

Tomato plant roots/ carboxymethyl cellulose (CMC) method for the removal and recovery of phosphate from agricultural wastewater

University of Windsor
Chemistry and Biochemistry

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Mutus¹





The goal of this project:

Reduce nutrient loadings from agricultural streams before it drains into rivers and lakes.

Accumulation in aquatic ecosystems leads to *eutrophication*.

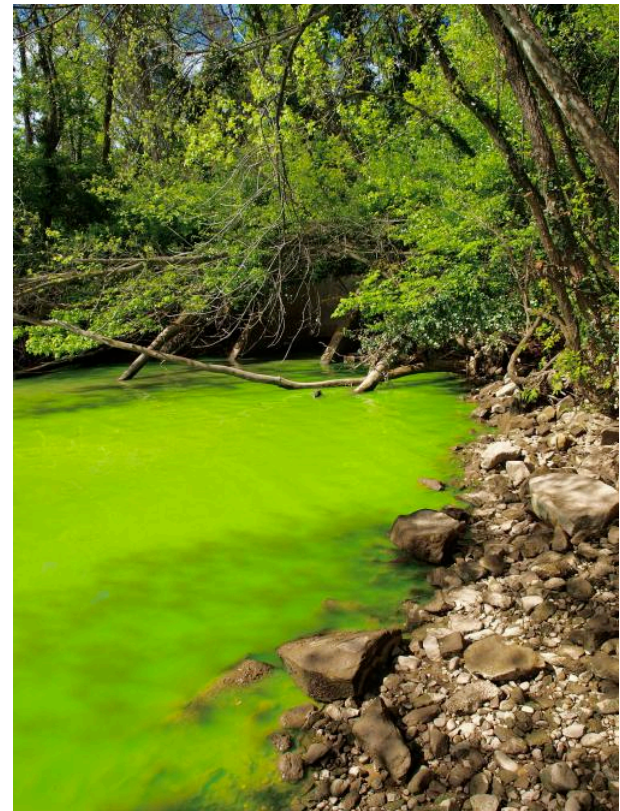


Eutrophication

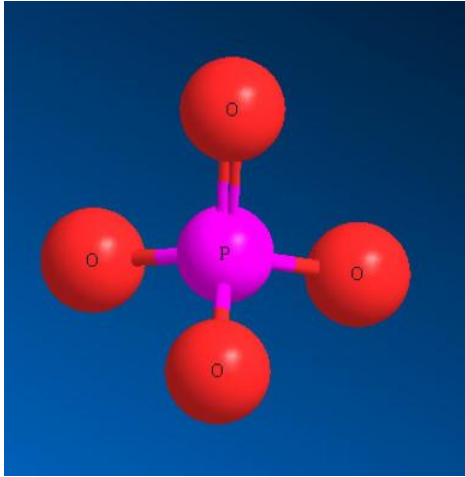
Eutrophication occurs when ecosystems accumulate too many nutrients

Aids the formation of harmful algal blooms

algal toxins > dead algae >
bacteria > depletion of
oxygen > kill of aquatic
animals



Causes many, our focus = P



Phosphate is important in many aspects of biology

Therefore, it is used in fertilizers

Like crops, algae depends on phosphate for growth and development

Therefore, the accumulation of phosphate promotes algal growth



Phosphate Binders

Chitosan matrix with chelated iron



From shell fish exoskeleton



Phosphate Binders

Chitosan matrix with chelated iron



Drastic price increase

Leeching of iron to environment

Unstable: digested by microorganisms



Phosphate Binders

Ideal binding matrix should;

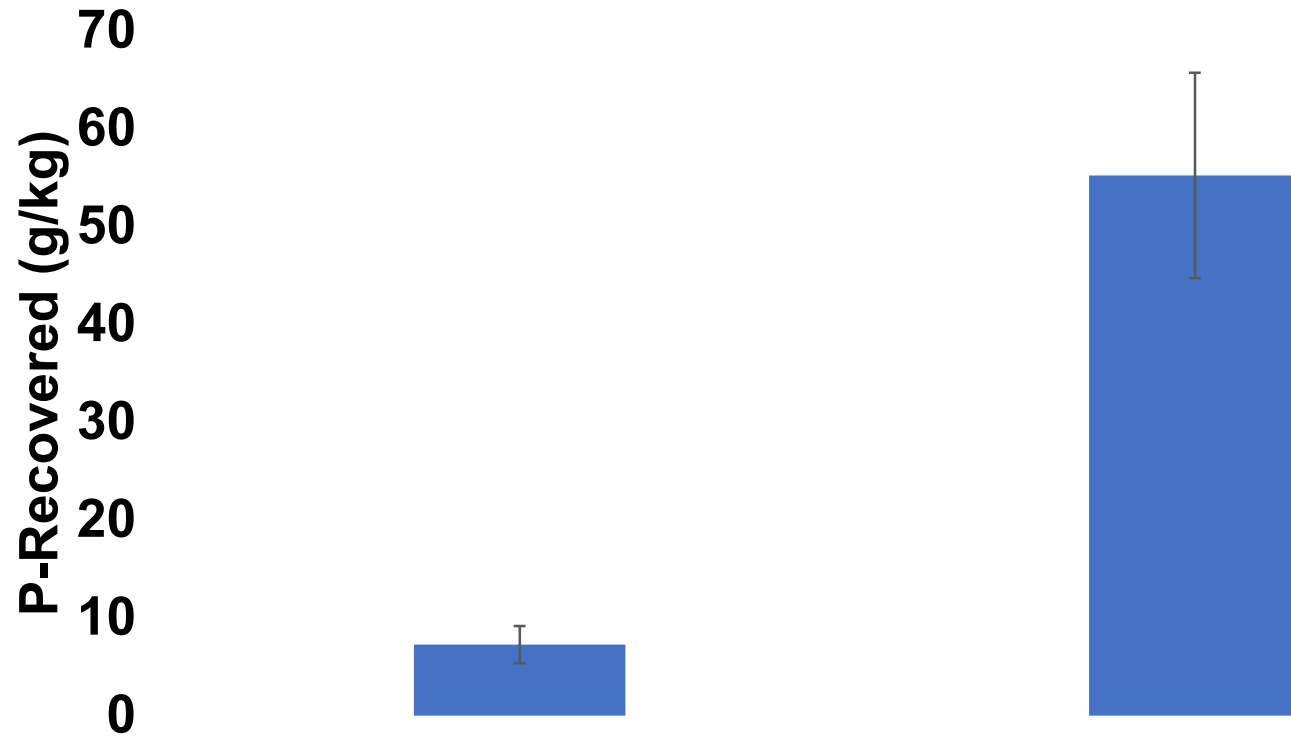
1. Bind large quantities of phosphate
2. Inexpensive
3. Safe for the environment



Tomato plant roots



Binding Capacity



Phosphate Binders

Ideal binding matrix should;

1. Bind large quantities of phosphate
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3. Safe for the environment

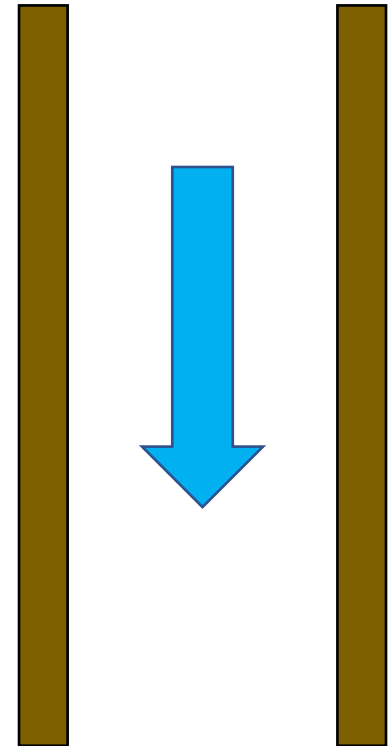


Probably



Tomato plant roots





Plant Roots – Phosphate Binding Capacity: ~ 55 g/kg





P

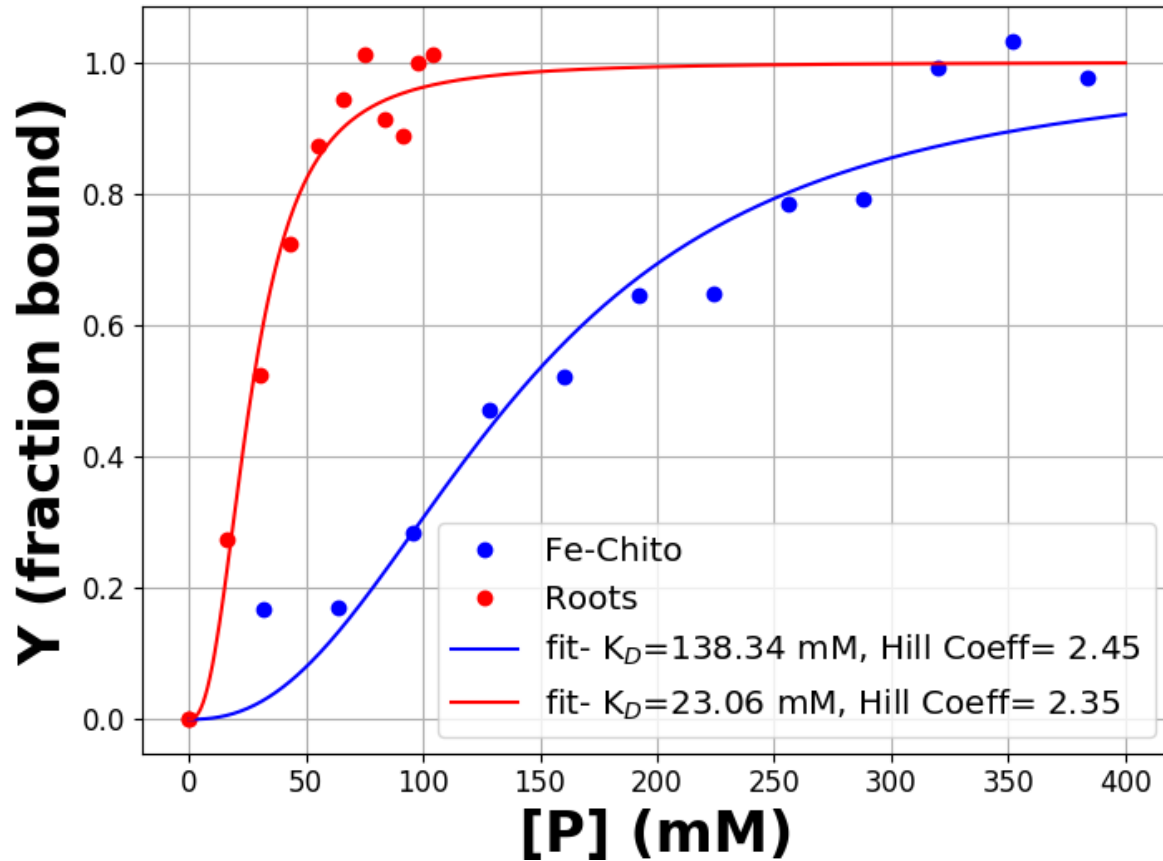


Plant Roots – Phosphate Binding Capacity: ~ 55 g/kg



Tightness of Binding

K_D Estimation: Roots and Fe^{3+} -chitosan



K_D App

Iron-Chito:
138.3mM

Roots: 23.1mM



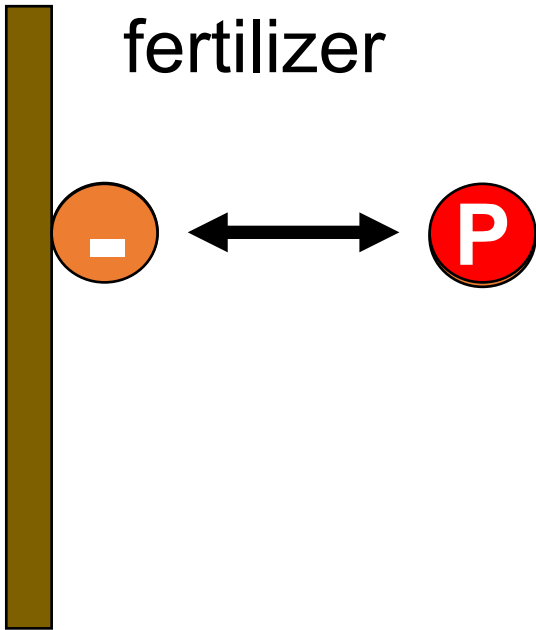
Methods of P Recovery

**Direct
reapplication of P-
saturated roots as
fertilizer**



Recovery and Regeneration of Binding Capacity

P replaced with counter anion – maybe liquid fertilizer

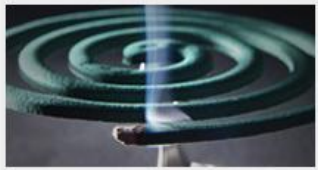


Typically, acid/base or conjugate salt



Carboxymethyl Cellulose (CMC)

