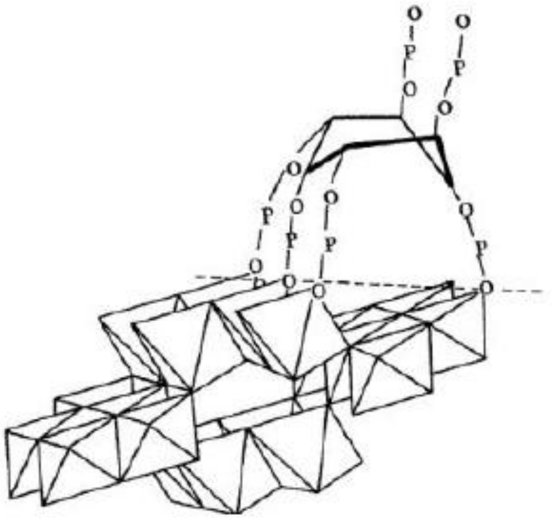
Organic Phosphorus
Solid phase interactions

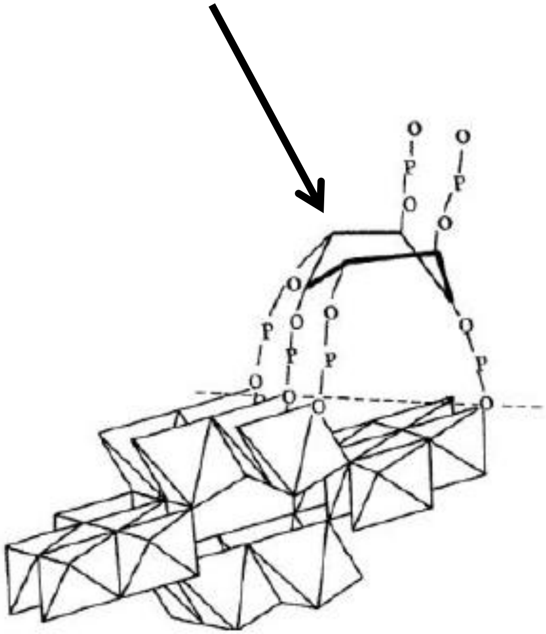
Courtney Giles, PhD Candidate
School of Engineering, Environmental Engineering

Geochemistry of Natural Waters (GEOL235)
Tuesday 25 October 2011, 2:30-3:45pm Delehanty 219



What I Study:

Organic P:
PHYTATE



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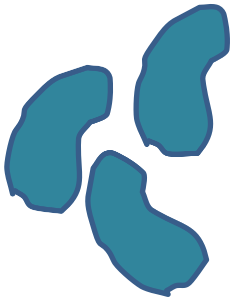
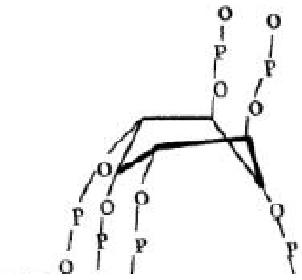
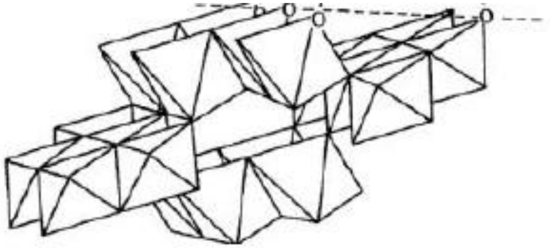
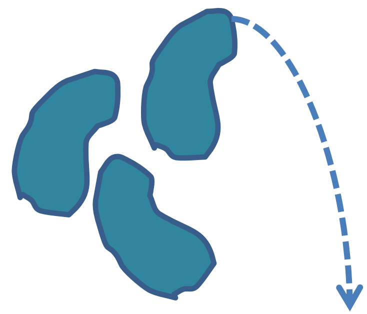


How can soil bacteria do this?

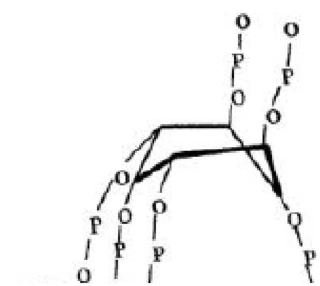


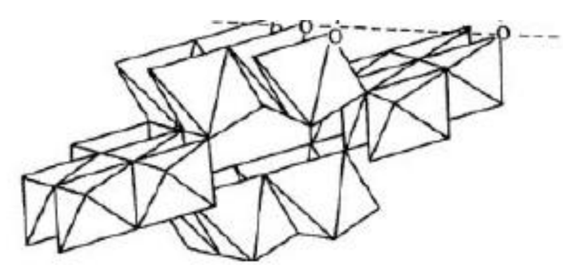


What I Study:



Siderophores/**Organic Anions**





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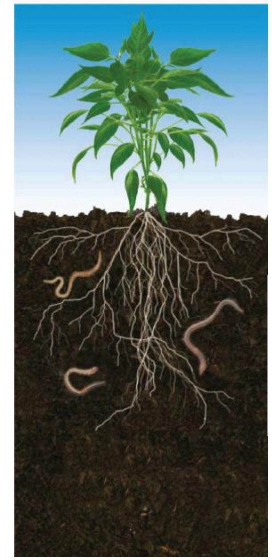
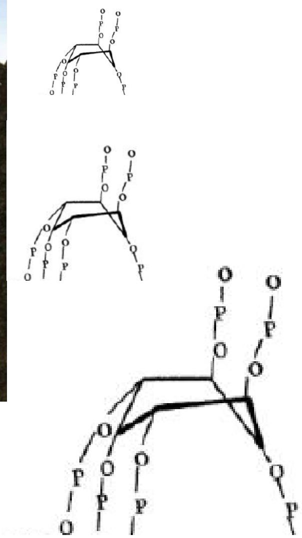
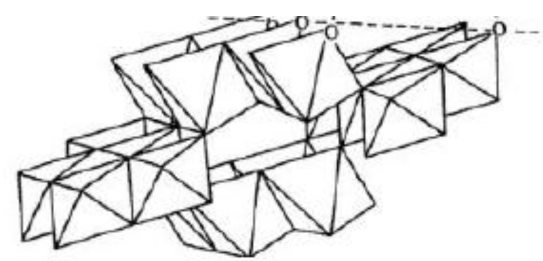




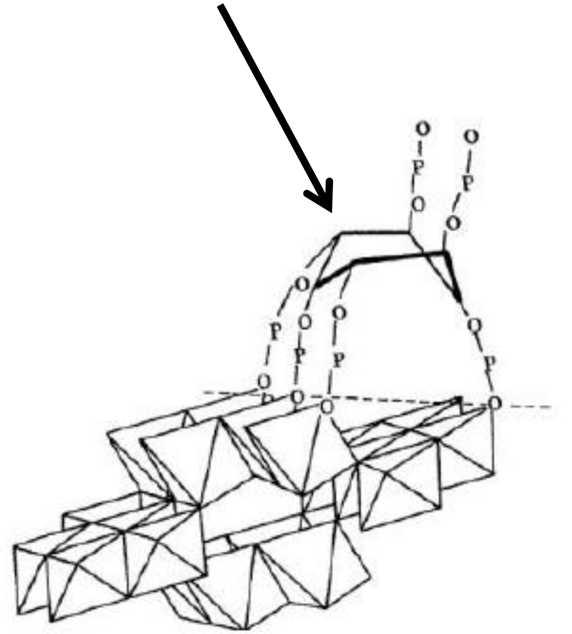
Result:

Plant availability ***INCREASES***

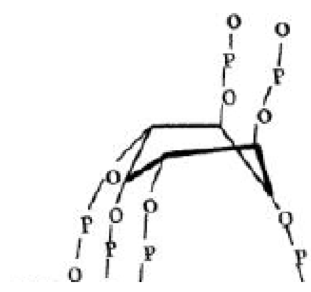


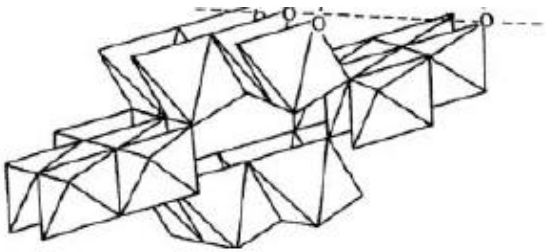
How does Organic P get there in the first place?

Organic P:
PHYTATE

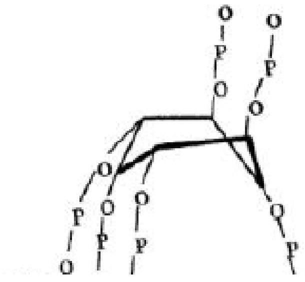


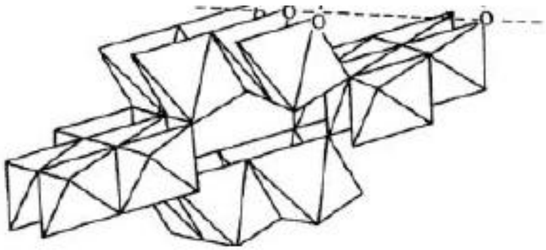
How is it removed?





How is it removed? **DE**SORPTION





Today

Soil **Organic P**

Forms/Sources

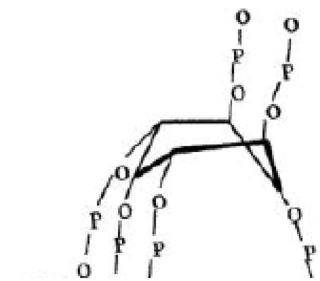
Behavior in Soils

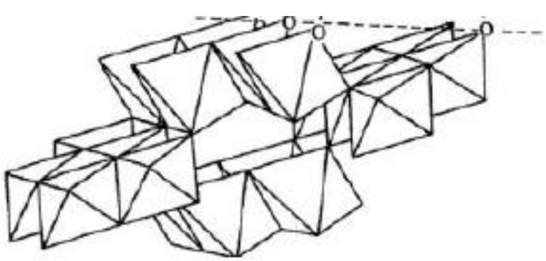
Measurement

DESORPTION (e.g. phytate)

