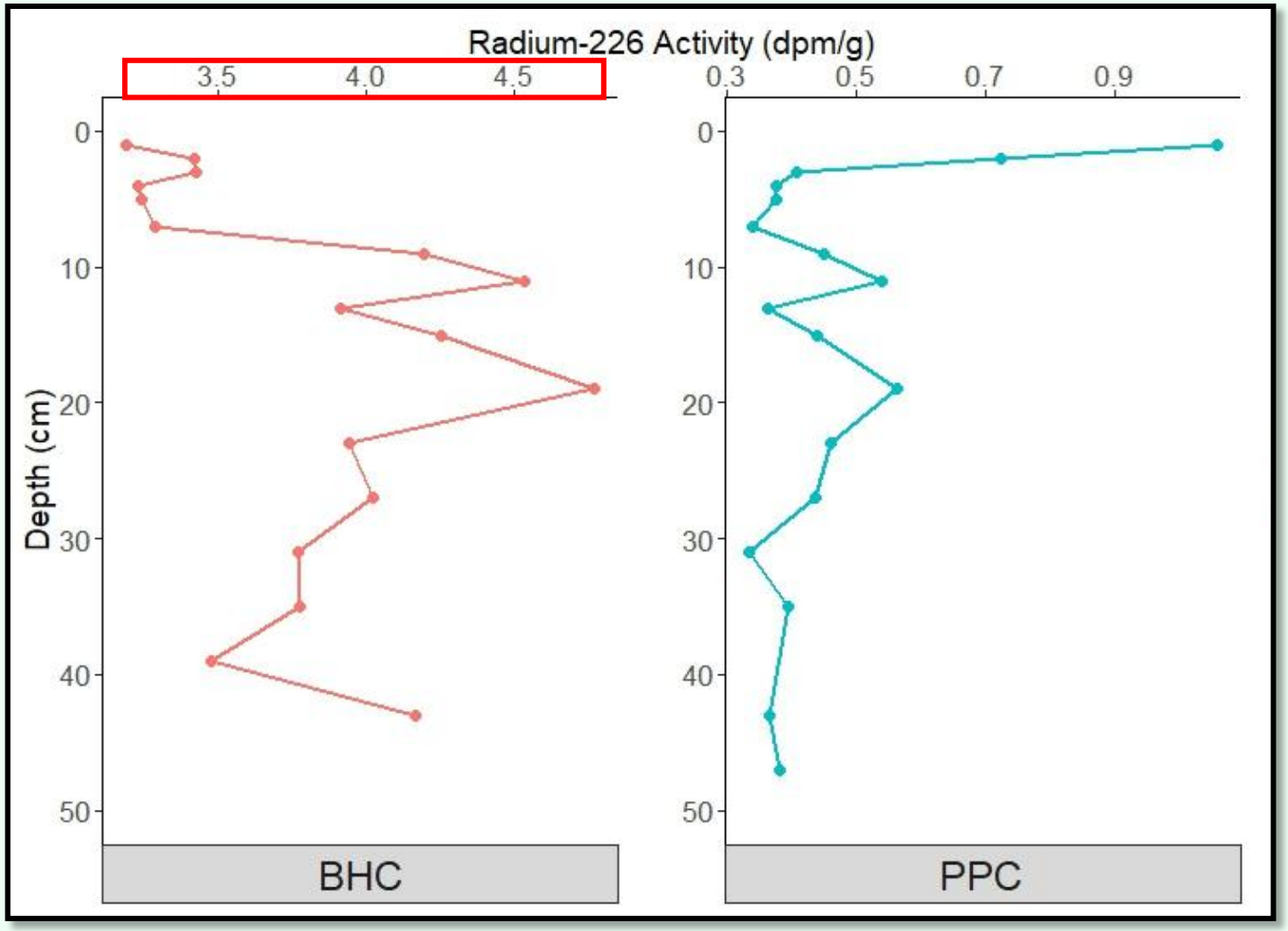
- Further reinforces the excess ^{210}Pb activity measured in the upper portion of cores showing bioturbation or a **"dump"** of homogenized sediment from an episodic event (Dellapenna et al. 1998)

- Ghost Shrimp bioturbation not suspected (Klerks et al. 2007)



Preliminary Downcore Data

^{226}Ra Activity

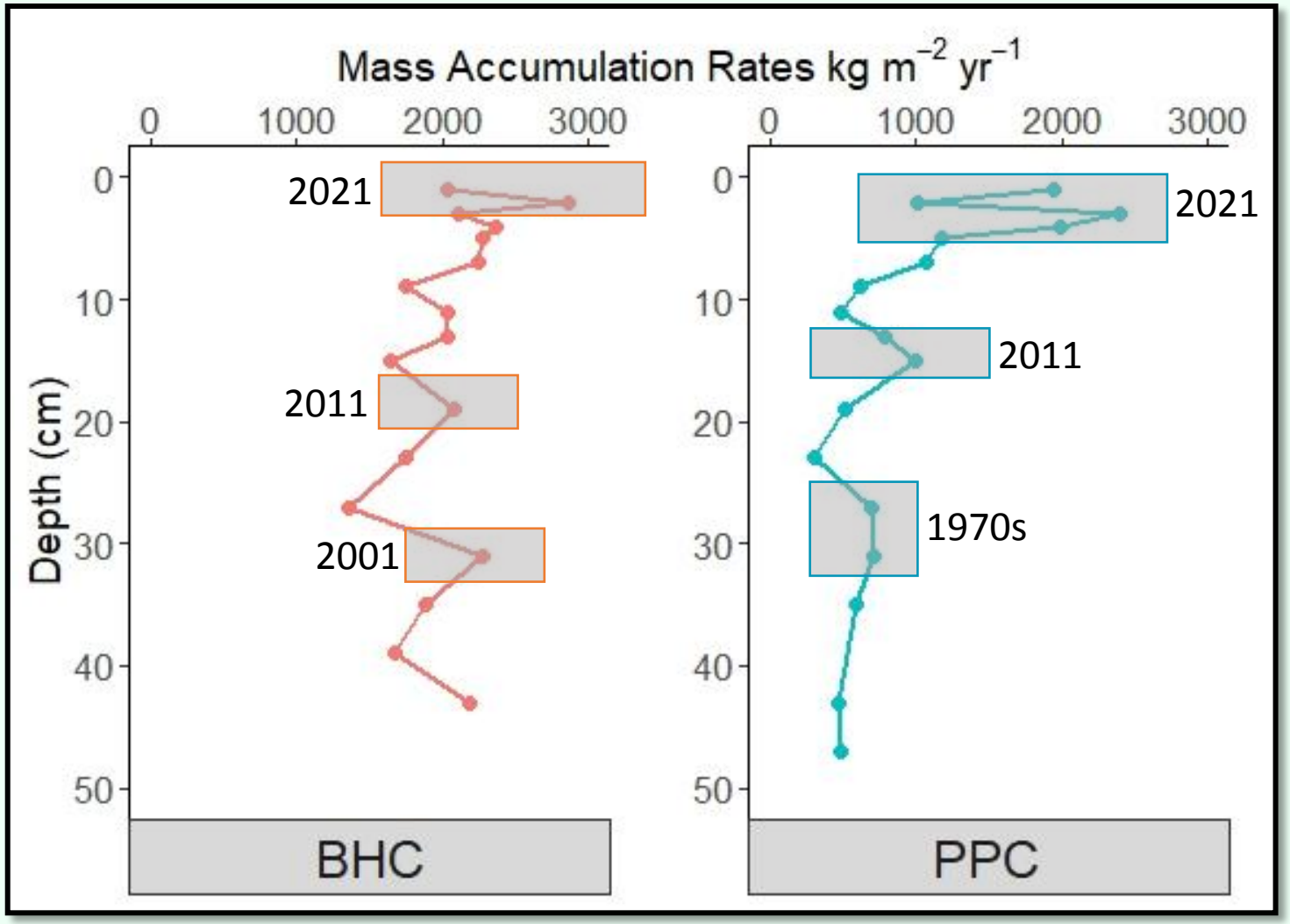


- Represents supported ^{210}Pb
- Activity in undisturbed systems is relatively low and constant
  - < 1 dpm/g
  - ^{226}Ra soluble in seawater
  - ^{226}Ra half-life = 1600 years
  - Activity should be relatively stable over a century

Episodic event(s) bringing radium in excess into the system is plausible

Preliminary Downcore Data

Mass Accumulation Rates



- Mass accumulations rates are 3 orders of magnitude larger than other tropical estuaries

(Robbins et al. 2000, Sabaris & Bonotto 2011, Corcho-Alvarado et al. 2014)

- Rate peaks correspond to discharge events from Piney Point

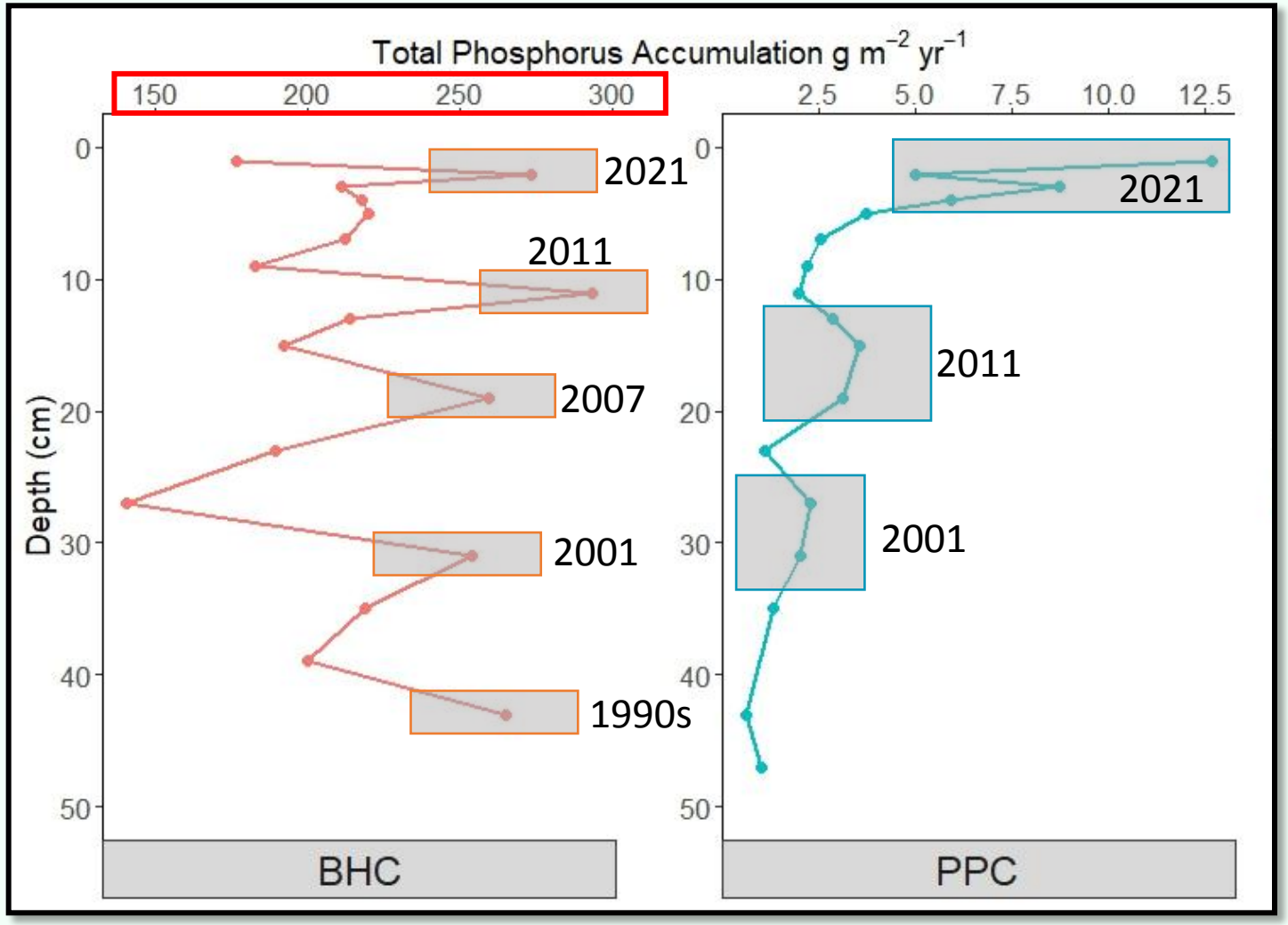
2021, 2011, 2001, and 1970s

- Enhanced bottom resuspension events support imperfect sediment records

(Baskaran & Swarzenski 2007)

Preliminary Downcore Data

Total Phosphorus Accumulation



TP accumulation rates have strong peaks corresponding to historical discharge events from Piney Point

TP Concentrations:

BHC: 8,680-14,398 µg/g

PPC: 130-651 µg/g

TAKEAWAYS & NEXT STEPS

- **Tampa Bay is acting as a natural archive**
  - Sediment cores are recording wastewater discharge events from the Piney Point facility
  - Large quantities of radium and total phosphorus are getting deposited and buried in the coastal sediments

- Does this create a potential for legacy phosphorus to impact the Bay's health in the future?

- Next steps: sedimentary algal pigment & $\delta^{18}O$-phosphate analysis
  - Correlation to harmful algal bloom events?
  - Evaluate the source, fate, and transformation of legacy phosphorus

Acknowledgments

- Center for Coastal Solutions Field Technicians
- Morrison Lab Personnel
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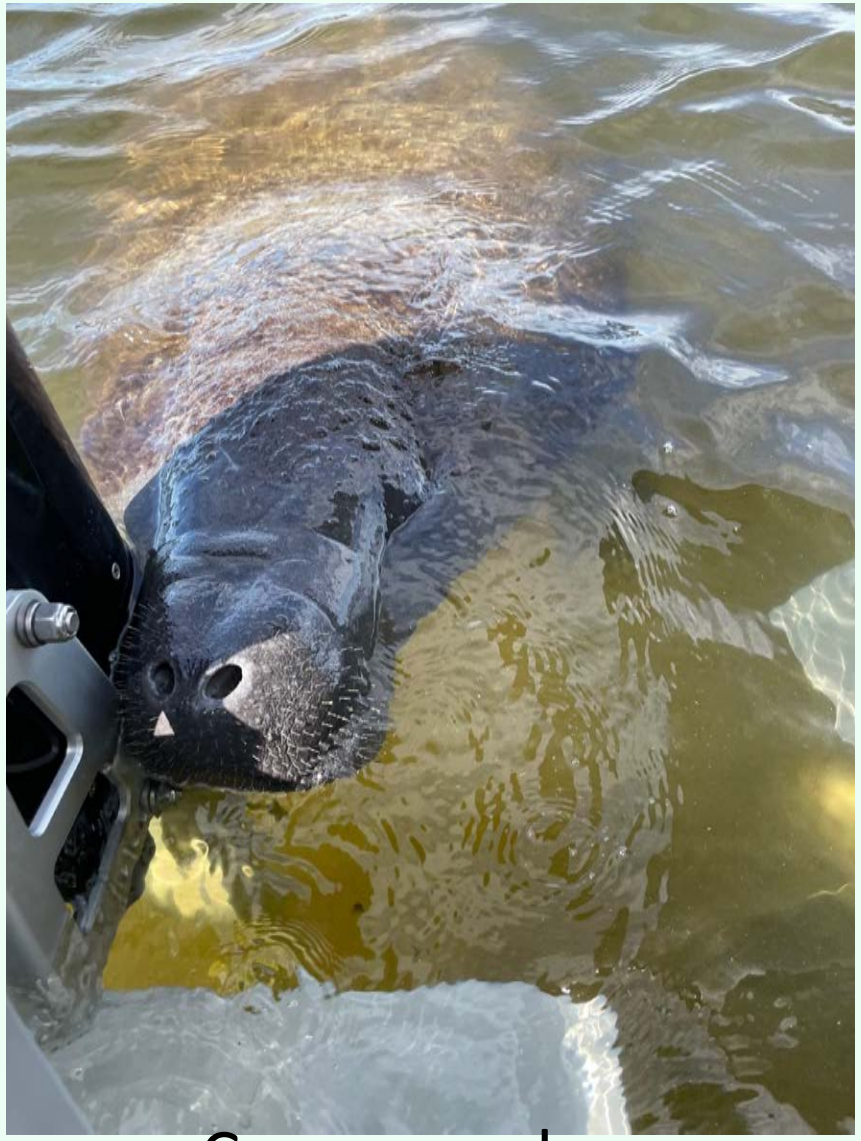
- UF Analytical Research Lab
- Tampa & Sarasota Bay Estuary Programs
- UF Geology Department
- Tampa Bay Manatees

RAPID 2130675



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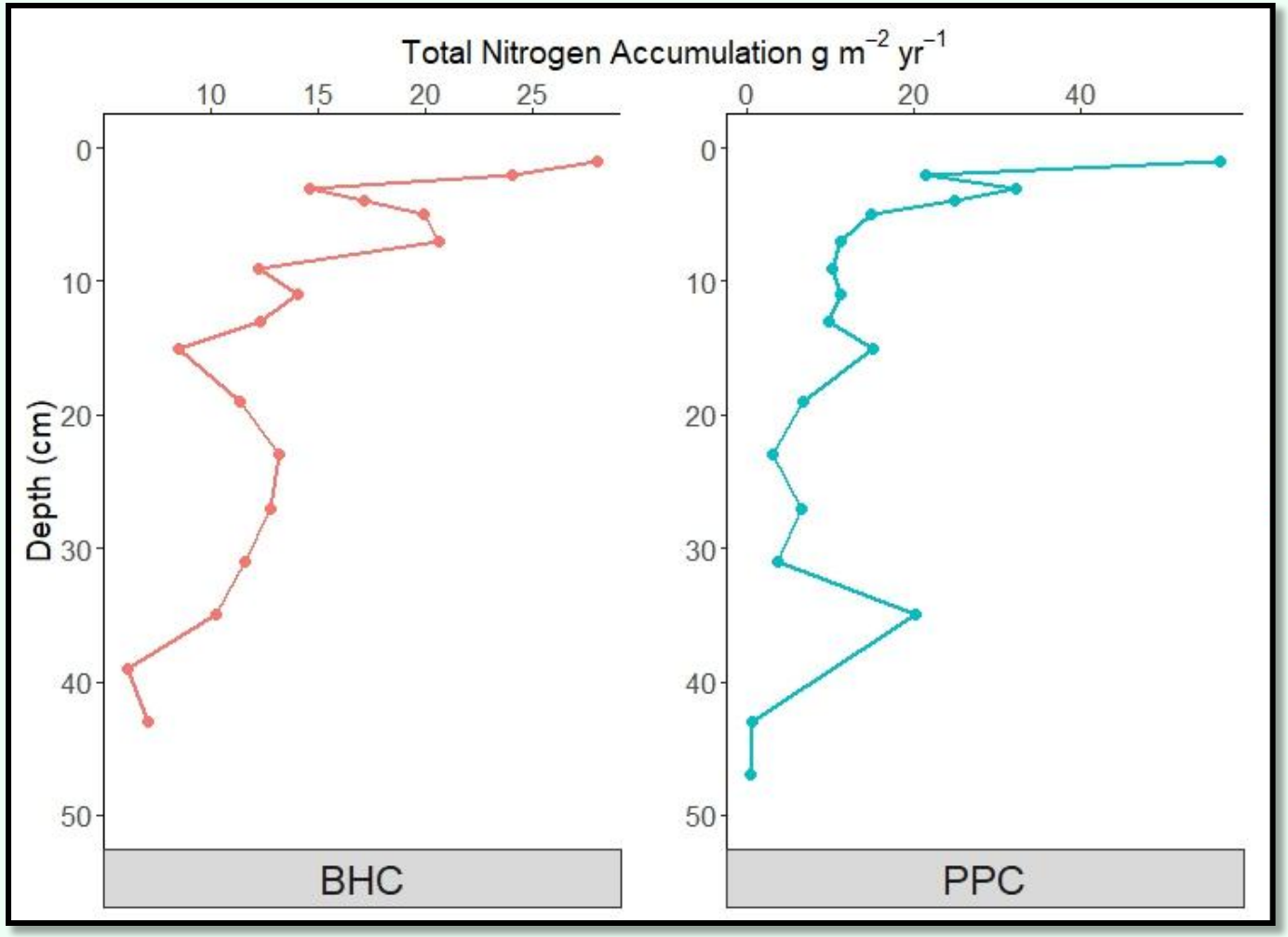
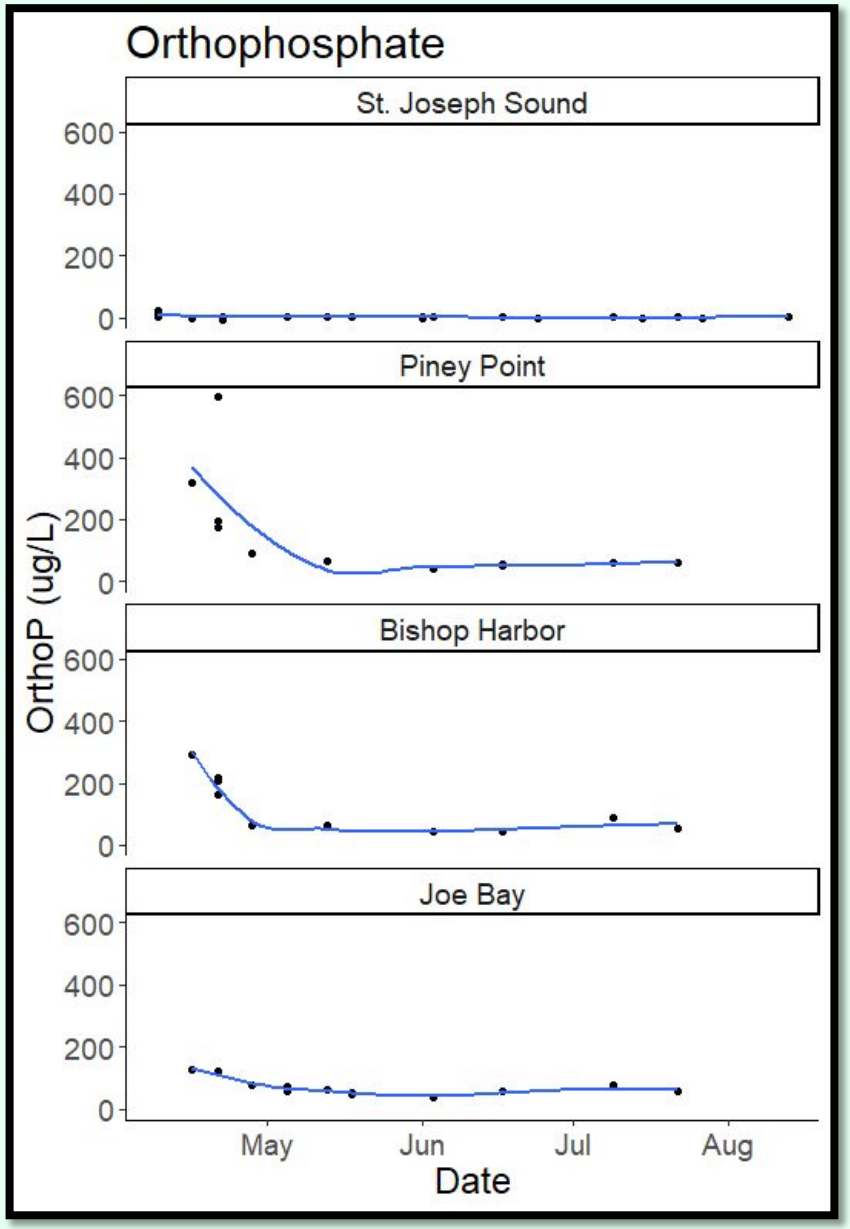
Preliminary Downcore Data
Total Nitrogen Accumulation



- More TN accumulation compared to TP accumulation in the PPC core
- Peaks in the top 5 cm of both cores correspond to the 2021 discharge event
- Other discharge-related peaks:
  - 2011, 2001, 1990s

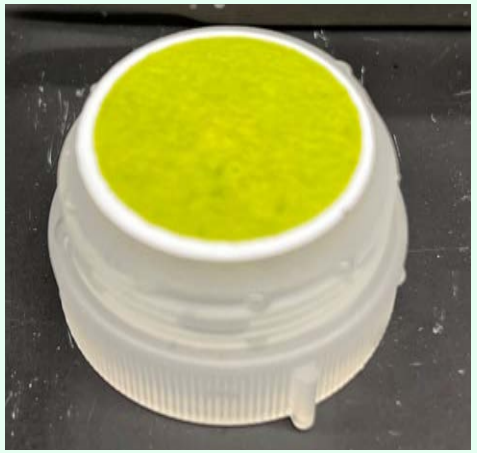


Morrison et al. In Prep

Preliminary Data

April –July 2021

Increases in orthophosphate were seen within the Bay with Piney Point and Bishop Harbor showing the greatest response



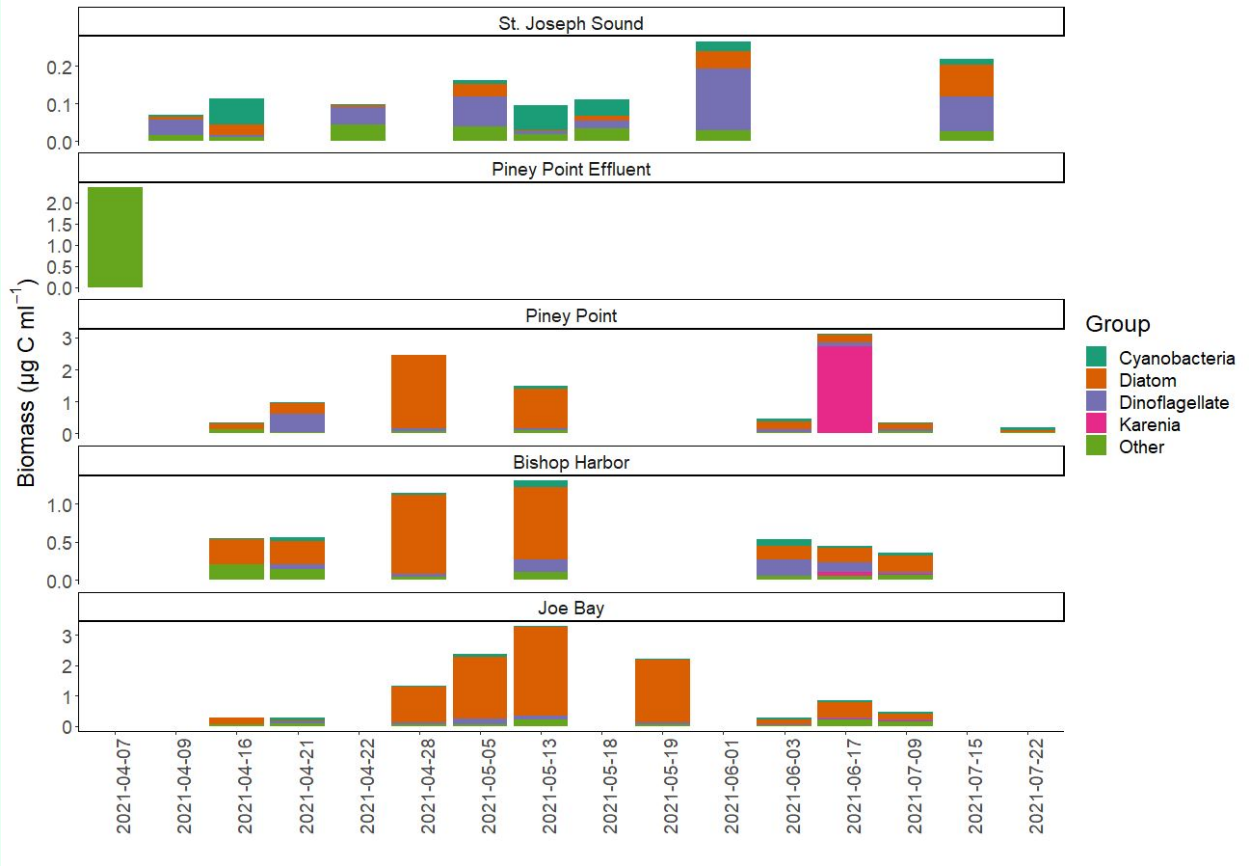
PP effluent orthophosphate concentrations: 140 mg L^{-1}

Preliminary Data

April –July 2021

Phytoplankton Community Composition

- Effluent was dominated by chlorophytes
- Localized diatom growth was seen soon after discharge
- *Karenia brevis* has the highest biomass in mid-June
  - Harmful algal bloom
- *Prorocentrum* were seen in high abundance
  - Also seen after the 2003 discharge into Bishop Harbor (Garrett et al 2011)



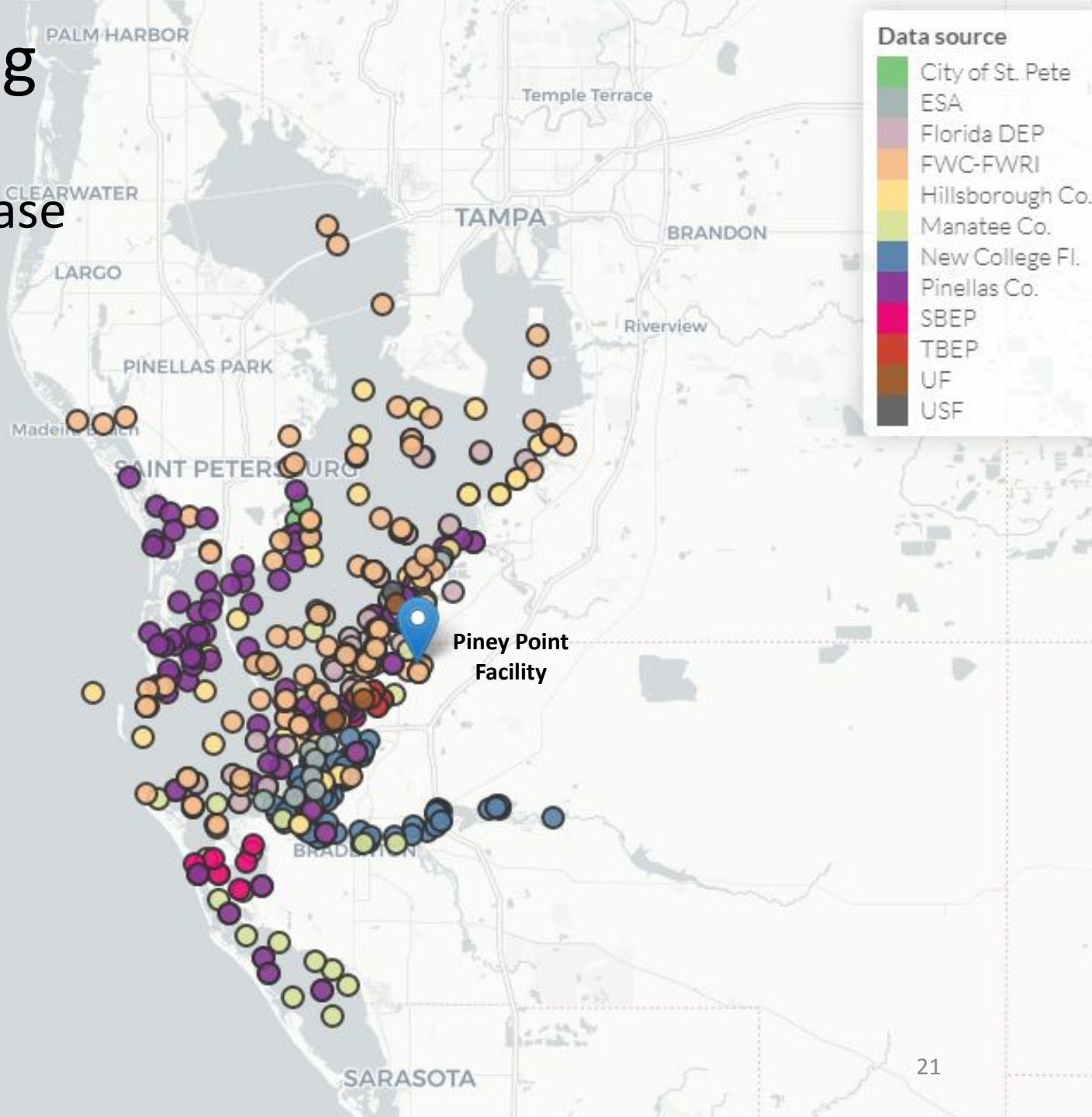
Morrison et al. In Prep

Collaborative Monitoring Efforts

To capture the effects of the release

- Tampa Bay Estuary Program (TBEP) led initial field efforts to ensure Bay-wide coverage of potential impact locations
- Many local institutions and agencies involved
- Data Collected:
  - Suite of water quality parameters
  - Macroalgae
  - Phytoplankton
  - Seagrass
  - Hydrodynamic data
- Monitoring dashboard created to aid in data sharing and analysis