INDUSTRIAL GRADE CMC



FOOD GRADE CMC



TOOTHPASTE GRADE CMC



DETERGENT GRADE CMC



CERAMIC GRADE CMC



PAINTING GRADE CMC



MINING GRADE CMC



PAPER MAKING GRADE CMC

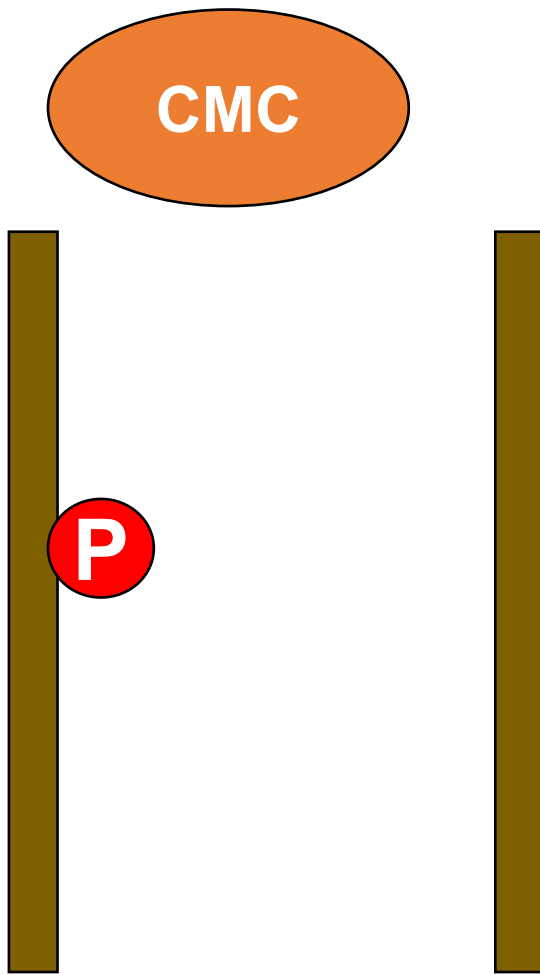


OIL DRILLING GRADE CMC



TEXTILE DYEING GRADE CMC



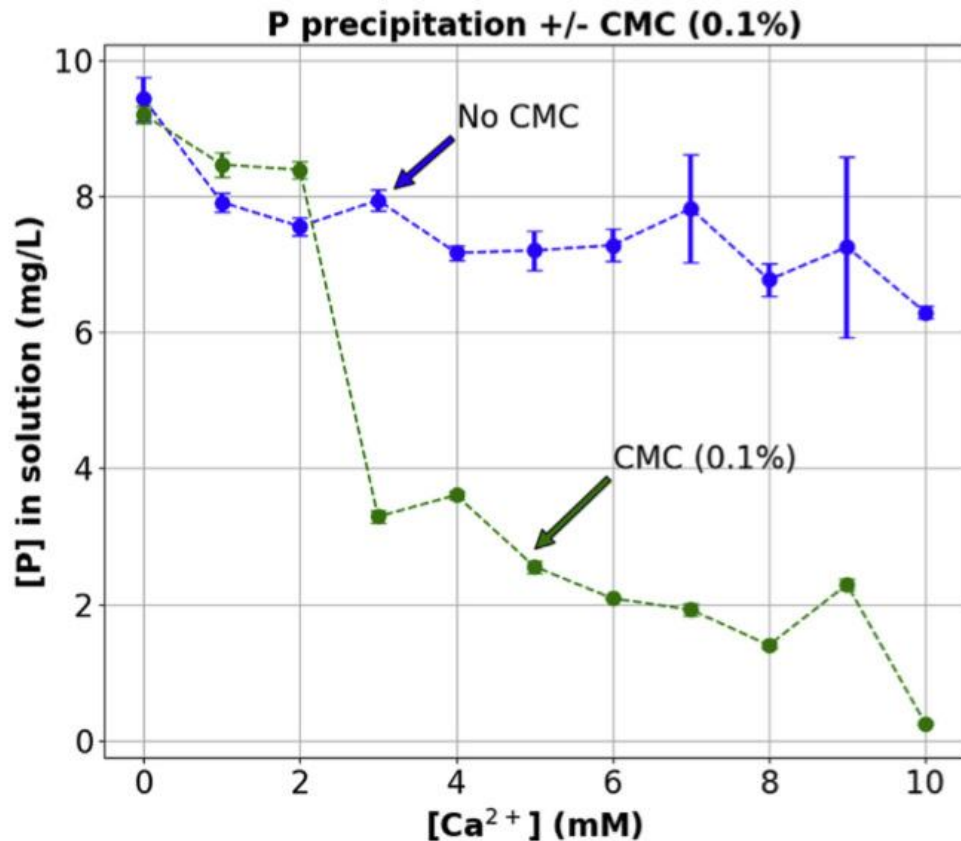


CMC displaces P

P can be collected and the root material reused



Precipitation of P as Calcium-Phosphate

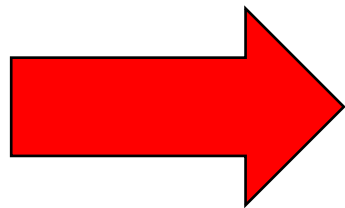


CMC enhances calcium-phosphate precipitation

Less calcium to harvest P

Lower cost





**Increasing calcium
(0-10mM)**



Lion's Head On Site Testing