Mechanisms

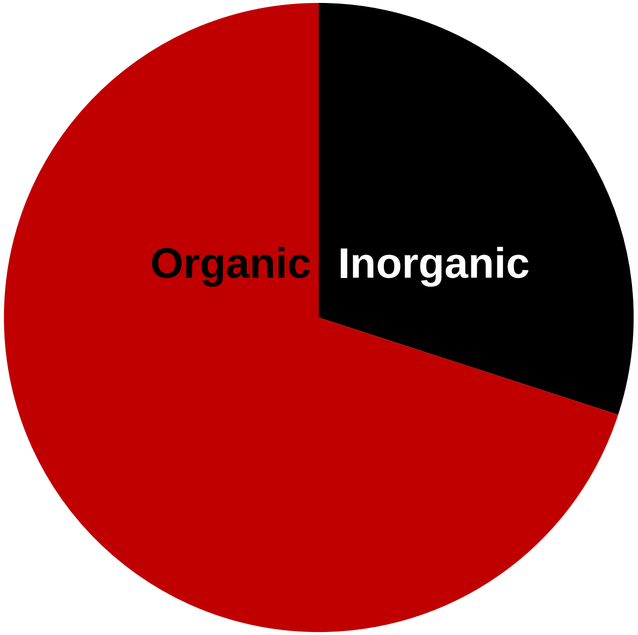
Kinetics





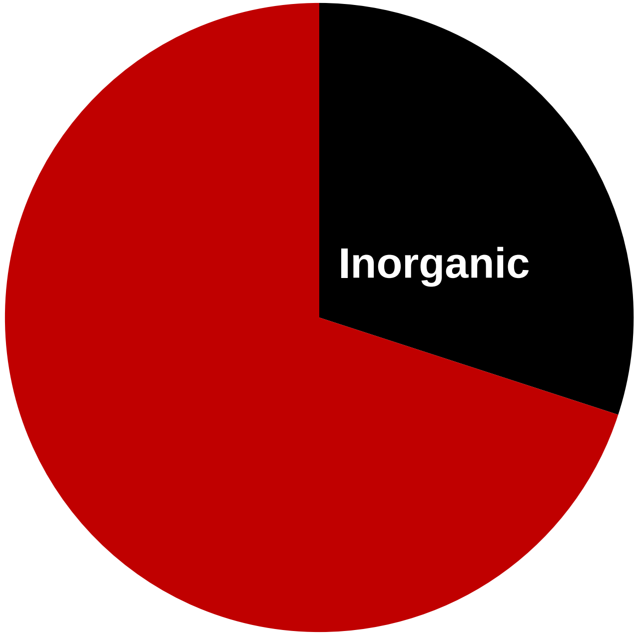
Soil Phosphorus

Soil Phosphorus



Total Soil P

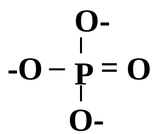
Inorganic Phosphorus

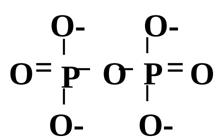


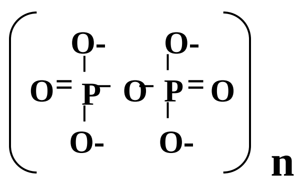
Total Soil P

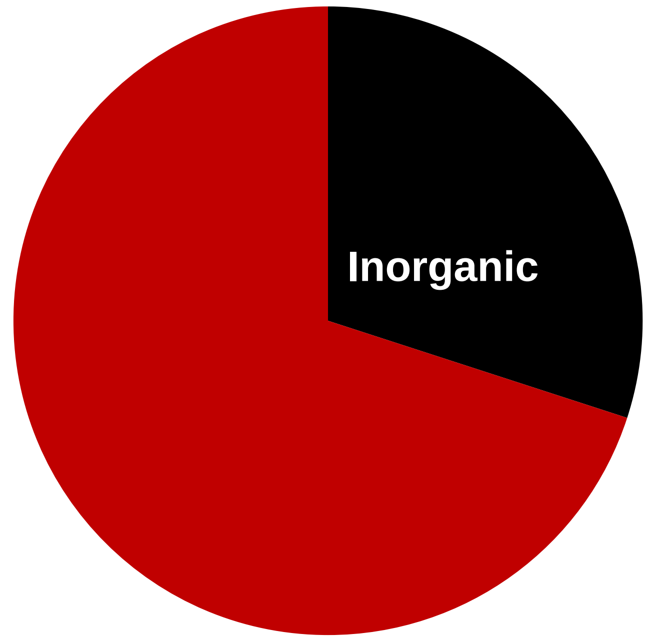
Inorganic Phosphorus

FORMS

Mono-Phosphate 

Pyro-Phosphate 

Poly-Phosphate 

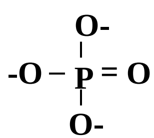


Total Soil P

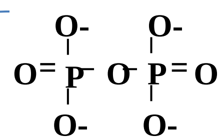
Inorganic Phosphorus

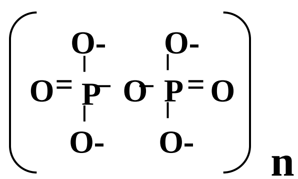
SOURCES

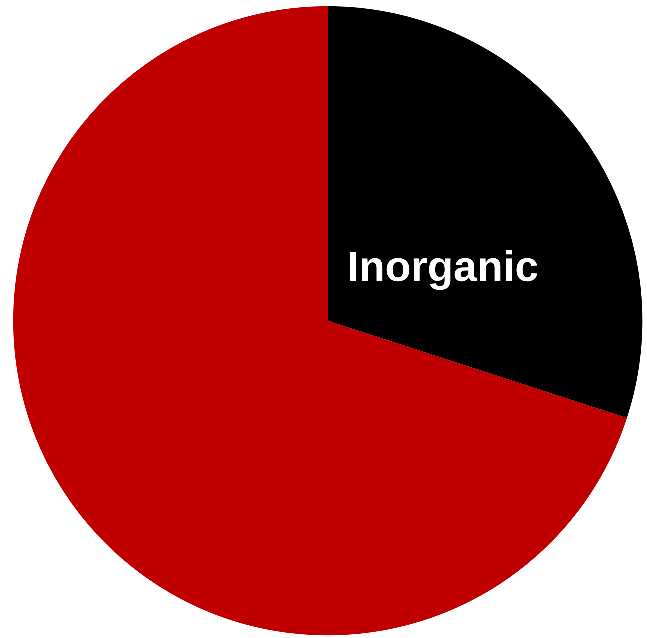
Fertilization
Mineral P
Organic breakdown



Microbial storage

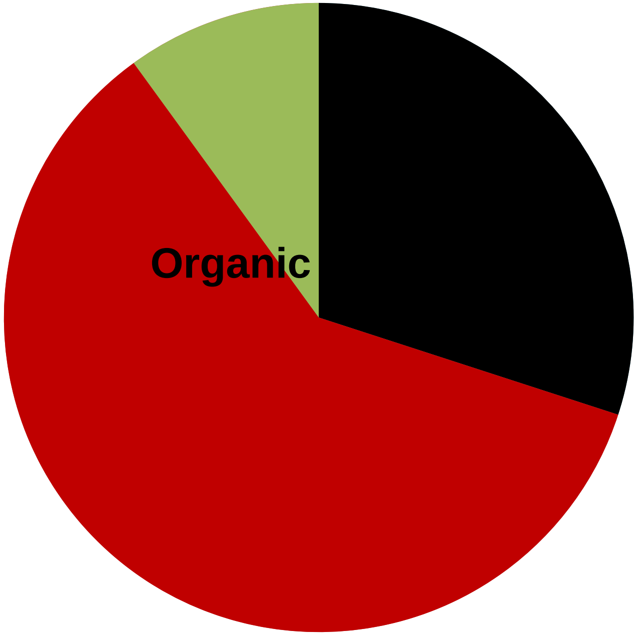






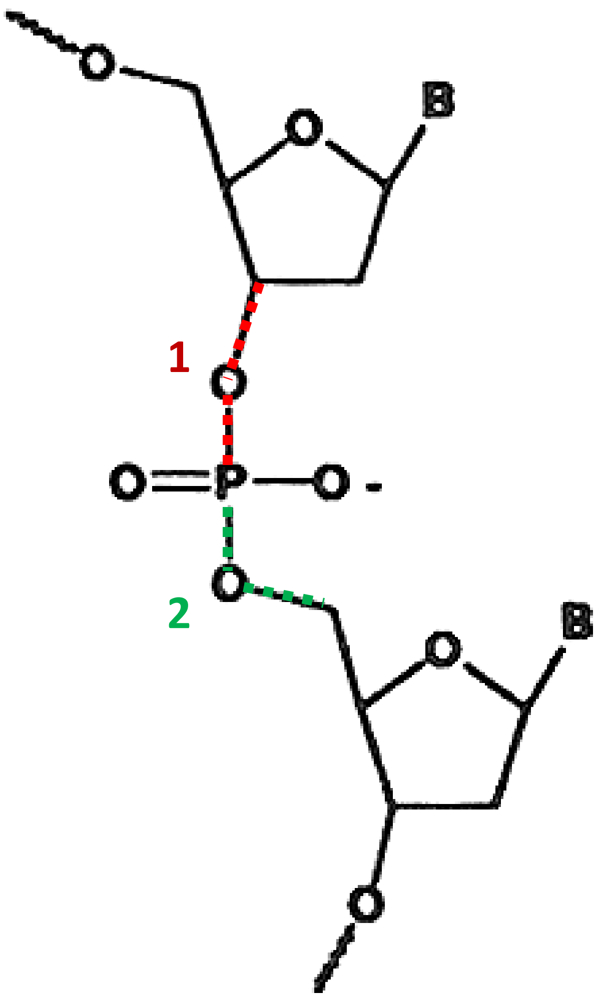
Total Soil P

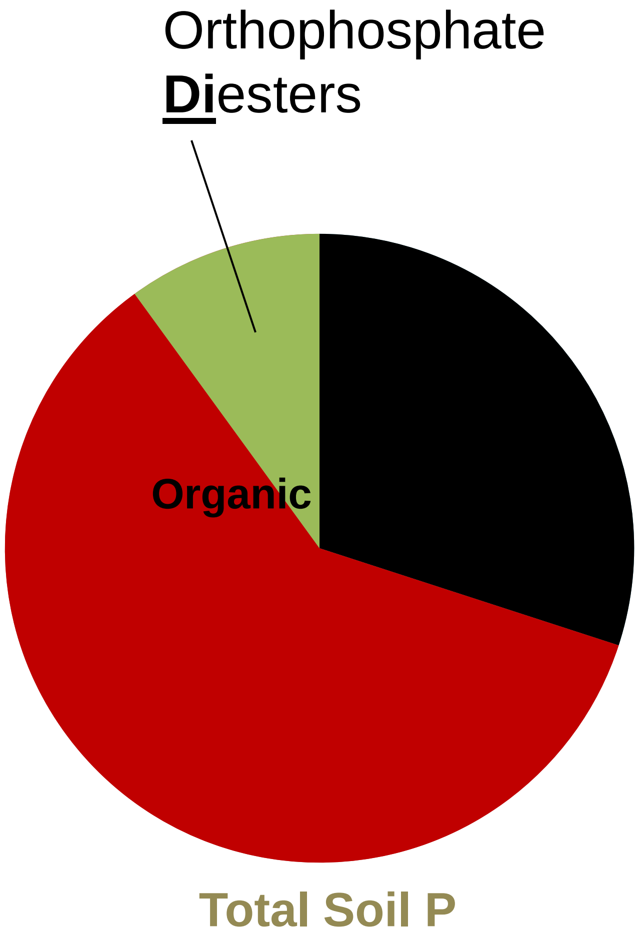
Organic Phosphorus



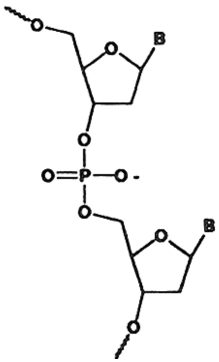
Total Soil P

Organic Phosphorus

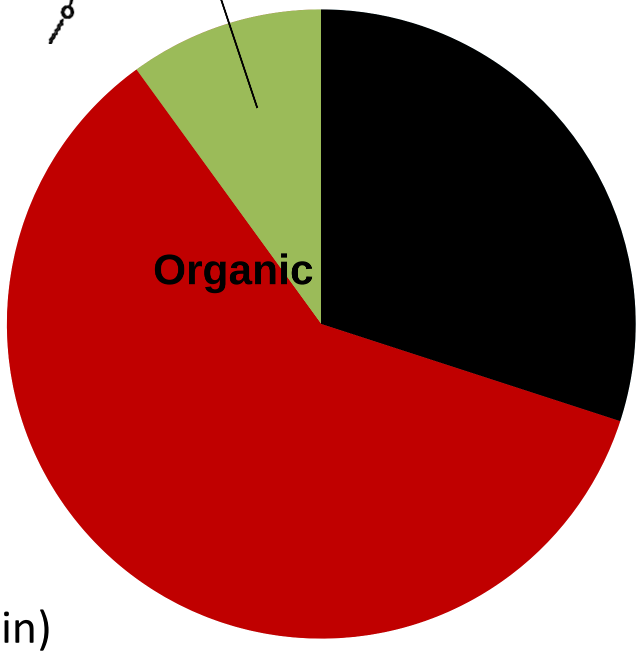




Organic Phosphorus



Orthophosphate
Diesters



FORMS

Nucleic Acids (0.2 – 2.4% Organic P)

DNA, RNA

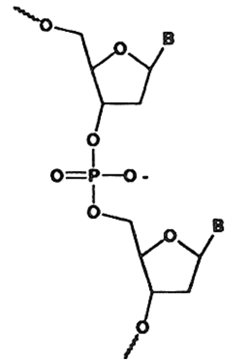
Phospholipids (0.5 – 7% Organic P)

phosphatidylcholine (lecithin)
Phosphatidylethanolamine (cephalin)