[PINEY POINT ENVIRONMENTAL MONITORING DASHBOARD (tbep.org)]

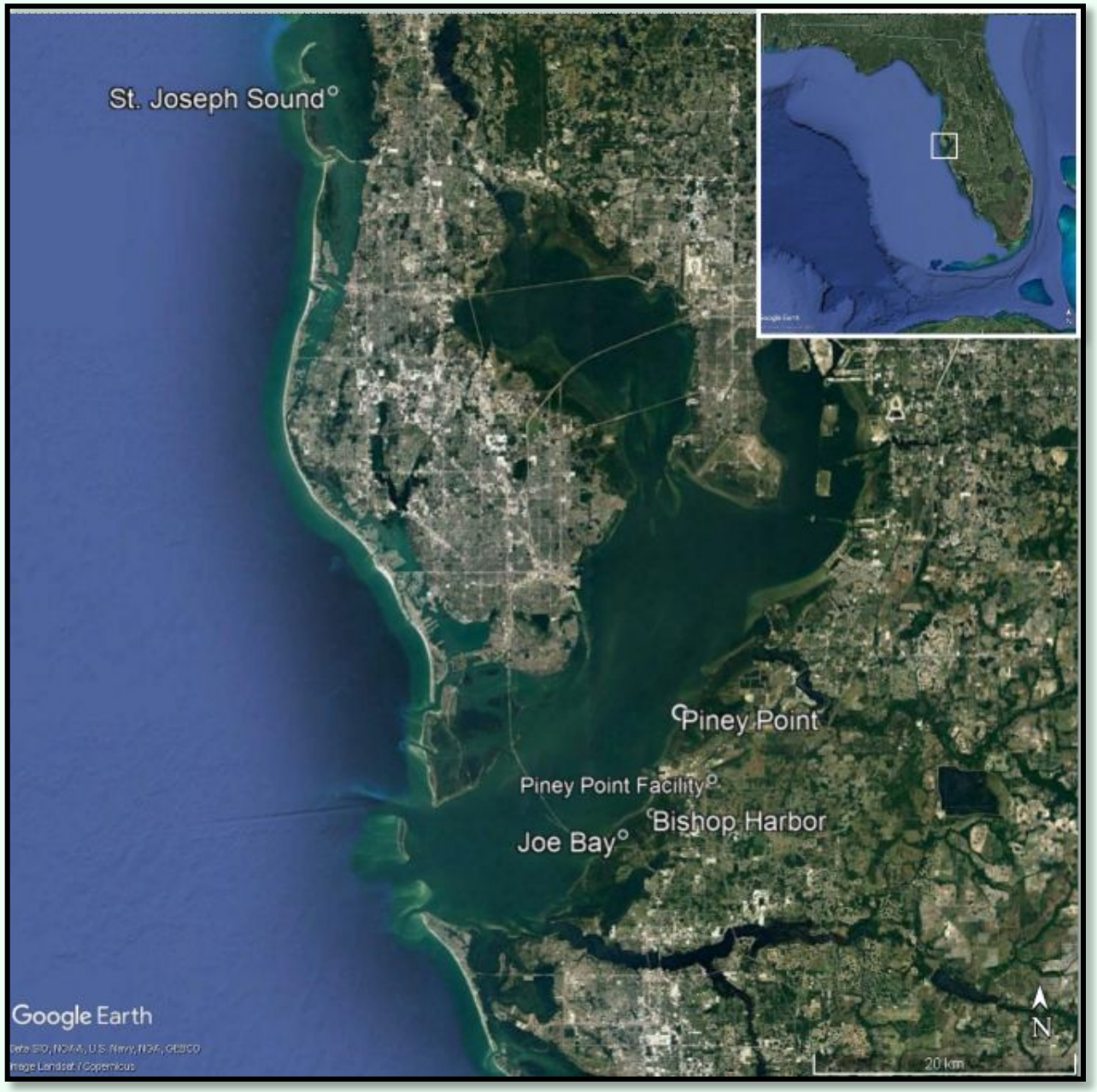


SITE MAP

UF Center for Coastal Solutions

- Lower Tampa Bay sites
  - Piney Point
  - Bishop Harbor
  - Joe Bay
- Reference site
  - St Joseph Sound
- Bi-weekly sampling
  - April 2021 – October 2022

- Sediment coring locations
  - Piney Point
  - Bishop Harbor
  - October 2021 and February 2022



Sediment Coring Sites

PPC Coring Site

BHC Coring Site

Technische Universität Berlin

Urban Water Interfaces (UWI)

IGB
Leibniz Institute of Freshwater Ecology and Inland Fisheries

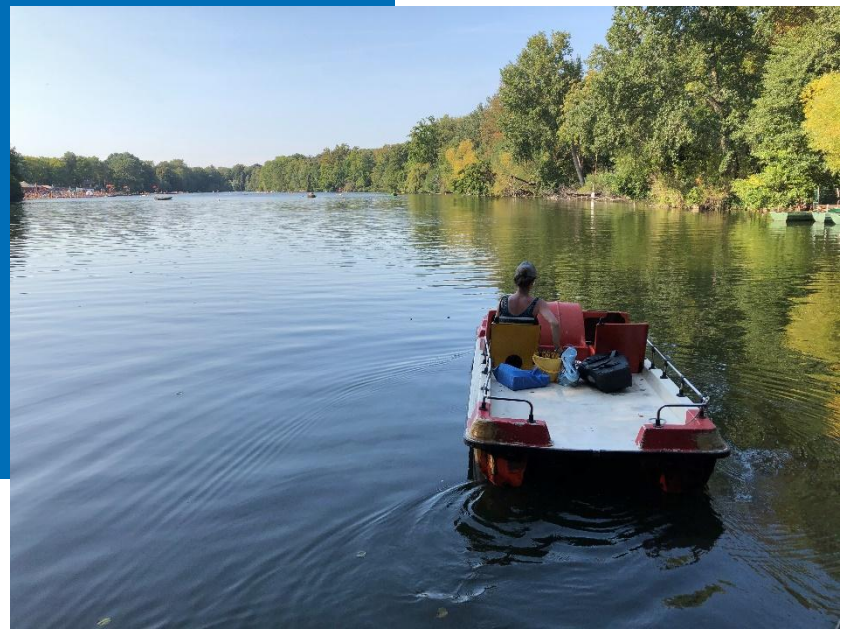
Universität Potsdam

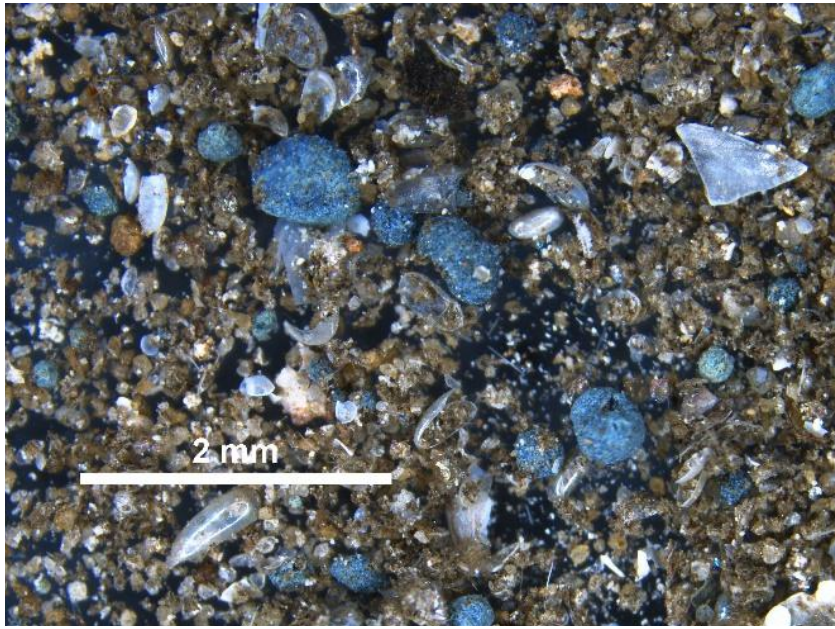
The long-term effect of iron amendments on sedimentary phosphorus retention

Lena Heinrich, Michael Hupfer

Phosphorus week

Raleigh, 4 November 2022





Water Research 189 (2021) 116609

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

Transformation of redox-sensitive to redox-stable iron-bound phosphorus in anoxic lake sediments under laboratory conditions

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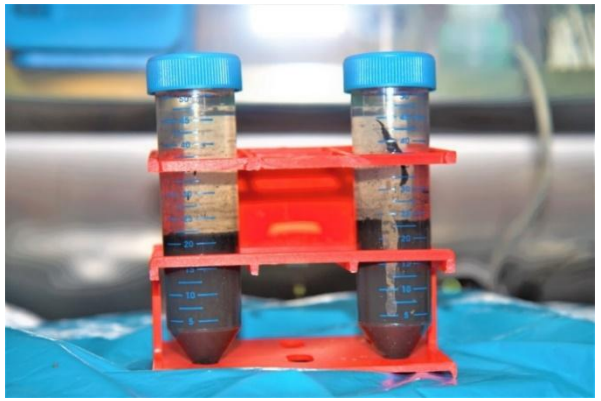


Journal of Soils and Sediments
https://doi.org/10.1007/s11368-021-03099-3

SEDIMENTS, SEC 2 • PHYSICAL AND BIOGEOCHEMICAL PROCESSES • RESEARCH ARTICLE

Sulphate reduction determines the long-term effect of iron amendments on phosphorus retention in lake sediments

Lena Heinrich[1,2] · Jan Dietel[3] · Michael Hupfer[1]

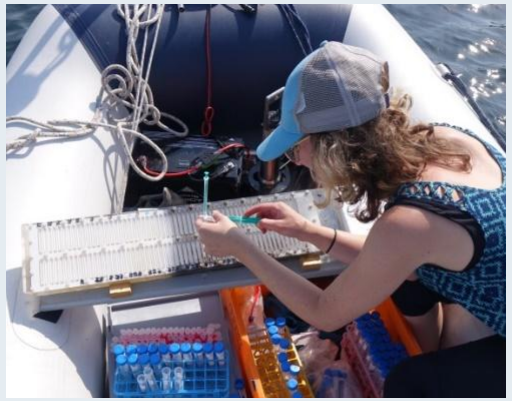
Received: 9 June 2021 / Accepted: 24 October 2021

Agenda

Background

In-lake P precipitation

Methods



Lab & field evidences

Vivianite

vs.

Pyrite

Management implications

Long-term P retention

Fe dosage estimate
Based on current sulphate reduction

Fe amendment
Check sulphate reduction after few months/years

Fe dosage adjustment
Understand interplay of Fe and sulphate reduction

Background – In-lake P precipitation by Fe

Fe dosing

Water - oxic

$Fe^{3+}O(OH) + PO_4^{3-}$

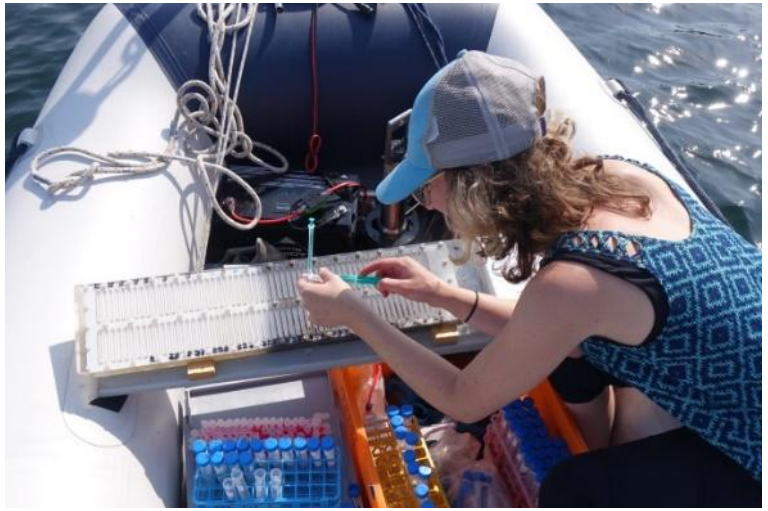
Fe^{2+} PO_4^{3-} Release?

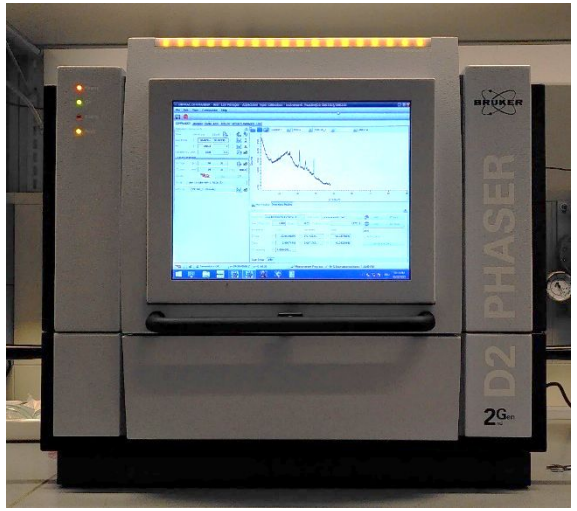
Sediment - anoxic

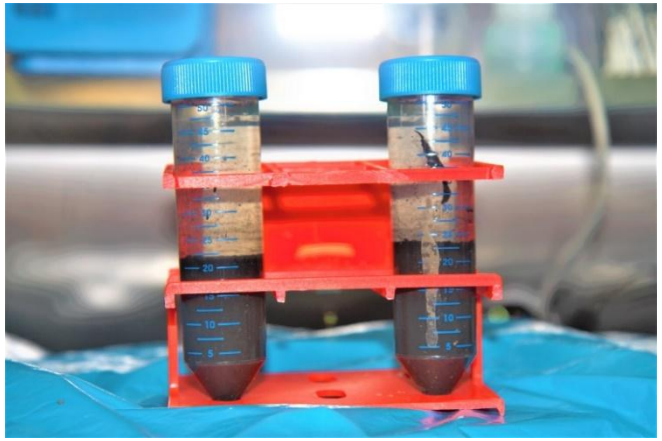
$Fe^{3+}O(OH) + PO_4^{3-}$ Long-term fate?

Low redox conditions limit the effectiveness of Fe dosing for long-term P retention?

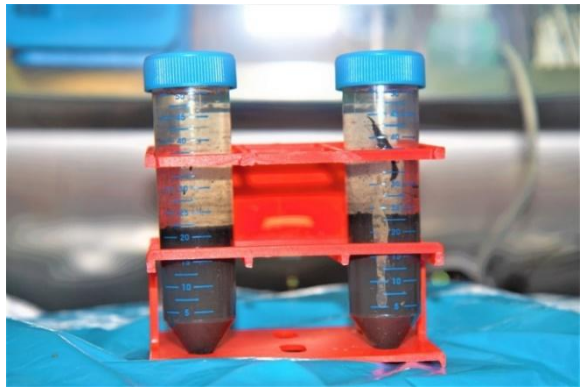
Methods







Laboratory experiment – Anoxic incubation



Fe dosing

Water - oxic

$Fe^{3+}O(OH) + PO_4^{3-}$

Sediment - anoxic

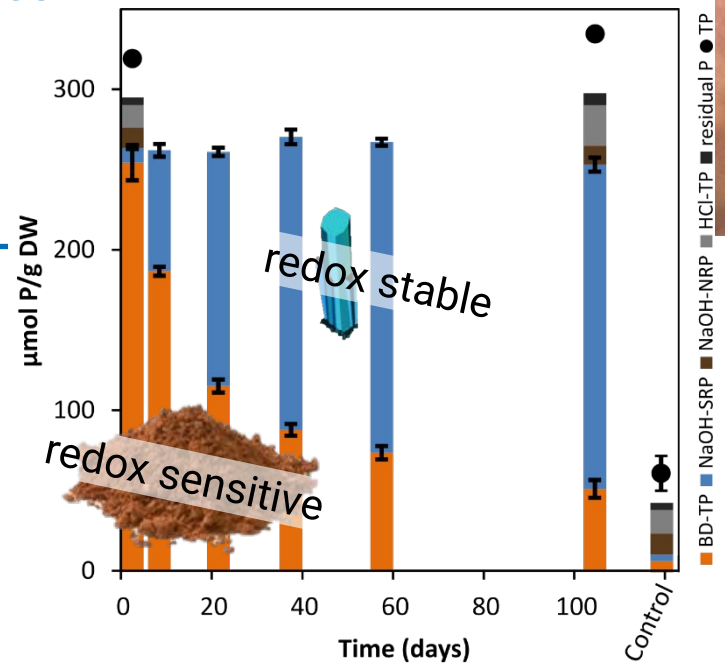
$Fe^{3+}O(OH) + PO_4^{3-}$

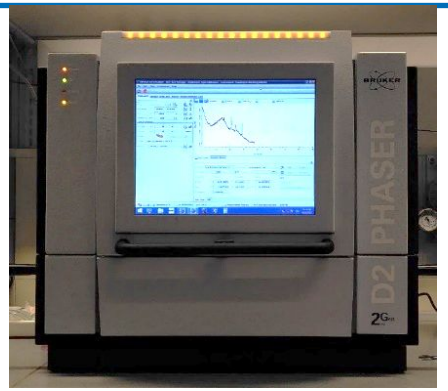
Lab scale evidence – Fe-P sink-switch

Fe dosing

Water - oxic

$Fe^{3+}O(OH) + PO_4^{3-}$





Sediment - anoxic

$Fe^{3+}O(OH) + PO_4^{3-} \xrightarrow{\sim 70\%,\ >40\ \text{days}} Fe^{2+}_3(PO_4)_2 \cdot 8\ H_2O$

PRECURSOR **LONG-TERM P SINK**

Vivianite

- **Fe dosing can initiate the formation of the precursor.**
- **Fe-P can be immobilized within anoxic lake stratification periods.**

Figure: Heinrich et al. 2021. Water Res 189, 116609.

IGB

Conclusion - Long-term P retention by Fe under anoxic conditions

Water - oxic

Sediment - anoxic

$Fe^{3+}O(OH) + PO_4^{3-}$

$Fe^{2+}_3(PO_4)_2 \cdot 8\ H_2O$

What happens outside the laboratory under more realistic conditions?

Field study - Sites

80ies	eutrophic
1992	**Fe dosing** 500 g Fe/m^2 as $Fe(OH)_3$ and $FeCl_3$ + other management measures
2010	Long term improvement

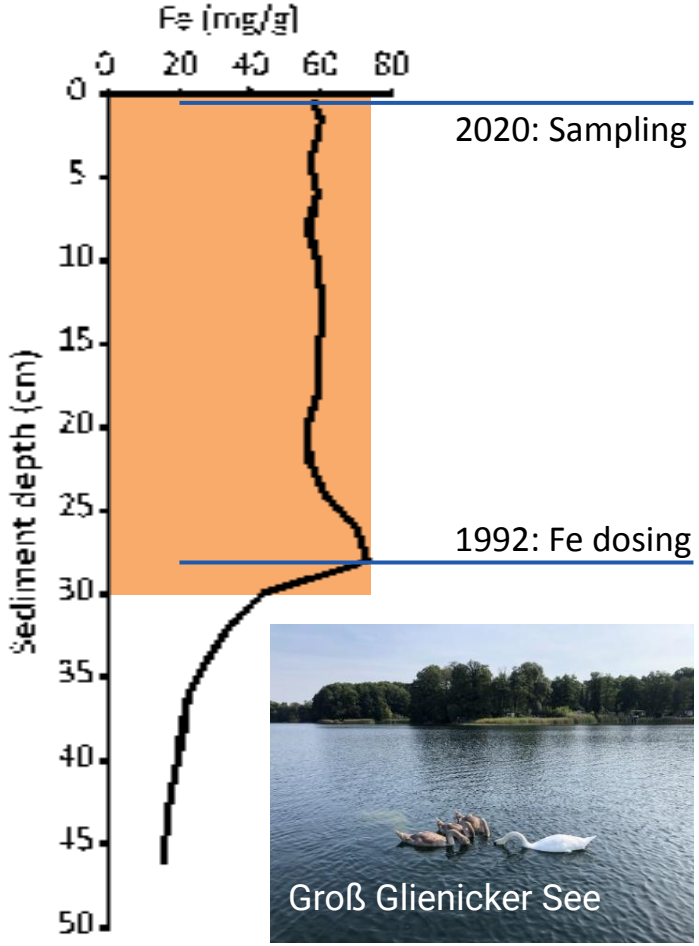
90ies	eutrophic
2000	**Fe dosing** 150 g Fe/m^2 as $Fe(OH)_3$ + other management measures
2002	Short term improvement
2018	Long term improvement

Information: Wolter 2010 in Restoration of Lakes, …, pp 85-99.

Information: ILAT, Berlin, 2003. & enviteam & LimPlan, Berlin, 2018.

IGB

Field scale evidences – Sediment stratigraphy



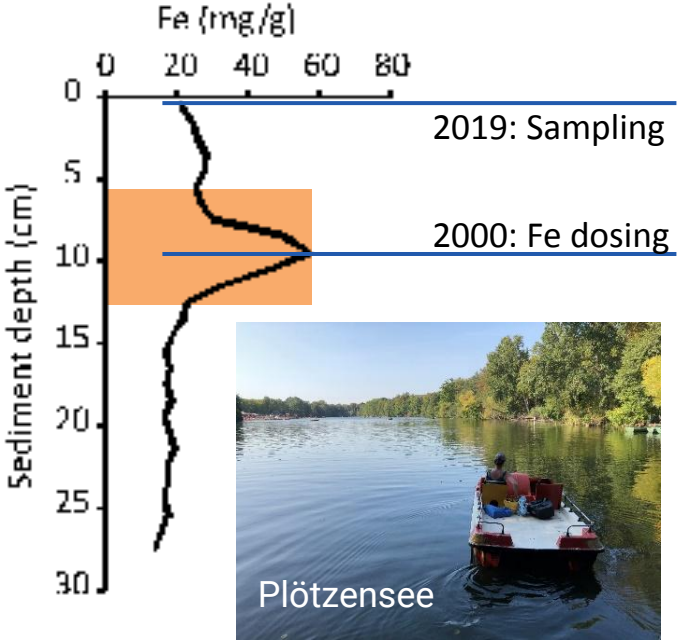
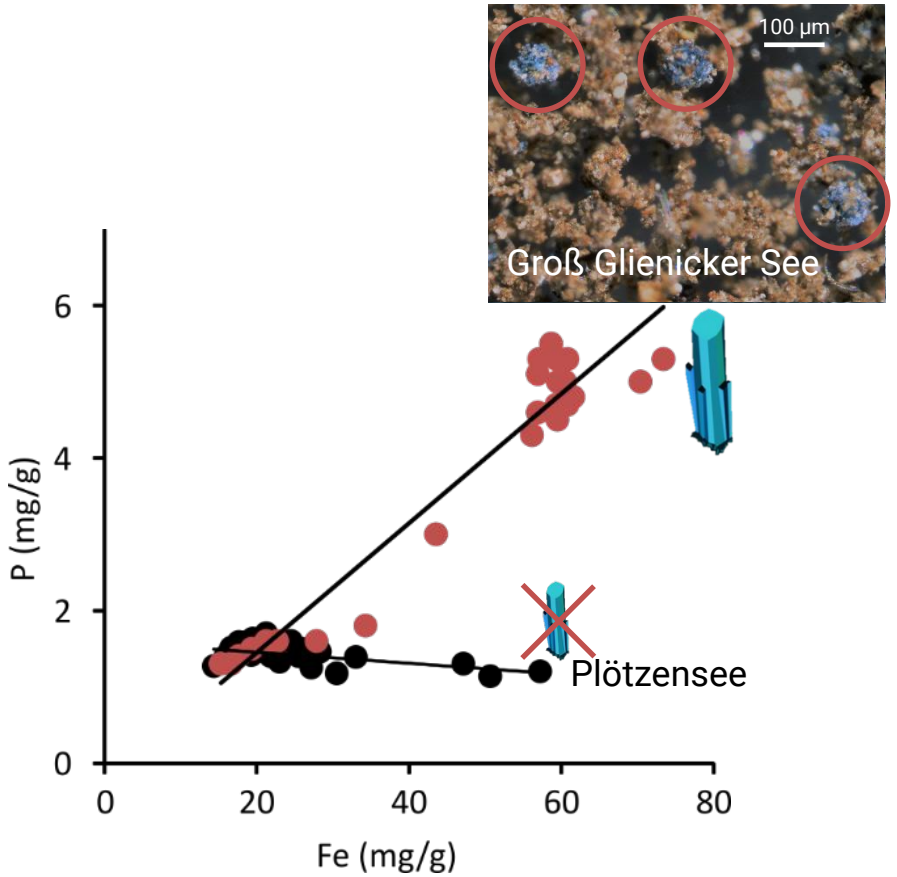
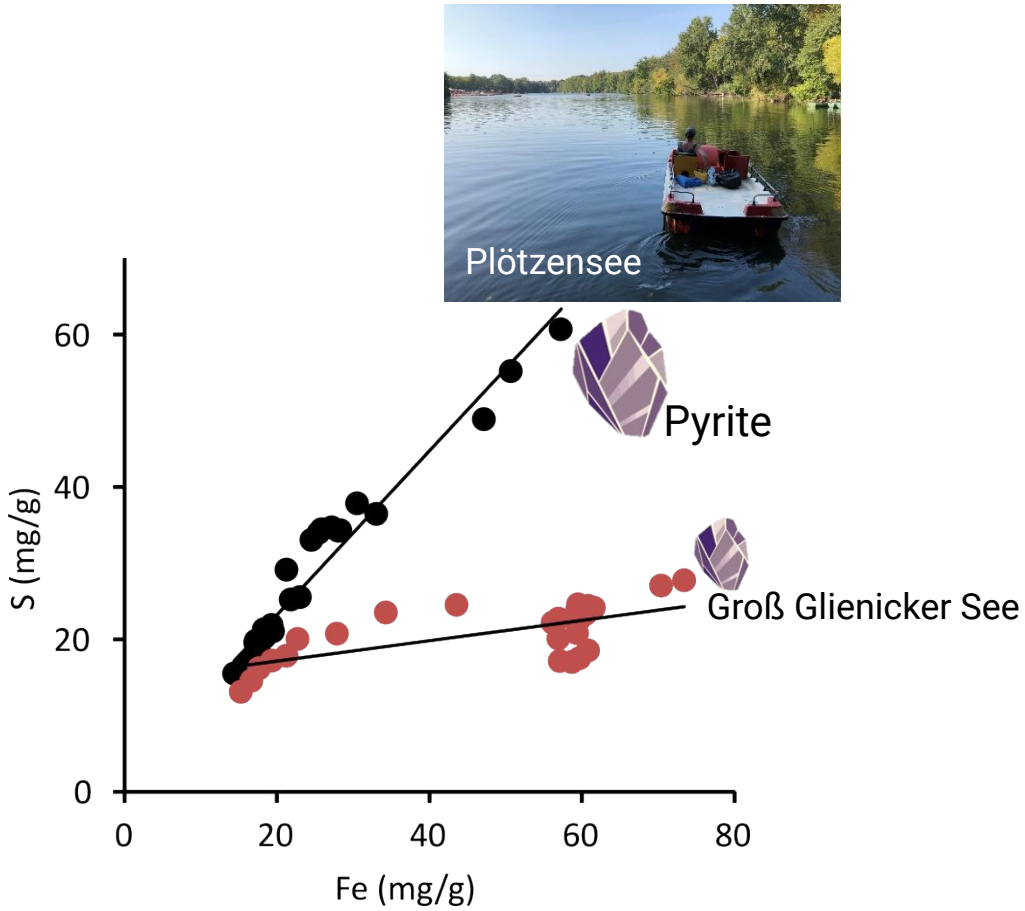


Figure: Heinrich et al. 2022. J Soils Sediments 22(1), 316-333.

Field scale evidences – Element correlations & Fe minerals





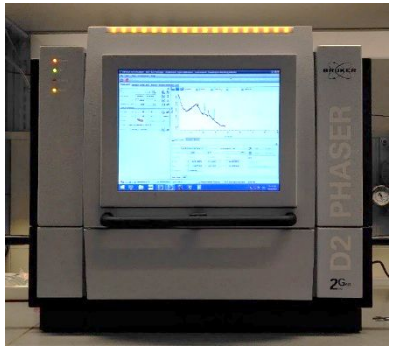
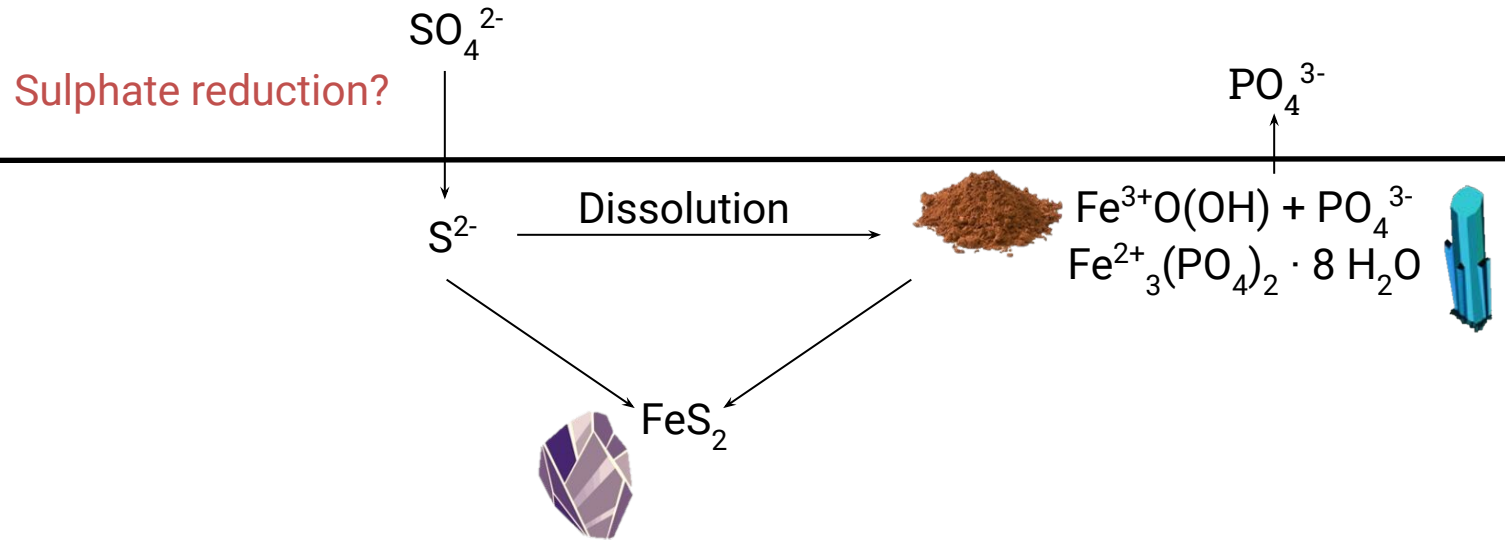


Figure: Heinrich et al. 2022. J Soils Sediments 22(1), 316-333.