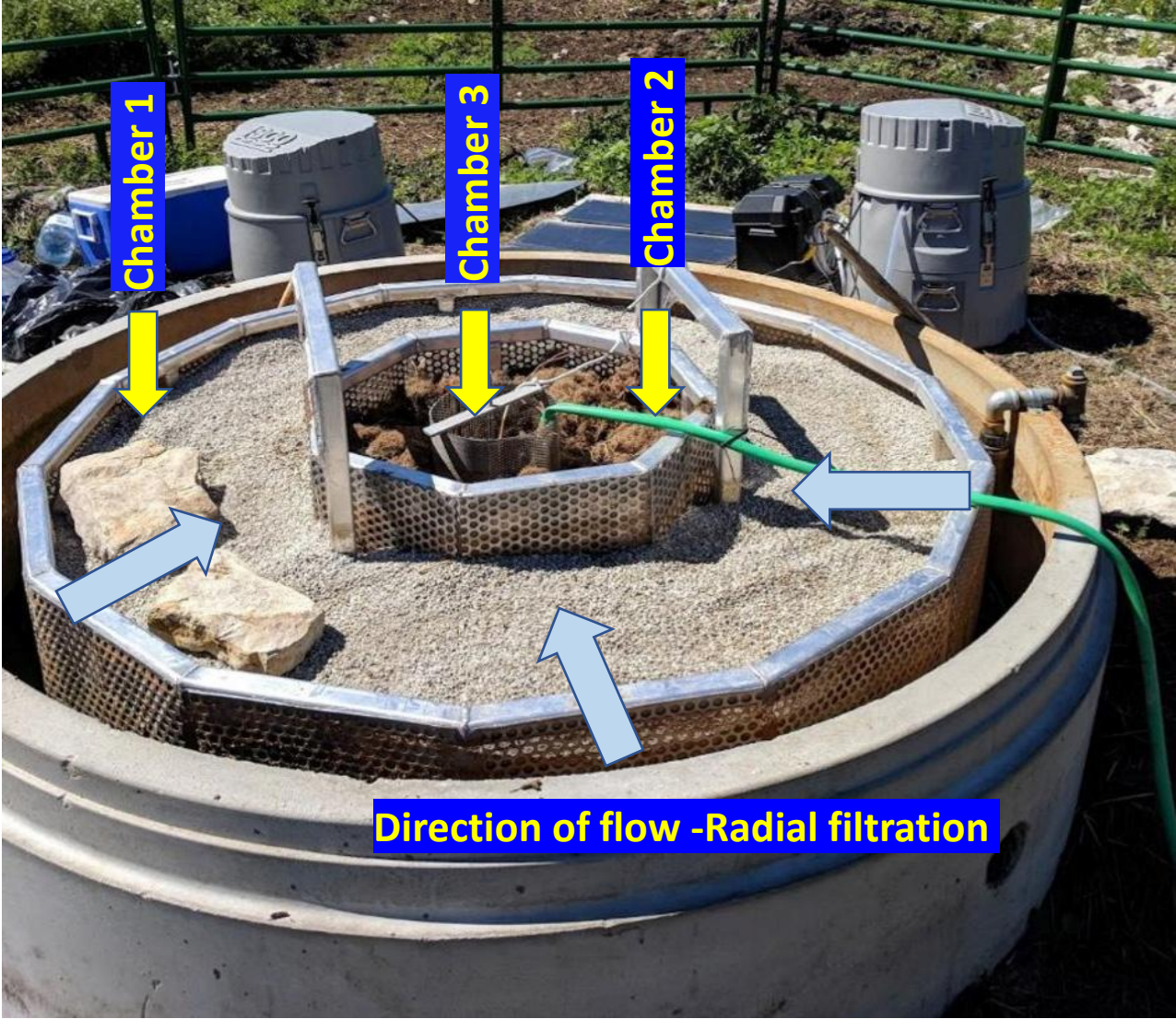


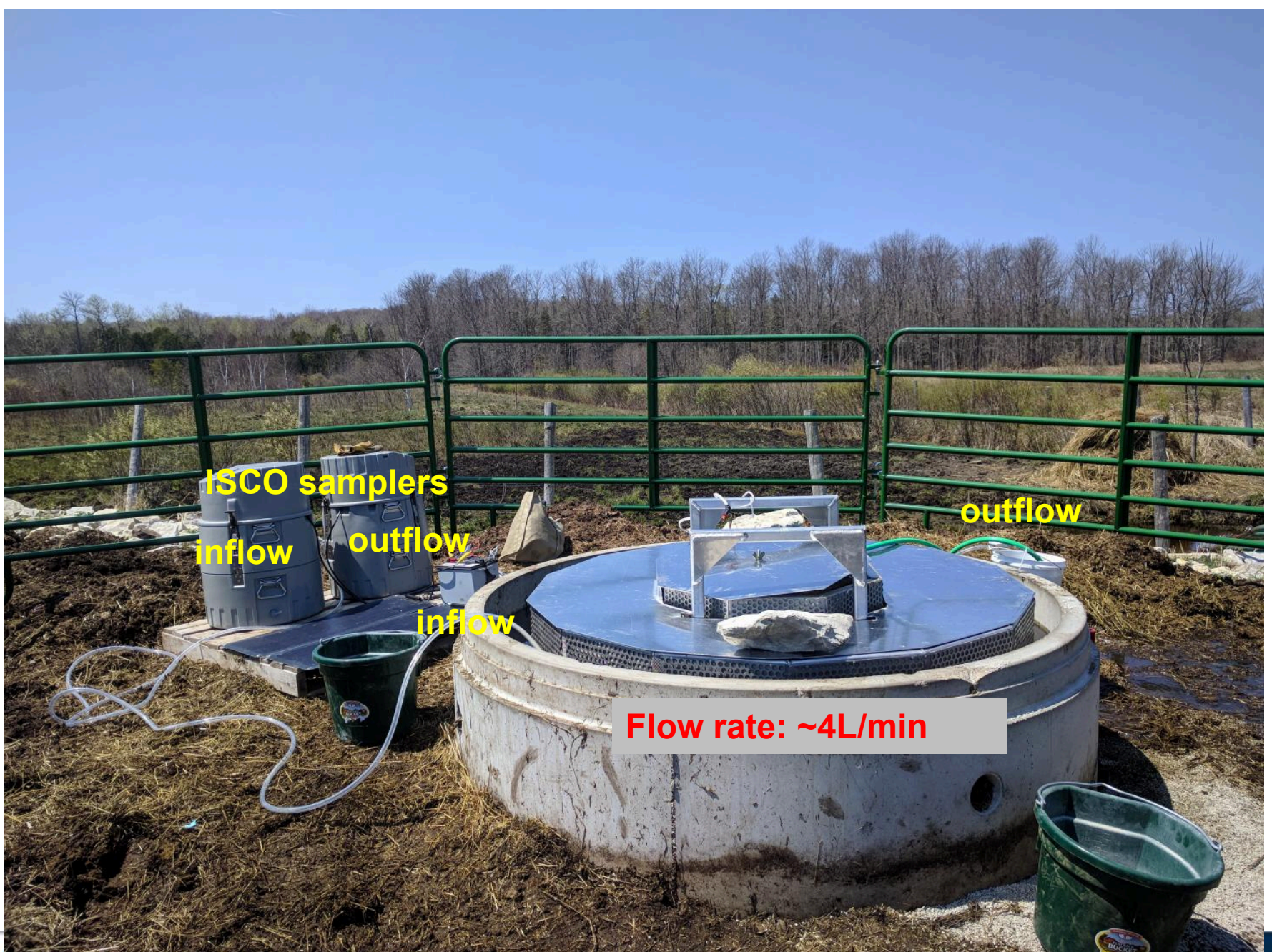
Lion's Head On Site Testing

Water source on site contaminated with manure.



Biofilter-Idea: Neils Munk; Design: Mutus; Build: UW Tech Support Centre





ISCO samplers
inflow

outflow

inflow

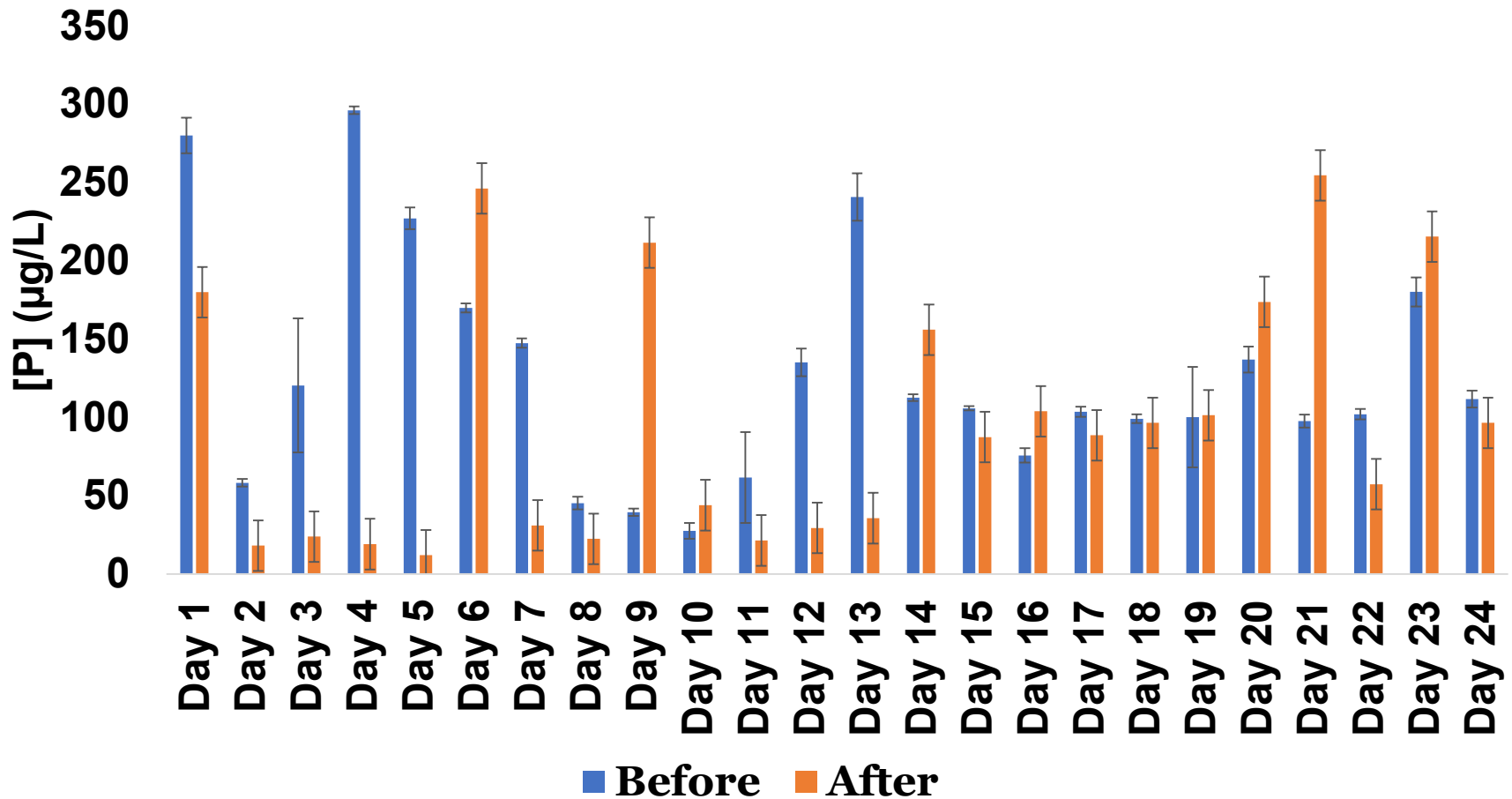
outflow

Flow rate: ~4L/min



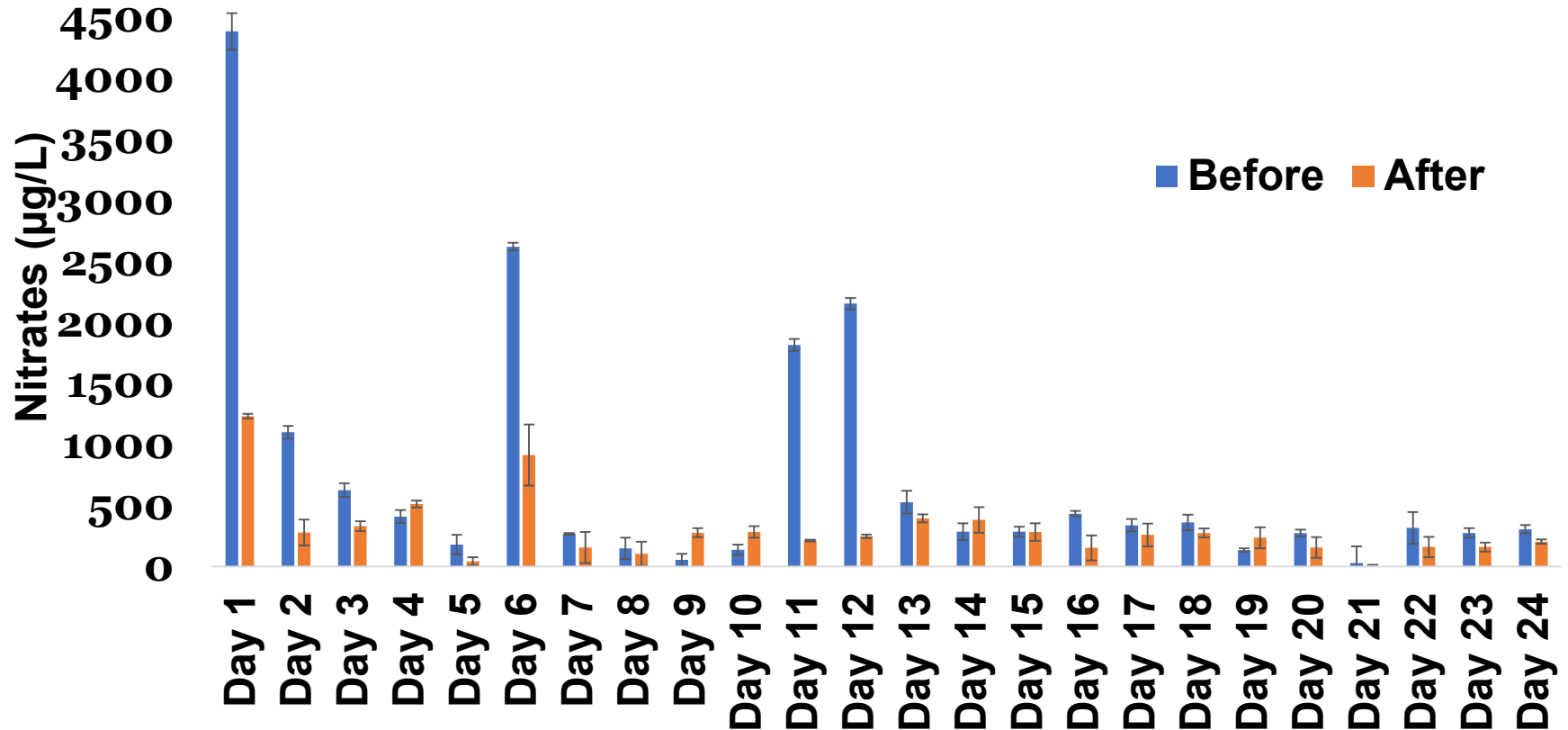
Lion's Head On Site Testing

Iron-Sawdust **Phosphate** Levels – Before and After Filtration



Lion's Head On Site Testing

Iron-Sawdust Nitrate Levels – Before and After Filtration



Summary

Phosphate
Removal (%)