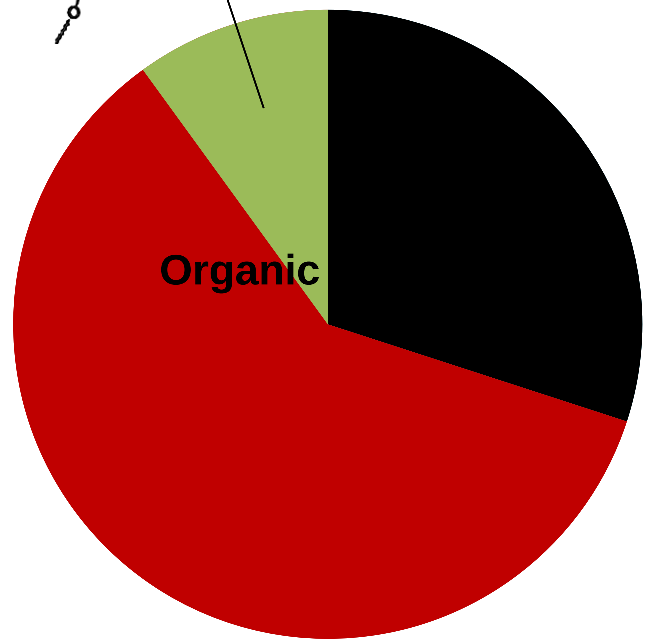
Fatty Acids

Teichoic acids

Organic Phosphorus



Orthophosphate
Diesters



Total Soil P

SOURCES

Nucleic Acids (0.2 – 2.4% Organic P)

Biological

Phospholipids (0.5 – 7% Organic P)

Cell membrane

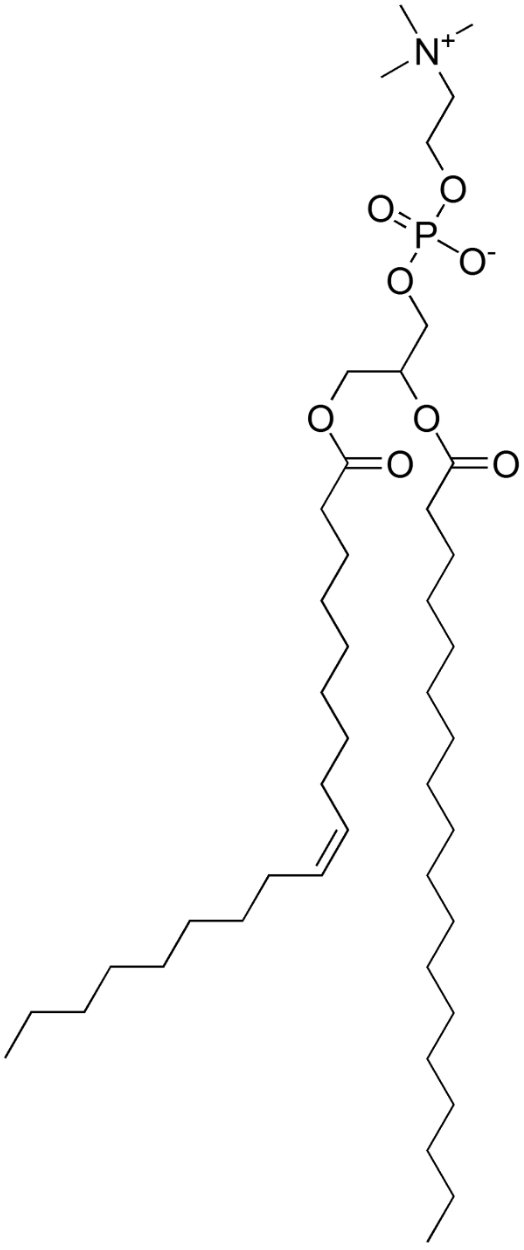
Cell membrane

Fatty Acids

Microbial cell wall/membrane

Organic Phosphorus

Find the phospho-**di-ester** bonds…..

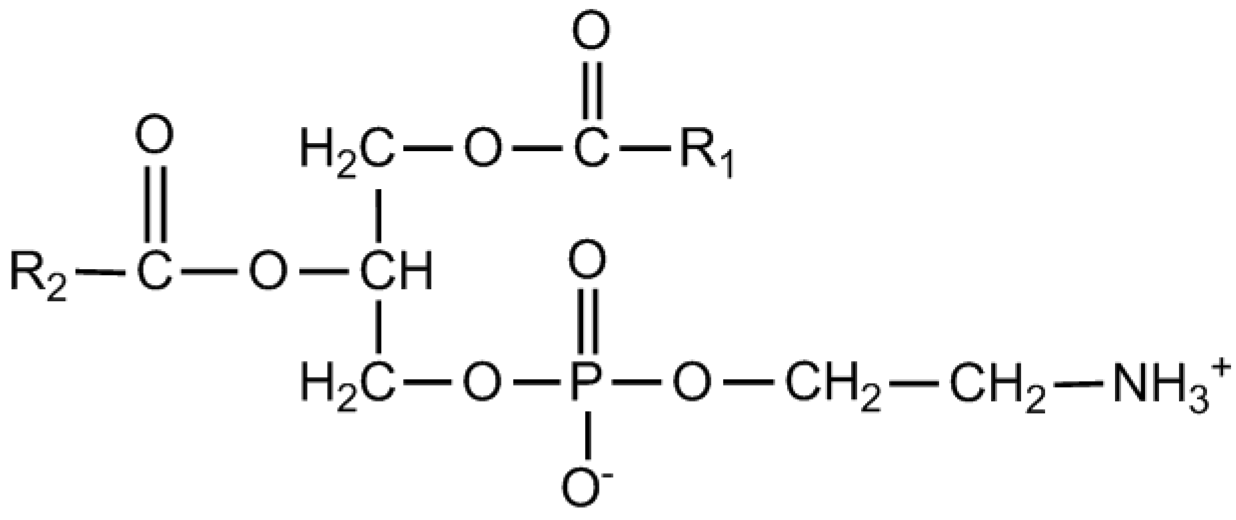


Phospholipids (0.5 – 7% Organic P)

phosphatidylcholine (lecithin)

Organic Phosphorus

Find the phospho-**di-ester** bonds…..

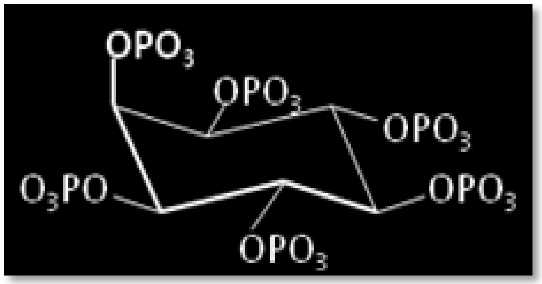


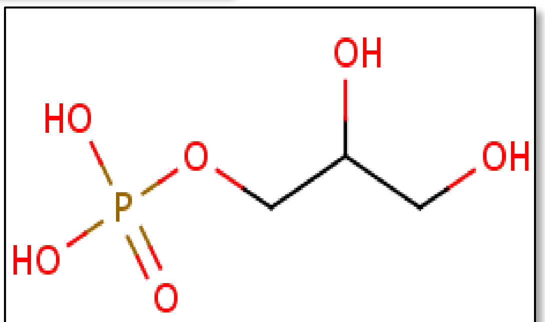
Phospholipids (0.5 – 7% Organic P)

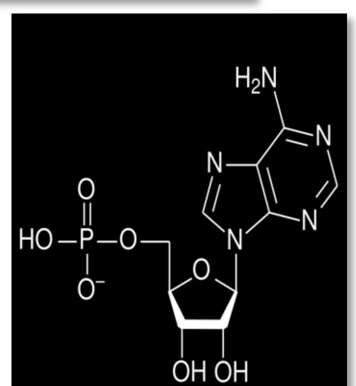
Phosphatidylethanolamine (cephalin)