Conclusion – S competition

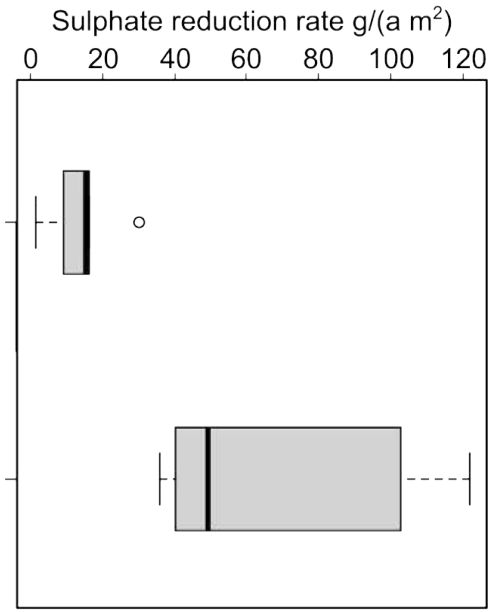
Water - oxic

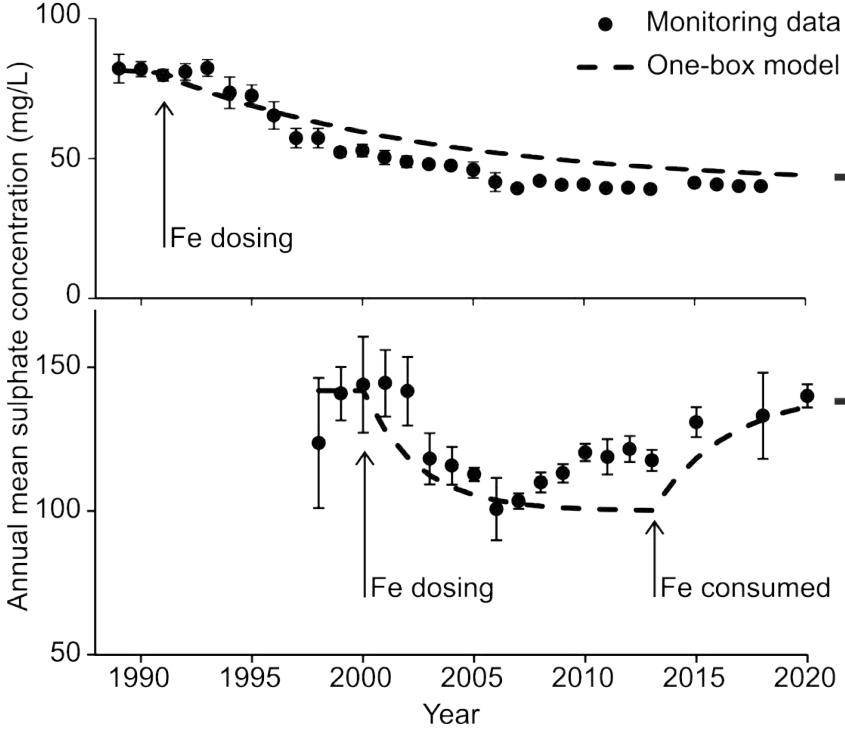
Sediment - anoxic

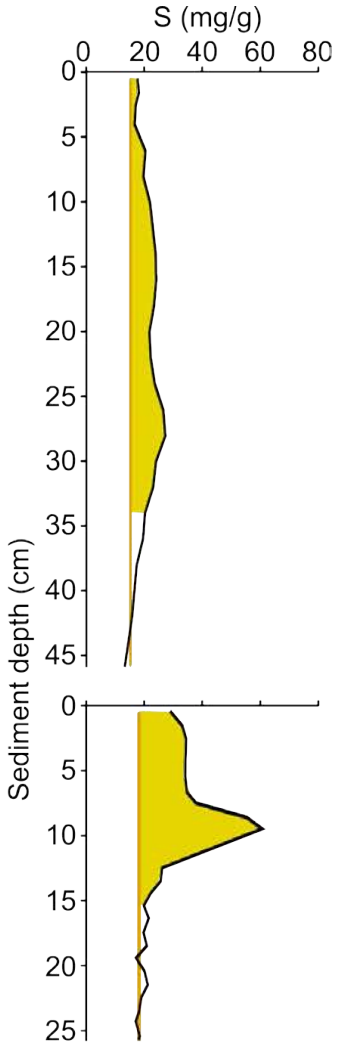


Result: Wilfert et al. 2019. Water Res 171, 115389.

One-box model – S fluxes at the sediment water interface







Method: Gächter and Imboden, J. Wiley & Sons, 1985.
Figure: Heinrich et al. 2022. J Soils Sediments 22(1), 316-333.

Conclusion – S competition

Water - oxic

Sulphate reduction!

SO_4^{2-}

PO_4^{3-}

Sediment - anoxic

S^{2-} → Dissolution →

$Fe^{3+}O(OH) + PO_4^{3-}$

$Fe^{2+}{}_3(PO_4)_2 \cdot 8\ H_2O$

FeS_2

Management implications – Long-term P retention after Fe dosing

Low redox conditions limit the effectiveness of Fe dosing for long-term P retention?

- Anoxic conditions and microbial Fe reduction – NO PROBLEM
- Sulphidic conditions due to intensive sulphate reduction – PROBLEM

More Fe needs to be dosed to account for the competition by S

Fe dosage calculation

Fe dosage = Fe consumption by P + Fe consumption by OM + ***Fe consumption by S***

Fe consumption by S *= sulphate reduction/year · 0.66 Fe/S in pyrite ·* ***years***

Fe dosage calculation based on: Kleeberg et al. 2012. Water Res 47(3), 1491-1502.

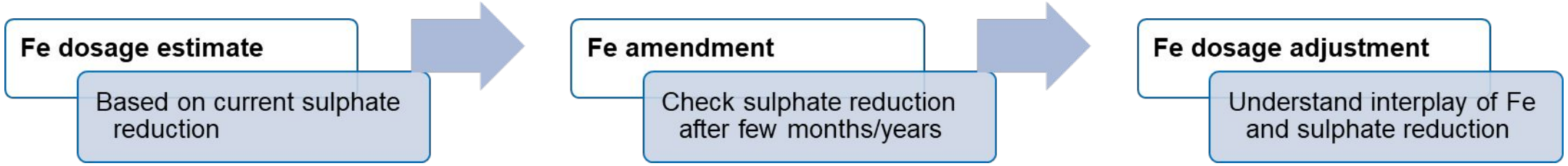
Management implications – Interplay of dosed Fe and sulphate reduction

Challenge – Does Fe dosing affect sulphate reduction?

- Stimulation? e.g. by preventing product inhibition of sulphate reduction by providing a sink for the toxic sulphide
- Decline? e.g. because P binding by Fe decreases primary production and availability of organic matter as electron donor

- **Possibly**

- **Suggested workflow**



Management implications – Controlling sulphate reduction

Could be more sustainable and cost-effective than increasing Fe dosages

- Plötzensee: 50% sulphate reduction Fe dosage –44%
- Groß Glienicker See: 50% sulphate reduction Fe dosage –20%

** How to control sulphate reduction?**

** Research perspective: Organic matter and/or sulphate availability!**

Take Home Message

	Low microbial Fe reduction	High microbial Fe reduction	
Low sulphate reduction	Fe(oxi)hydroxides bind P on the long term 	Vivianite binds P on the long term. 	Fe dosing works well
High sulphate reduction	Sulphide releases P from Fe, immobilizes Fe a prevents long-term P retention. 		Additional planning!

Thanks for your attention!

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IGB

Prof. Dr. Michael Hupfer

Universität Potsdam

Contact and Travel Funding:
Working group Soil Science and Geoecology – Aquatic biogeochemistry

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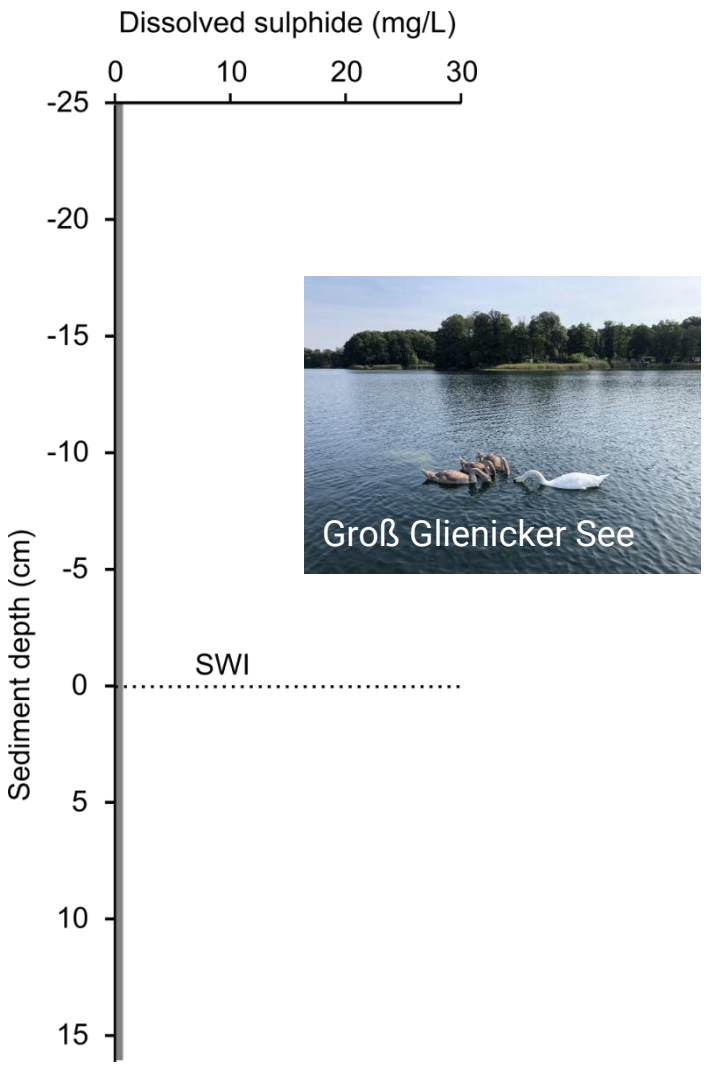
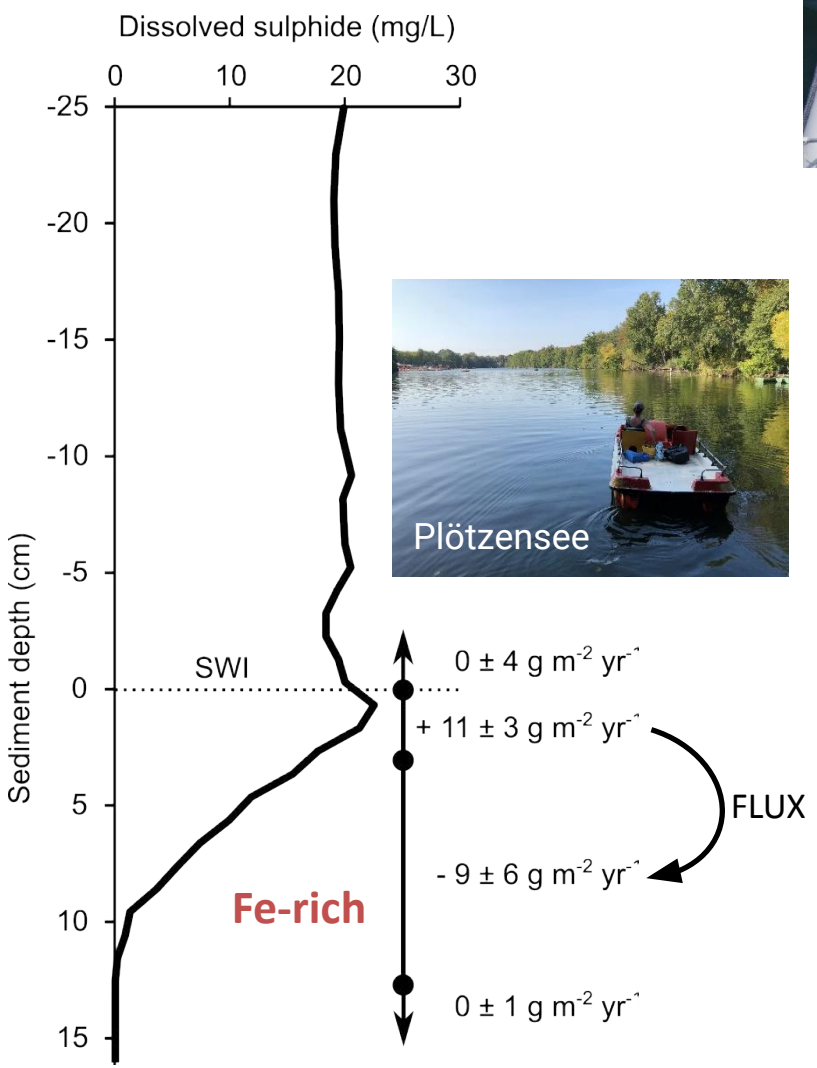
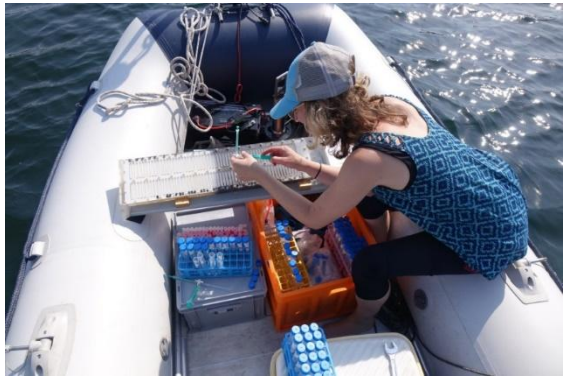
LenaLikesLakes

Prof. Dr. Stefan Norra

Field scale evidences – Sulphide production

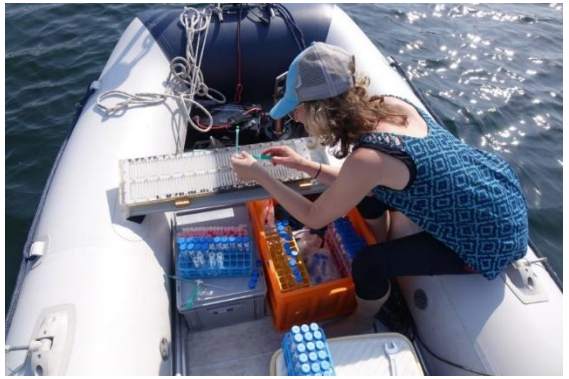


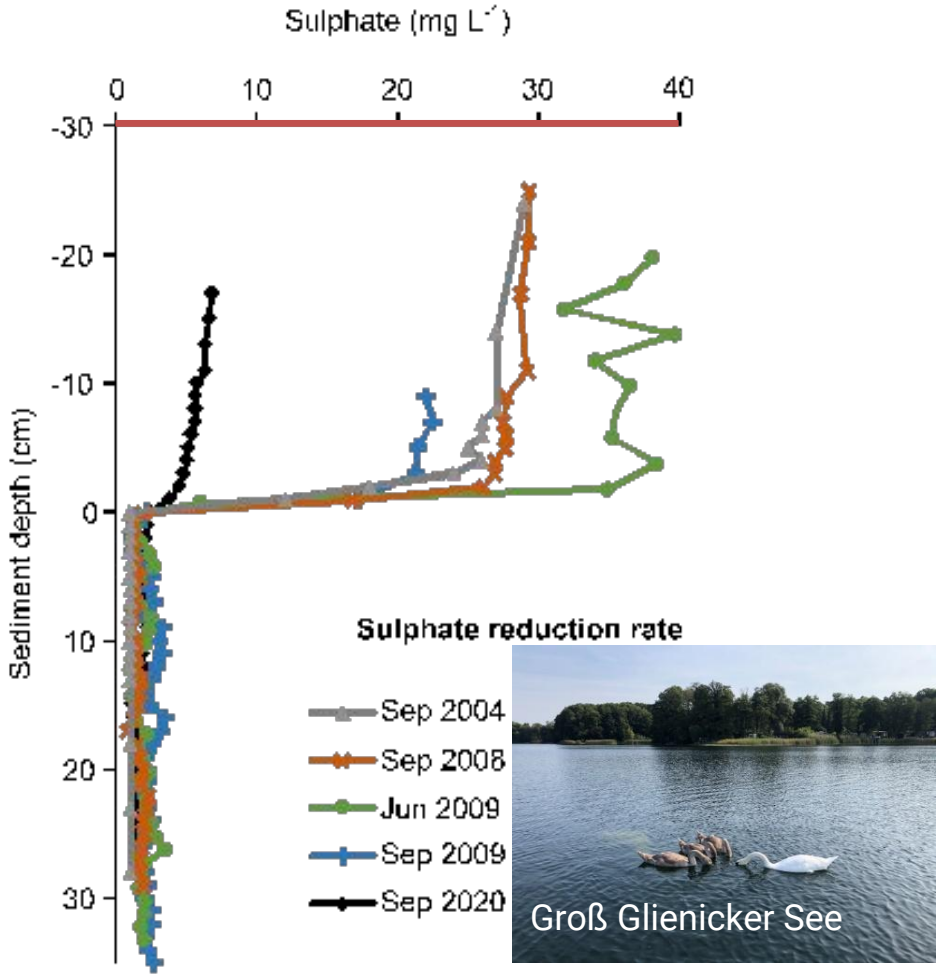


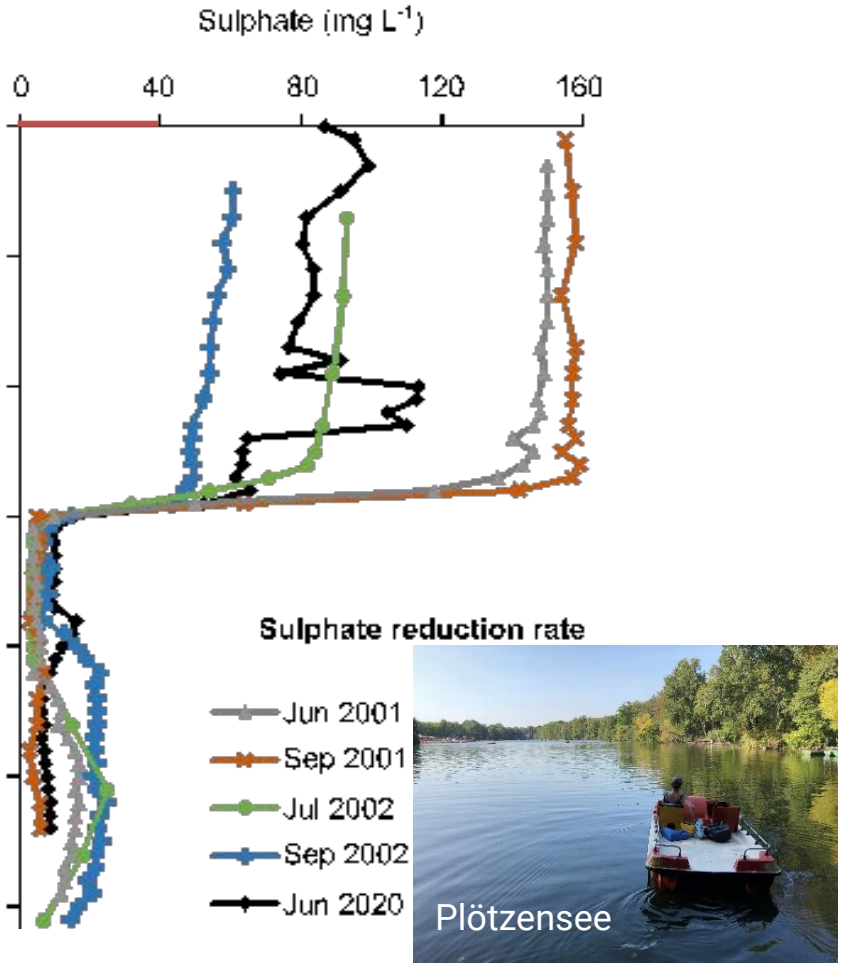


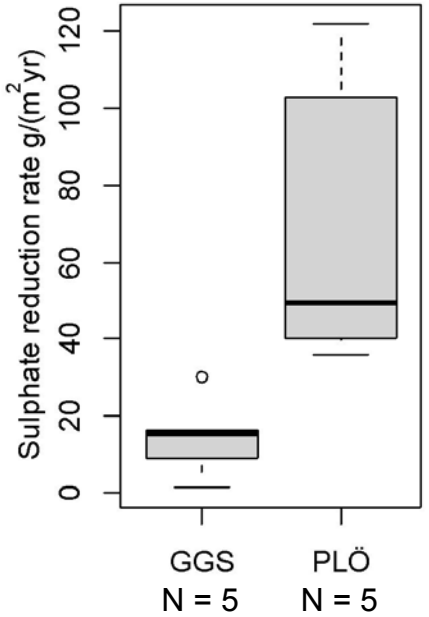
Method: Wang et al. 2008. Water Res 171, 115389.
Figure: Heinrich et al. 2022. J Soils Sediments 22(1), 316-333.

Field scale evidences – Sulphate reduction





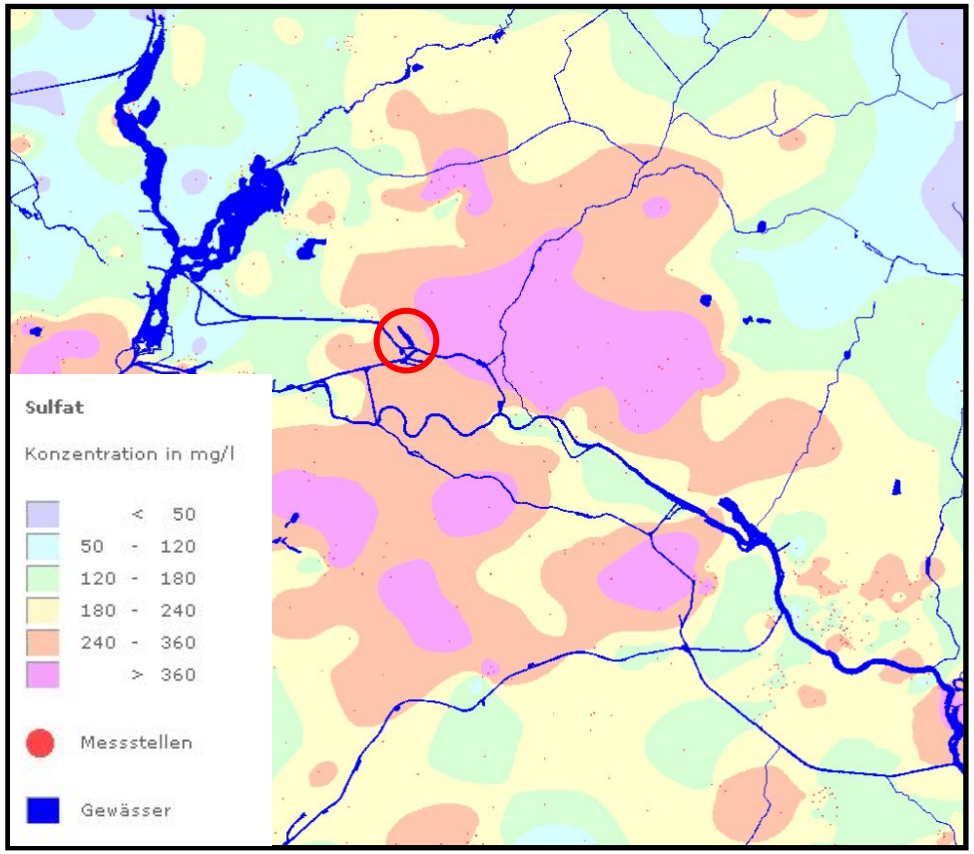




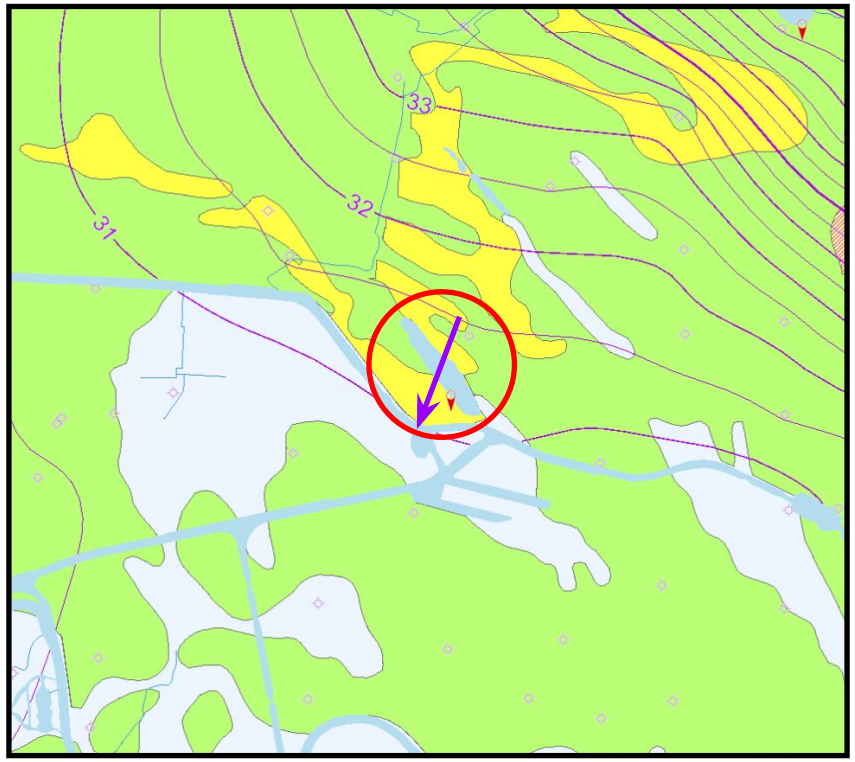
Wilcoxon rank sum exact test
W = 25, p-value < 0.01

Method: Wang et al. 2008. Water Res 171, 115389.
Figure: Heinrich et al. 2022. J Soils Sediments 22(1), 316-333.

Origin of sulphate - Groundwater

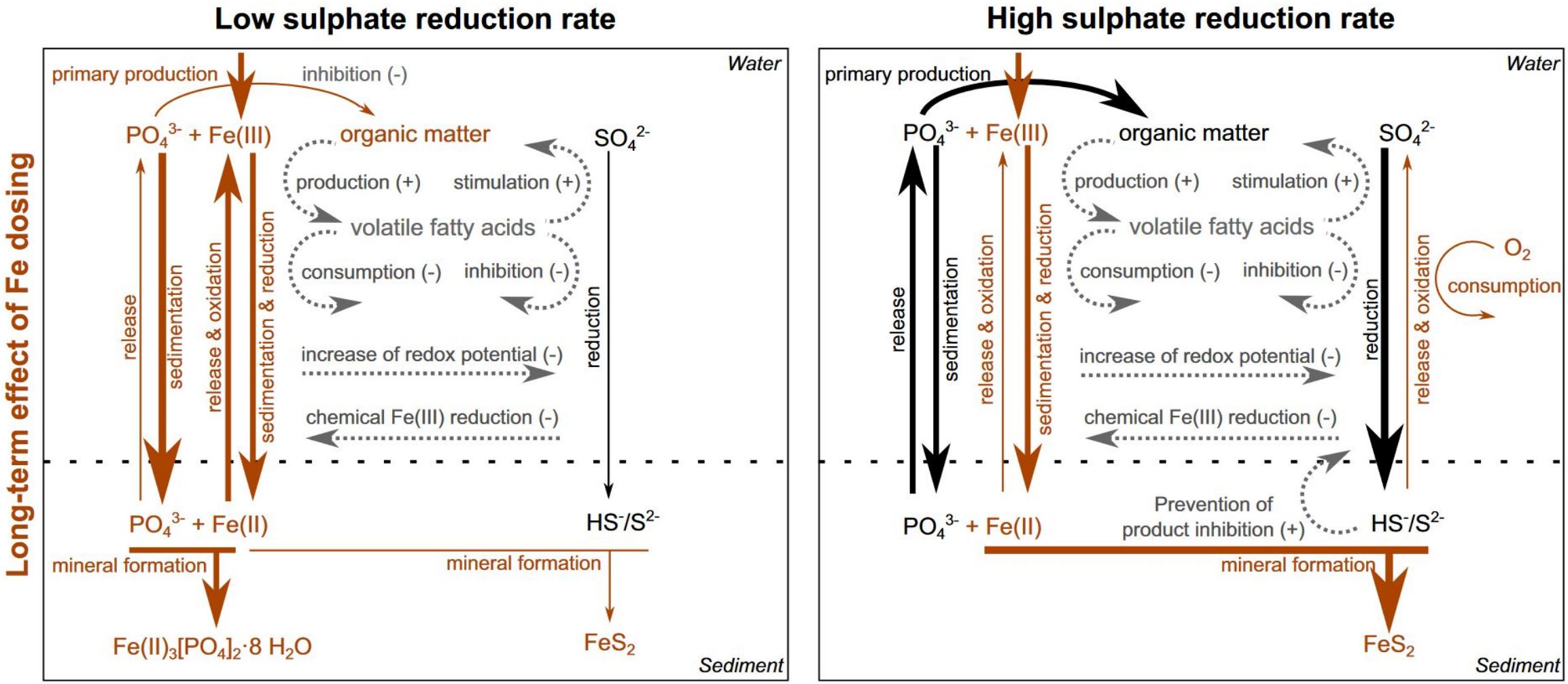


Geoportal Berlin / Grundwassergüte Sulfat

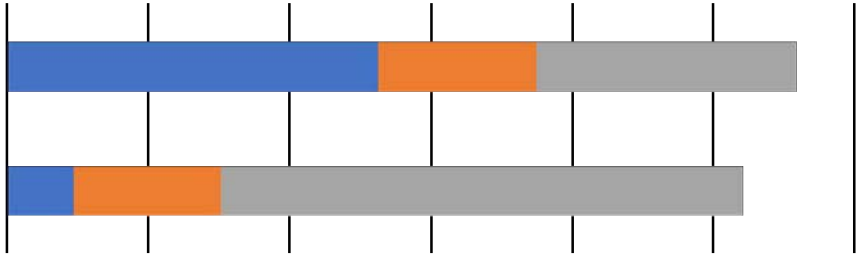


Geoportal Berlin / Grundwassergleichen 2018

Interactions between Fe dosing, P retention and sulphate reduction

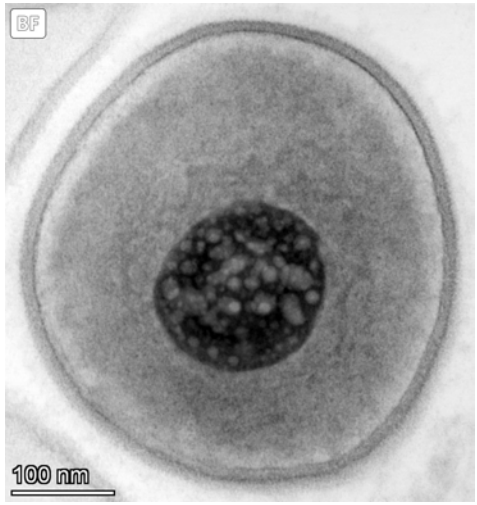


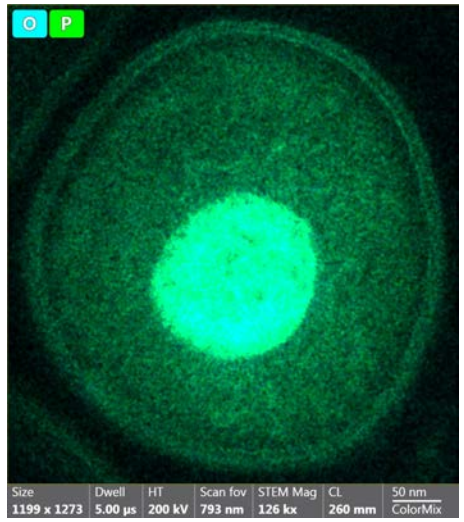
Re-calculated Fe dosages



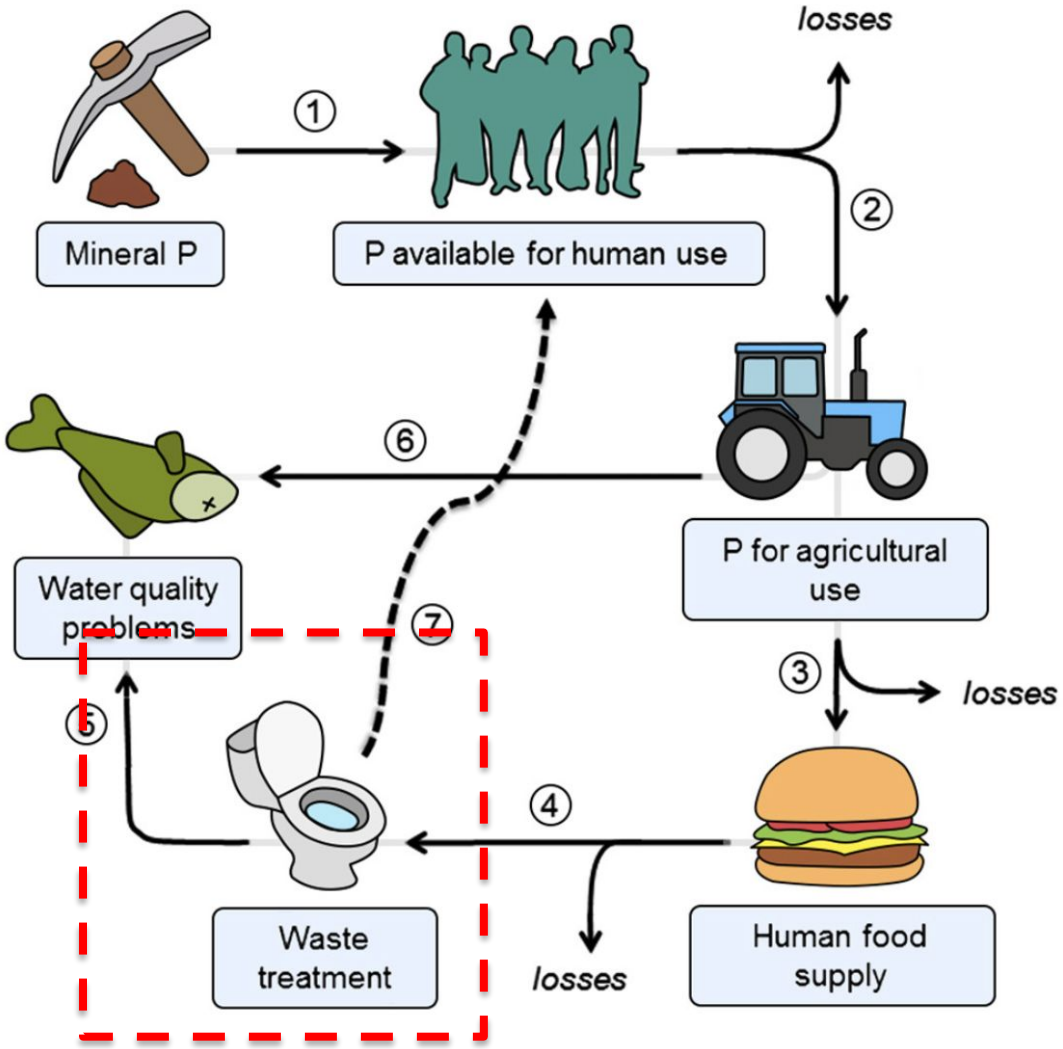
Evaluating the diversity of metal cations in microbial polyphosphate granules and their role in enhanced biological phosphorus removal processes at wastewater treatment facilities