Nitrate Removal
(%)

Iron-Sawdust

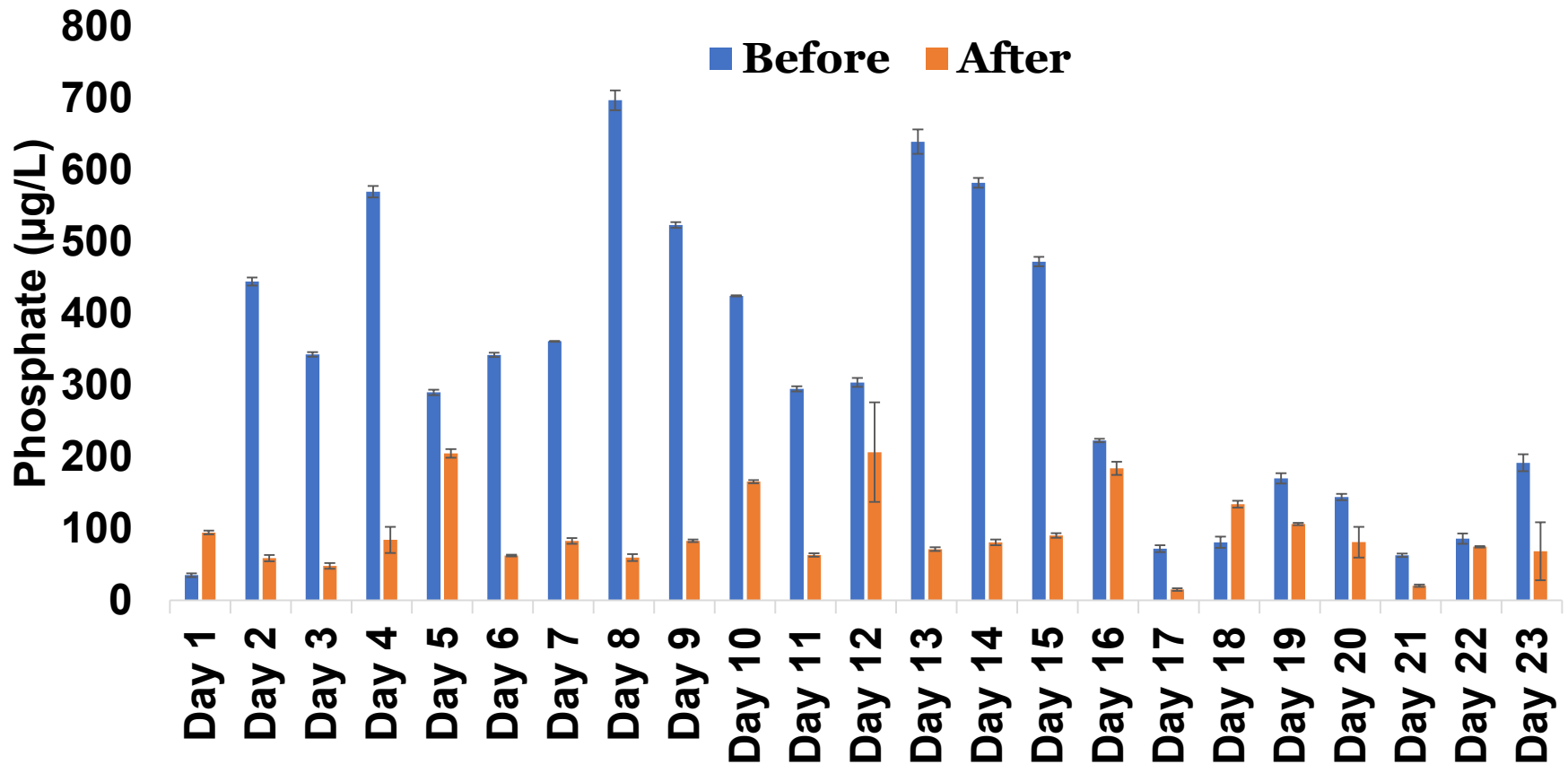
26.2%

58.5%



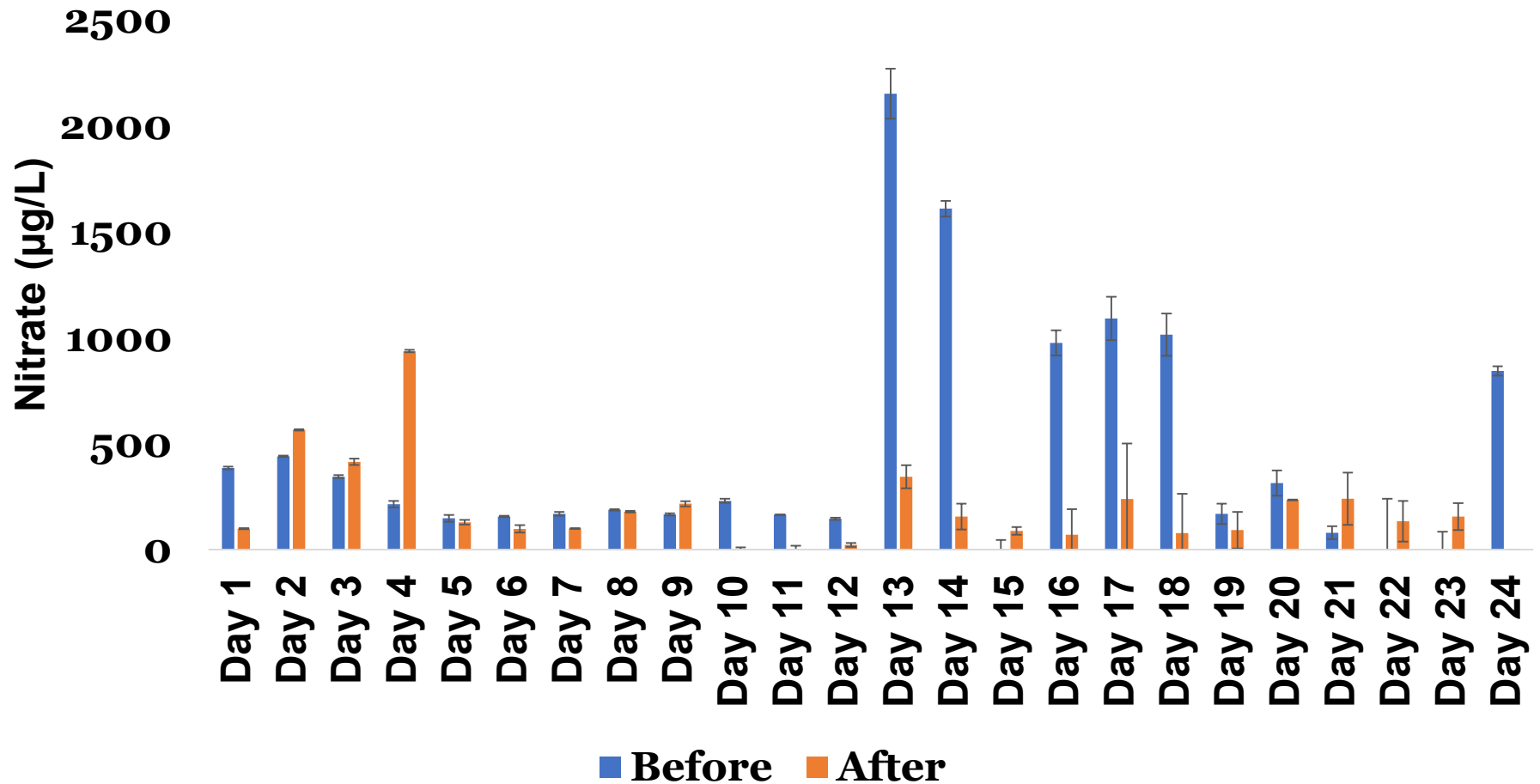
Lion's Head On Site Testing

Roots **Phosphate** Levels – Before and After Filtration



Lion's Head On Site Testing

Root Nitrate Levels – Before and After Filtration



Summary

	Phosphate Removal (%)	Nitrate Removal (%)
Iron-Sawdust	26.2%	58.5%
Plant Roots	70.8%	58.2%



What in plant roots binds phosphate?

In collaboration with Dr. Robert Schurko,
Austin Peach and Michelle Quan



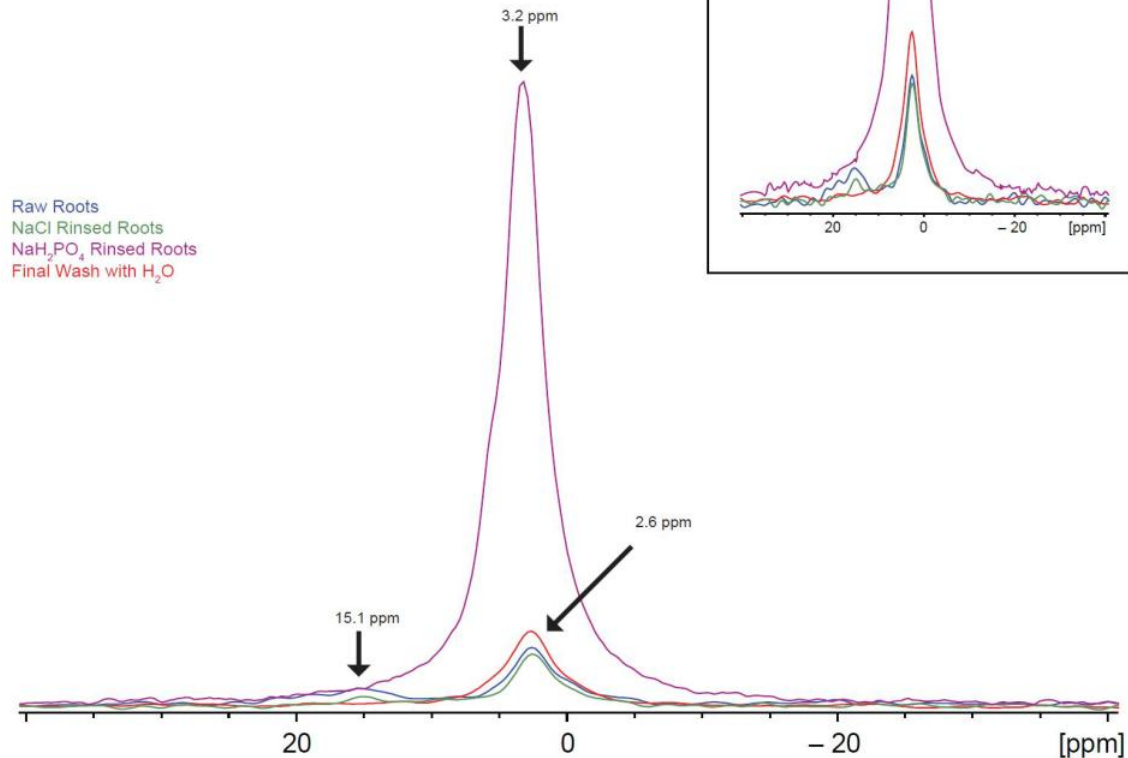
Used solid state
nuclear magnetic
resonance