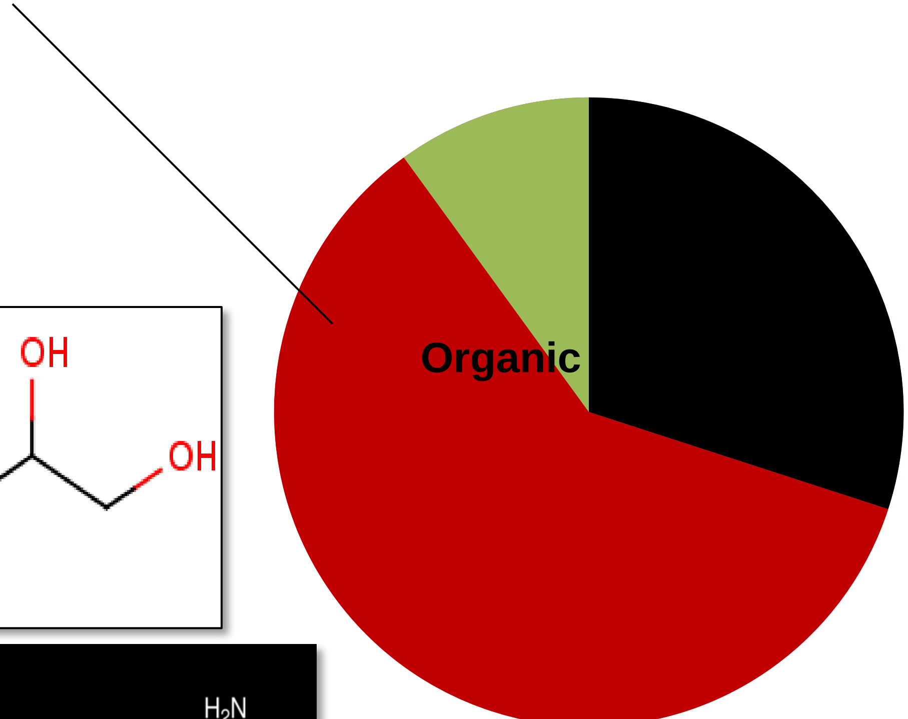
Organic Phosphorus

Orthophosphate **Monoesters**





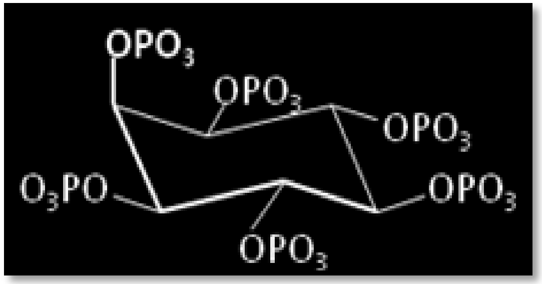




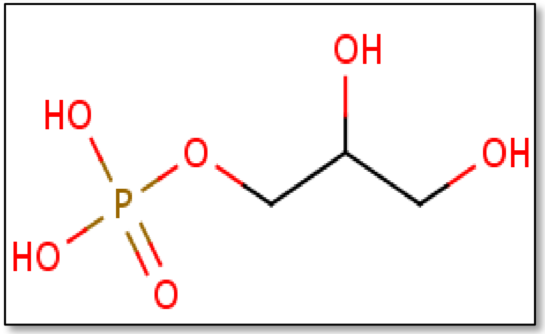
Total Soil P

Organic Phosphorus

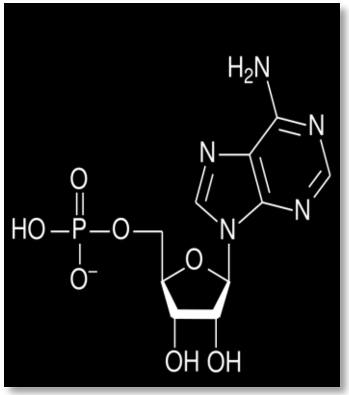
Orthophosphate **Mono**esters **FORMS**



Inositol phosphates



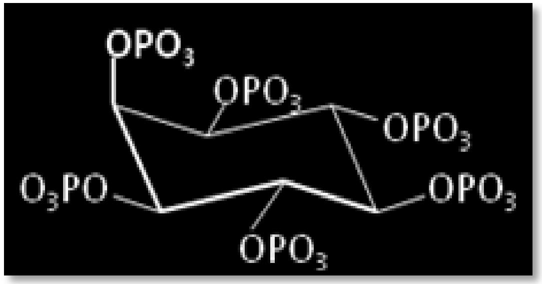
glycerophosphates



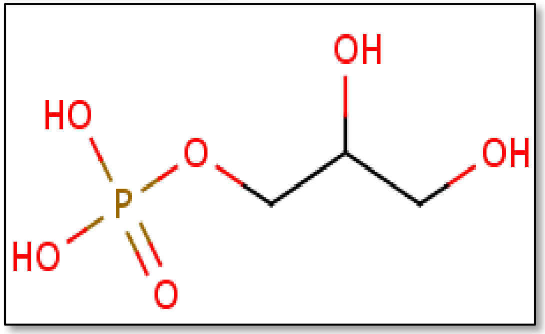
AMP

Organic Phosphorus

Orthophosphate **Mono**esters **SOURCES**

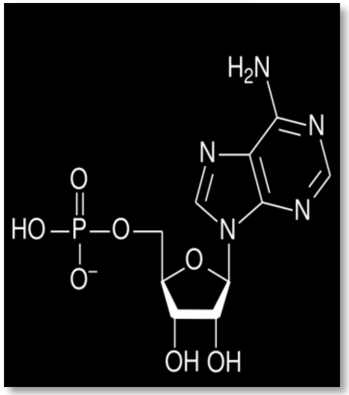


Seed/grain, eukaryotes



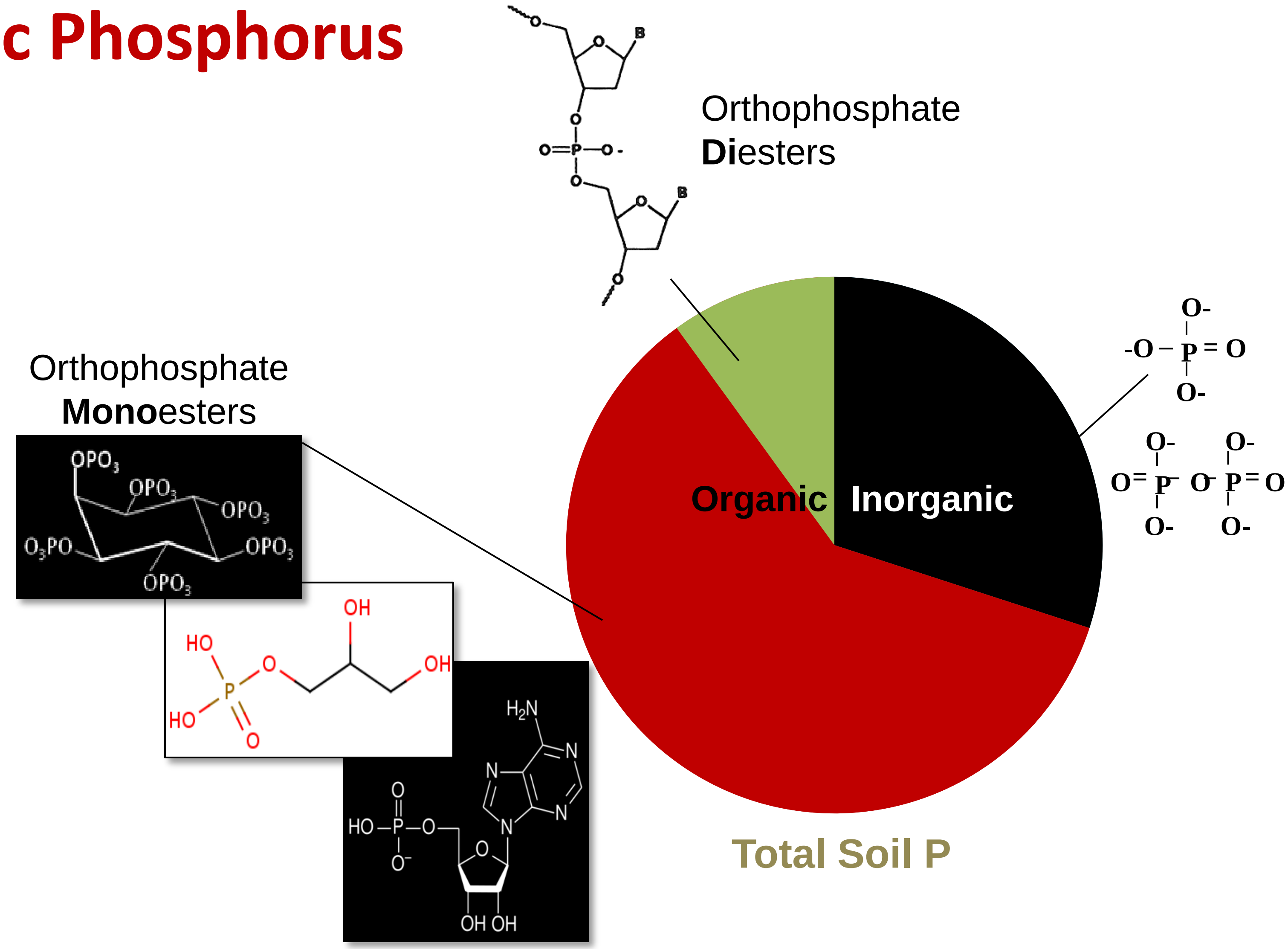
Biological →

Phospholipid break-down



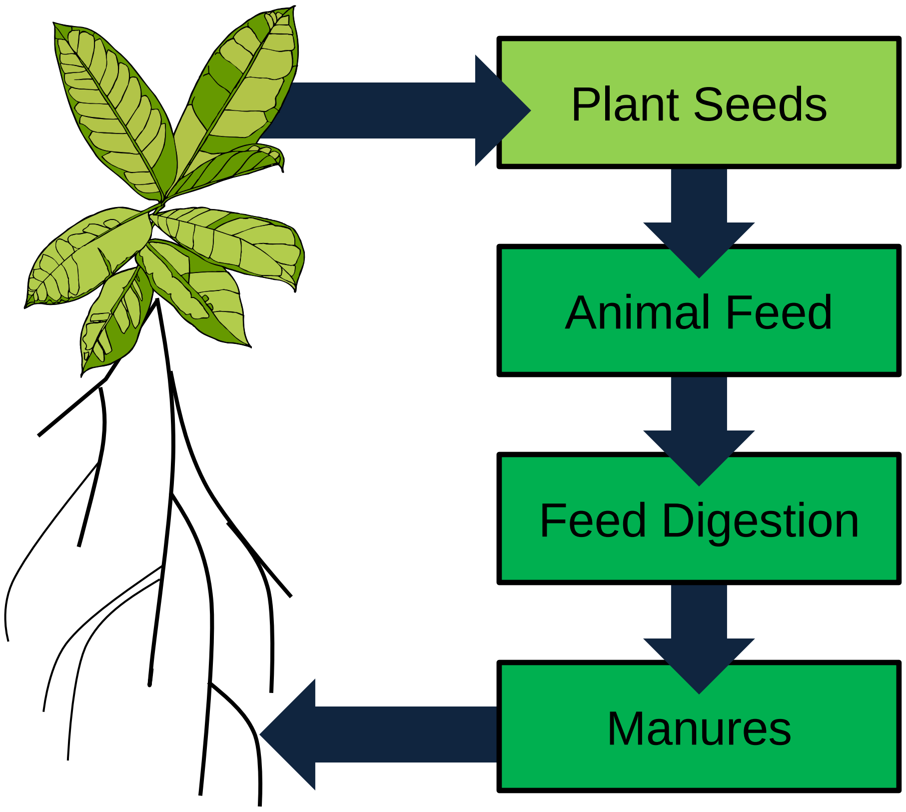
Biological

Organic Phosphorus



Organic Phosphorus ORIGINS in SOIL

The Phytate Story



Today

Soil **Organic P**

Forms/Sources

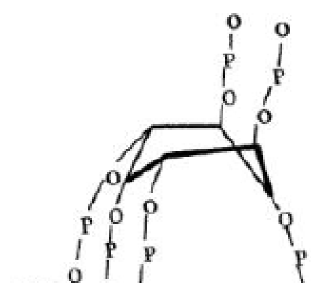
Behavior in Soils

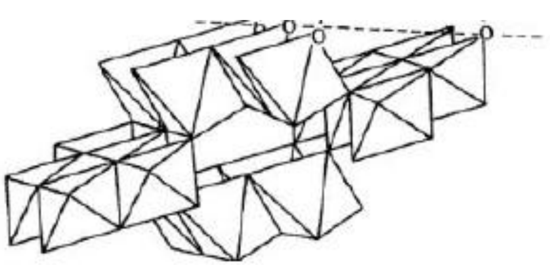
Measurement

DESORPTION (e.g. phytate)

Mechanisms

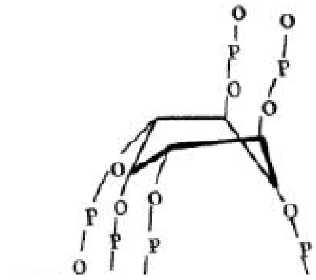
Kinetics



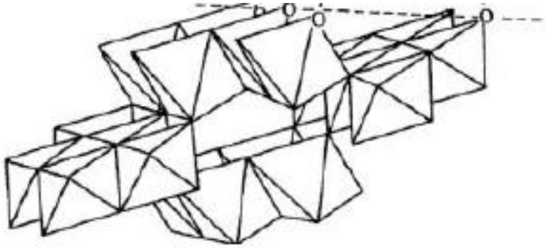


Behavior in Soils

PHYTATE

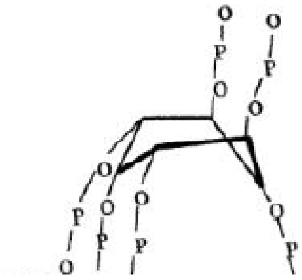


GOETHITE



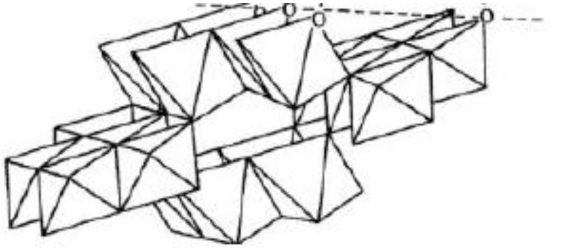
Behavior in Soils

PHYTATE



PROCESSES → Abiotic → Biotic

GOETHITE

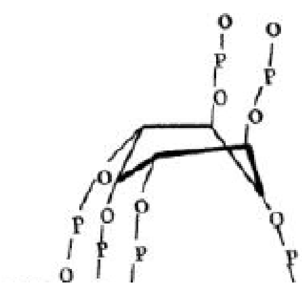


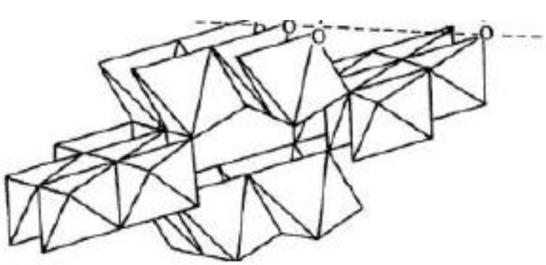
Abiotic

Sorption and **Desorption** influenced by:

P Concentration
Mineral surface characteristics
pH
Ionic strength
Temperature

PHYTATE





GOETHITE

Celi *et al*. 2001a

Abiotic

Sorption and **Desorption** influenced by:

P Concentration
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pH
Ionic strength
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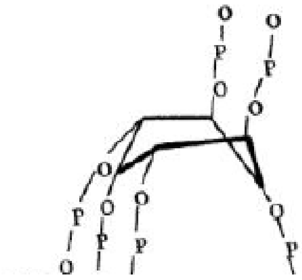
PHYTATE