Jessica Deaver, PhD
Postdoc, Call Lab
Department of Civil, Construction, and Environmental Engineering
Sustainable Phosphorus Summit
4 November 2022



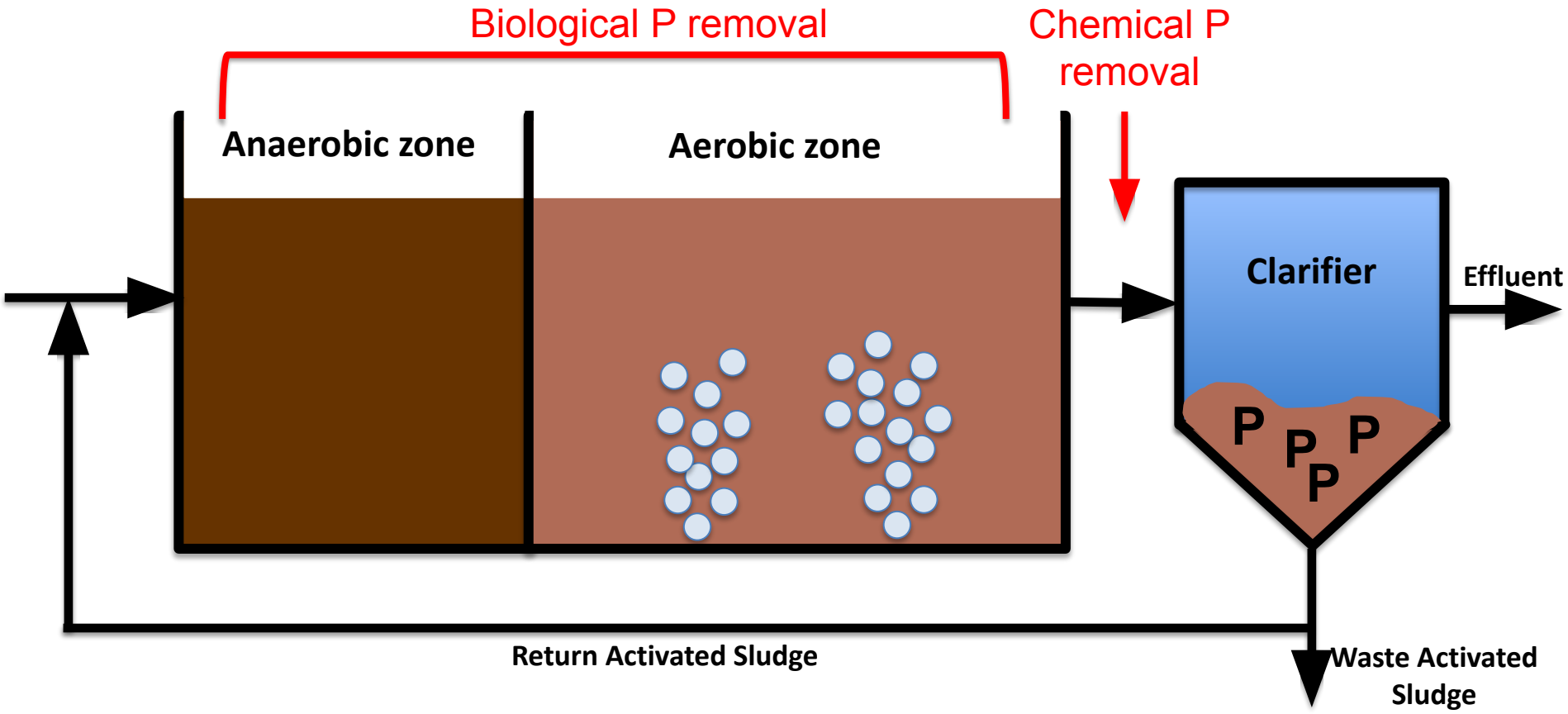


Anthropogenic P Cycle



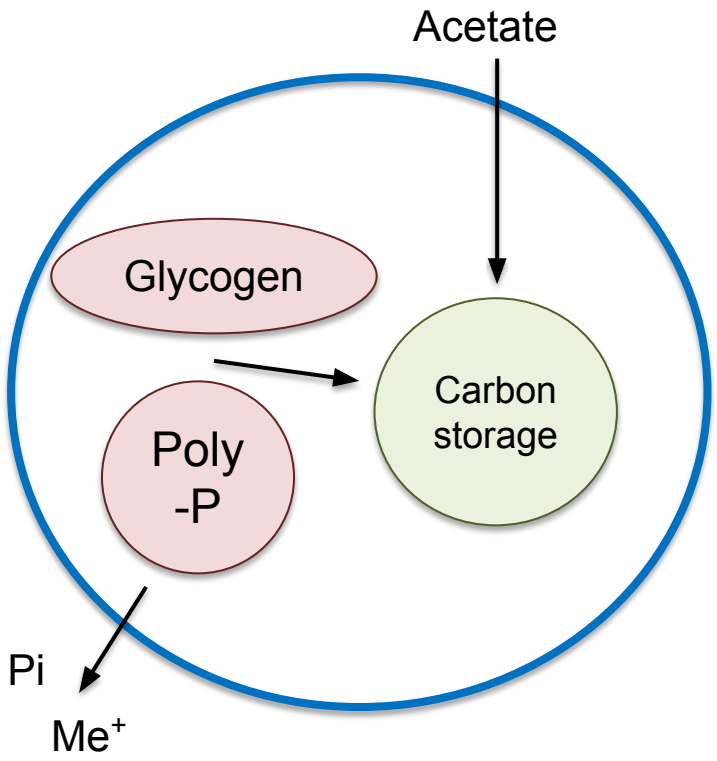
Bunce et al. (2018). *Front. Environ. Sci.* 6:8.

Enhanced Biological Phosphorus Removal (EBPR)

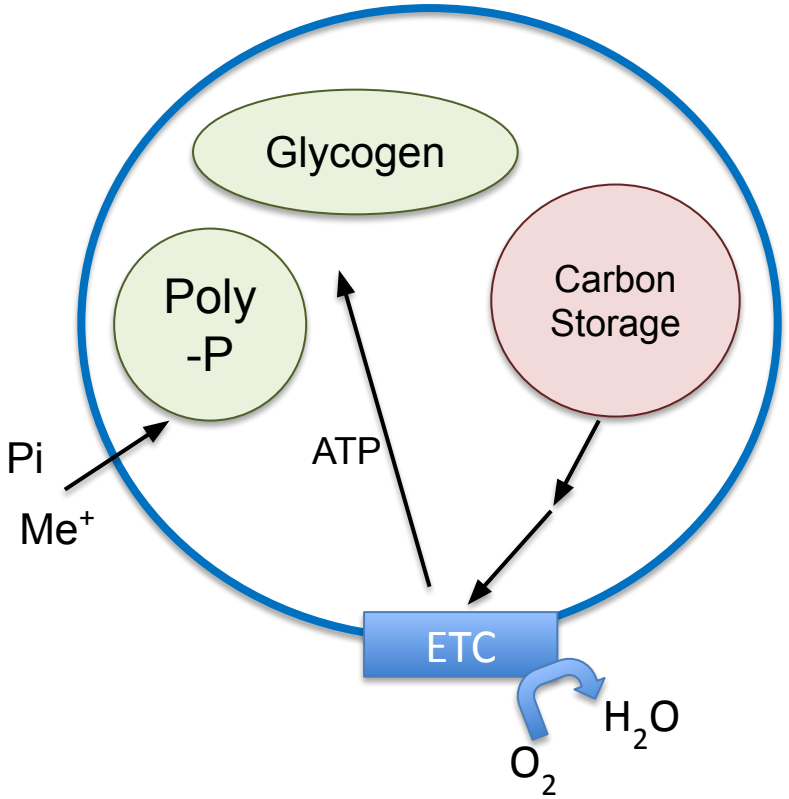


Polyphosphate Accumulating Organisms

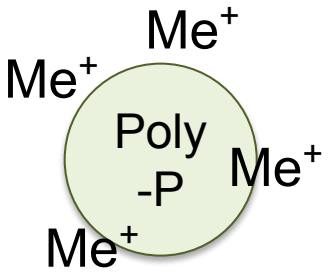
Traditional PAOs

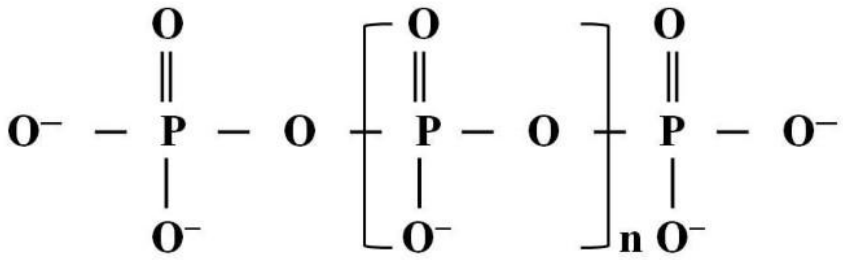


Anaerobic

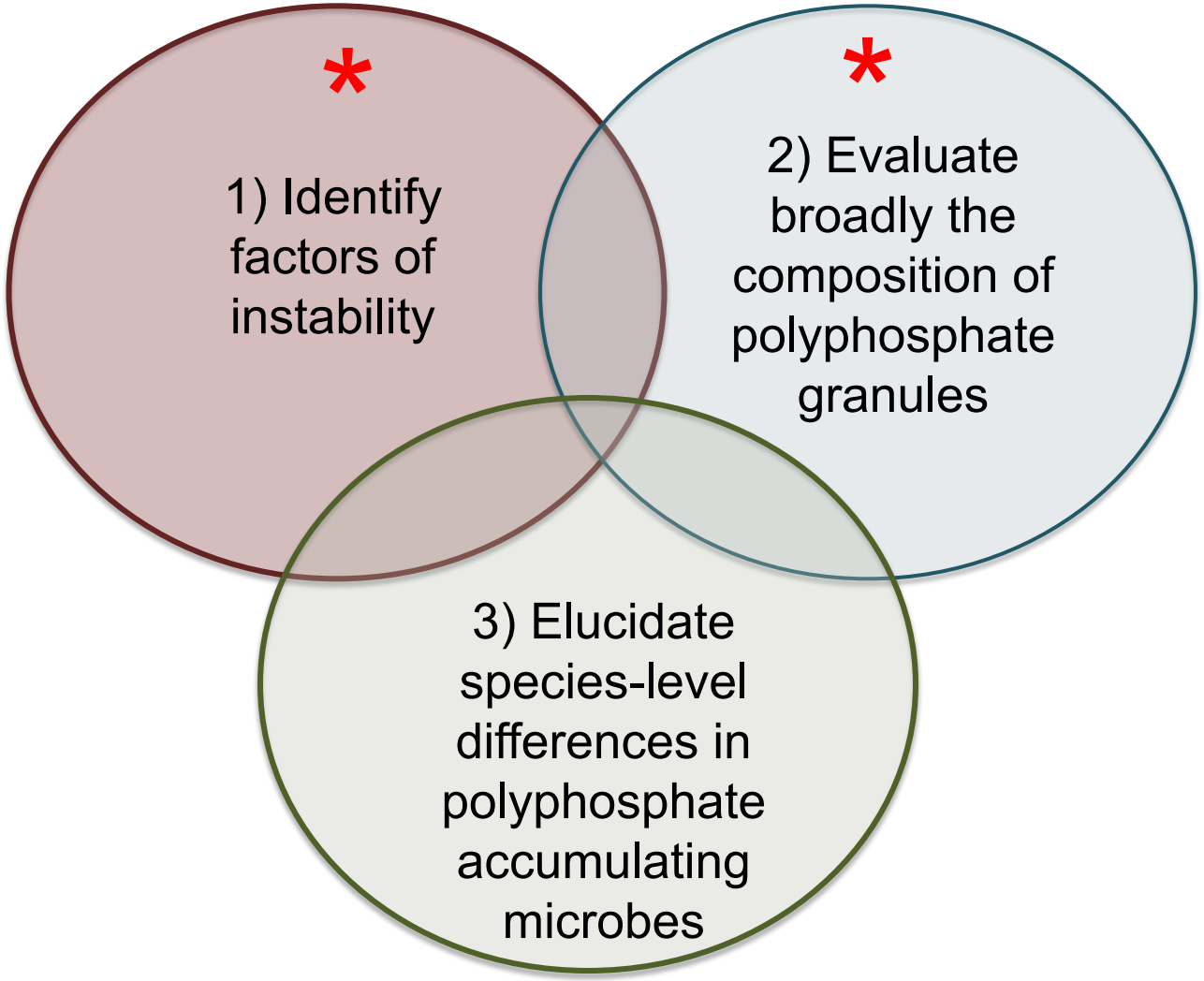


Aerobic

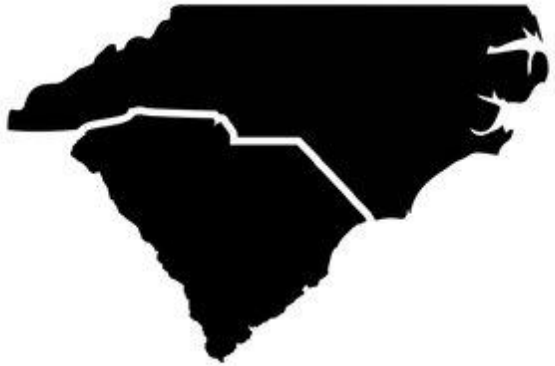




Objectives


*
1) Identify factors of instability
*
2) Evaluate broadly the composition of polyphosphate granules
3) Elucidate species-level differences in polyphosphate accumulating microbes

Results of Stakeholder Survey



Source of carbon- sewage fermentation, side stream, acetic acid addition

Variable configurations

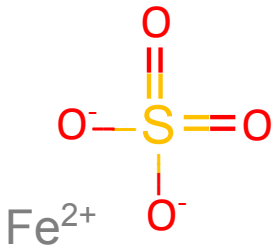
~50% report problems with unstable biological phosphorus removal

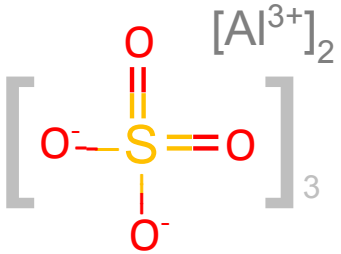
SRT 2-20 days

Average **flow rates** 2-20 MGD

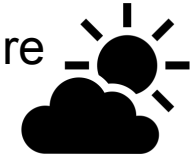
Mostly **residential** + **commercial** influent

Chemical precipitation





>Seasons/temperature



>Influent changes

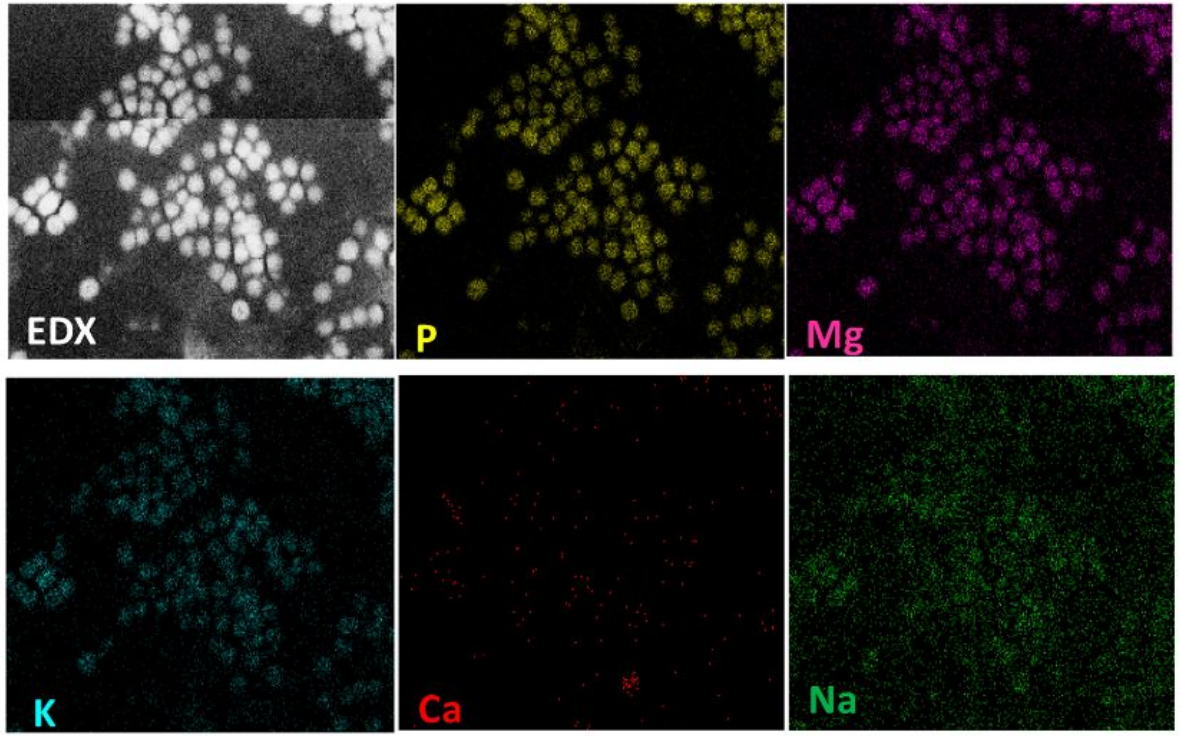
Studying EBPR

Problems: seasonal instability, changes in P removal when influent changes due to storm water, reduced flow, etc.

Question: Does polyphosphate granule composition change under different operating conditions?

Knowledge Gaps

- SEM/EDS* image of activated sludge sample from a lab scale EBPR reactor
- Fed synthetic wastewater with known composition

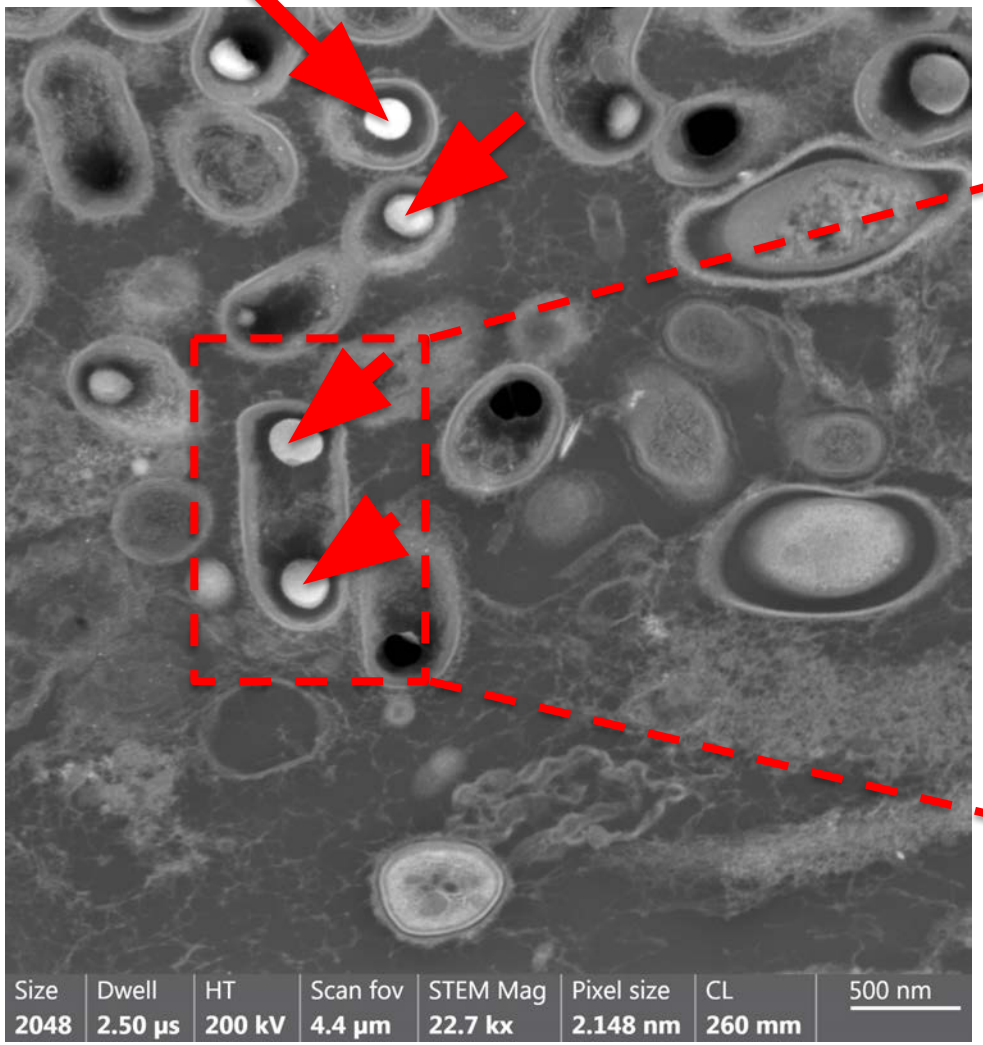


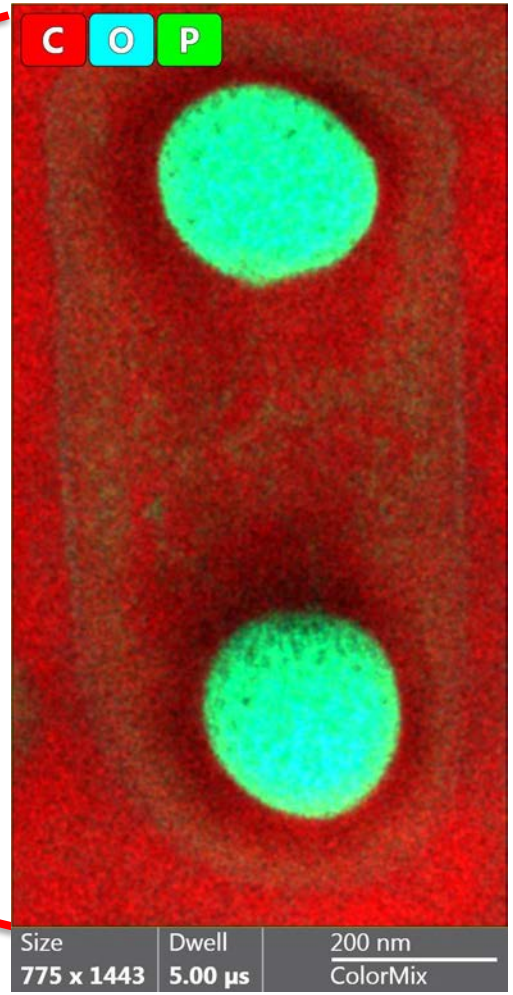
Li et al. (2019). *Environ. Sci. Technol.* 53, 1536−1544.

*SEM/EDS = Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy

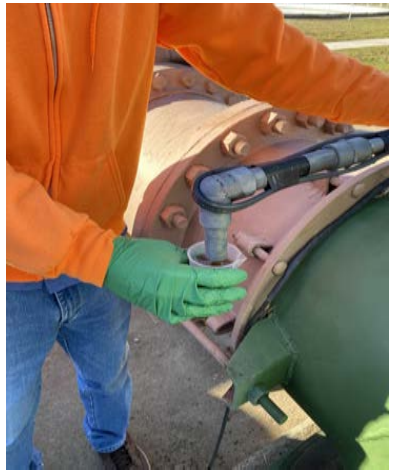
Scanning Transmission Electron Microscopy (STEM)/Energy Dispersive X-ray Spectroscopy (EDS)

Polyphosphate granules

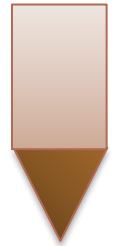




Microscopy Methods

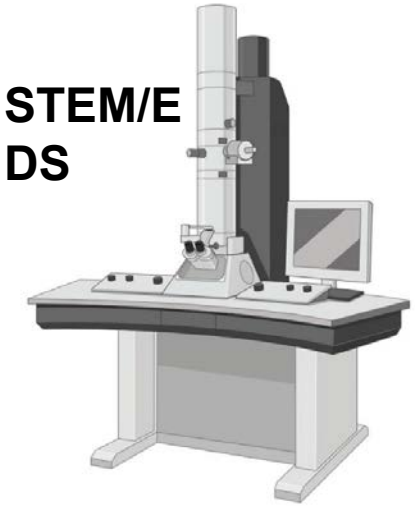


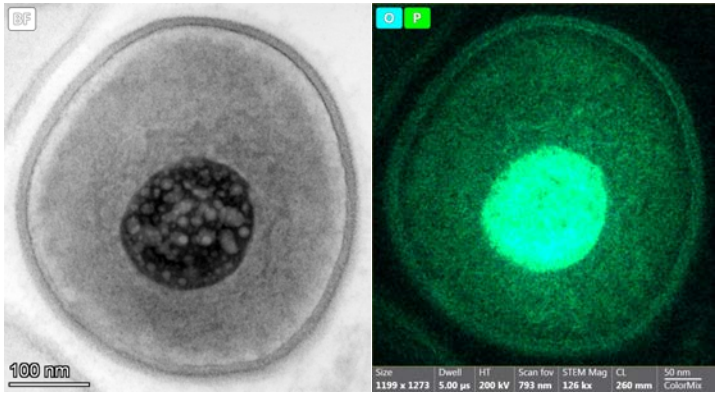
Fixed biomass pellet



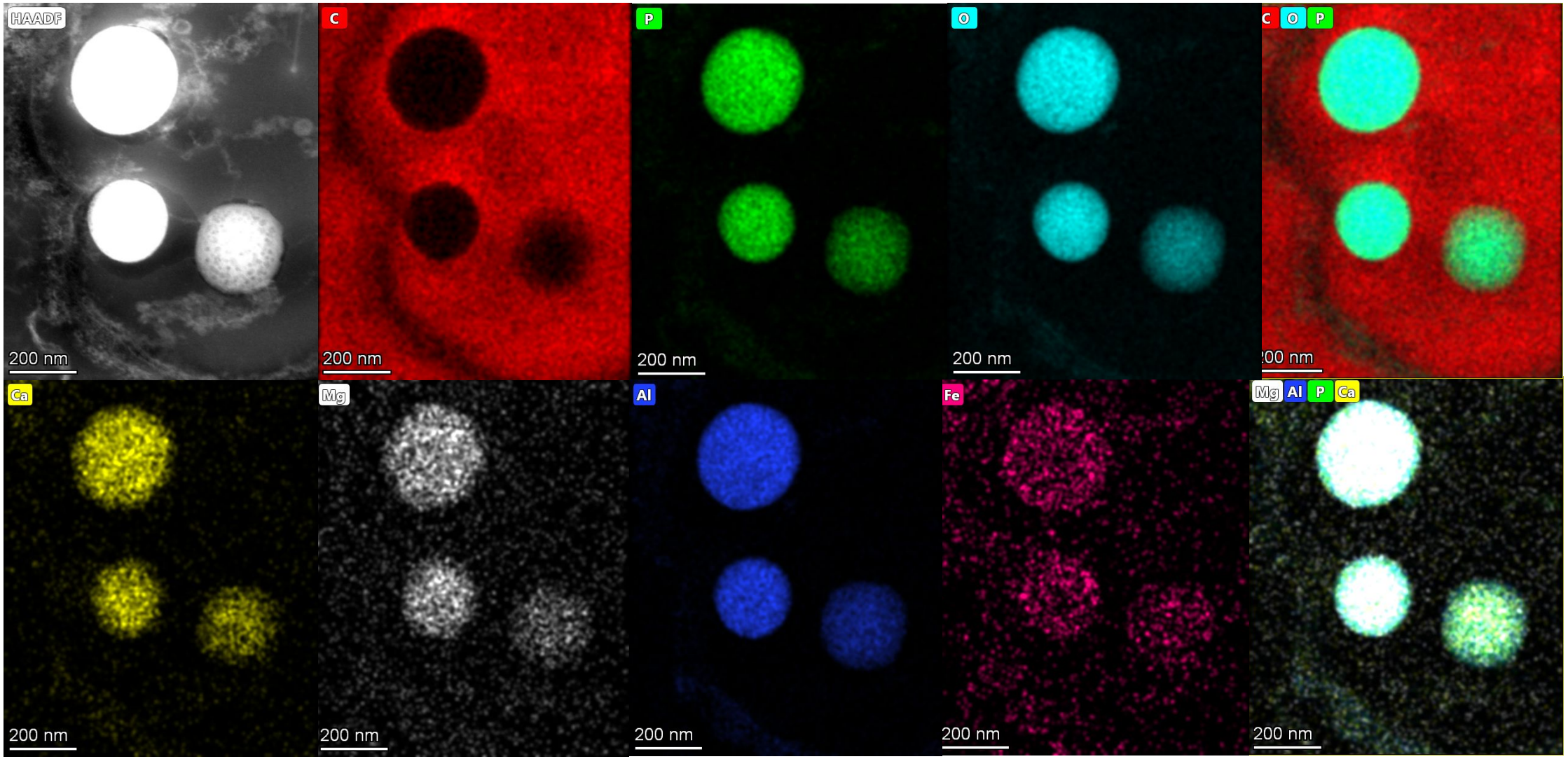
micrometry

STEM/EDS



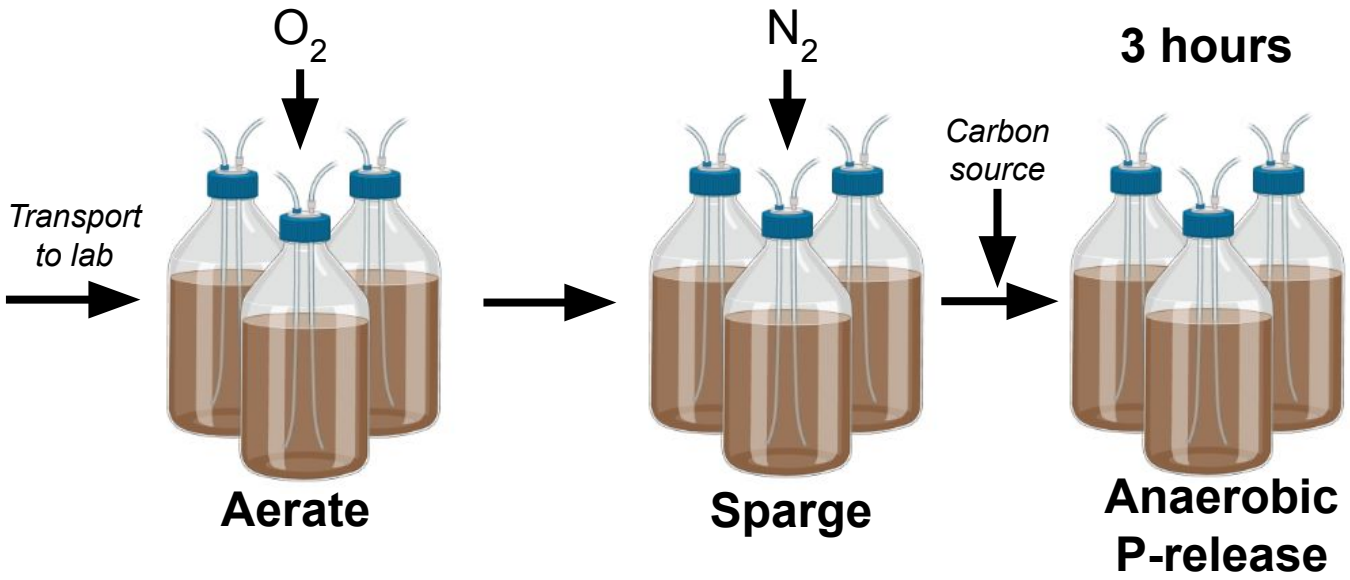


Microscopy


HAADF
200 nm
C
200 nm
P
200 nm
O
200 nm
C O P
200 nm
Ca
200 nm
Mg
200 nm
Al
200 nm
Fe
200 nm
Mg Al P Ca
200 nm