Probe the chemical
environment of P
atom



ssNMR of Plant Roots Throughout Binding-Elution Cycle

^{31}P - $\{^1\text{H}\}$ SSNMR
MAS - 10 kHz

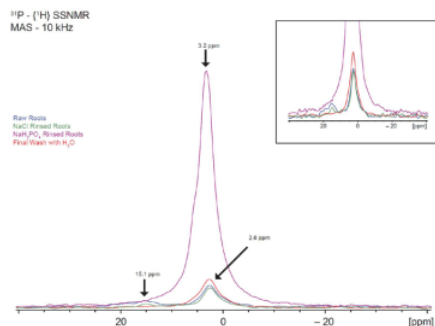


Demonstrates strong uptake and removal of phosphate throughout the binding-removal cycle

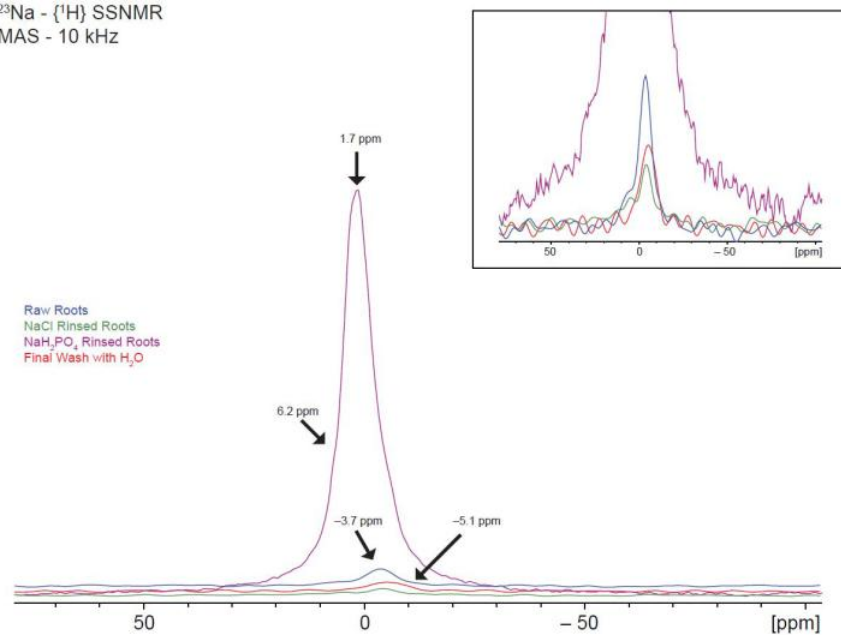


ssNMR of Plant Roots Throughout Binding-Elution Cycle

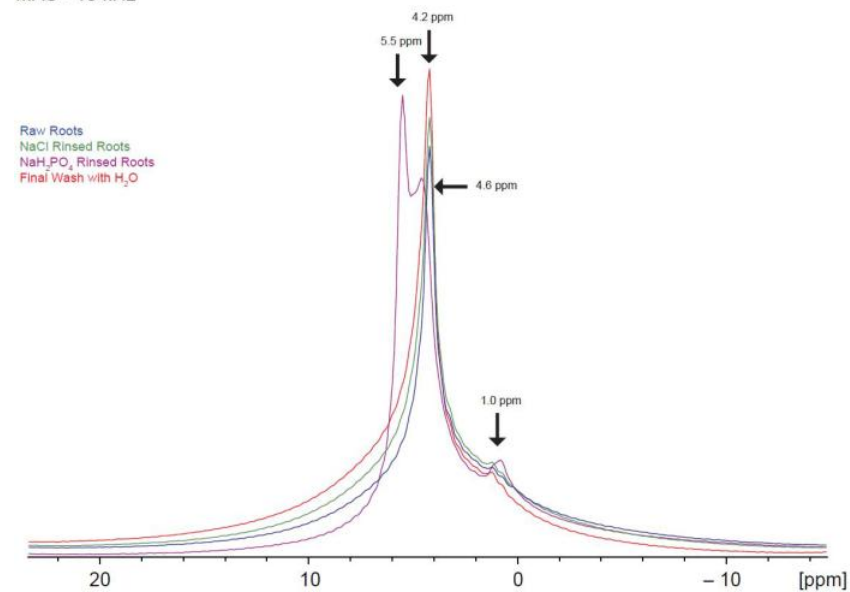
Not definitive on what binds P
Co-run Na and H atom NMR



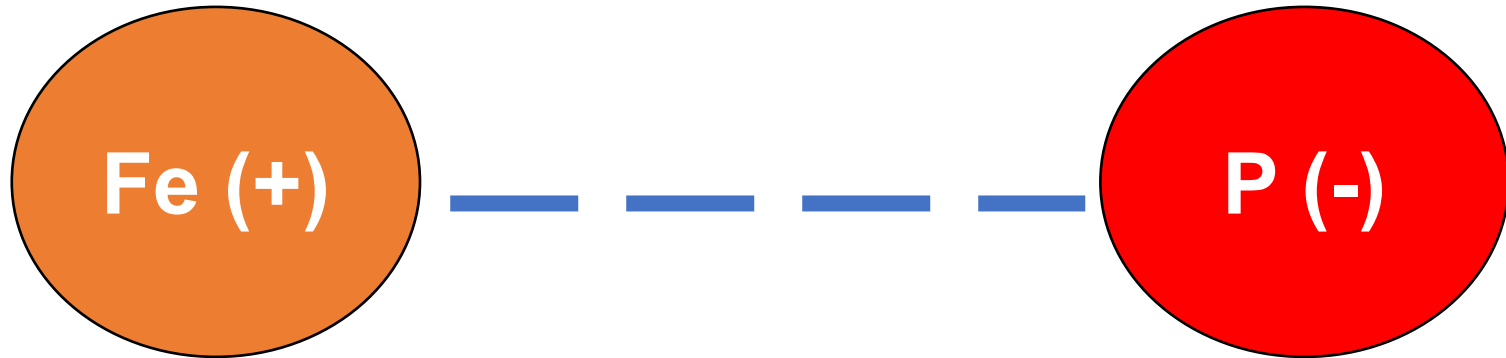
²³Na - {¹H} SSNMR
MAS - 10 kHz



¹H SSNMR
MAS - 10 kHz



Iron-chito – iron interacts with P



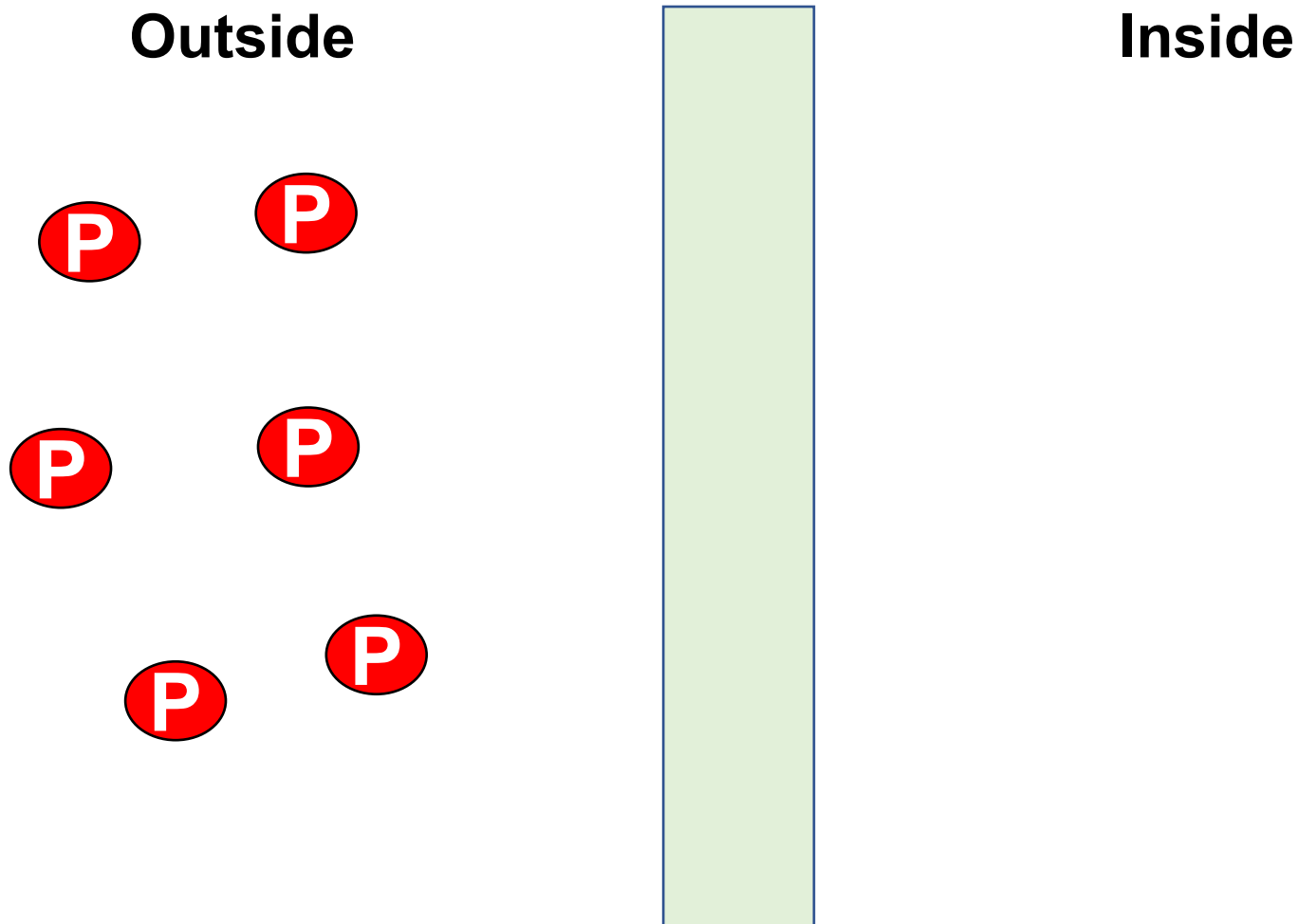
The NMR signal of metal – P interactions is distinct and not occurring in roots

NMR data suggests the formation of H-bond(s)