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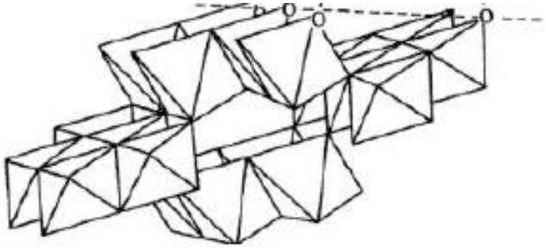
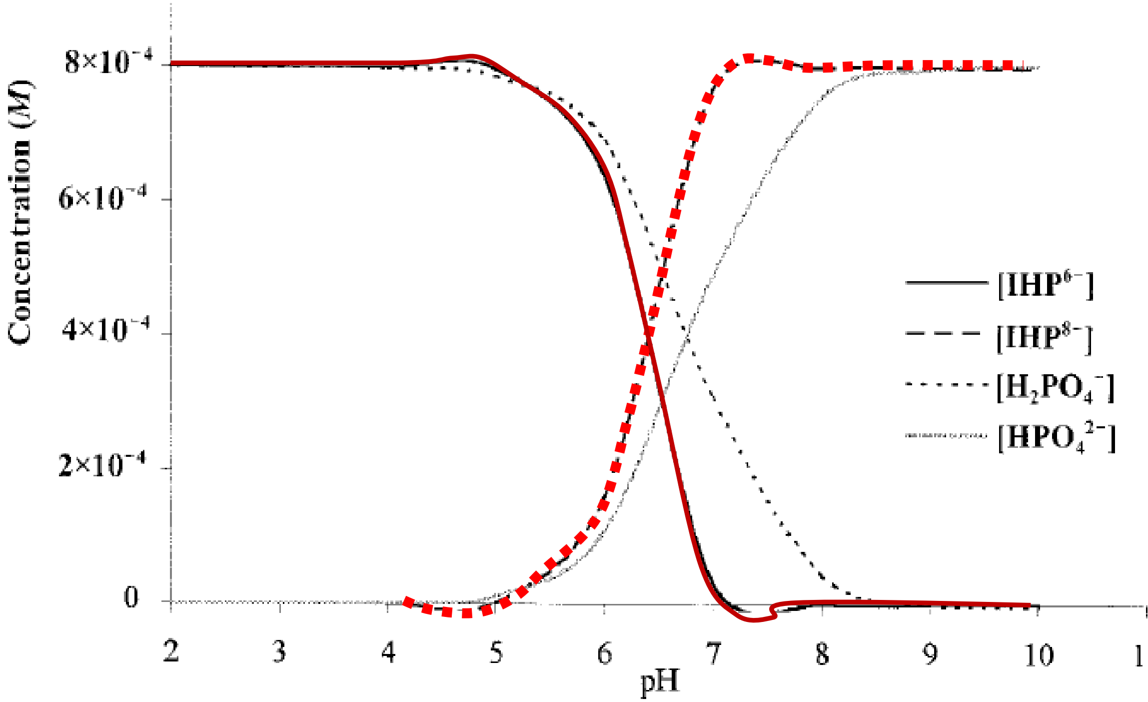


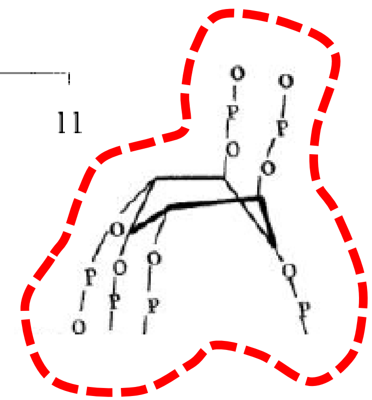
Celi *et al*. 2001a

Abiotic

1. **Depends on** aqueous **CHARGE SPECIES**



PHYTATE



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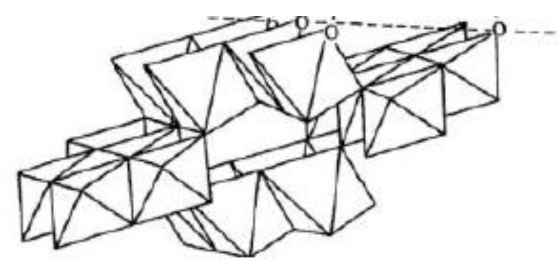
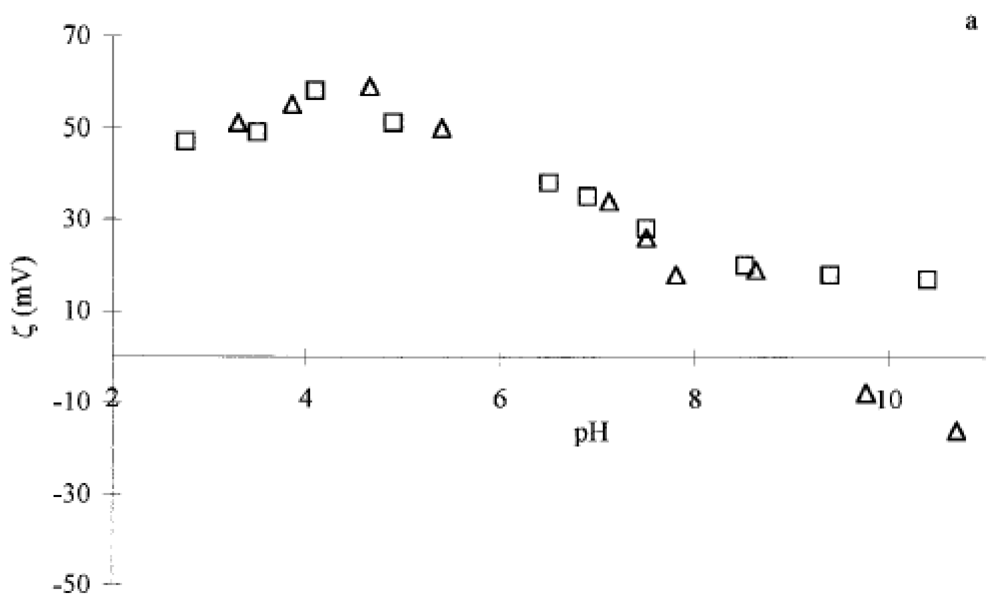


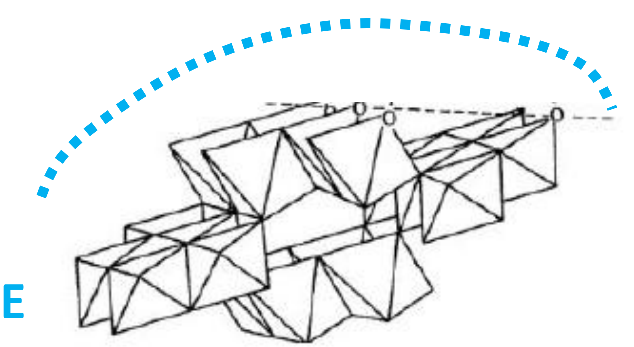
Celi *et al*. 2001a

Abiotic

2. Depends on mineral surface **CHARGE**



PHYTATE

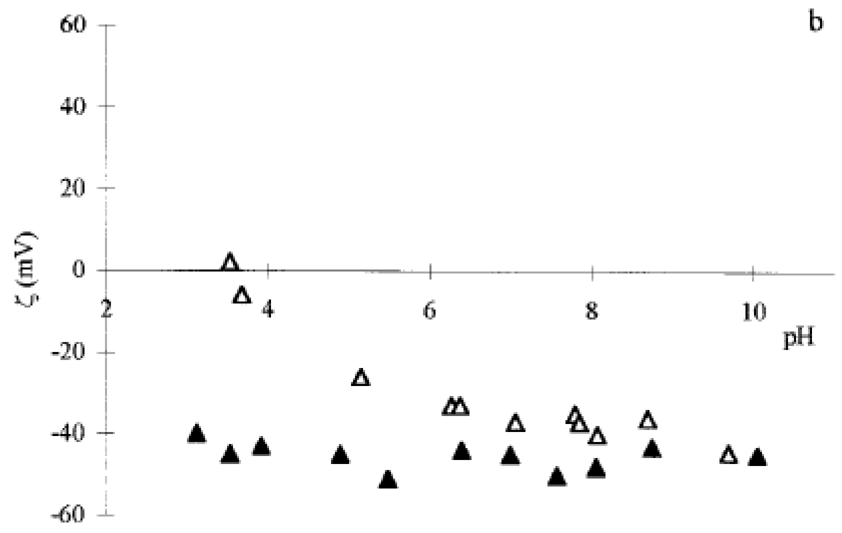


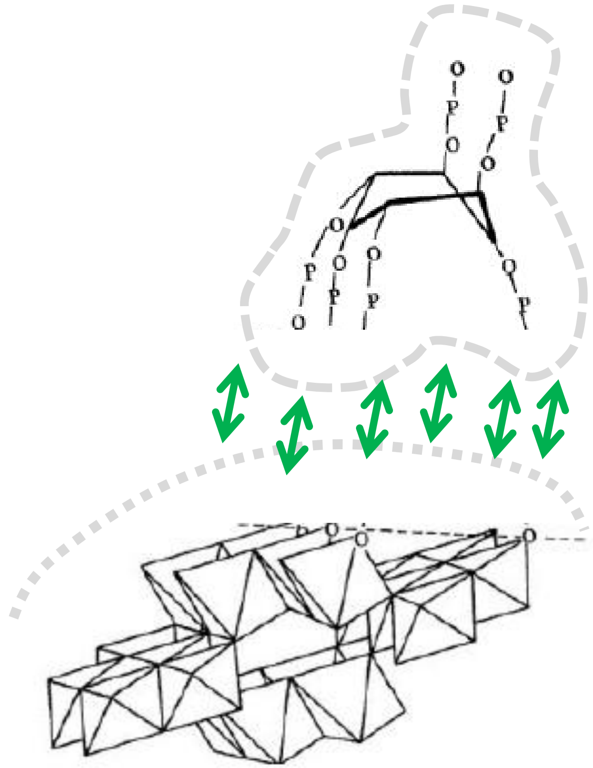
GOETHITE

Celi *et al*. 2001a

Abiotic

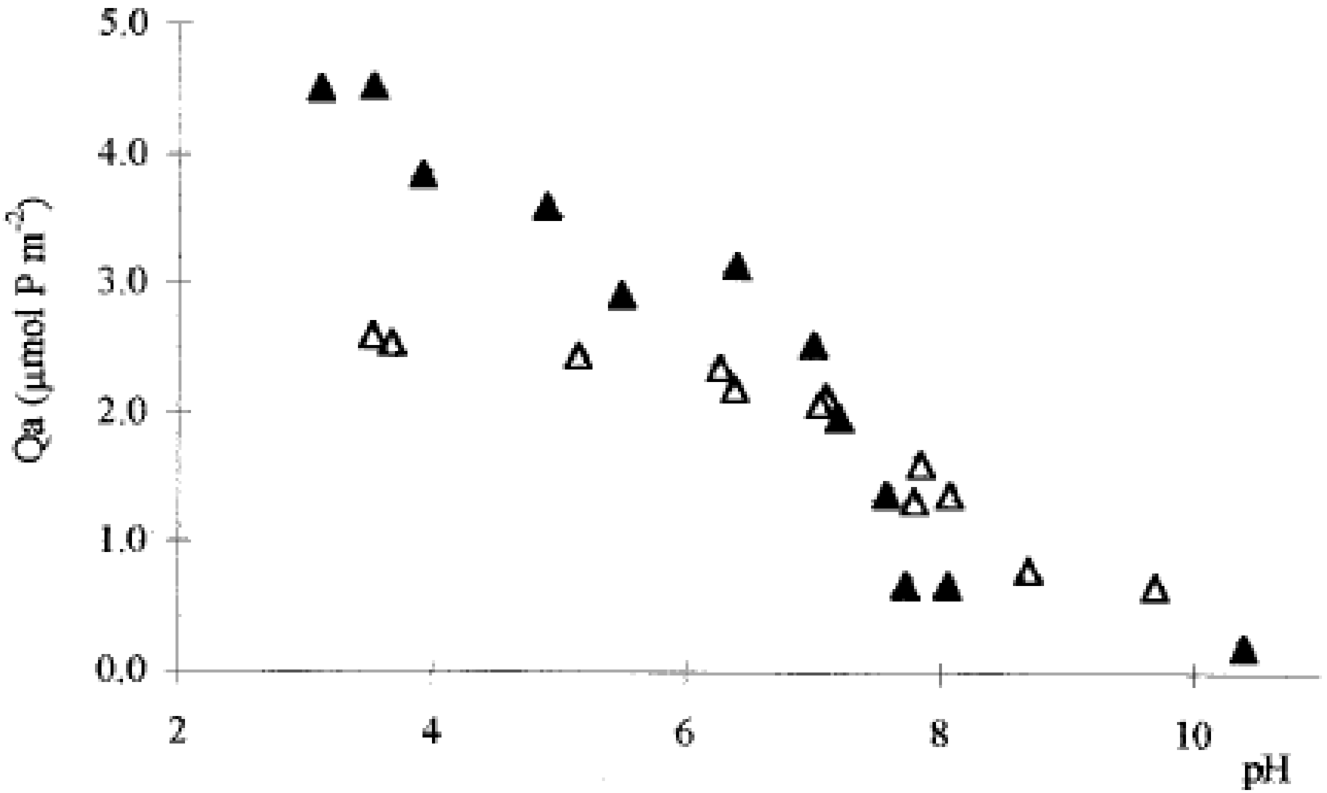
3. **Depends on** electrostatic **INTERACTIONS**