P-release tests

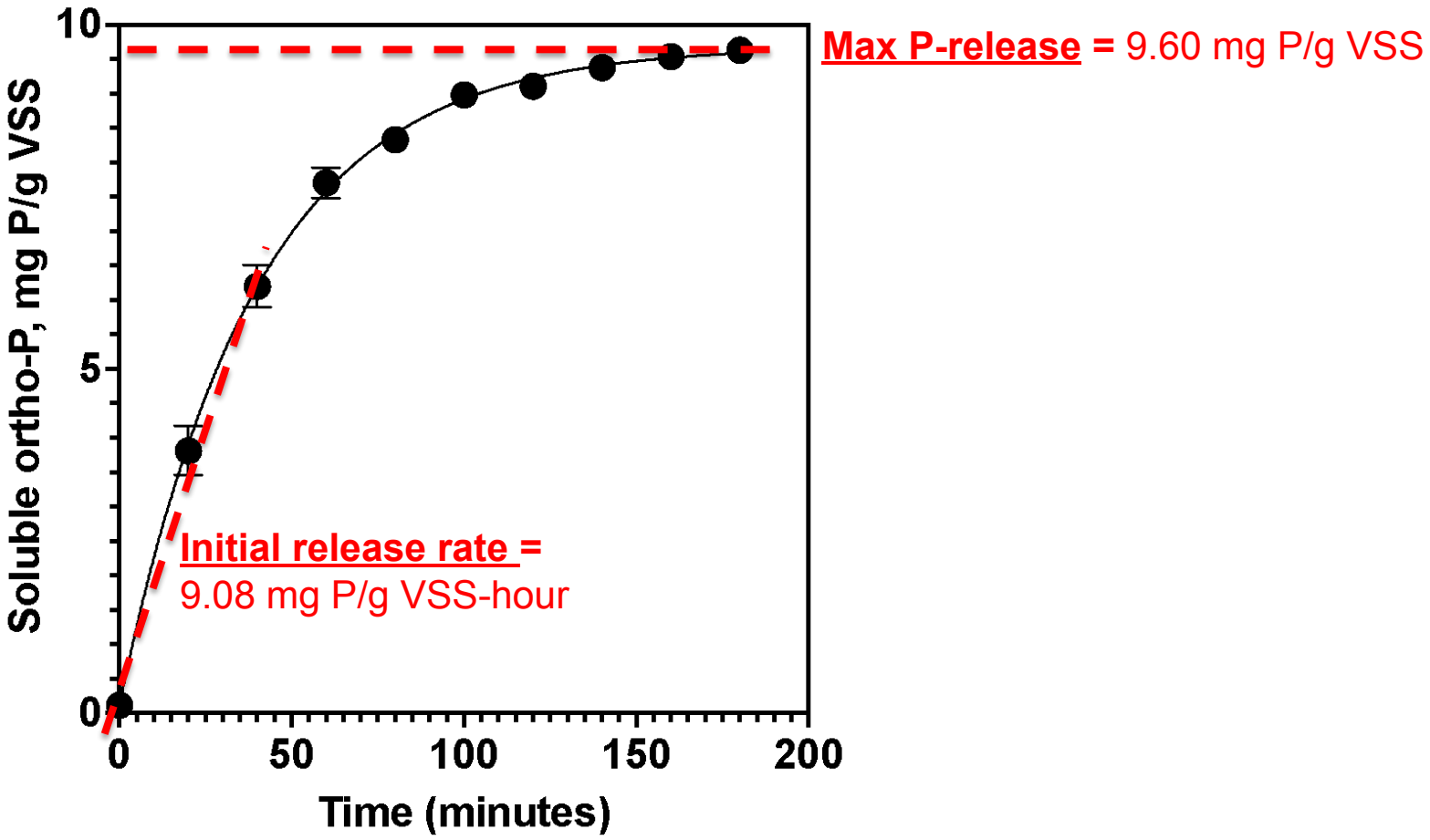
Objective: Measure phosphorus and corresponding metal release of different sludges; compare across facilities operating under different conditions



Constant pH = 7
Constant temp = 22°C

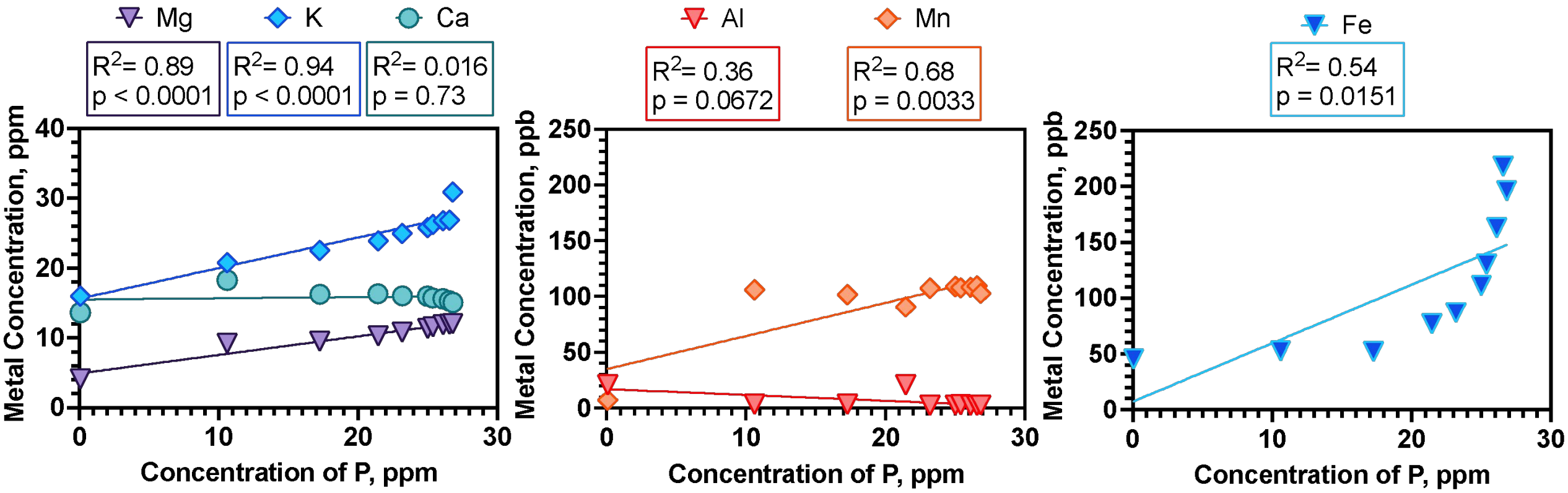
Measure soluble phosphorus and metals released every 20 minutes

Soluble Phosphorus Release



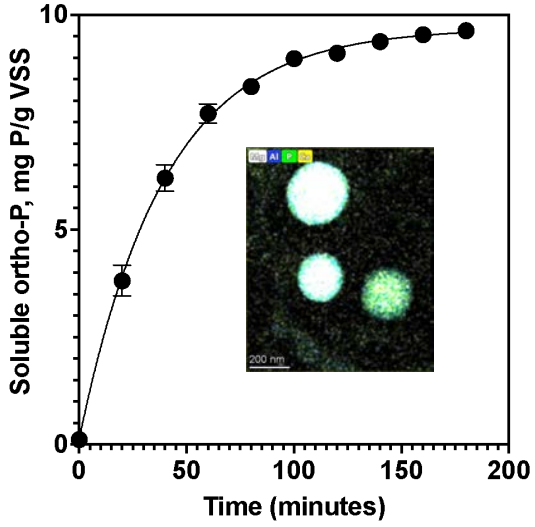
Soluble ortho-phosphate as P release

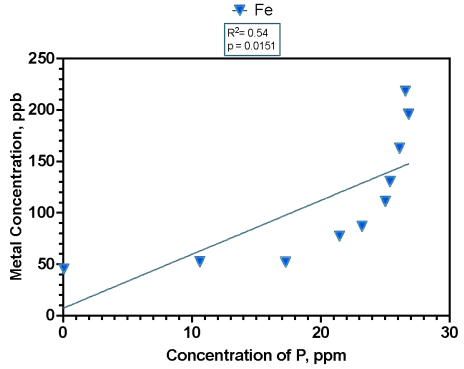
Soluble Metals Release



Soluble metal concentrations as a function of soluble ortho-P concentrations

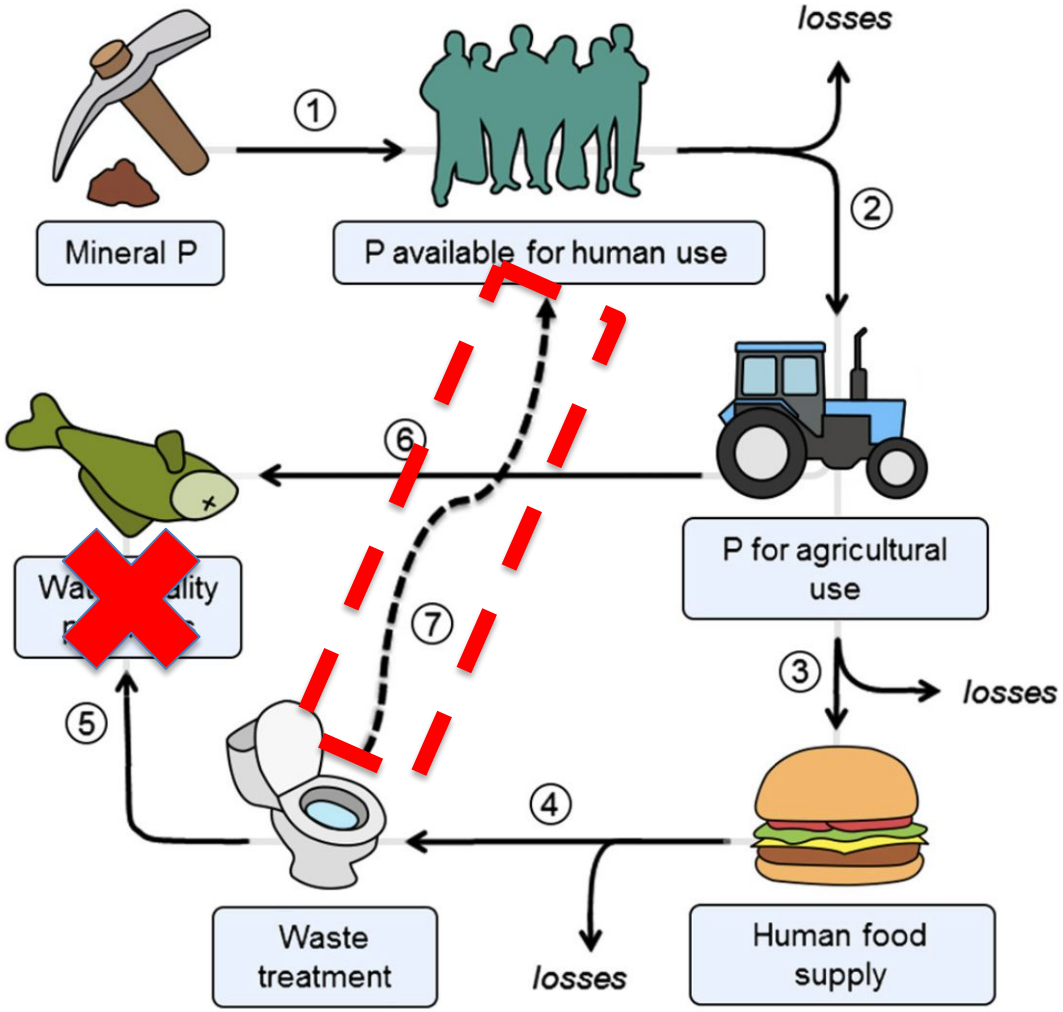
Future Work





- Phosphorus release tests in conjunction with STEM/EDS from several partner facilities using variable operating conditions
- Goal is to understand the influence of metal cation usage on biological P storage
- Eventually, sample over time to capture an instability event

Conclusions



Bunce et al. (2018). *Front. Environ. Sci.* 6:8.

Acknowledgements

Call Research Group

Dr. Doug Call

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Dr. Christopher Winkler
Dr. Jin Nakashima

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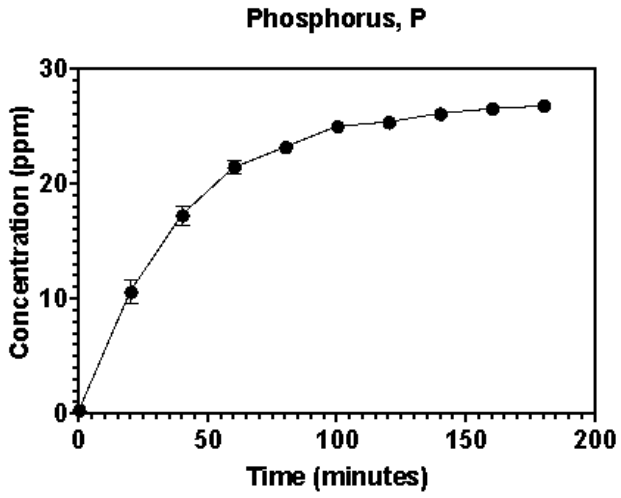
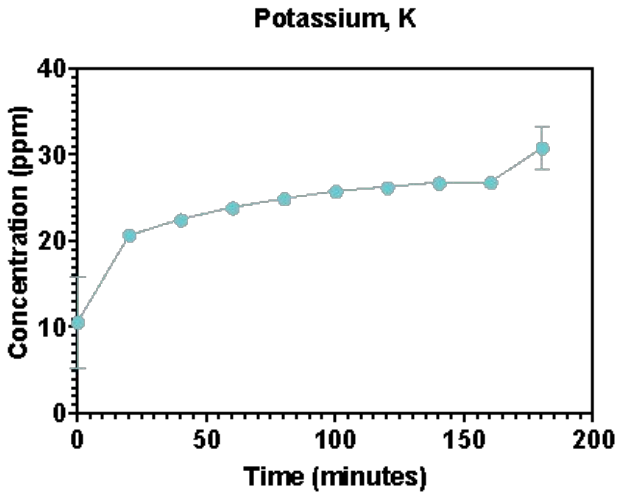
Theme 3 Collaborators- Dr. Anna Marshall, Dr. Khara Grieger

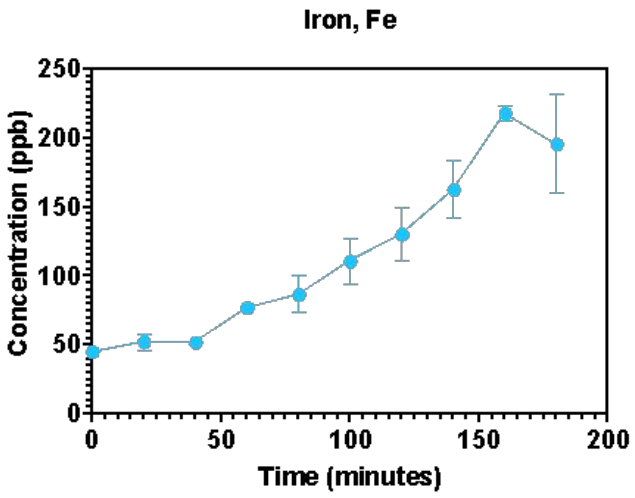
STEPS
Science and Technologies for Phosphorus Sustainability

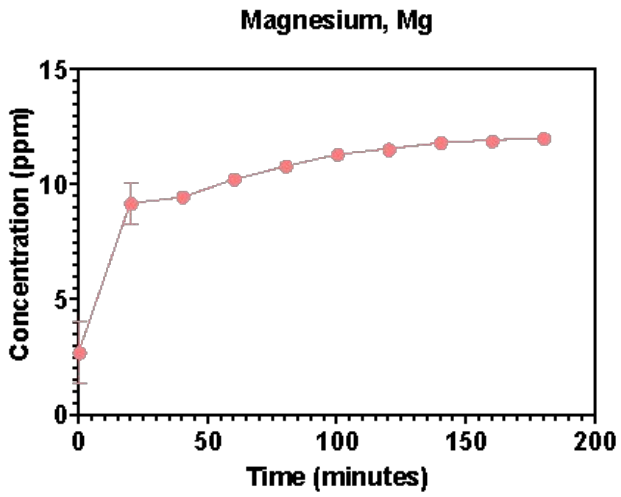
EXTRA SLIDES

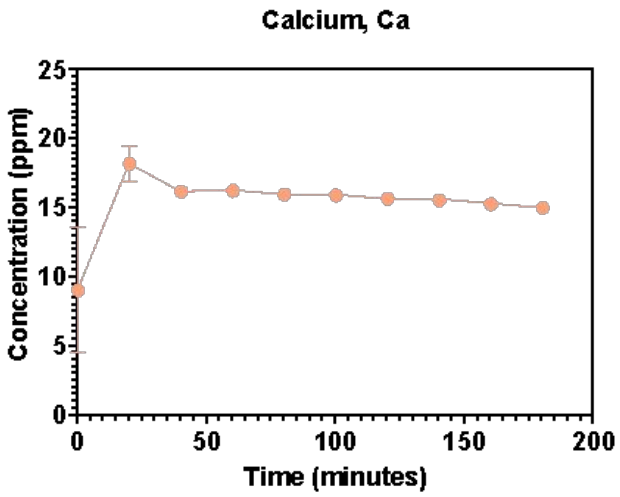
Soluble Metal Concentrations

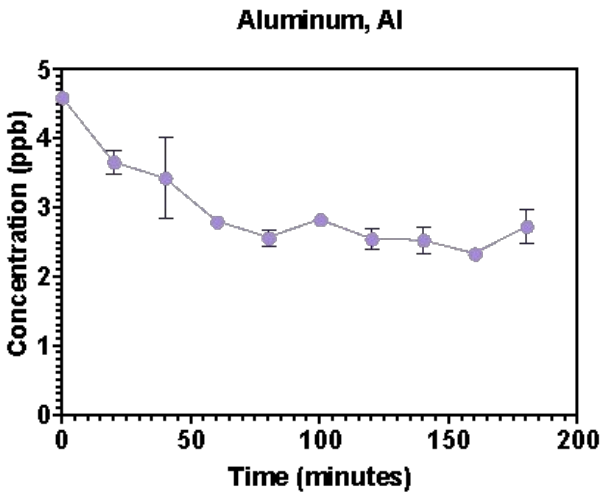












K_{sp} Values

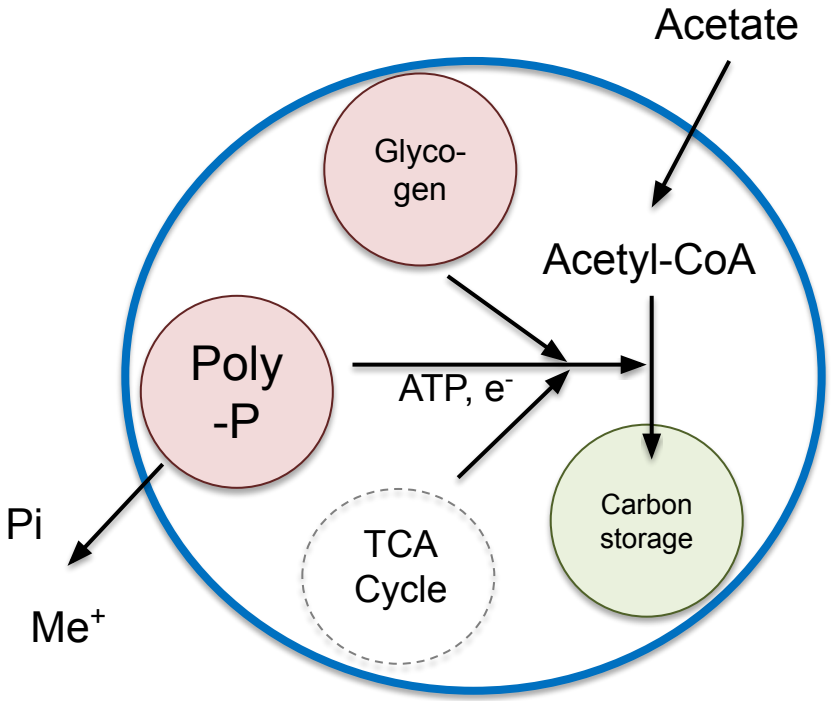
Low solubility

Soluble

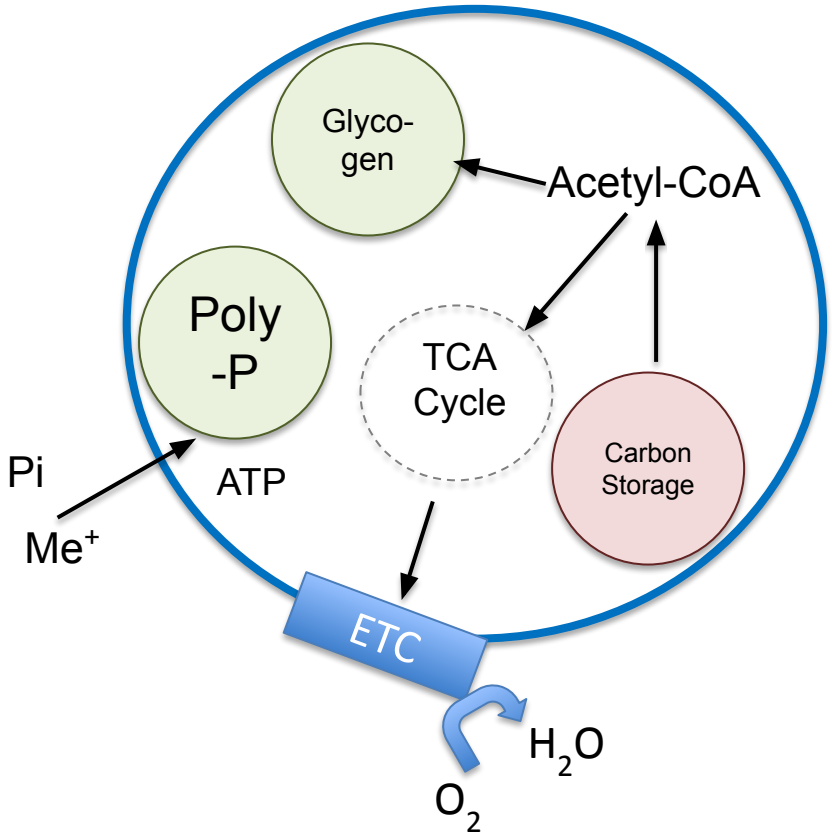
Name	Formula	K_{sp}
Calcium phosphate	$Ca_3(PO_4)_2$	1×10^{-26}
Magnesium phosphate	$Mg_3(PO_4)_2$	1×10^{-25}
Iron (III) phosphate	$FePO_4$	1.3×10^{-22}
Aluminum phosphate	$AlPO_4$	6.3×10^{-19}
Magnesium ammonium phosphate	$MgNH_4PO_4$	2.5×10^{-13}
Calcium hydrogen phosphate	$CaHPO_4$	1×10^{-7}
Sodium Phosphate	Na_3PO_4	2.24
Potassium Phosphate	K_3PO_4	8730

Polyphosphate Accumulating Organisms

Traditional PAOs



Anaerobic (no oxygen)

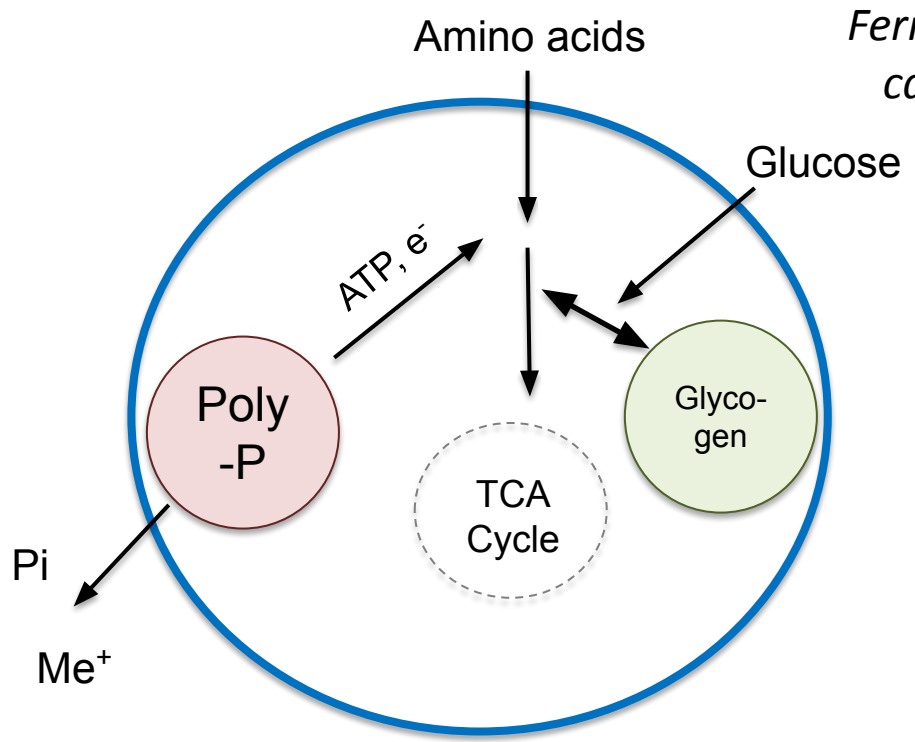


Aerobic (oxygen)

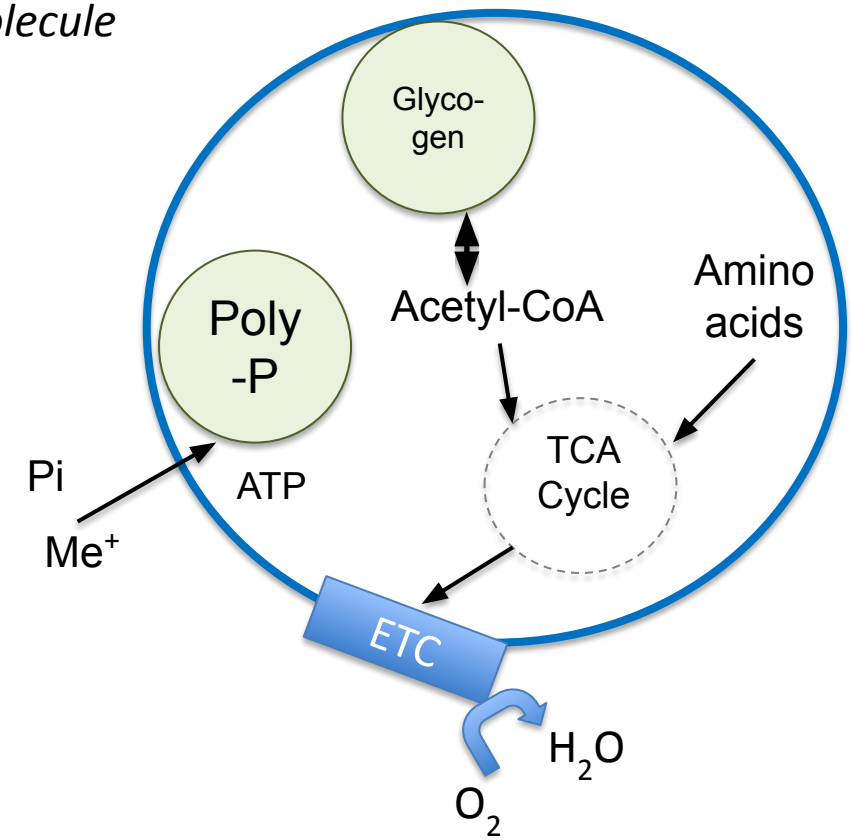
Polyphosphate Accumulating Organisms

Other PAOs

Fermentation, no traditional carbon storage molecule

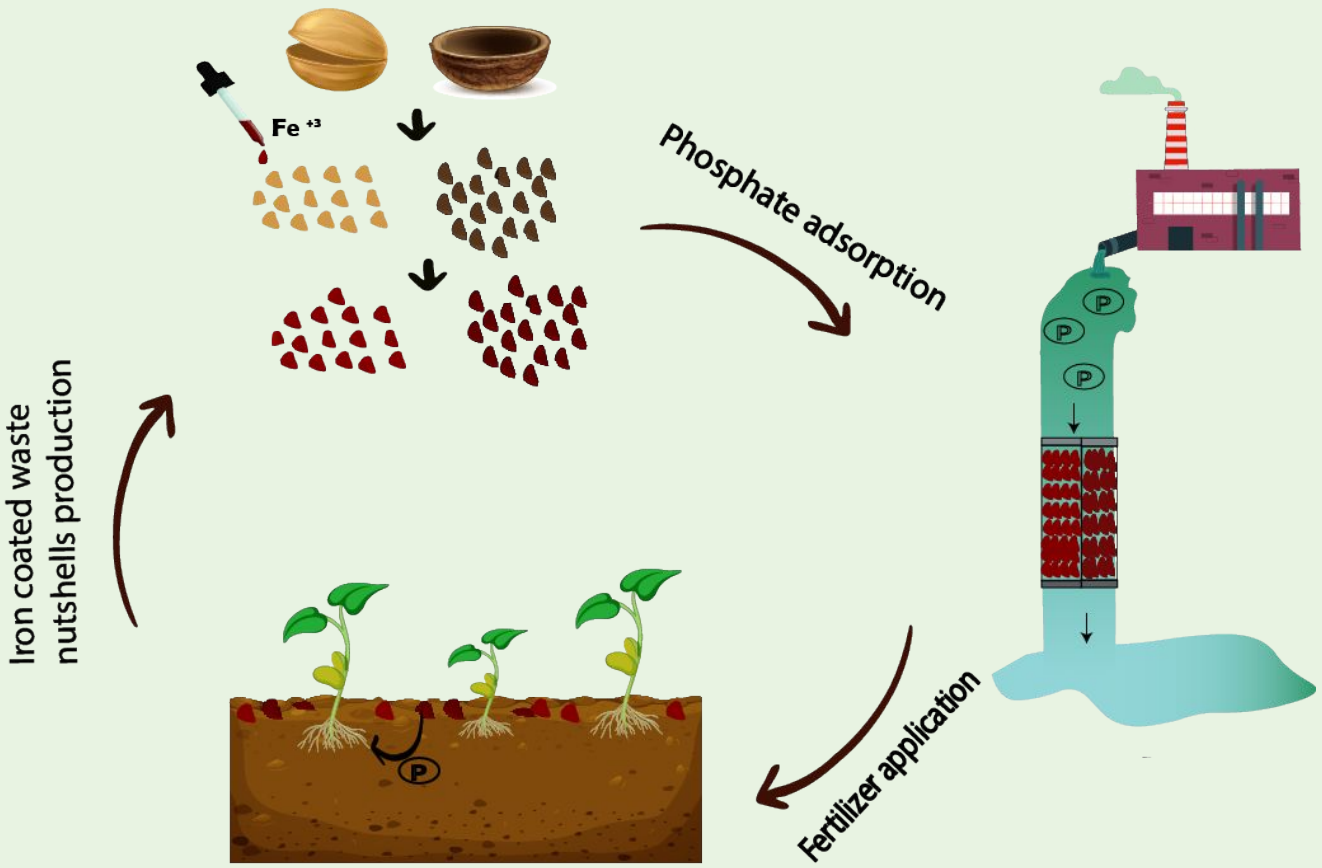


Anaerobic (no oxygen)