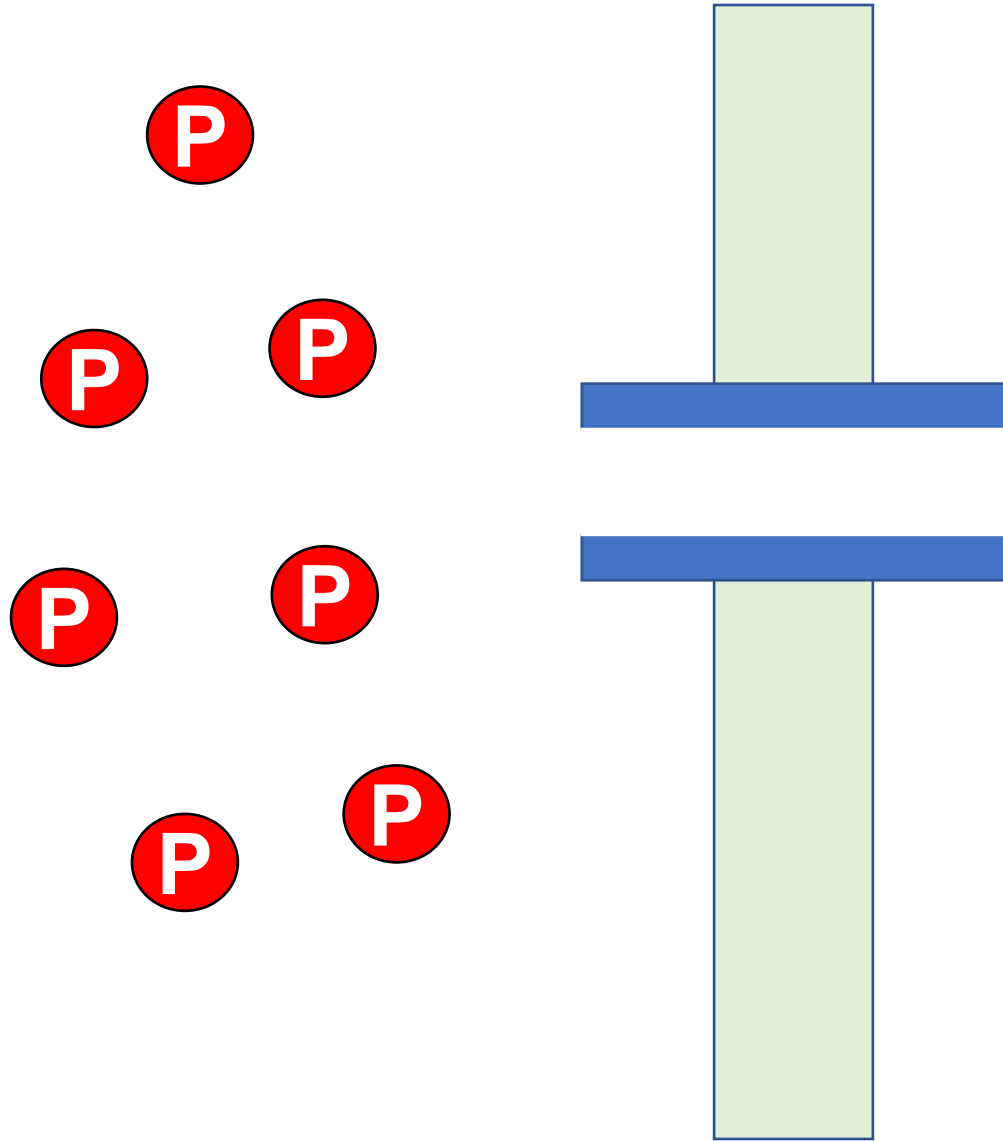
H-bonds suggest binding to a protein

All organisms, including tomatoes have phosphate transporter proteins that internalize phosphate