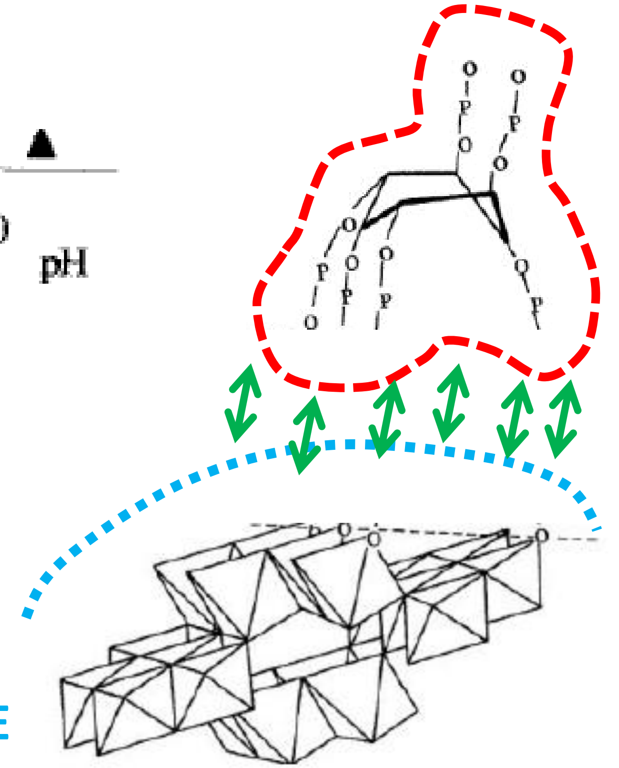




Celi *et al*. 2001a

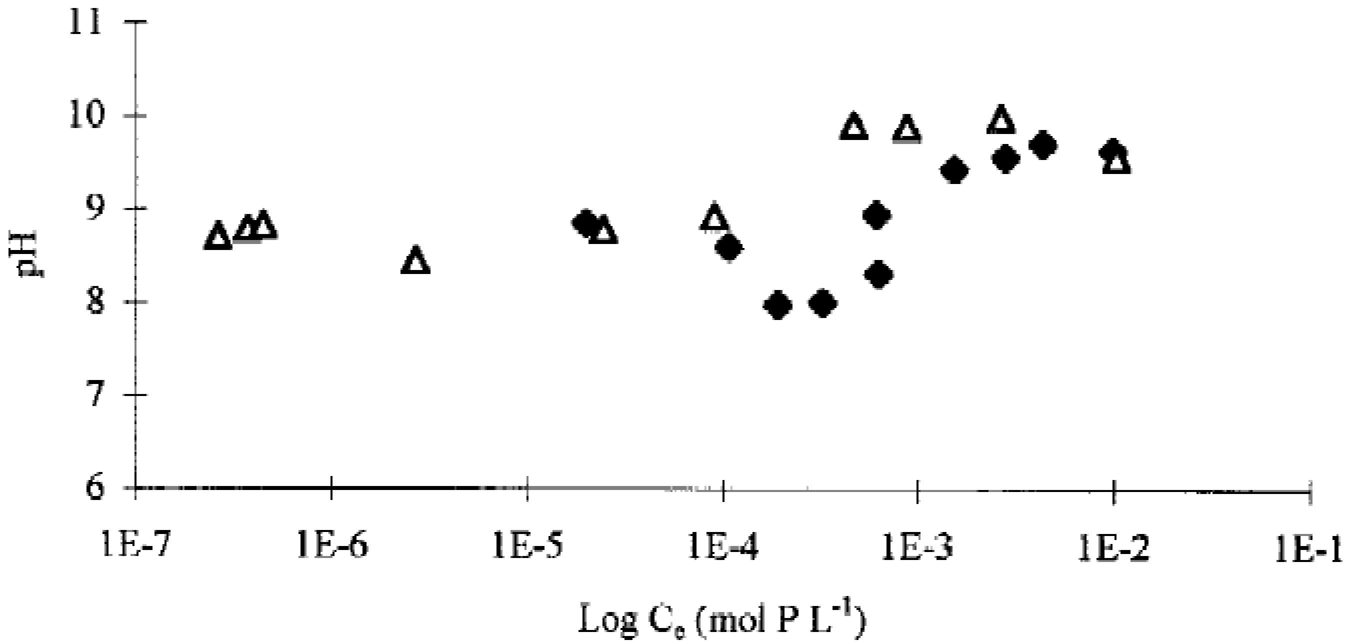
Abiotic

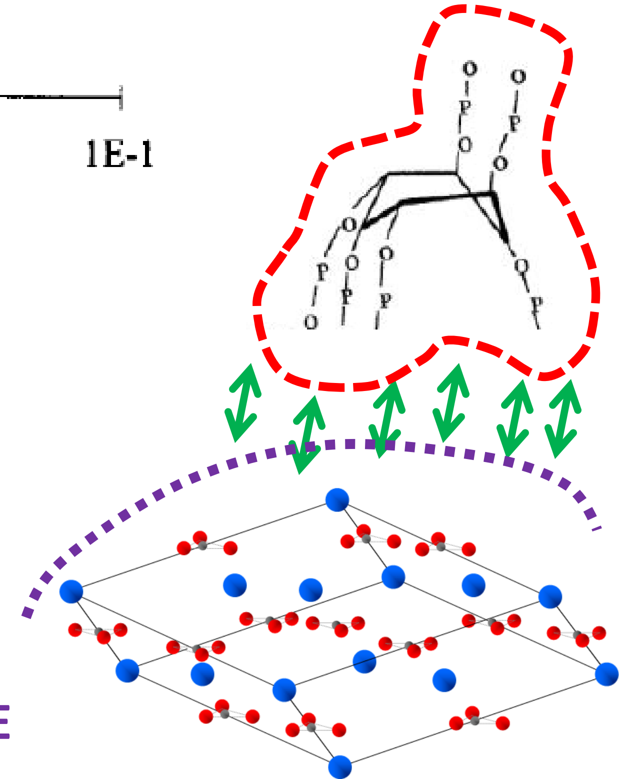




Celi *et al*. 2001a

Abiotic





Celi *et al*. 2001a

CALCITE

Abiotic

Phytate and Phosphate on Calcite

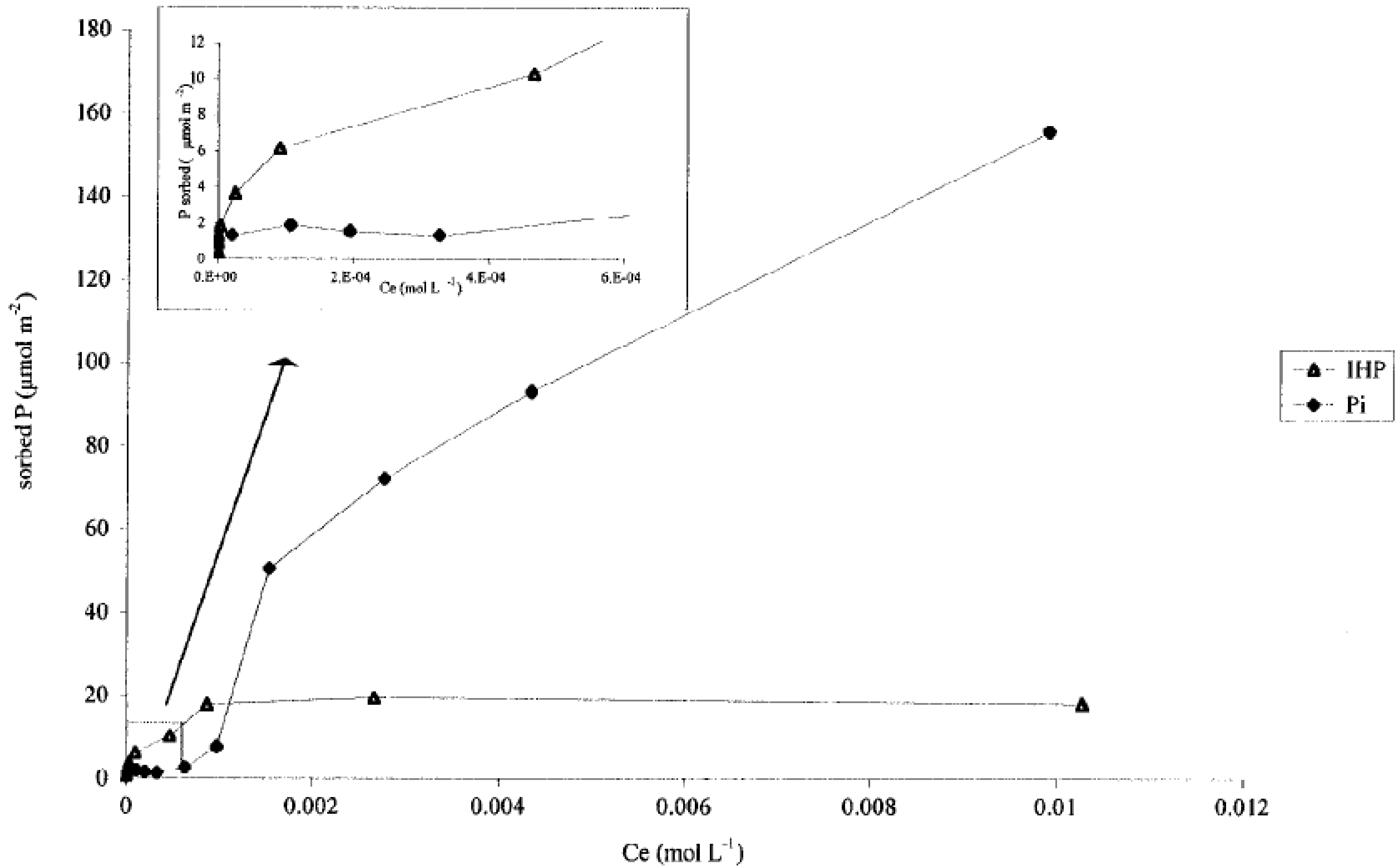


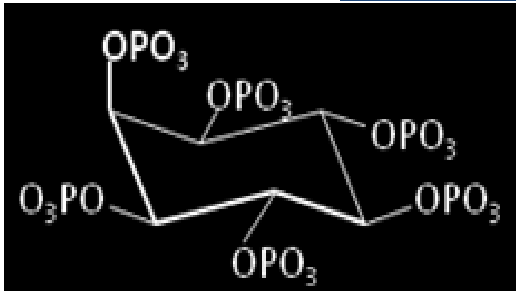
Figure 1. Adsorption isotherms of myo-inositol hexaphosphate (IHP) and orthophosphate (Pi) on calcite: variation of the sorbed amount (sorbed P) with the equilibrium concentration (C_e).