Aerobic (oxygen)

Iron enhanced biowaste to recover lost phosphate and its potential application as a slow-release fertilizer for agriculture



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Assistant professor, Wayne State University

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Introduction

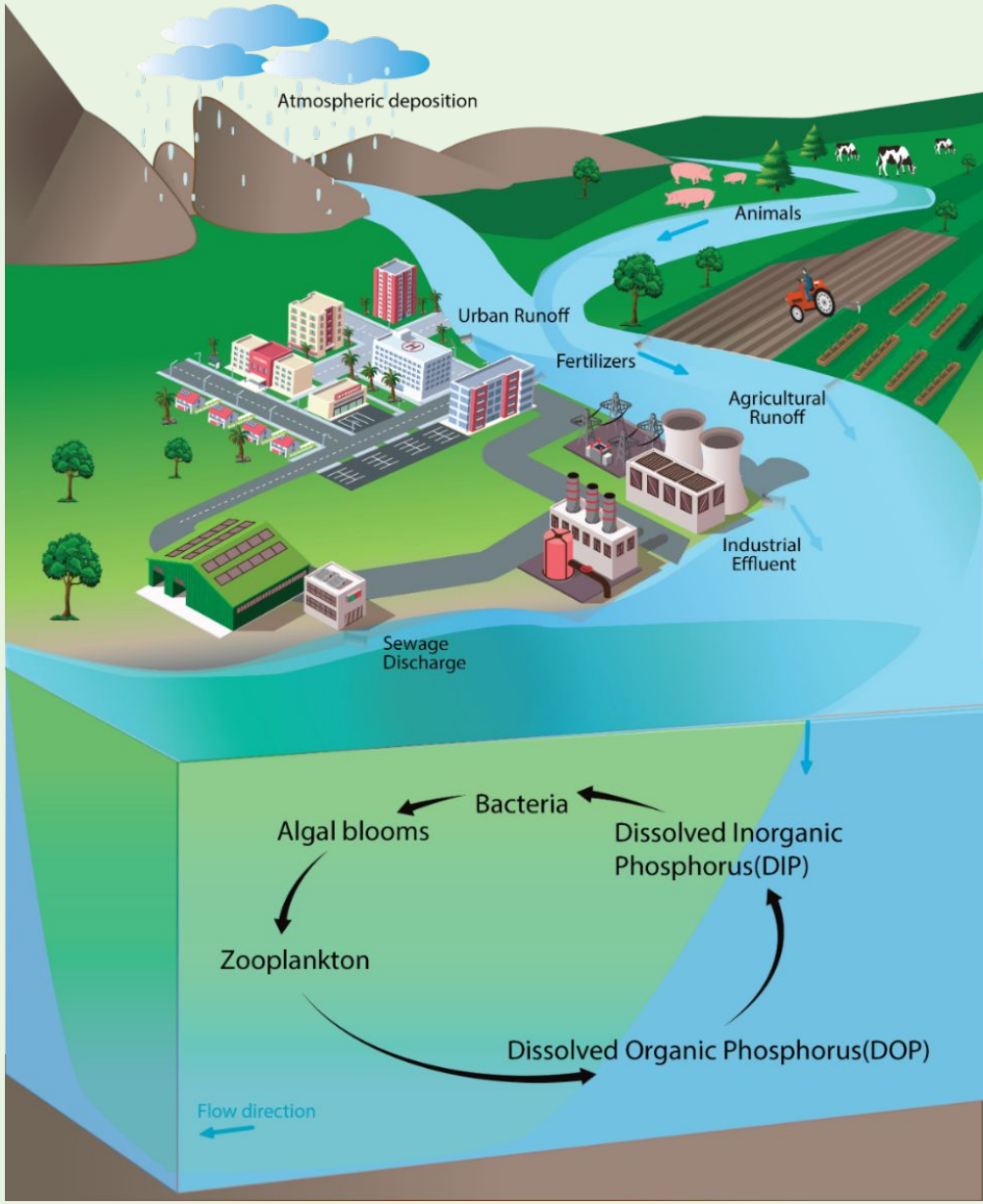
- Phosphate loads from non-point and point sources discharged into freshwater reason for the development of algal bloom growth

Sources: Agriculture runoff, industrial effluents, sewage discharge

- Phosphate limit in freshwater streams 0.1 ppm (EPA)

Health effects:

- Respiratory and neurological problems
- Can sometimes lead to death



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Elevated phosphate levels caused algal blooms

Toledo, Ohio

Algal blooms growth in Lake Erie due phosphate loads from agriculture runoff

- **Don’t drink water** order passed because of the algal bloom's growth in freshwater source
- Left **400000 people** without drinking water for three days

Source: https://glbusinessnetwork.com/harmful-algal-blooms-lake-erie-2/

Mulberry, Florida

- **215 million gallons** of wastewater was discharged into freshwater aquifer
- Excess of phosphates in the wastewater
- Can be potential reason behind the harmful algal blooms growth now

Mosaic- New Wales facility, Florida

Source: Google maps(coordinates :27.815674, -82.033218)

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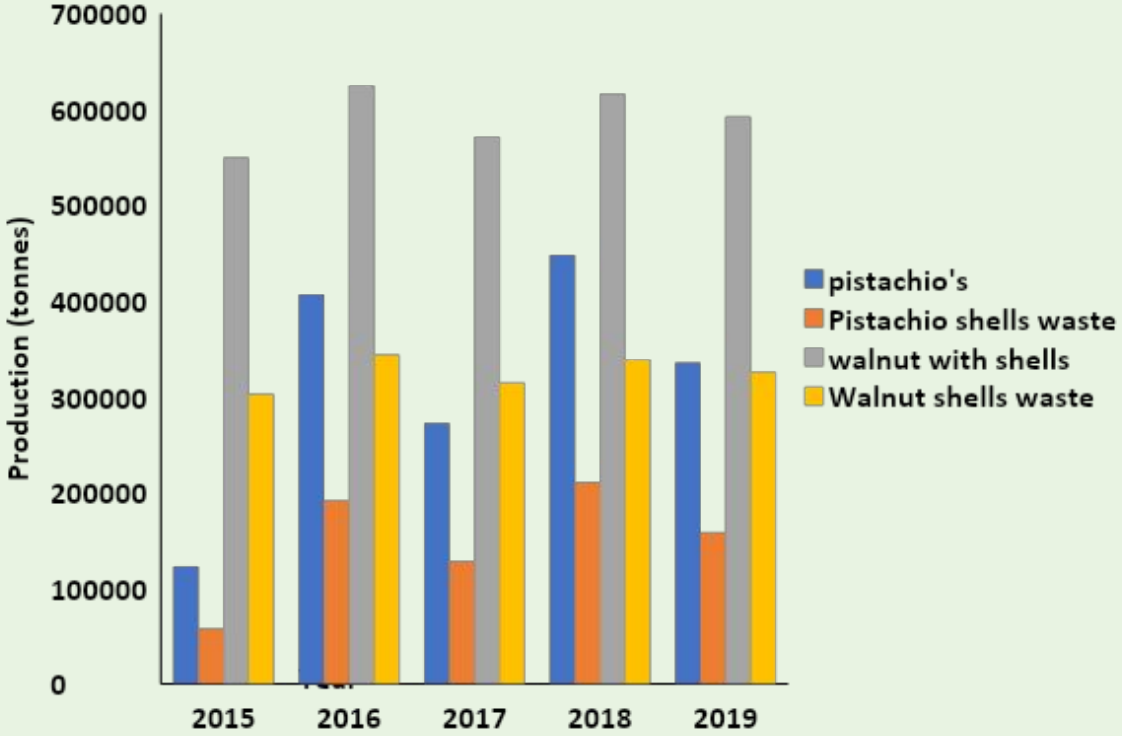
Nutshell waste can be used as a solid support

- United States produces **40% of world's pistachio** and **31% of world's walnuts** – 2nd largest producer of both nuts around the world

- Pistachio shell weight accounts up to 45% total weight of pistachio

- Walnut shell accounts up to 55-60% in the total weight of walnut

On an average **148968 tonnes (approx. 328million pounds)** of pistachio shells and **325017 tonnes (716 million pounds)** of walnut shells are produced



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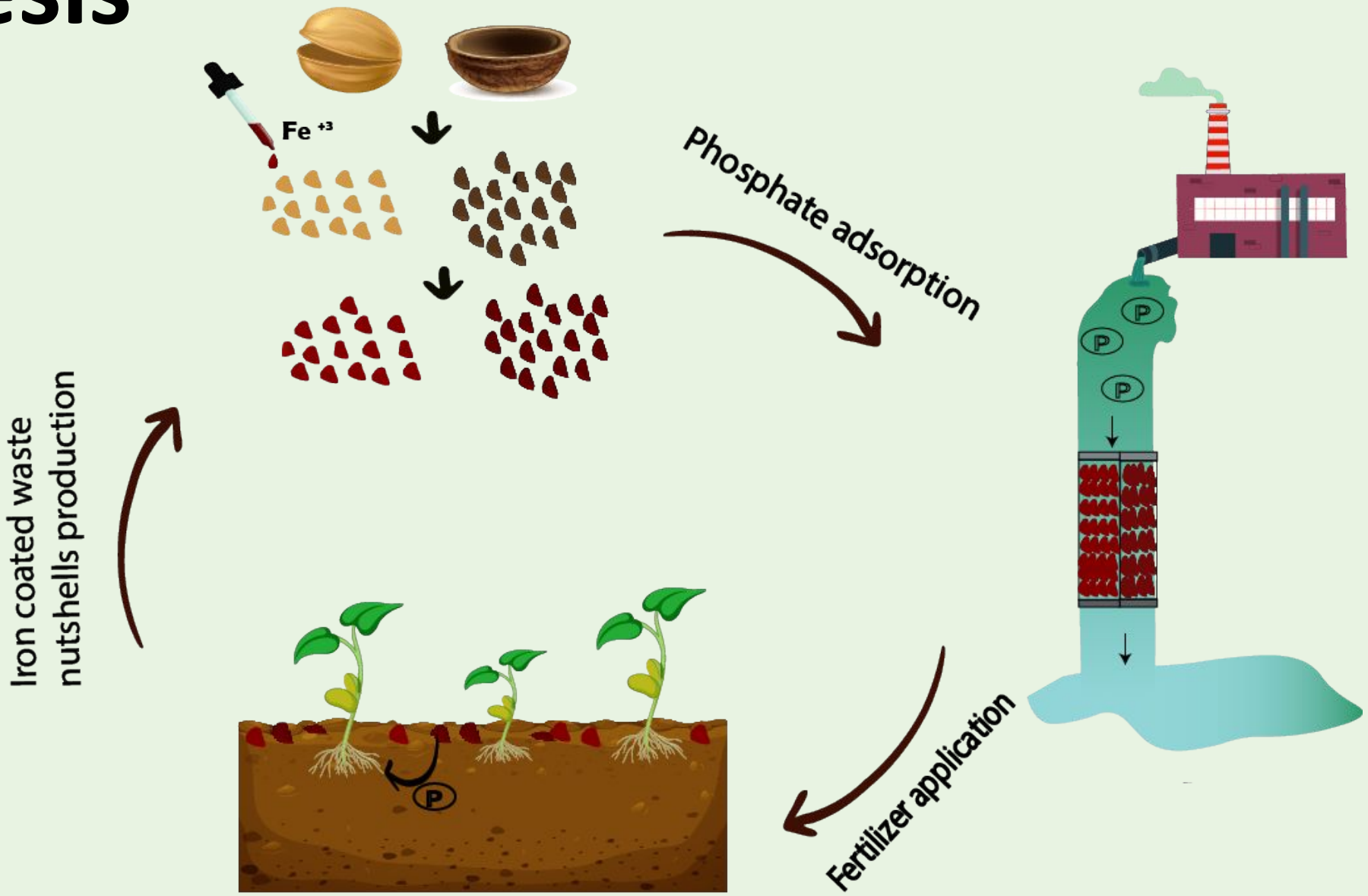
Hypothesis



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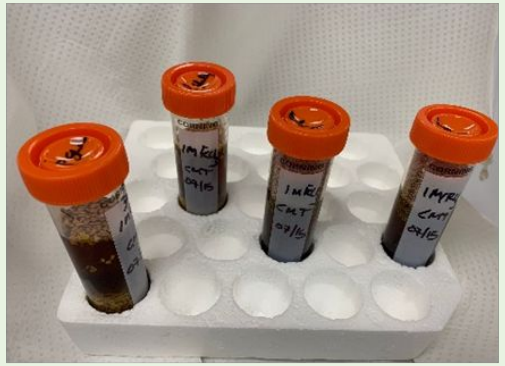
Preparation of Iron coated shells

Washed them with DI water and dried them at 50^0C for 24 hours



Nutshells were added to 1M $FeCl_3$ (solid : liquid = 1:3)

Rotated at 15 rpm for 4 hours at 50 ^0C

Heated to 205^0C

Cooled to room temperature

Washed iron nutshells with DI water(with approx. 7g/l) and dried at 50^0C

Stored in polyethylene bag

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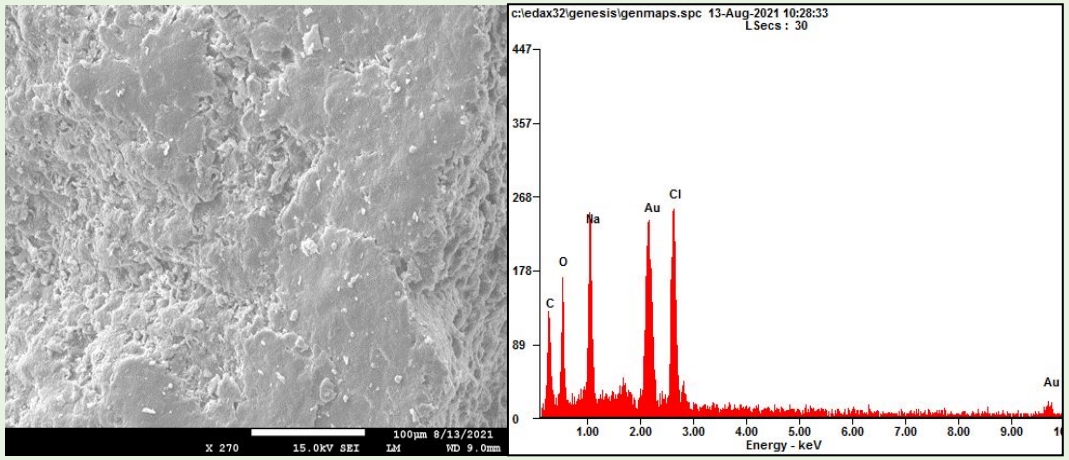
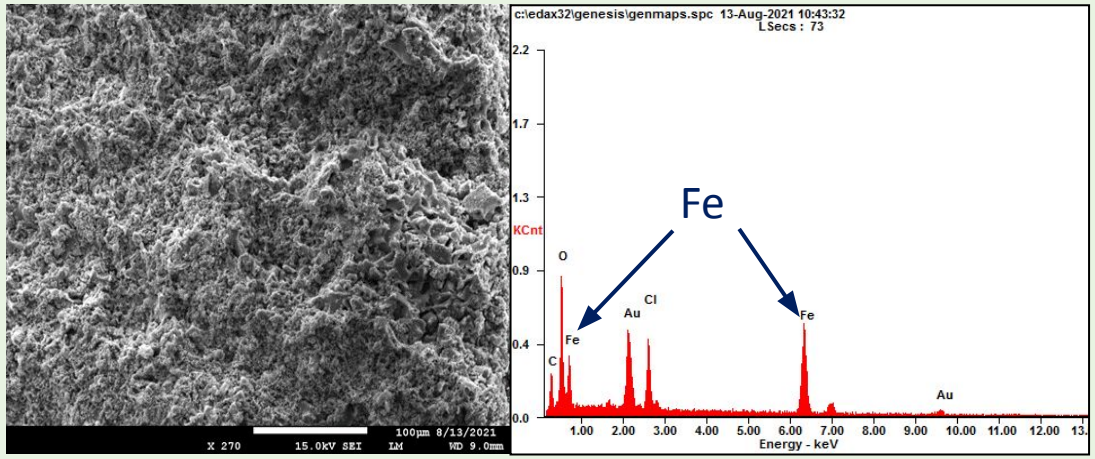
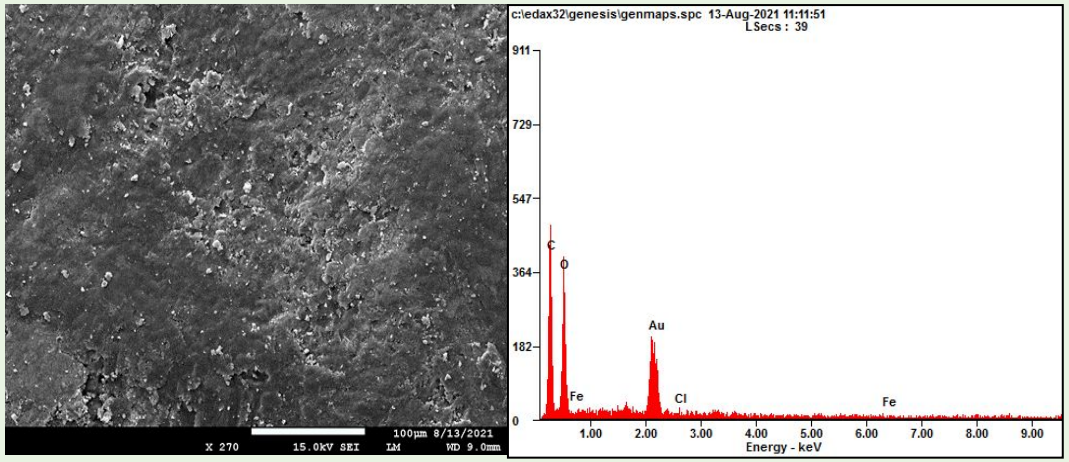
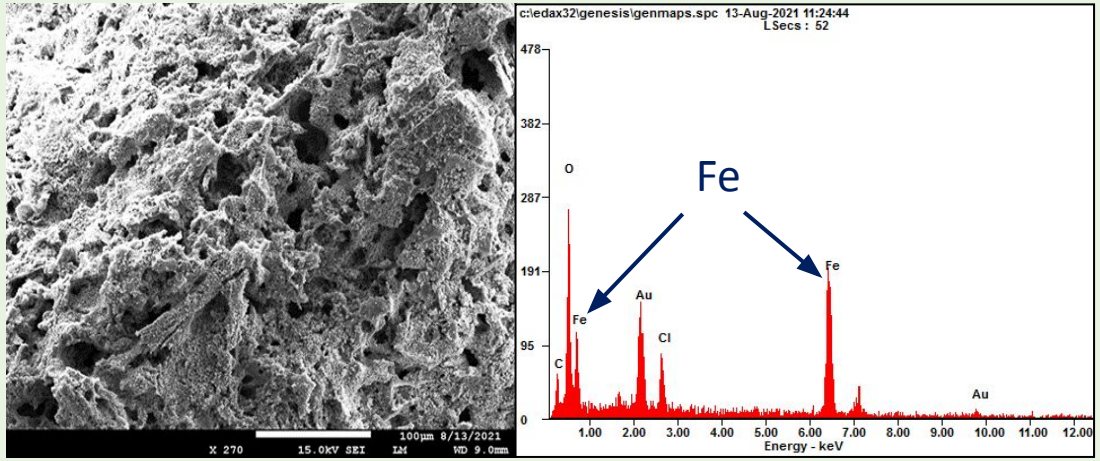
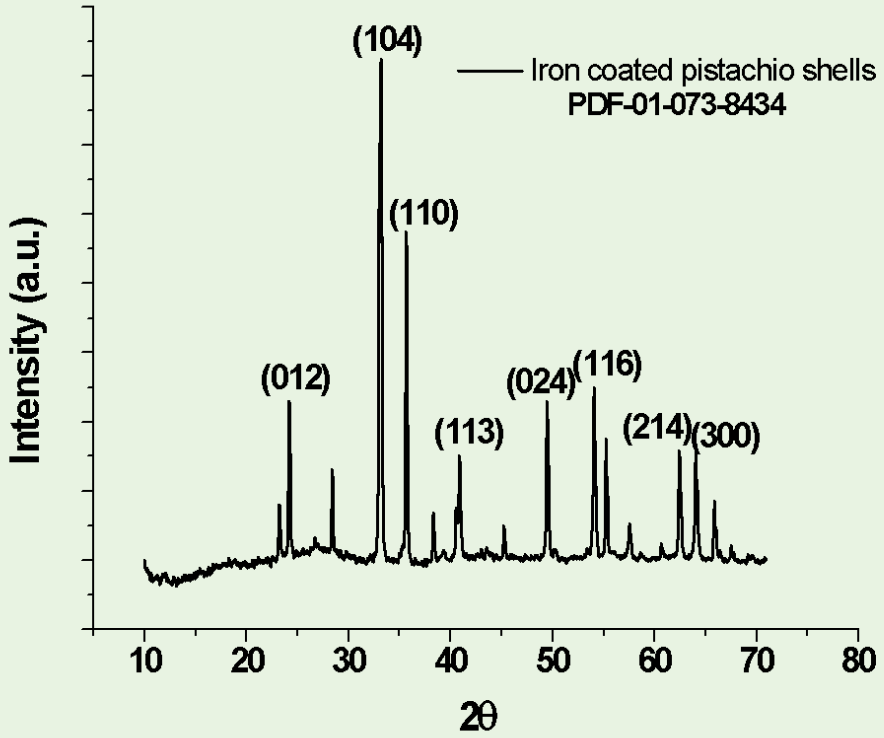
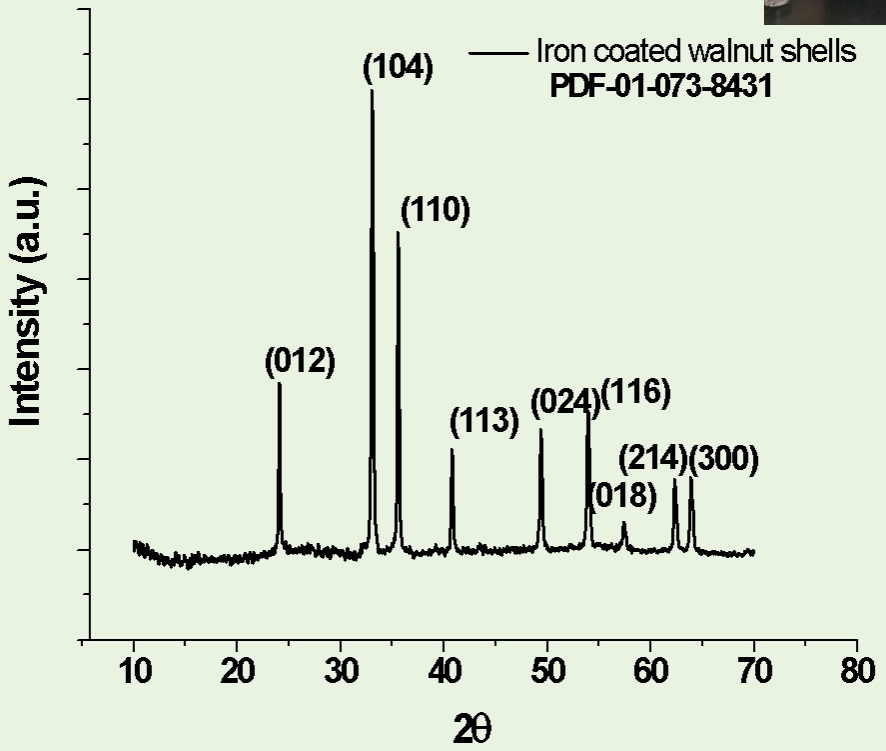
Iron coat confirmation using the SEM and EDS analysis

	Before Iron coat	After Iron coat
Pistachio shells		
Walnut shells		

Hematite mineral was formed on surface of waste nutshells due to the iron coat





Name	Mineral Name	Formula	System	Molecular weight	Density
Iron hydrogen oxide	Iron hydroxide(III) hematite	Fe1.98H0.06O3	Rhombohedral	158.63	5.229

Name	Mineral Name	Formula	System	Molecular weight	Density
Iron hydroxide(III)	Iron hydroxide(III) hematite	Fe1.67HO0.99O3	Rhombohedral	142.26	4.672

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Amount iron coated on the waste nutshells

- **EPA total digestion method 3050B** – Iron was completely dissolved to find out total Iron coated on the shells

- Iron coated on pistachio shells = **19.6±0.8 mg/g**
- Iron coated on walnut shells = **21.2±1.4 mg/g**

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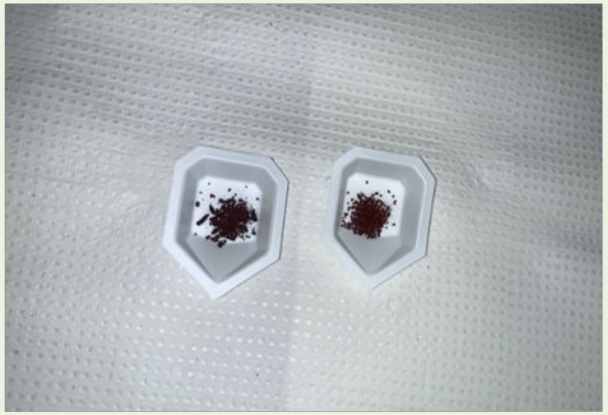
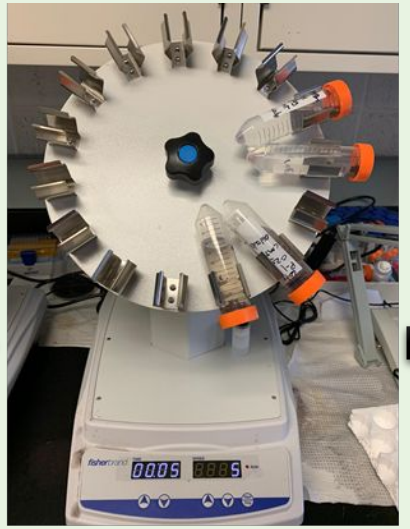
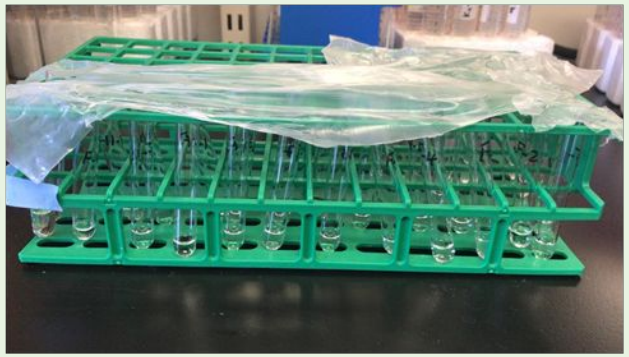
Batch experiments



0.2g of each sorbent added to 40ml of phosphate solution



Centrifuge tubes rotated at 5 rpm (Inclination 120^0)



Samples were collected at regular time intervals(0 minutes, 10minutes, 20 minutes…. 2880 minutes)

Samples are digested in an autoclave at 121^0C for about 35 minutes

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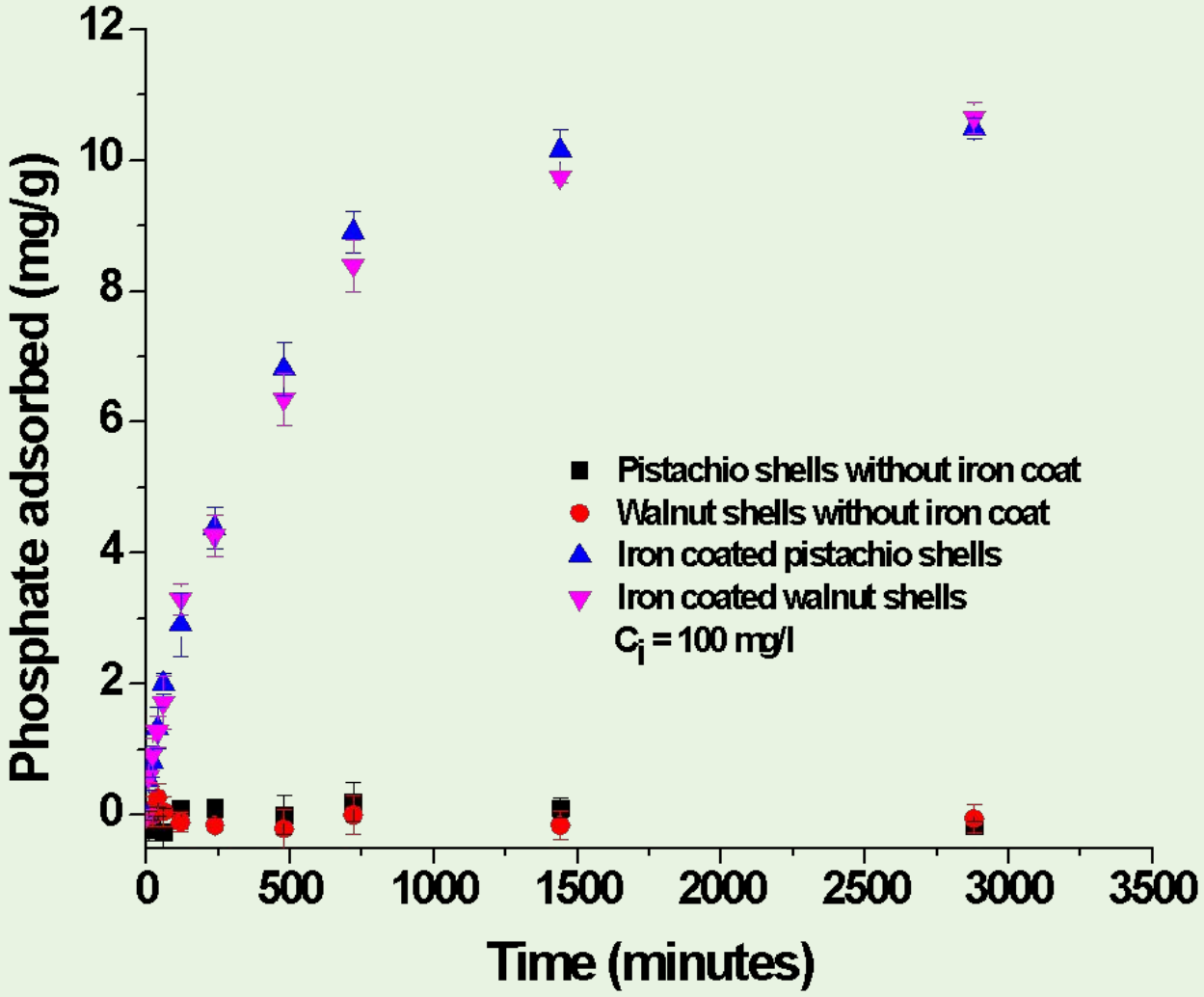
Enhancement of the waste nutshell phosphate adsorption capacity with the Iron coat