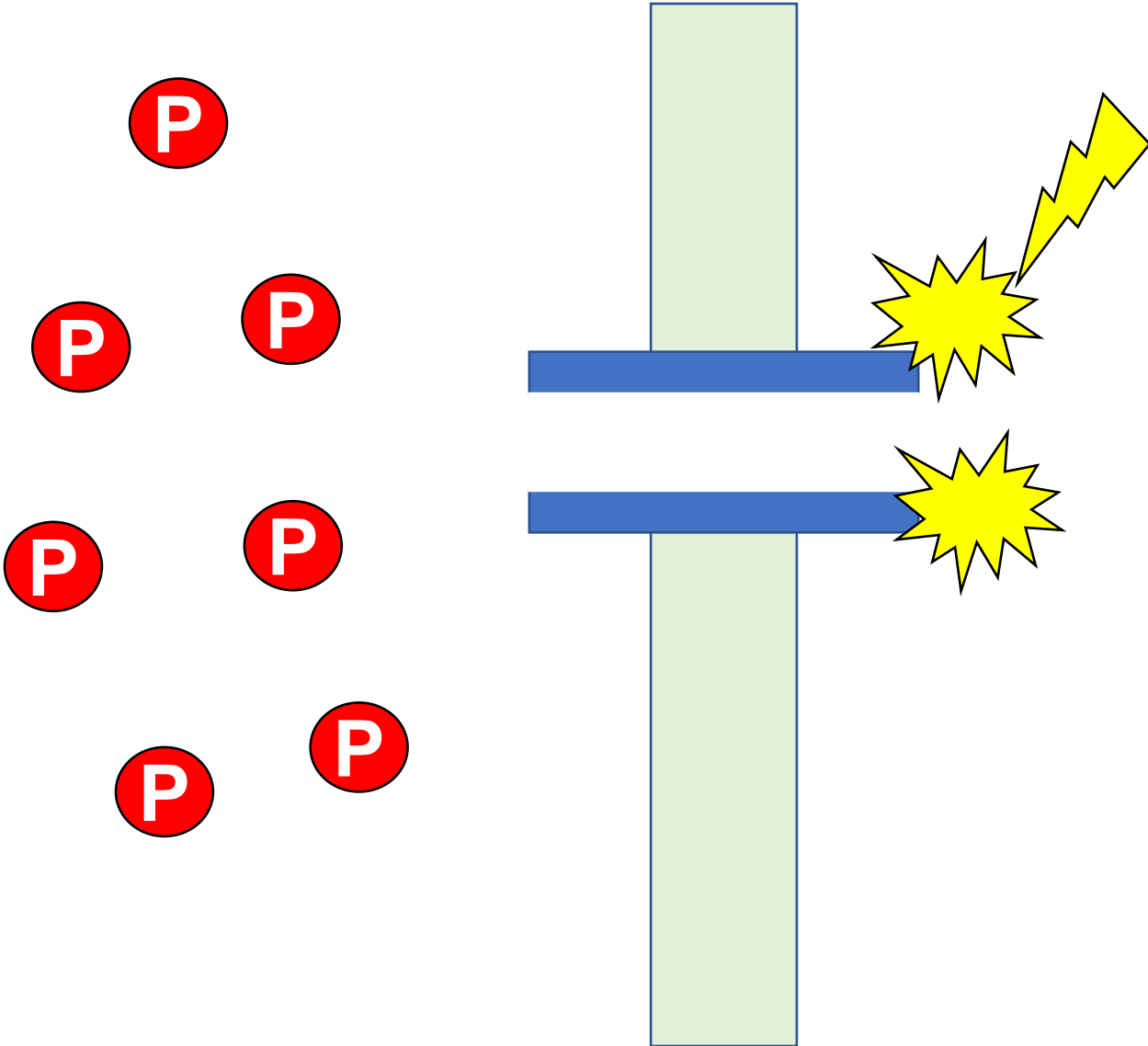
Outside

Inside



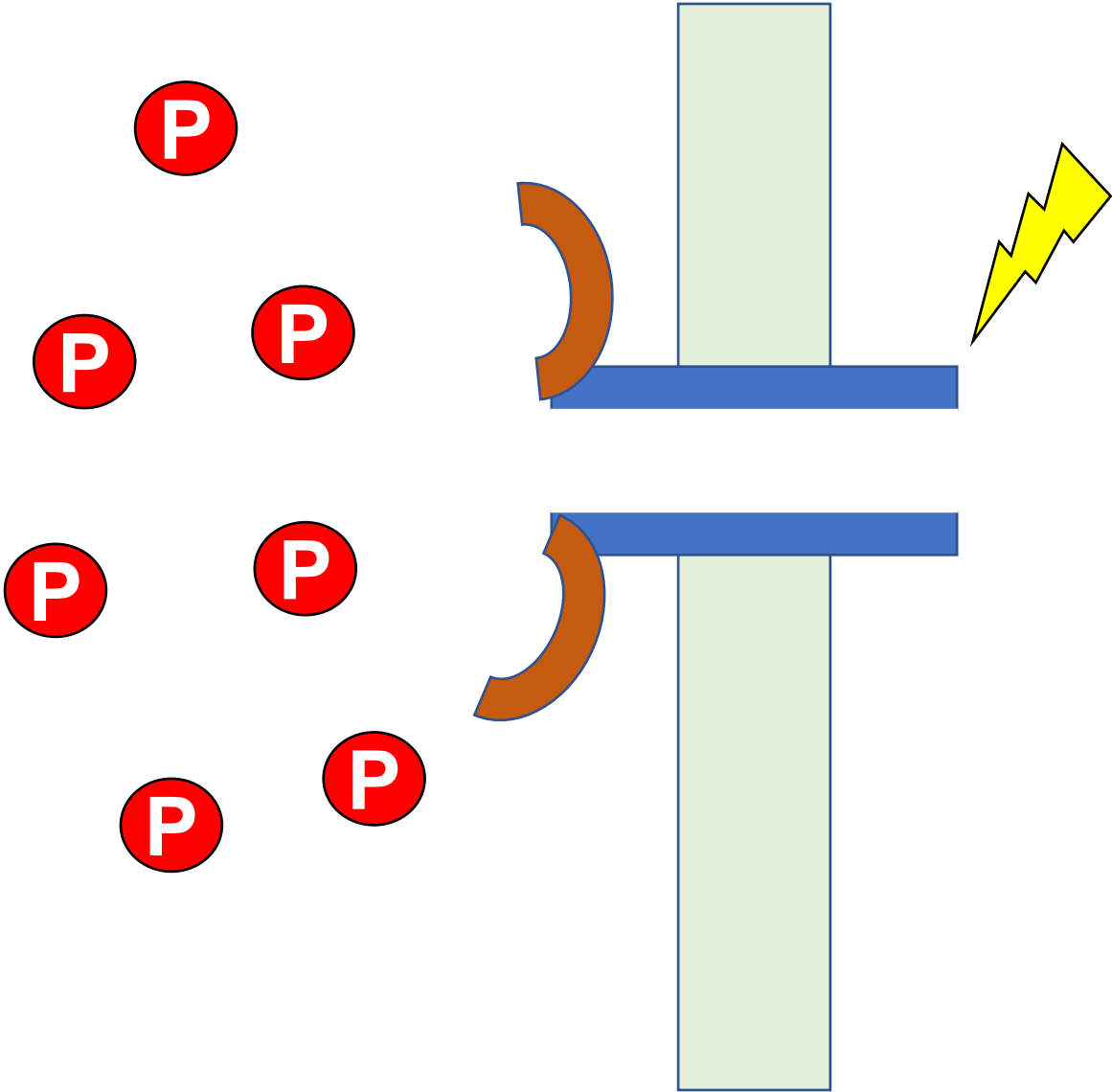
Outside

Inside



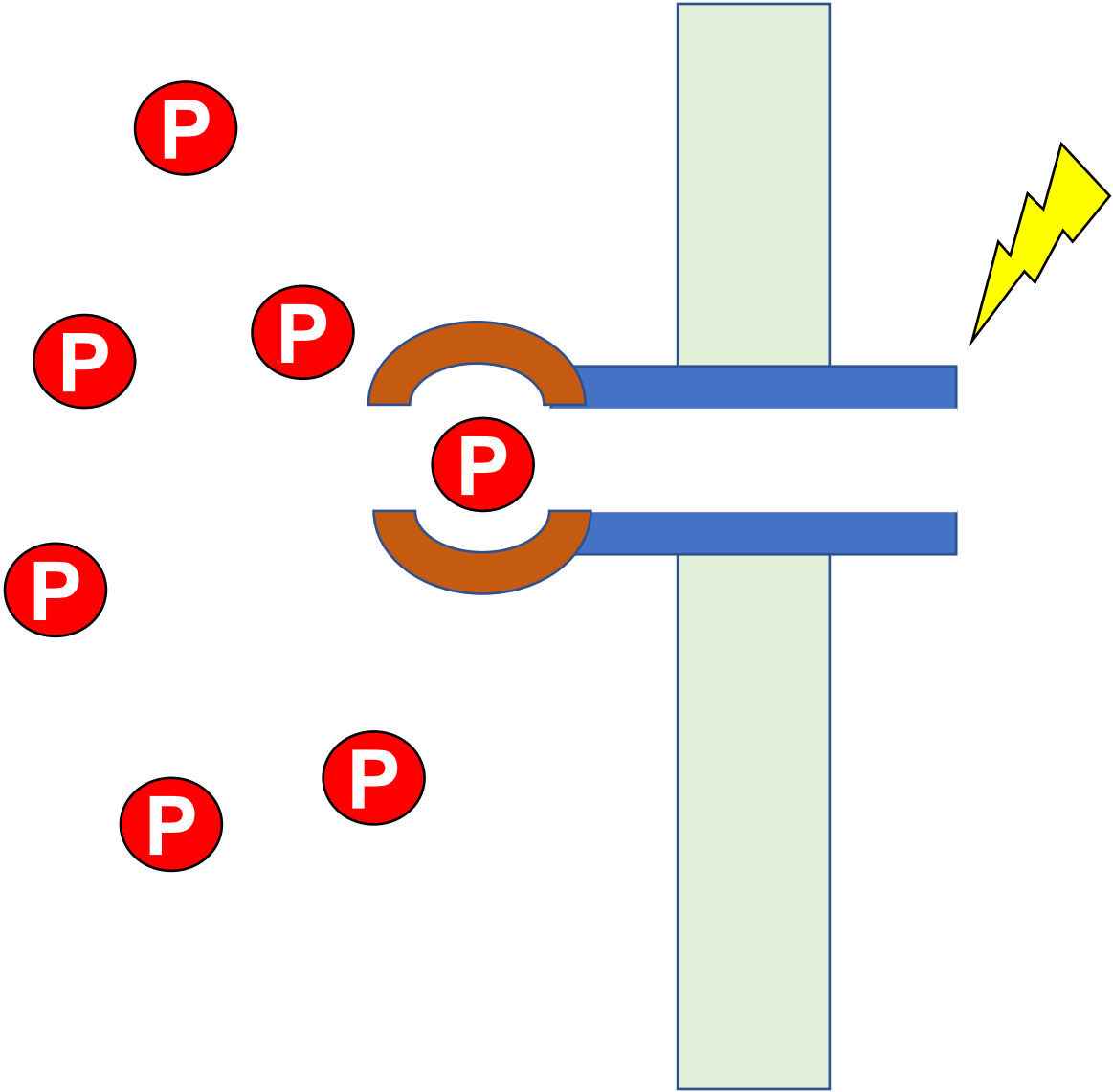
Outside

Inside



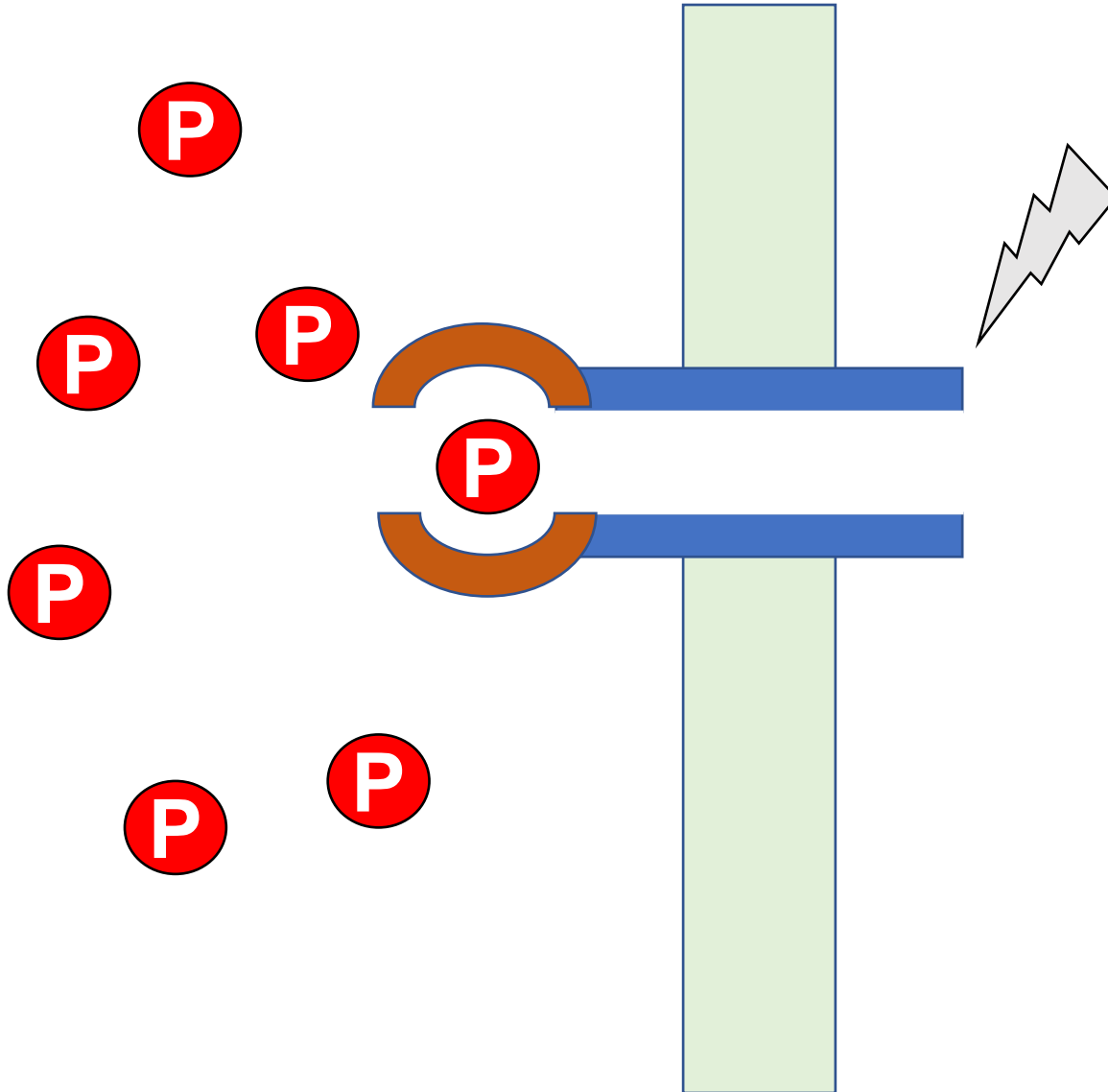
Outside

Inside



Outside

Inside



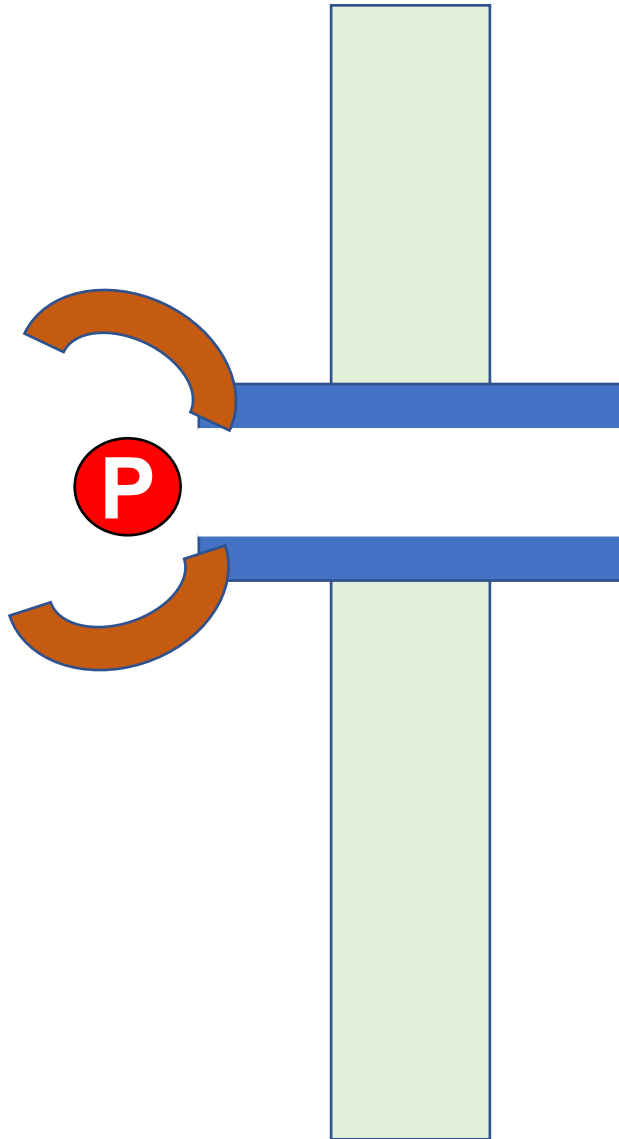
**Our roots are
dead**

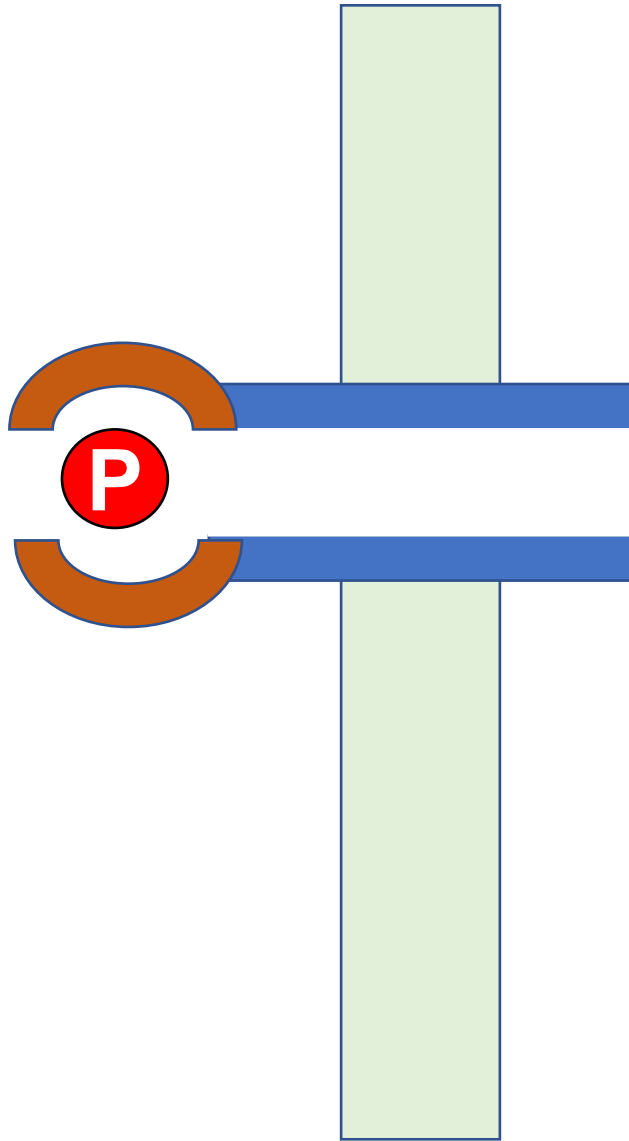
**No energy
available**

**But, the P
binding protein
works without
energy**



Phosphate binds

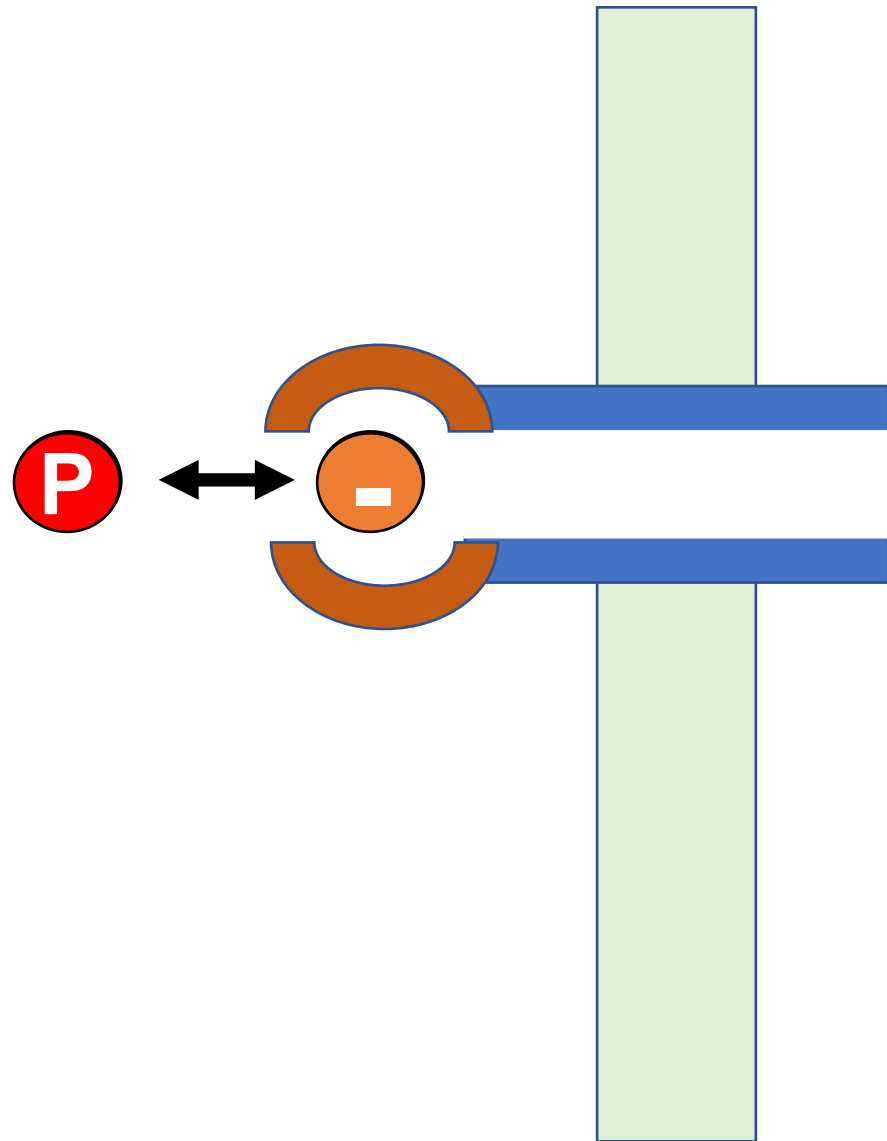




Phosphate binds

**Induce release with
counter anions (CMC
or Cl)**





Phosphate binds

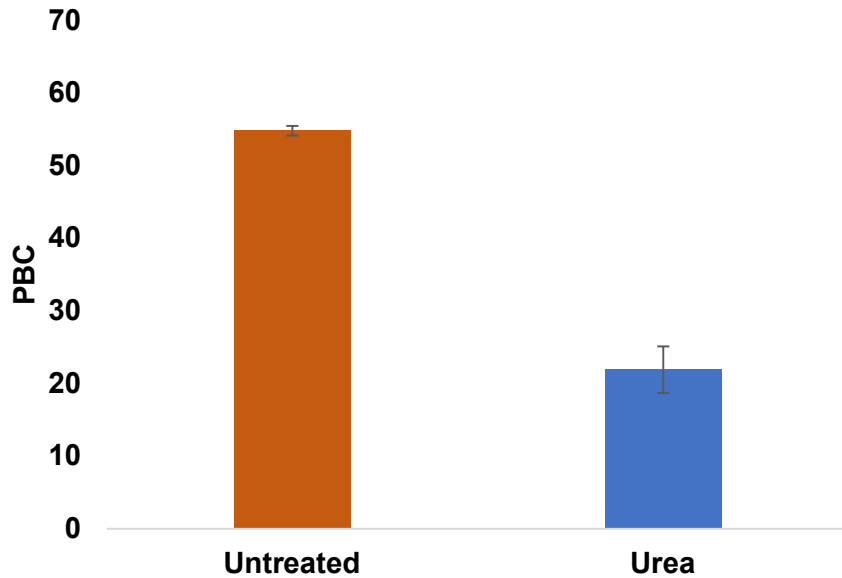
**Induce release with
counter anions (CMC
or Cl)**

Repeat

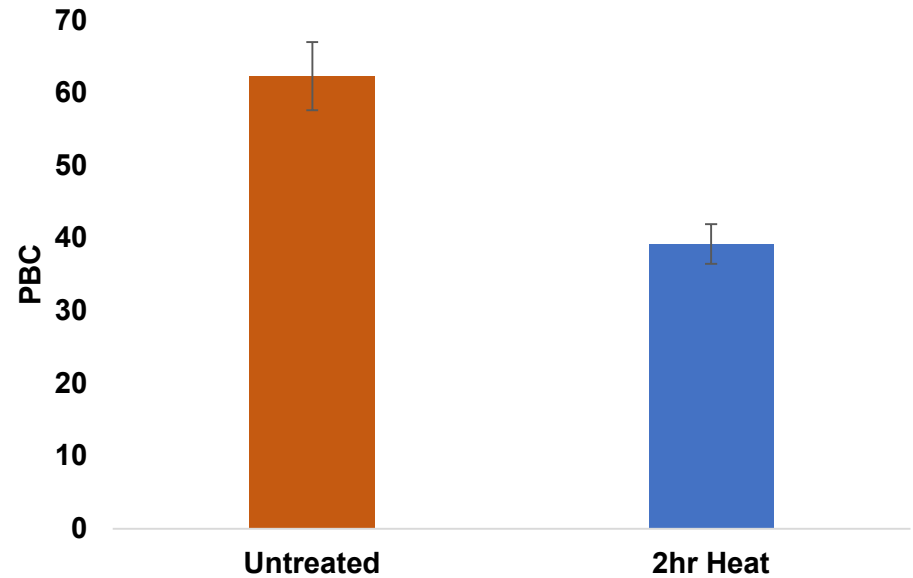


Disrupt proteins with urea or heat treatment

6 M Urea



150 ° C



Current and Future Objectives