Celi *et al.* 2000

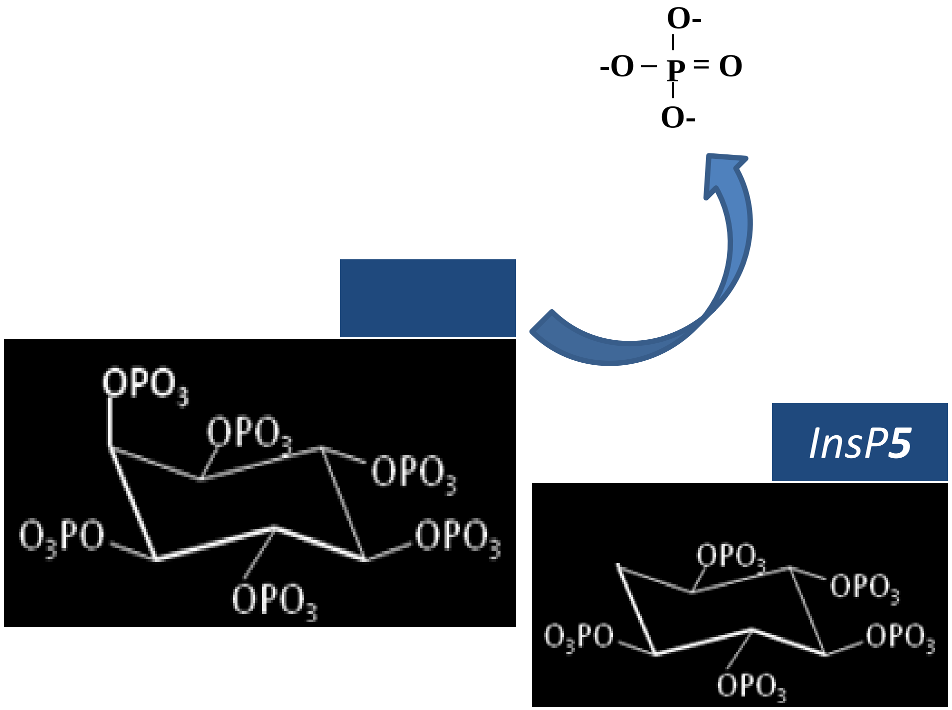
Biotic

Biotic → DEGRADATION

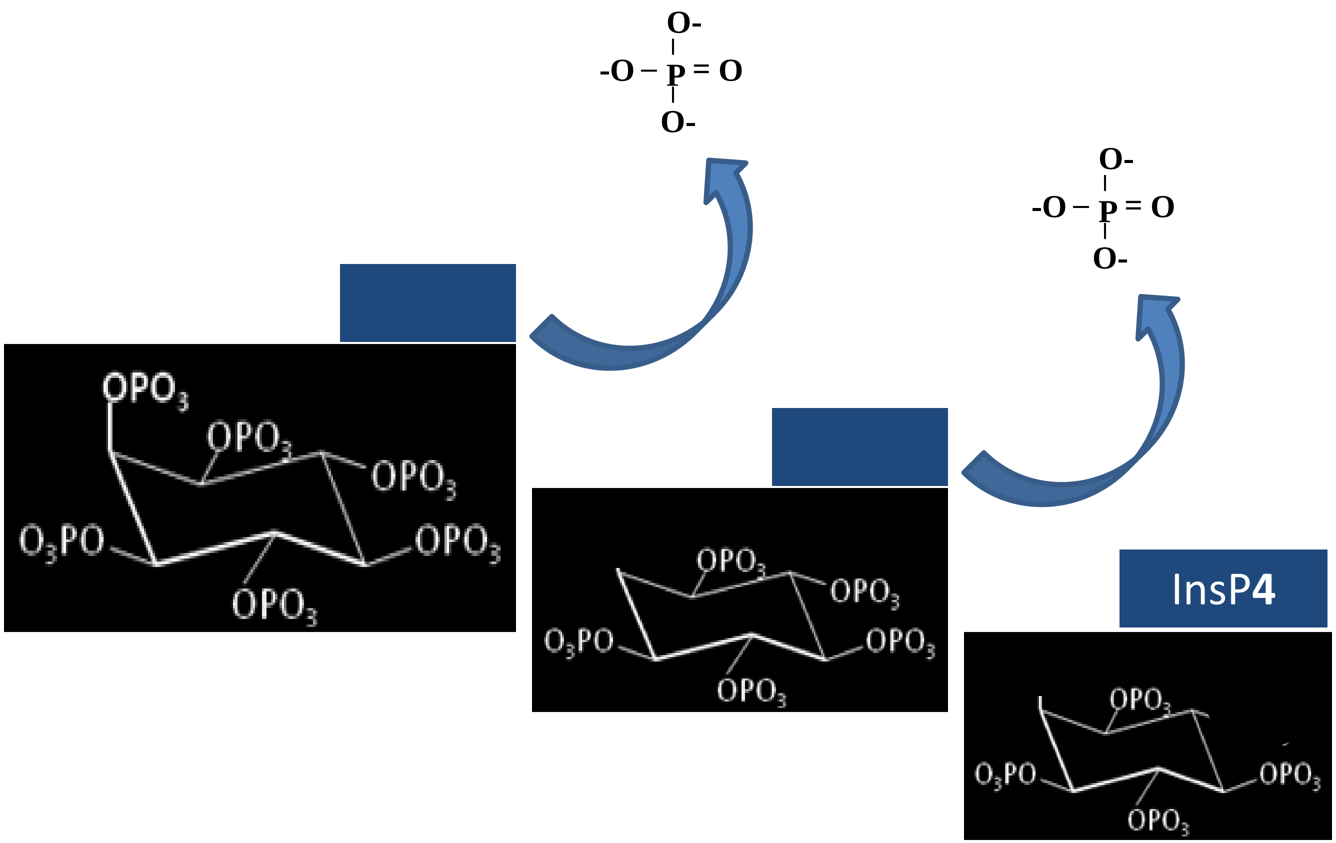
*InsP**6***



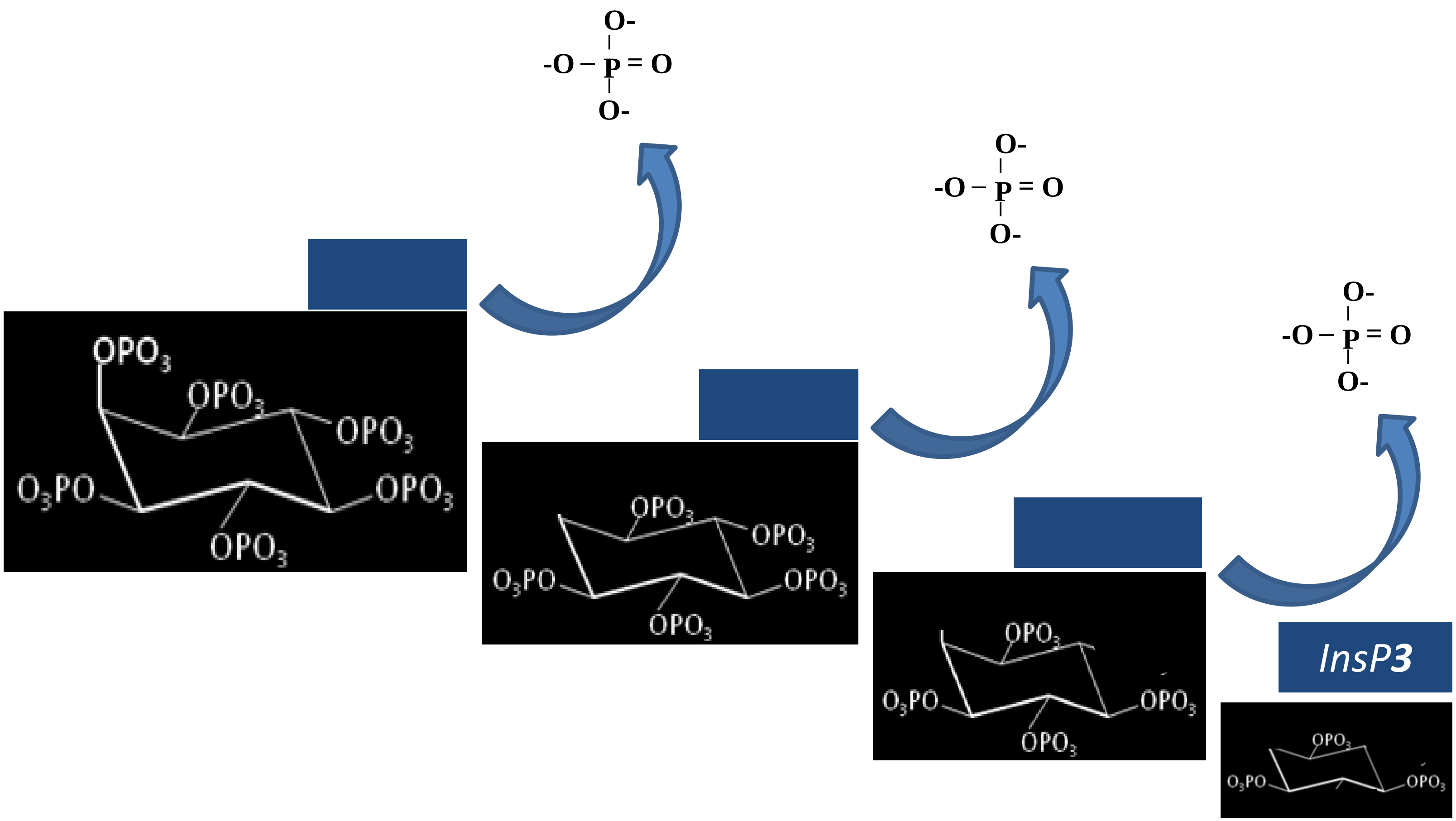
Biotic → DEGRADATION



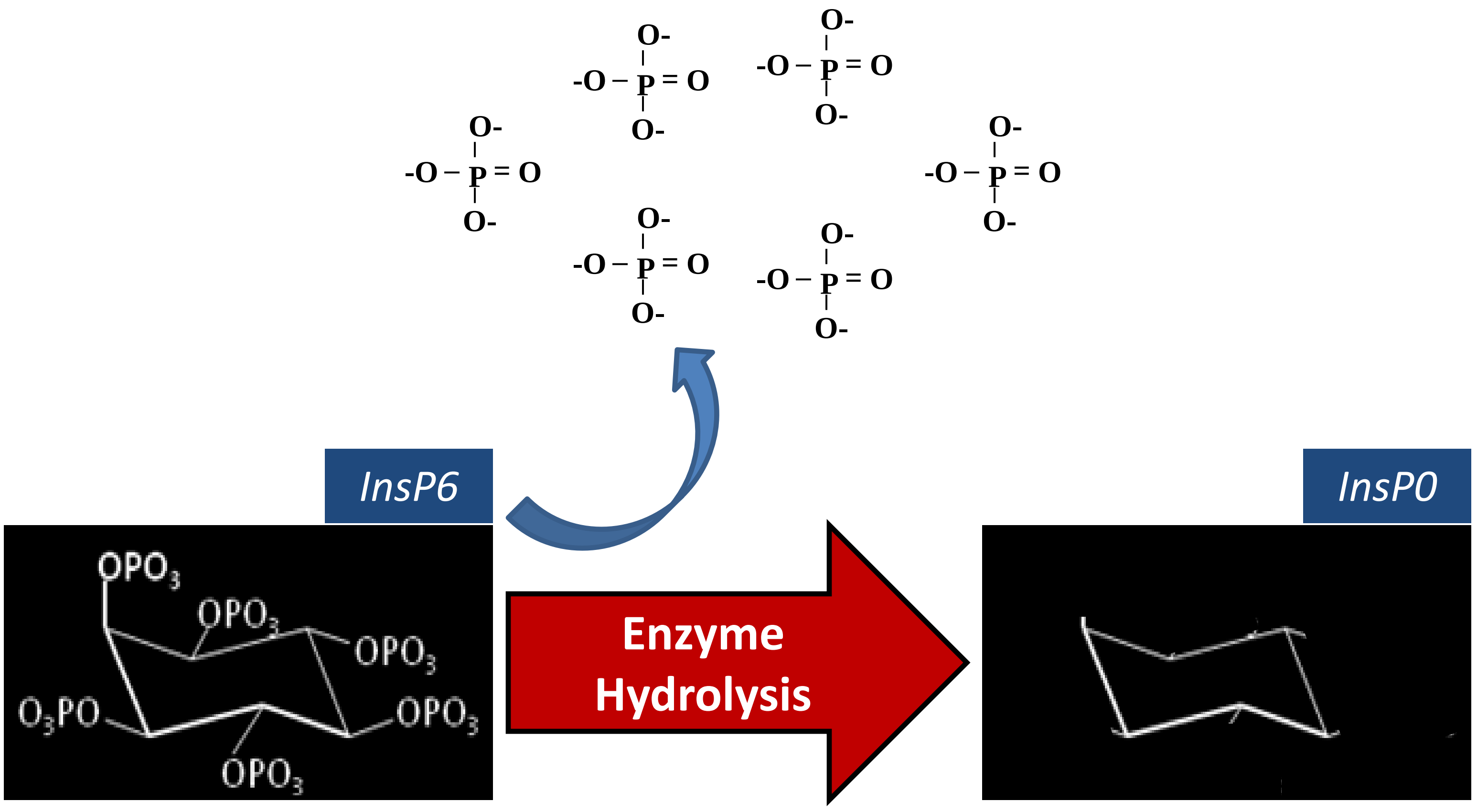
Biotic → DEGRADATION



Biotic → DEGRADATION



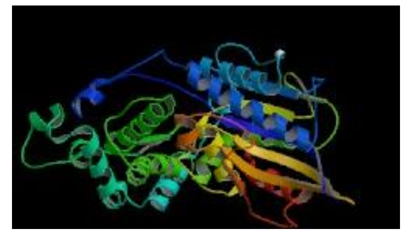
Biotic → DEGRADATION



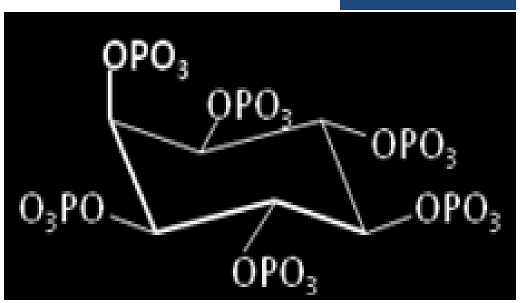
Biotic → DEGRADATION

PHYTASES

Fungus
Bacteria
Plants