- Pistachio shells and walnut shells didn't remove any phosphate from the aqueous solution
- Iron coat on the waste nutshells enhanced the adsorption capabilities of the waste nutshells



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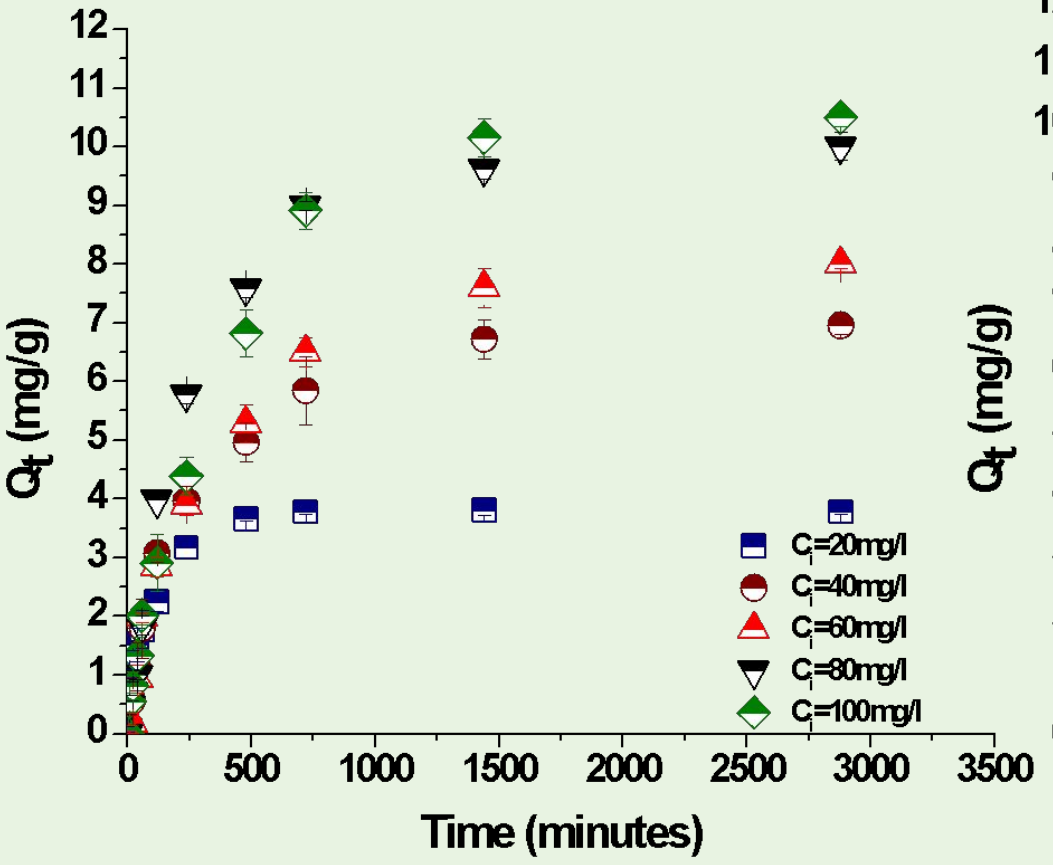
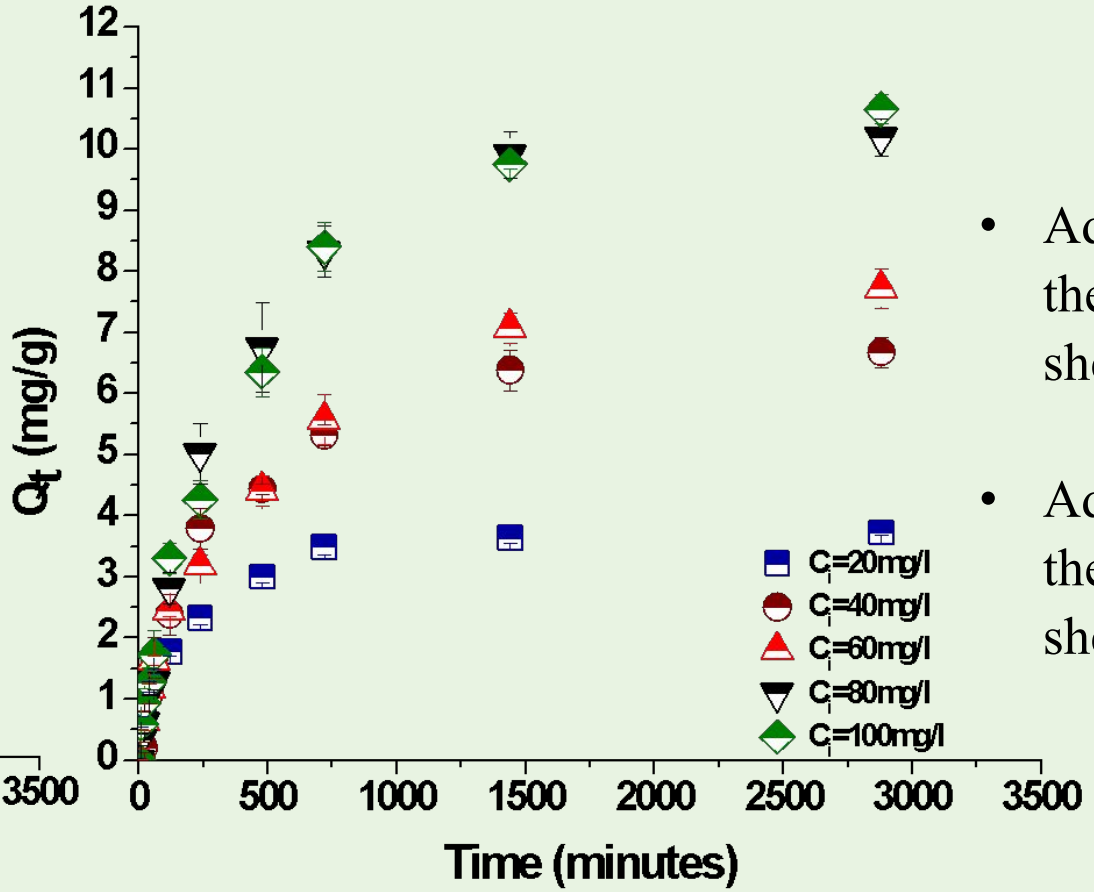
Time taken to reach equilibrium varied with the phosphate concentration



Iron coated pistachio shells



Iron coated walnut shells

- Adsorption capacity of the Iron coated pistachio shells = **12.63 mg/g**
- Adsorption capacity of the Iron coated walnut shells = **9.25 mg/g**

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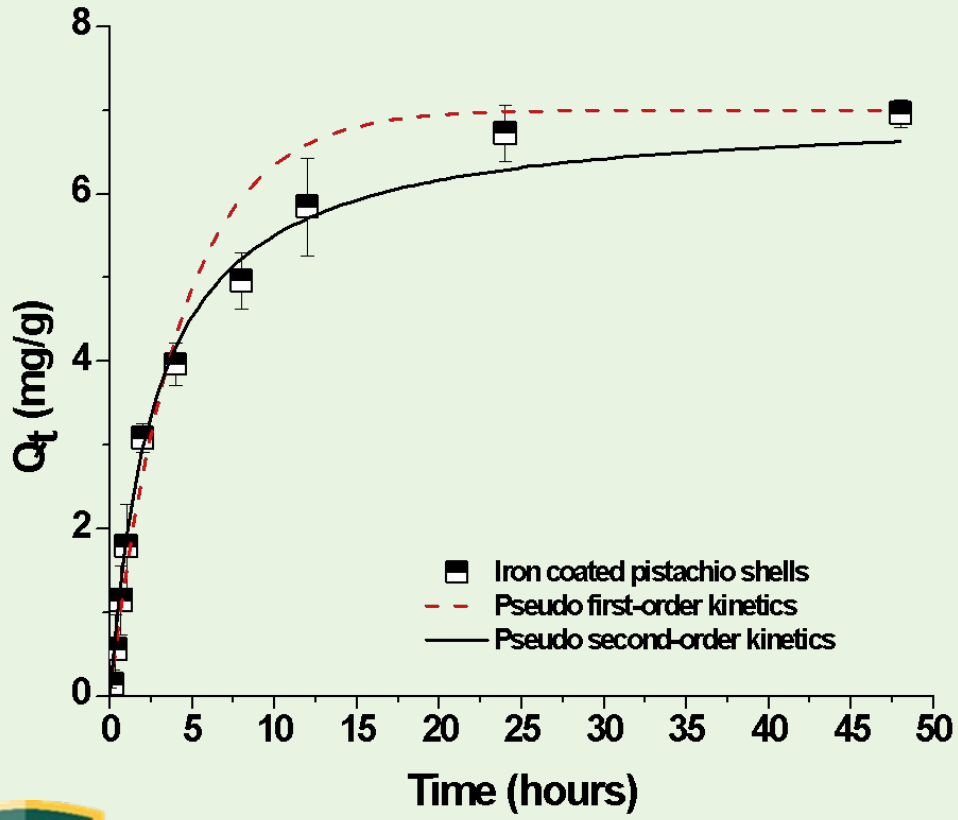
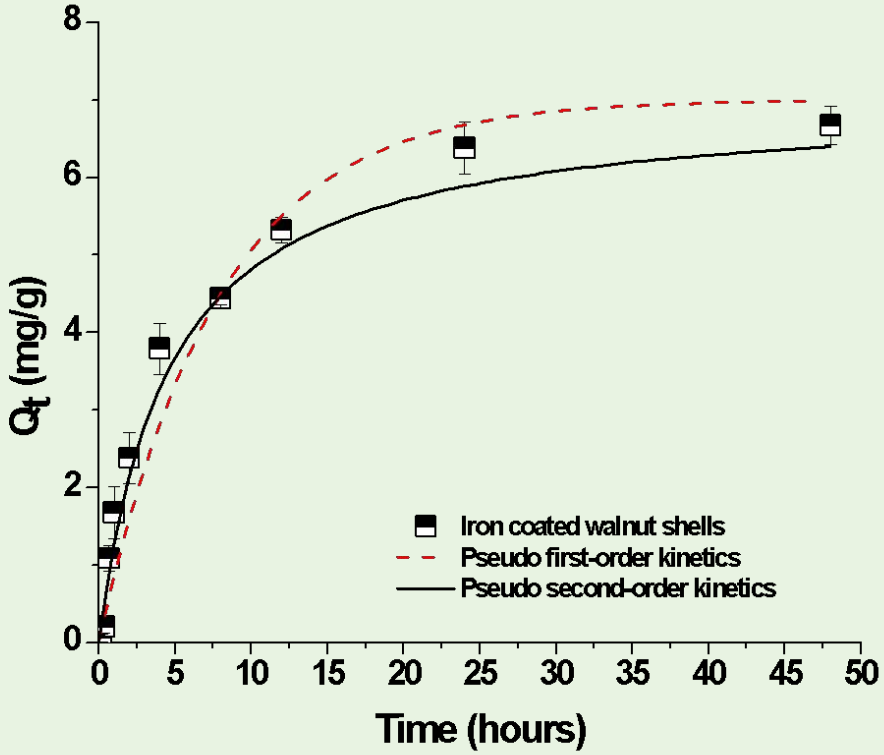
Both the iron coated waste nutshells followed pseudo second order kinetics

- Pseudo-kinetic first order equation $: Q_t = Q_e - e^{-K_1 t}$
- Pseudo-kinetic second order equation $: Q_t = \frac{K_2 Q_e^2 t}{1 + K_2 Q_e t}$





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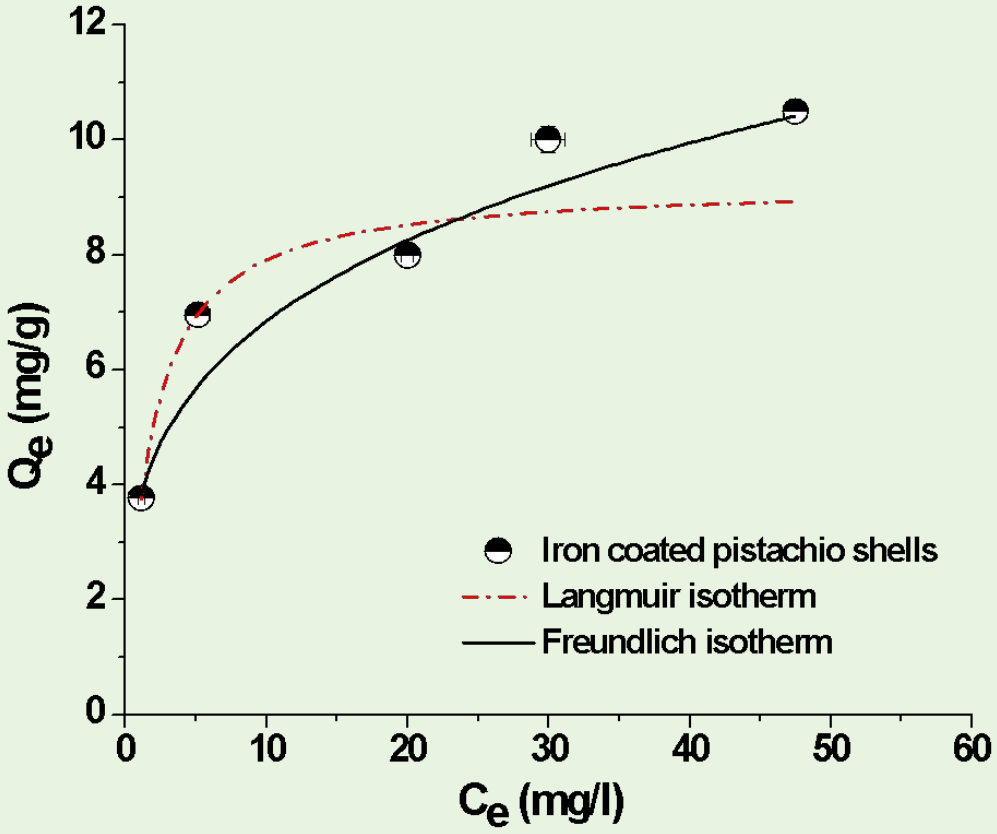
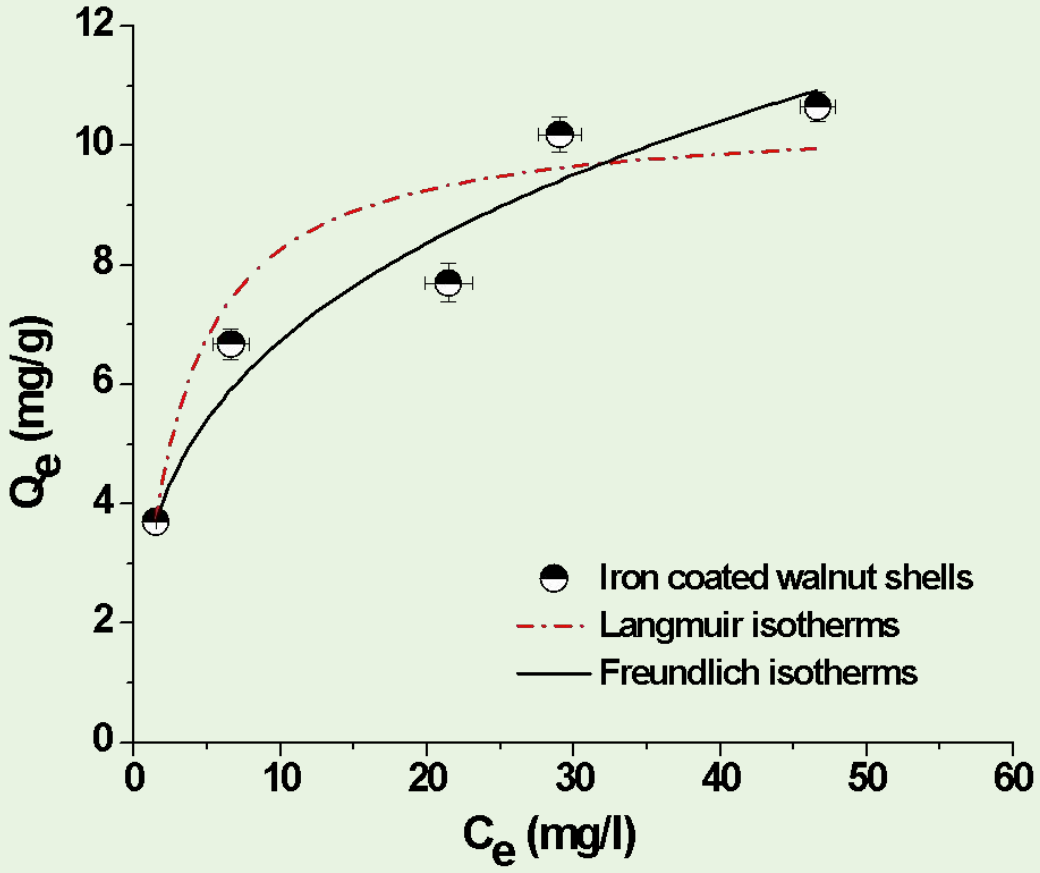
Freundlich isotherms model fits better based on the R-squared value





Adsorbents	Freundlich			Langmuir		
	R^2	k_F	1/n	R^2	Q_m	k_L
Pistachio shells	0.97	3.77	0.26	0.93	9.79	0.57
Walnut shells	0.97	3.33	0.30	0.95	10.2	0.40

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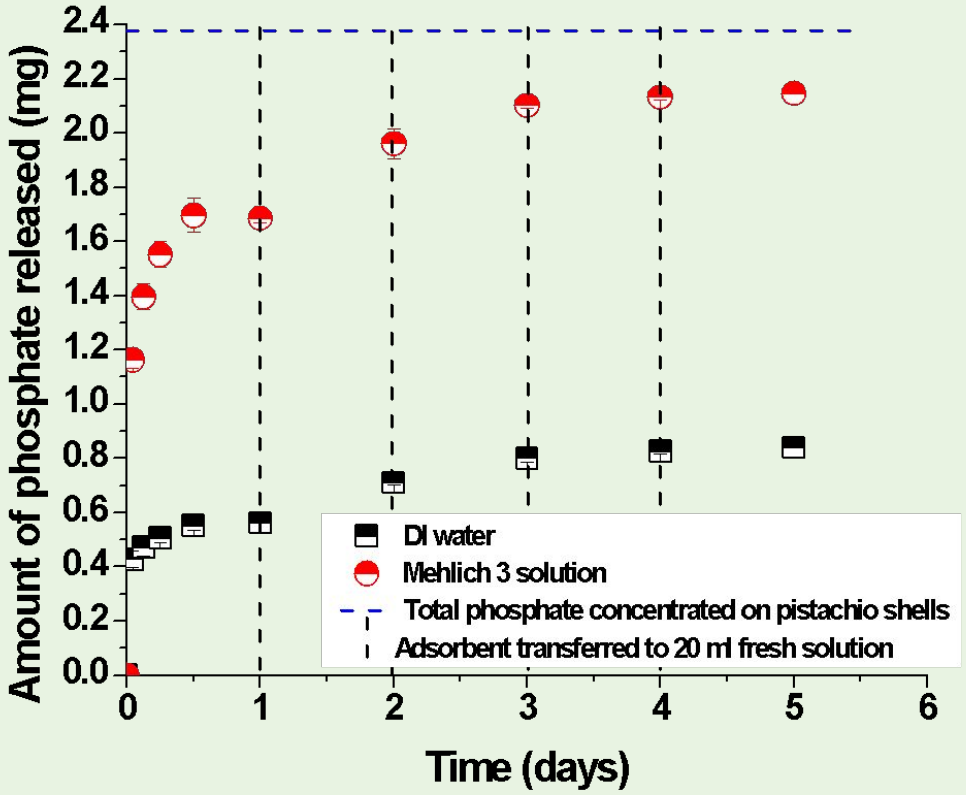
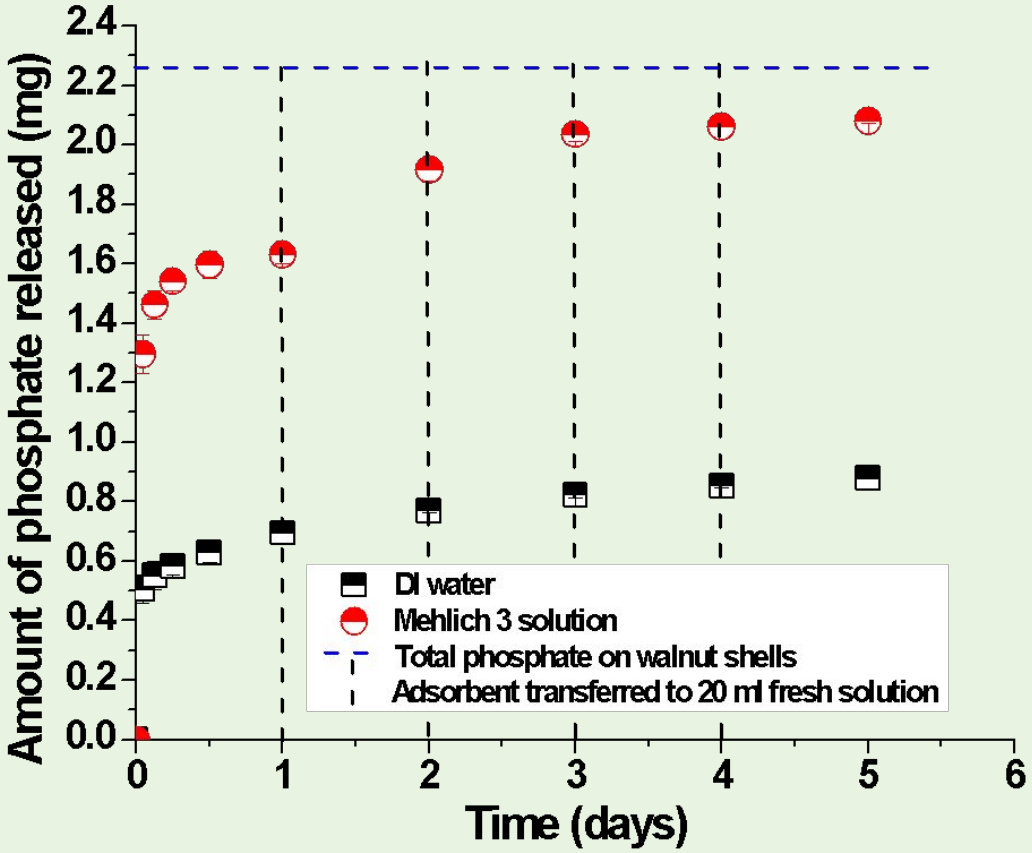
Sequential phosphate release experiments to demonstrate slow release





Mehlich 3 solution: 0.2 M glacial acetic acid, 0.25 M Ammonium nitrate, 0.015 M Ammonium fluoride, 0.013 M Nitric acid, 0.001M EDTA

- More than **90 %** of phosphate attached to the iron coated walnut shells was released slowly over a **5-day period**

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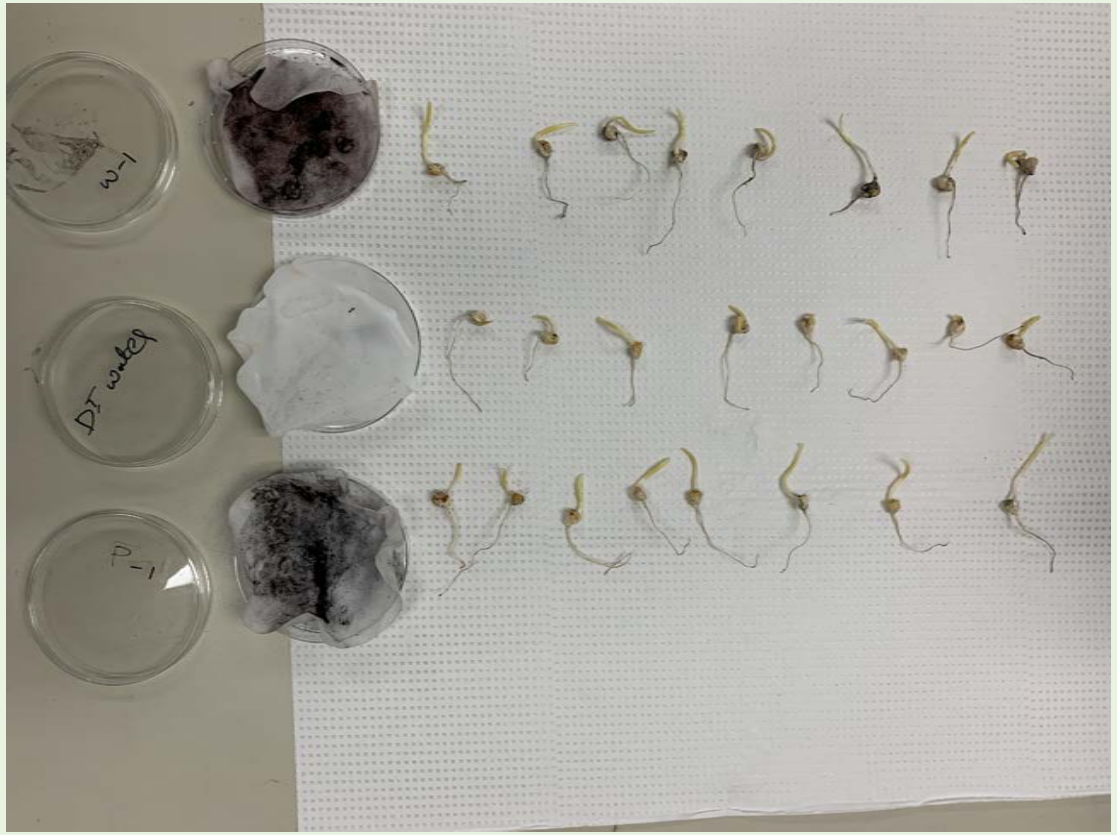
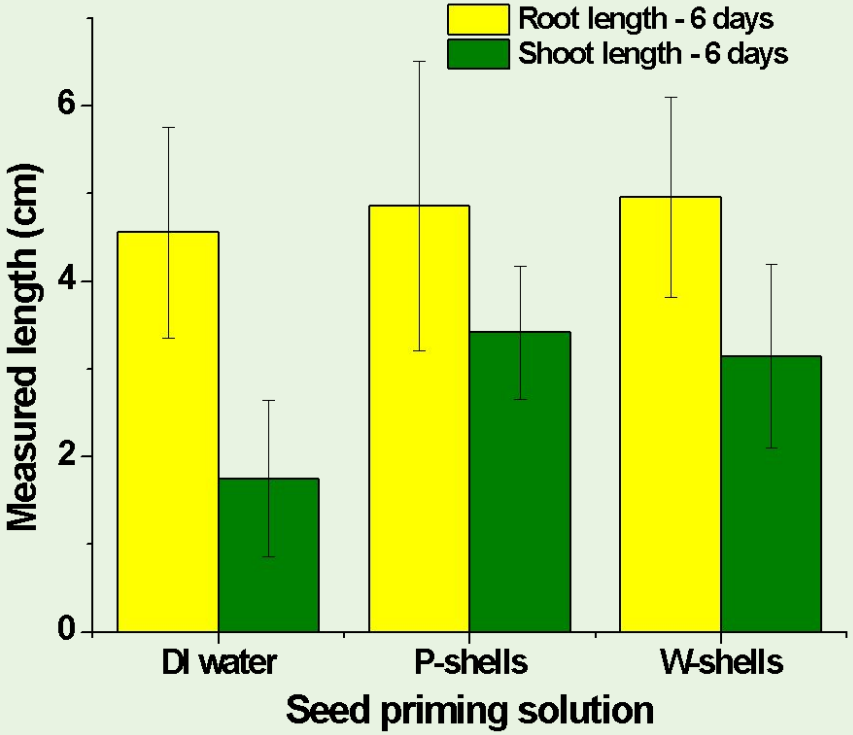
Nutrients released from iron coated adsorbents can enhance the growth in the plants





- Mean shoot length increased by **48%** when phosphate enhanced iron coated pistachio shells were used and **43%** increase was se when phosphate enhanced walnut shells used.
- Results were statistically significant with a **P<0.01(ANNOVA analysis).** No significant difference was observed in the root length

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Conclusion

- Adsorption experiments showed that iron coated nutshells successfully adsorbed phosphates from the water system
- Adsorption process is spontaneous and followed pseudo second order kinetics
- Iron coated nutshells can be potential low-cost adsorption media to filter phosphate from contaminated waters
- Large scale studies are planned to investigate to P-release kinetics and the applications for these materials as slow-release fertilizers.