Phosphate transporter protein expression is regulated by phosphate in soil

Study the effect on phosphate treatment on later use of roots for remediation

Working with Holy Names High School – STEM Academy (Ms Mary-Ellen Kavanaugh)



Current and Future Objectives

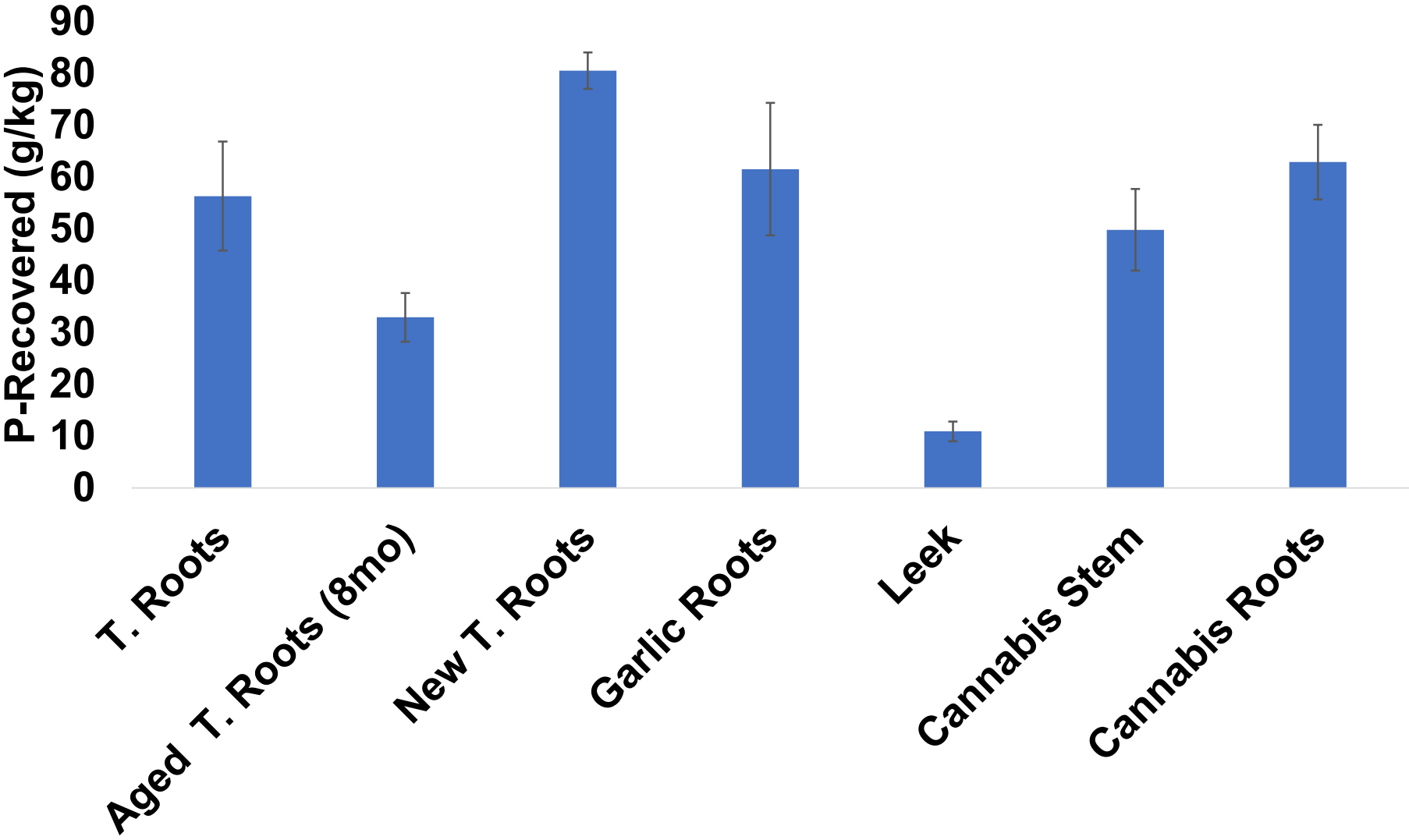


P and No P roots

Flow rates



Different Ages and Types of Plant Roots



Current and Future Objectives

Study different plant roots ie. cucumber

Study the degradation in binding capacity overtime



Acknowledgements:

WECO2 Parks: Matthew Posthumus, Sergey Postnikov

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Katherine McLeod, Amanda Stanger, Elizabeth Thorn and Neils Munk

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**Thank you very much for
listening**

Questions?

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