References

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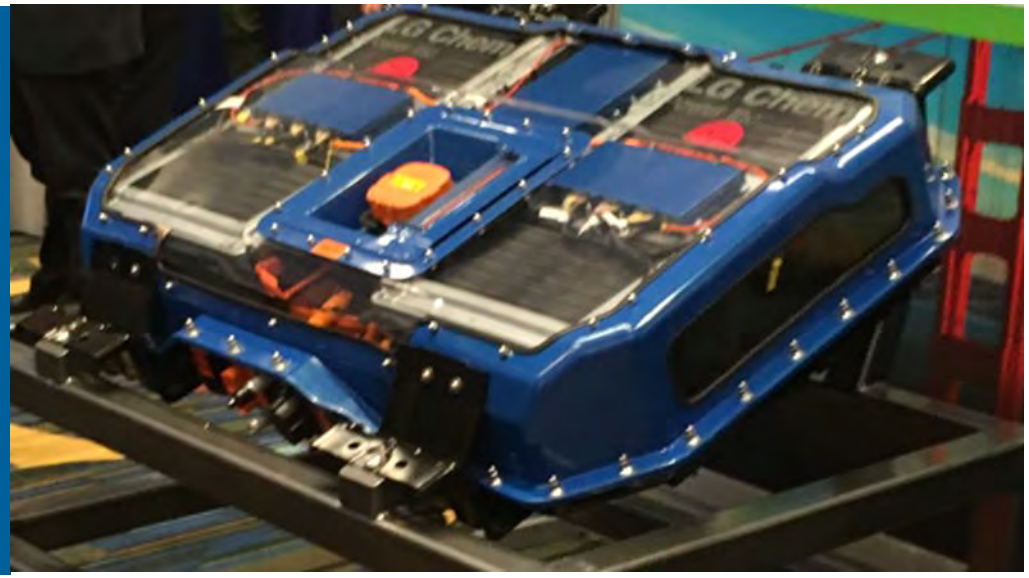
Thank you

COMPETITION FOR PHOSPHORUS FROM THE BATTERY INDUSTRY



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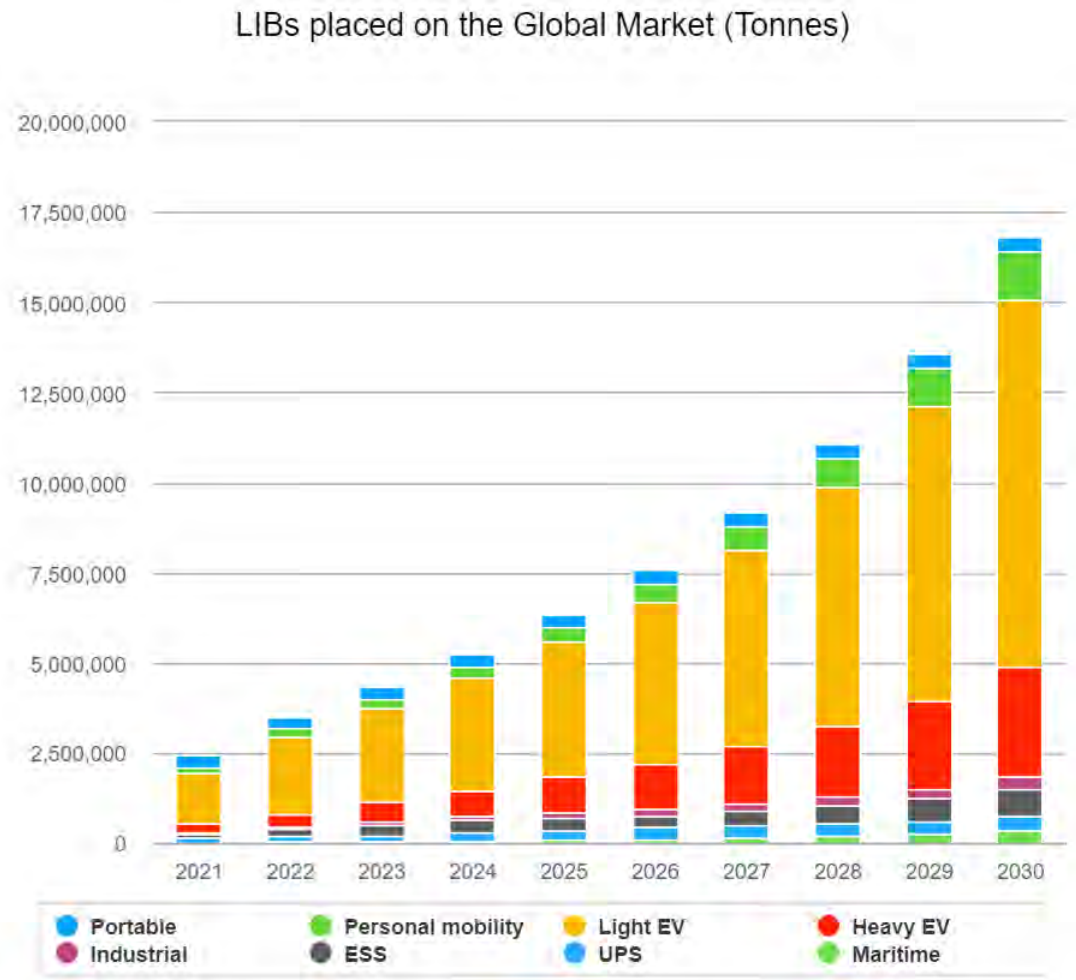
Sustainable Phosphorus Summit

November 4, 2022

BATTERIES WILL REQUIRE HUGE QUANTITIES OF MATERIAL

Demand stems from commitment to rapid displacement of fossil fuels

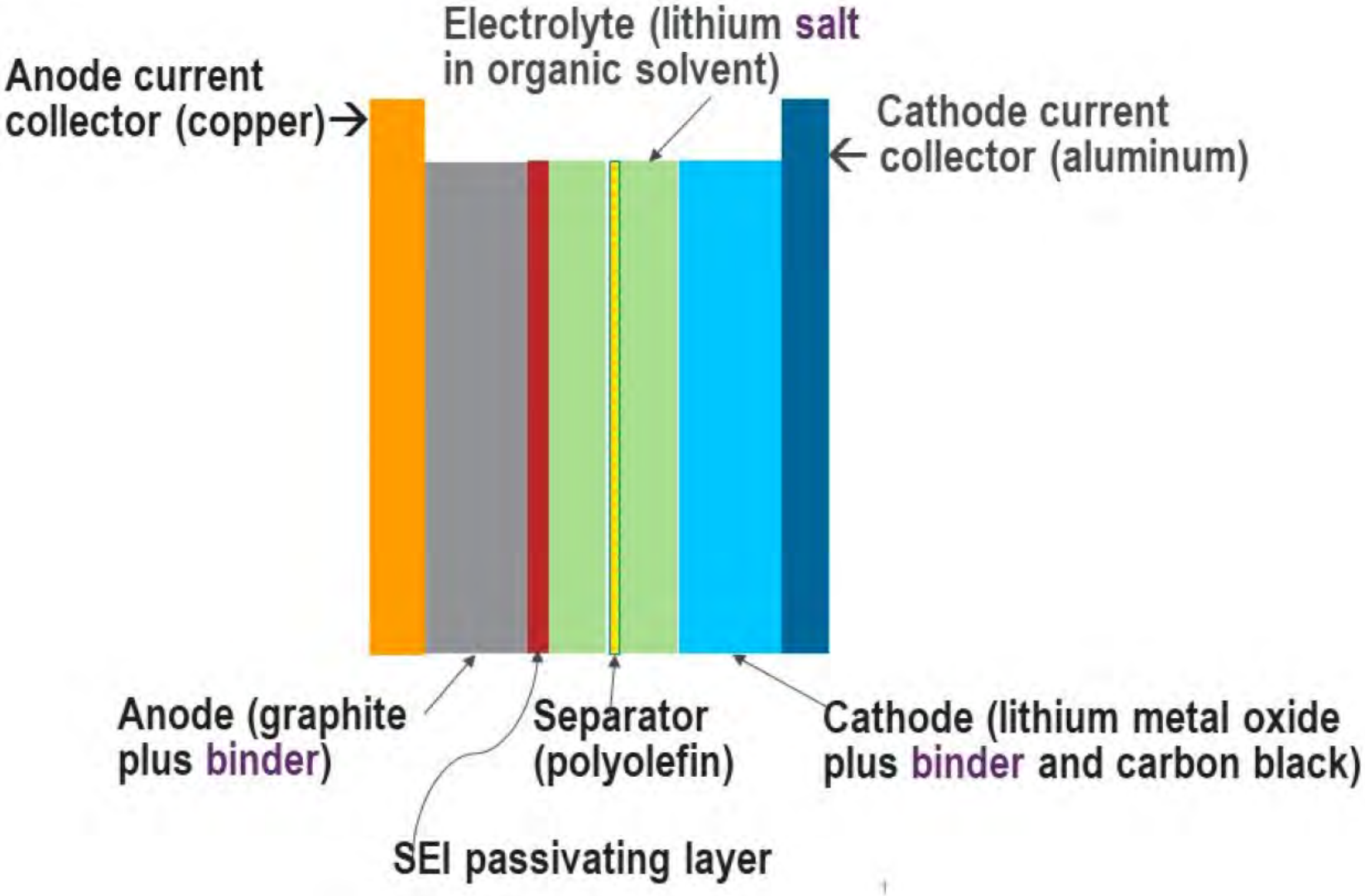
- Existing supply chains are inadequate and unstable
  - In a finite system, there is no such thing as sustainable growth
  - Disruptions happen from pandemics and war
- Alternative materials, technologies, and mobility options should be explored
- Use of domestic materials could reduce conflict from competition for materials
- Recycling can make a major contribution after demand growth slows



Source: https://www.circularenergystorage-online.com/global-pom-application

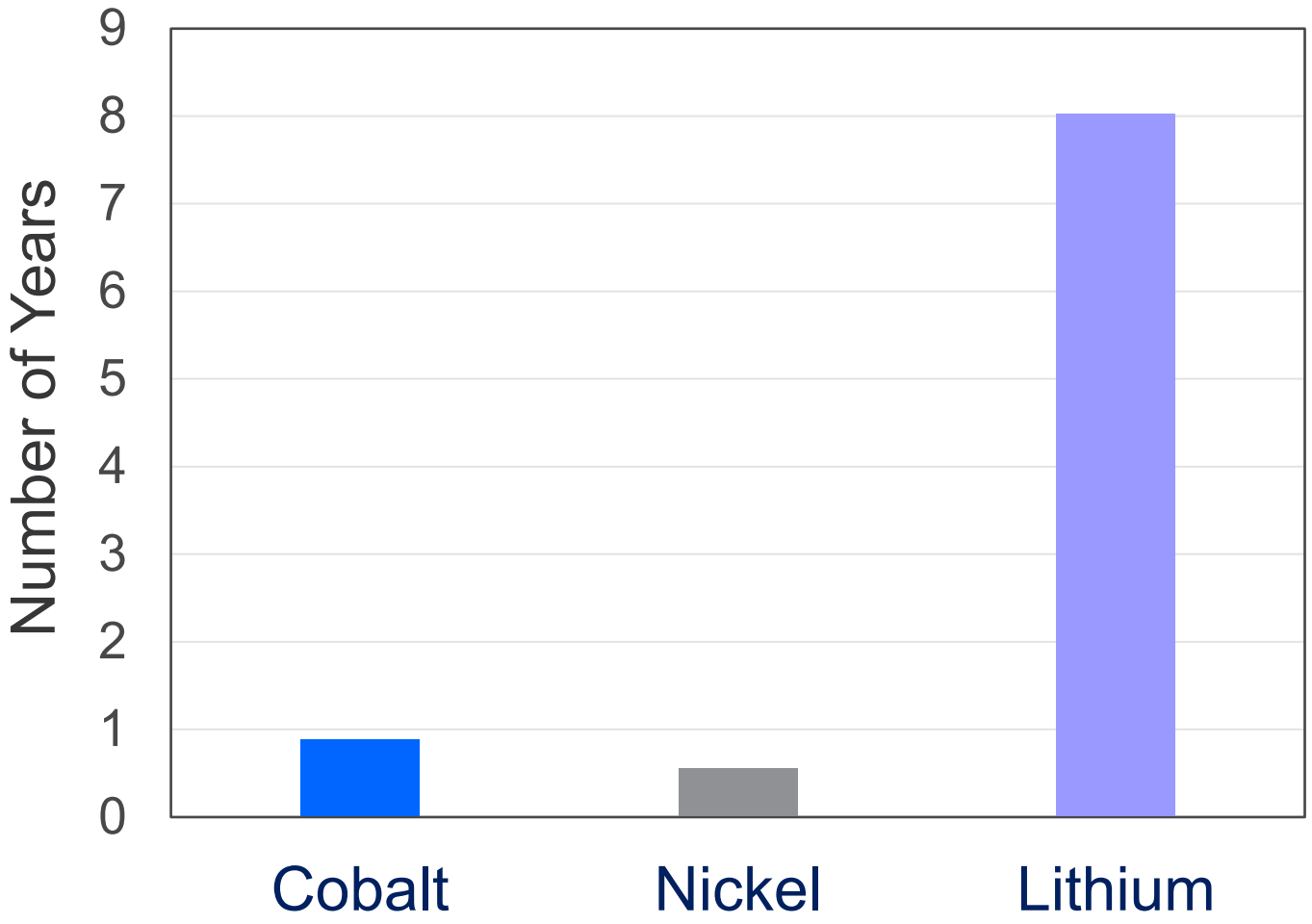
WHAT'S IN A LITHIUM-ION BATTERY?

Cathode [$Li(Ni_xMn_yCo_z)O_2$] is key to battery performance



US DEPENDS ON COBALT AND NICKEL IMPORTS

How many years could US make all cars as EVs with our reserves?



DOE SEEKS TO REDUCE CO AND NI CONTENT

Battery Technologies – Key R&D Emphasis

Significantly reduce battery cost	Reduce or eliminate dependence on critical minerals	Support domestic battery and materials supply chain

BATTERY 500 CONSORTIUM

Solid State Batteries

1. Accelerate and Scale-Up lithium Metal Battery R&D

- Reduce EV battery cell cost by 50% to $60/kWh by 2030 to achieve EV cost parity with ICE vehicles

Low/No Cobalt Cathode

2. Accelerate Next Generation Lithium-Ion

- Develop and Scale Up No Cobalt, No Nickel Cathodes
- Develop and Scale Up Silicon-based anode

ReCell ADVANCED BATTERY RECYCLING

3. Expand Lithium Battery Recycling R&D

- Establish a lithium battery recycling ecosystem to recover [illegible]es and re-introduce 90% of key materials into the battery supply chain by 2030

POSSIBILITES FOR NO COBALT, NO NICKEL CATHODES

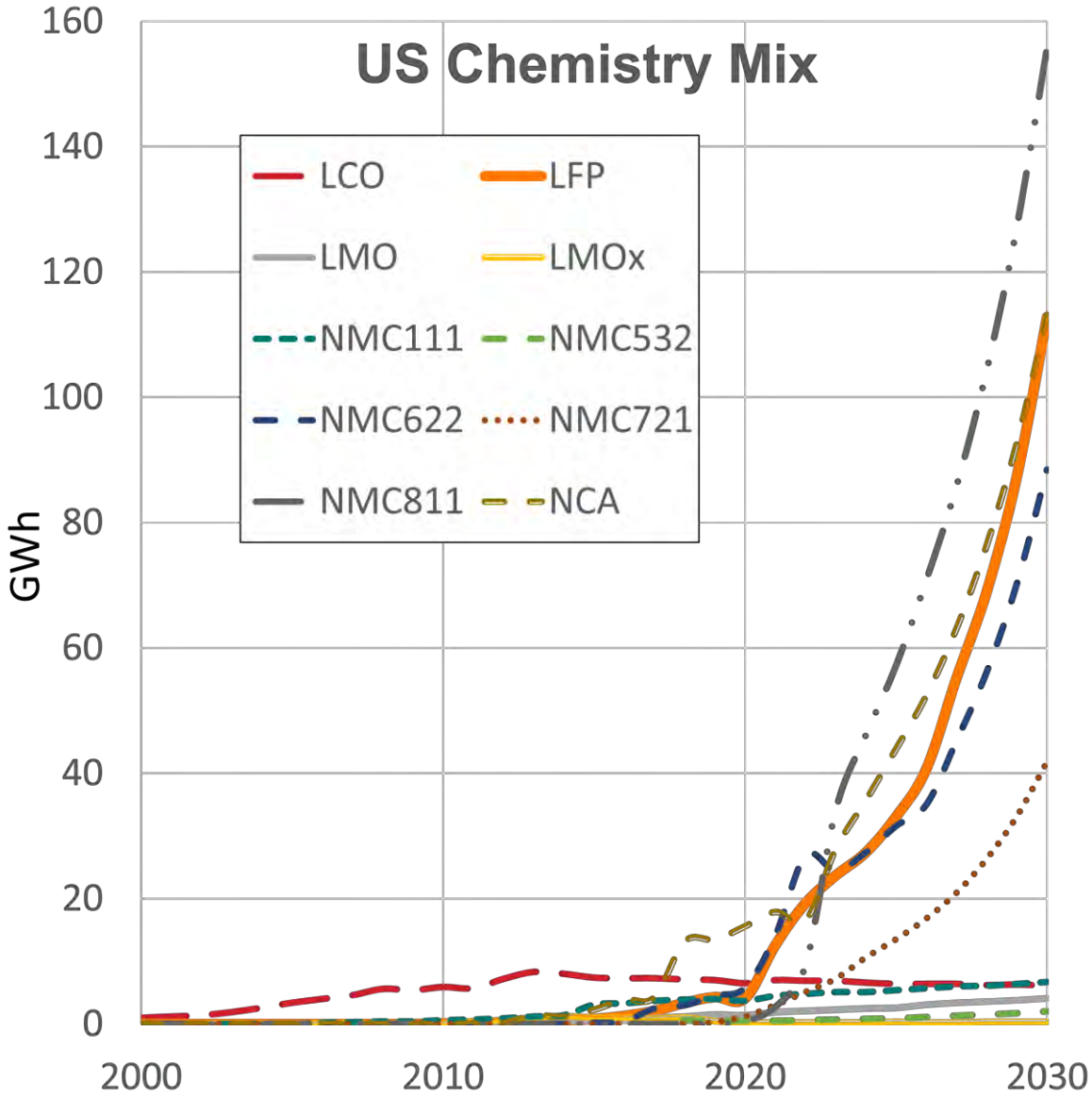
- Disordered structures
- Rock salts
- Manganese
- Li-S
- **Phosphates (e.g., LFP [Lithium Iron Phosphate])**

"There is lots of work being done, lots of challenges. So, there will be no single winner."

David Howell, MSPC Supply Chain Symposium

WHY LFP IS INTERESTING

- It could be made with all domestic materials
  - No worry about sourcing Ni and Co
- It is cheaper and safer than NMC
- Fewer GHG to produce
- New designs like BYD Blade compensate for lower energy density
  - Can fully charge/discharge
  - 400-mile range might not be needed
- It can be recycled directly at low cost
- First Phosphate will produce in NA



Projection courtesy of Circular Energy Storage, London

PHOSPHORUS COULD BE IMPORTANT FOR BATTERIES

US does have domestic phosphate rock (and iron)

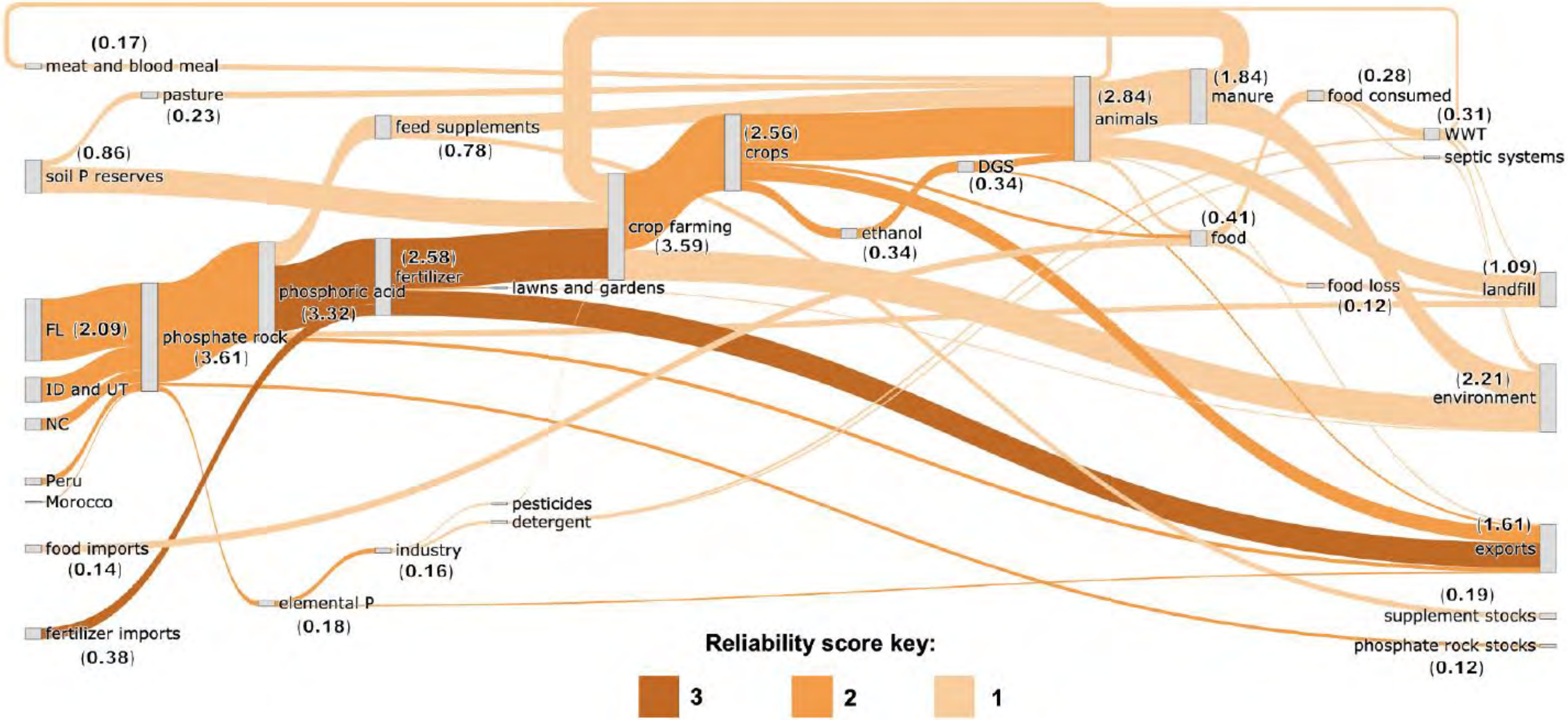
- EU classifies P as critical, with reserves but minimal production in Finland
- US also produces pure phosphoric acid
  - Precursor for LFP
  - Could develop complete domestic supply chain
- Major use is agricultural
- Major use for batteries could eventually impact fertilizer market
- There is potential to recover phosphorus lost in agricultural use
  - There would be ecological benefits
  - Research would be needed on methods

Country	Mine Production 2021	Reserves
United States	22,000	1,000,000
China	85,000	3,200,000
Morocco	38,000	50,000,000
Russia	14,000	600,000
World Total	**220,000**	**71,000,000**

USGS Phosphate Rock Data (1000 metric tons)
Contained phosphorus is about a 10X lower.

PHOSPORUS FLOWS IN US ECONOMY 2017

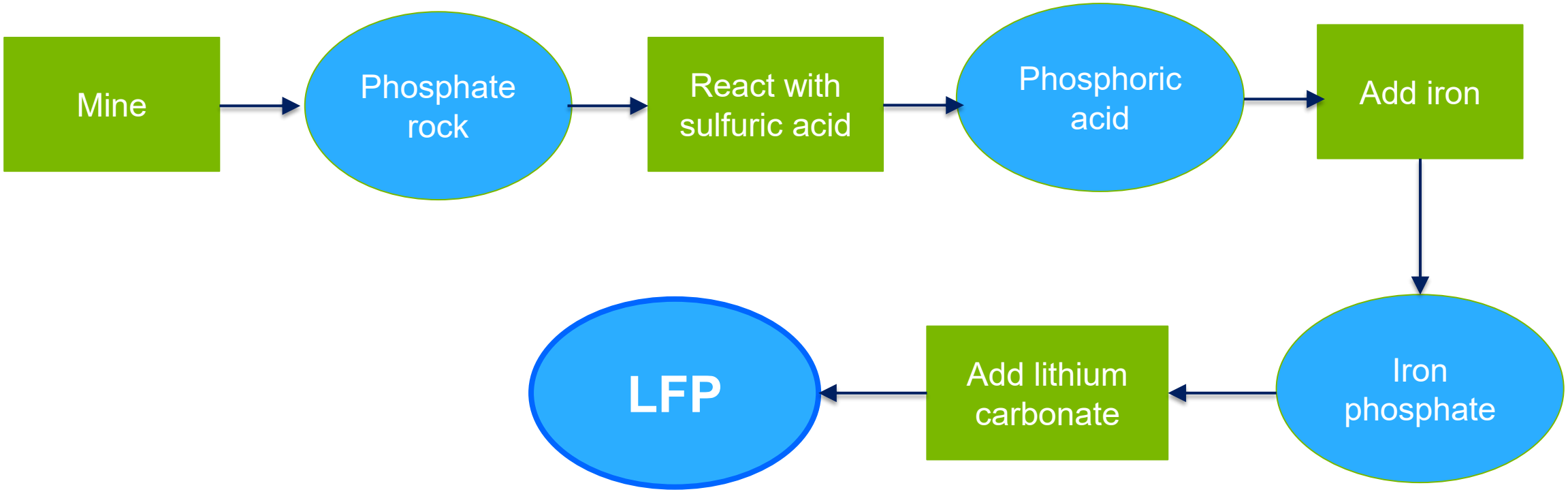
b) 2017 US P Flows (billion kg P)



Algren, M., T. T. Burke, Z. U. M. Chowdhury, C. Costello, and A.E. Landis. *Quantifying phosphorus flows in the United States to identify the major contributors to P loss and opportunities for improvement*. In journal peer review.

HOW IS LFP MADE?

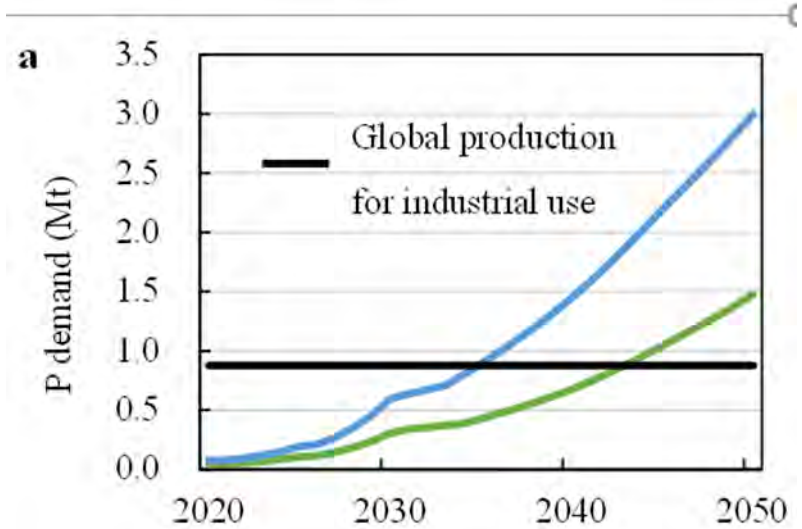
US has capacity to make all of the intermediate products

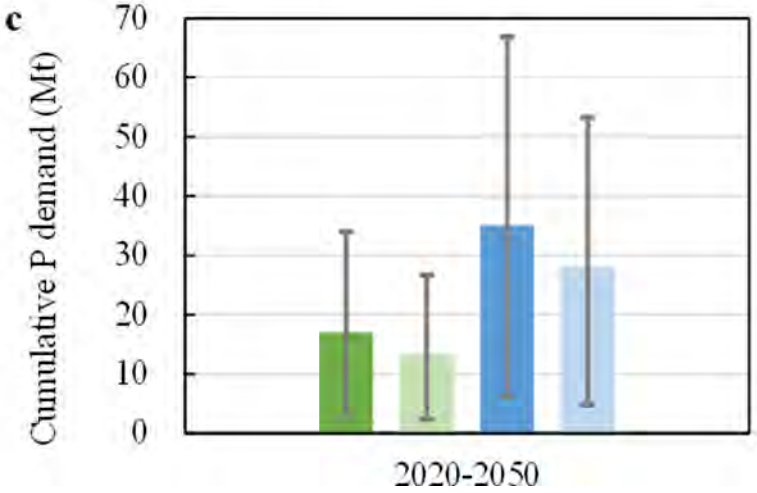


BATTERY USAGE MAY IMPACT PHOSPHORUS MARKET

Global demand could rival industrial uses within 10 years

- By 2050, LFP batteries could require >3 Mt/y of P
  - This estimate is highly uncertain
  - About 30% could be available from recycling
  - Cumulative demand could be over 35 Mt
- About 30 Mt P (223 Mt rock) was mined in 2020
  - Quantity could double by 2050
  - Resources are large but finite
  - Industrial grade production is under 1 Mt/y
- Competition most likely for industrial market



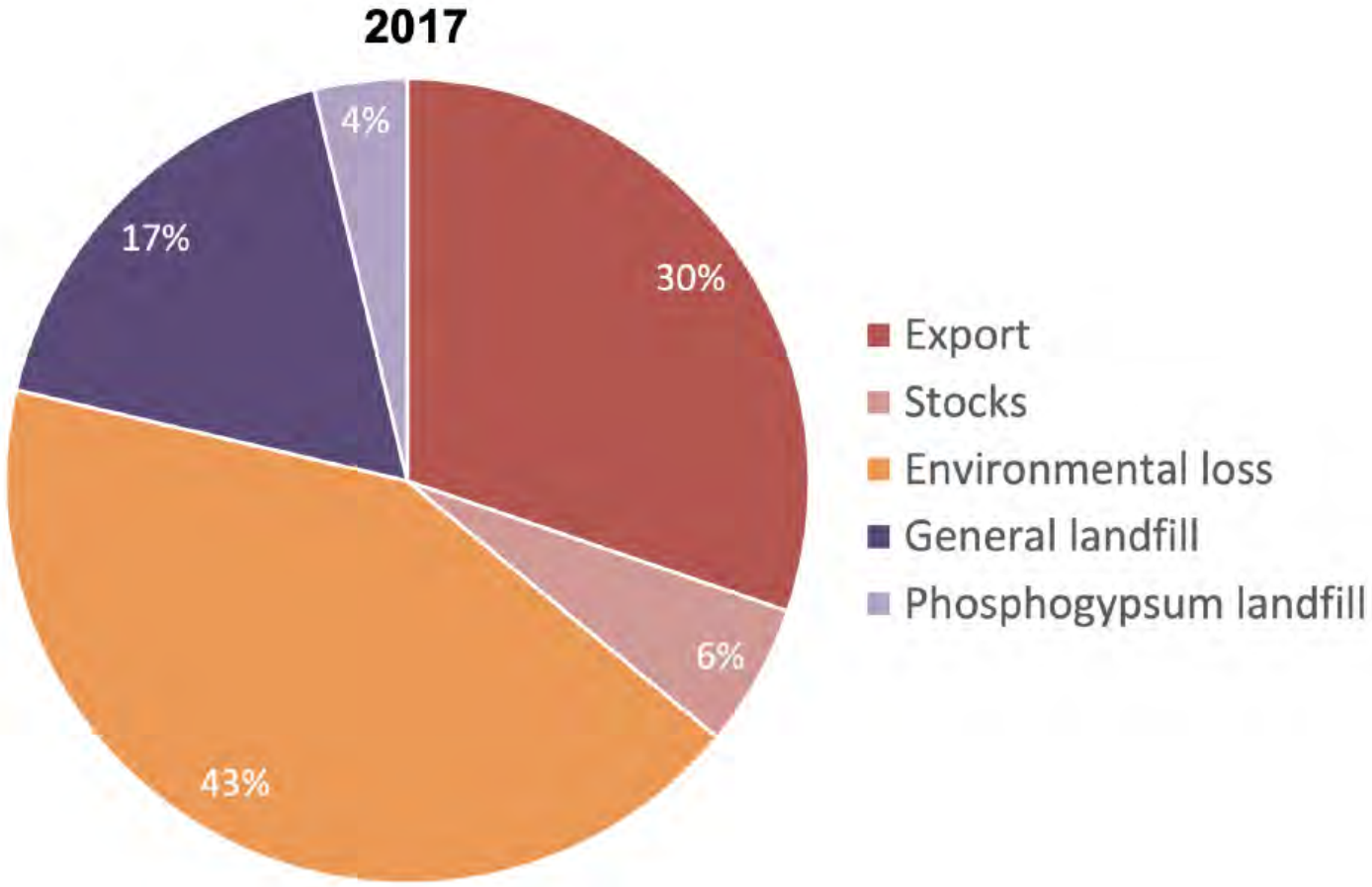


"Reply to: Concerns about global phosphorus demand for $LiFePO_4$ batteries," C. Xu, Q. Dai, L. Gaines, M. Hu, A. Tukker, B. Steubing, Communications Materials, 2022

MUCH P IS LOST TO THE ENVIRONMENT

More could be captured

- Lawn/garden runoff
- Septic system drainage
- Food waste
- Wastewater
- Phosphogypsum
- Animal processing
- Manure
- Cropland runoff



Fate of P in US

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PHOSPHORUS RECOVERY CAN MODERATE DEMAND GROWTH

Would also benefit environment by removal from waste stream

- Increased P recovery from wastewater would limit need for mining
  - Sewerage connections expected to increase by 4 billion globally by 2050
    - Connections with urine separation could double P recycled to 1.3 Mt/y
    - Vivianite (3 Mt/y), with high Fe content, could be input to LFP
- Sustainability could benefit from reduction in the P load to fresh waters (~5Mt/y)
- Potential synergy if agricultural P can be recycled to battery-grade raw materials or P from batteries for agricultural purposes
- P is not as critical a raw material as Li, Co, or Ni, especially if it can be recycled.

Thank you!
US Department of Energy, Vehicle Technologies Office