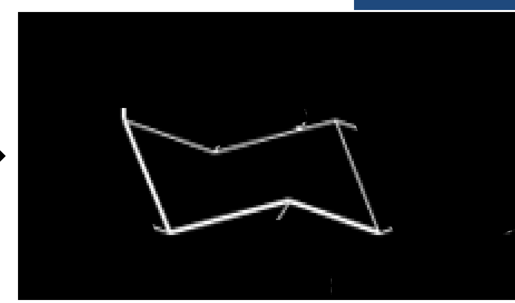


InsP6

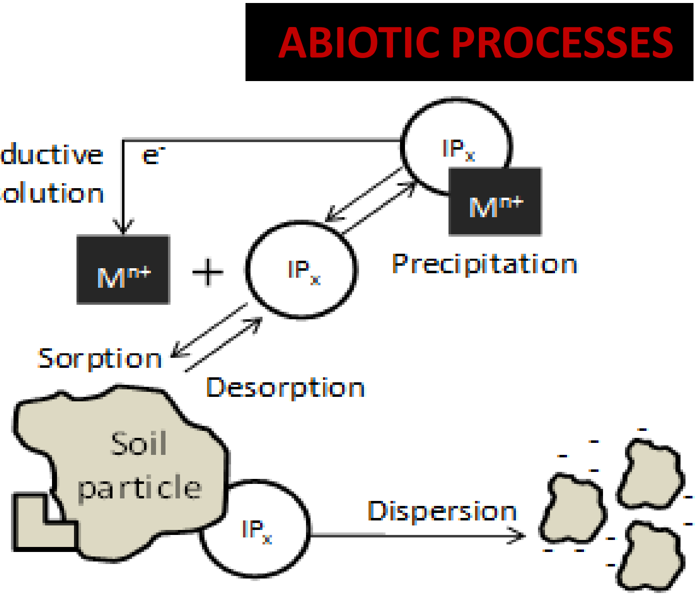


Enzyme Hydrolysis

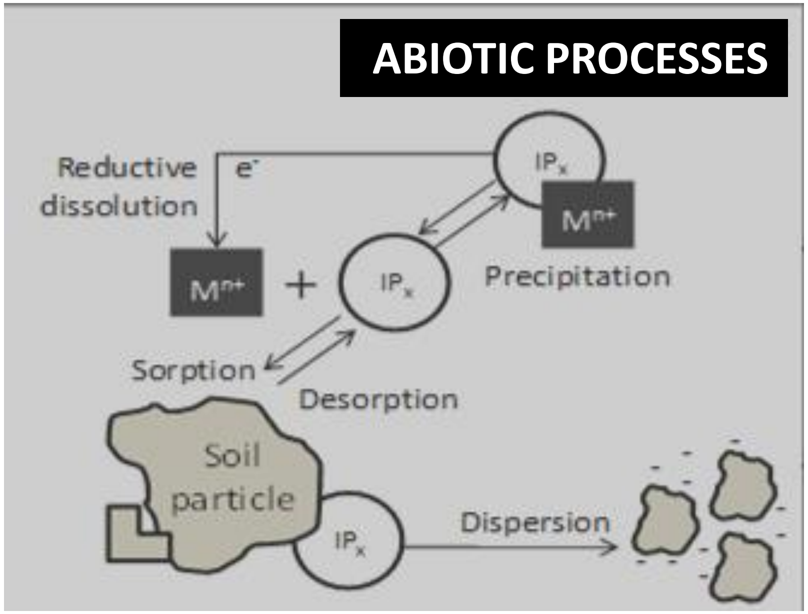
InsP0



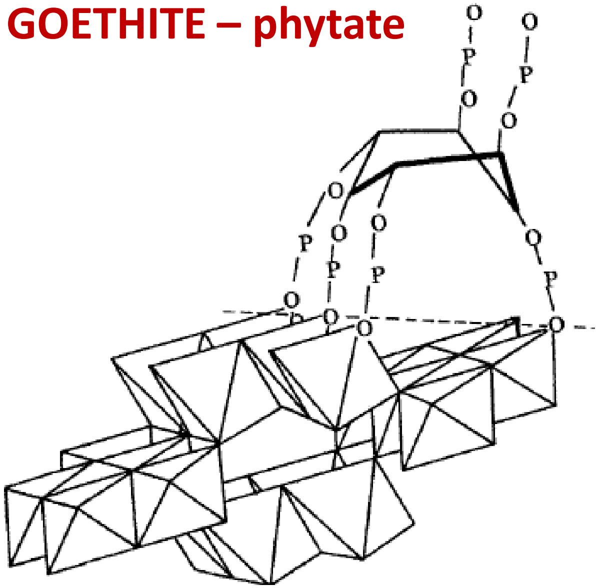
RECAP: Behavior in Soils



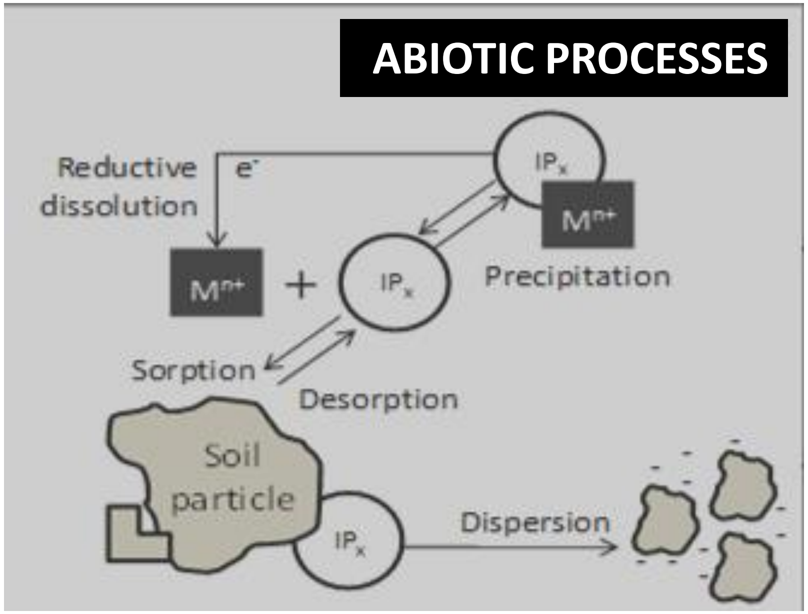
RECAP: Behavior in Soils

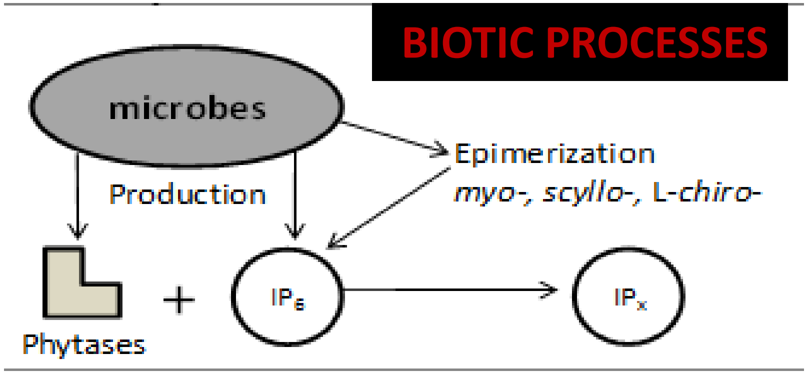


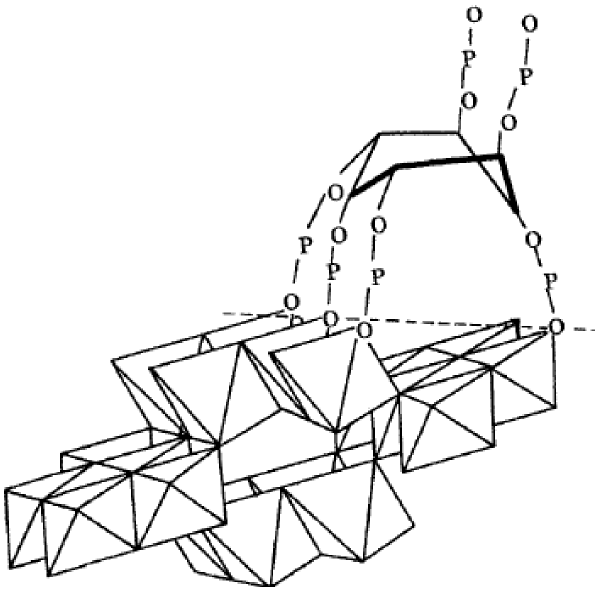
GOETHITE – phytate



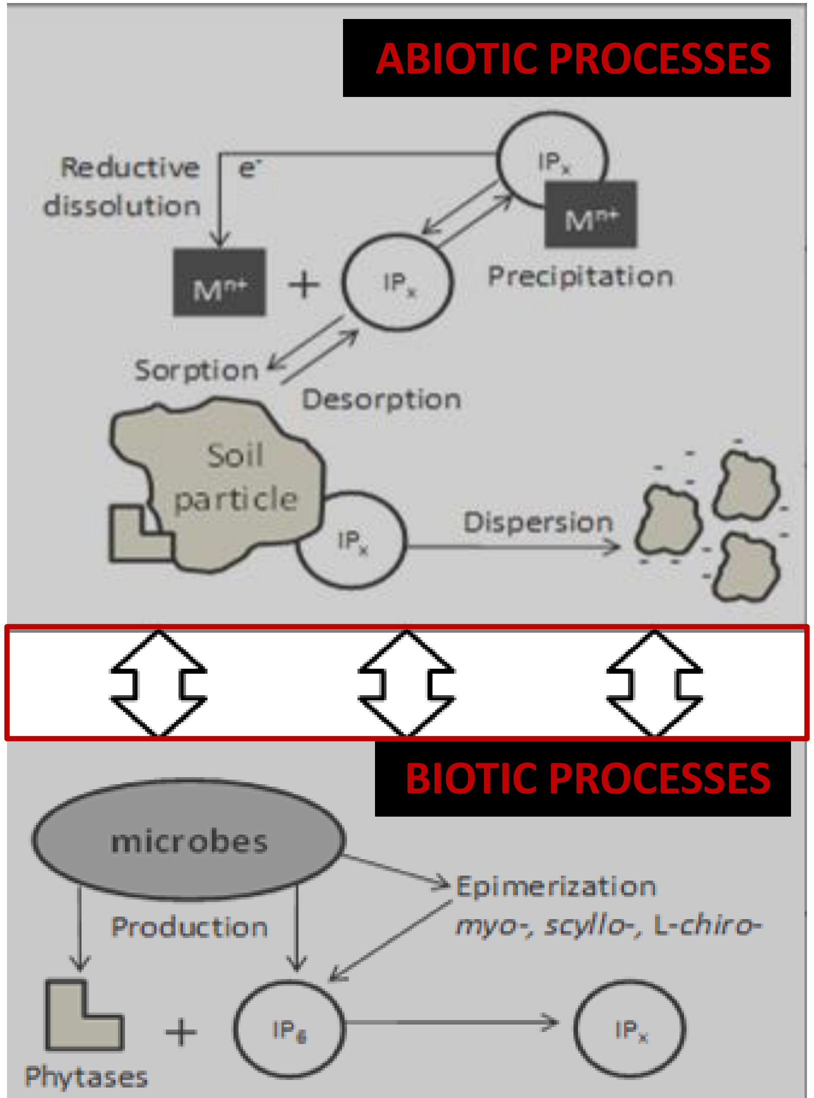
RECAP: Behavior in Soils

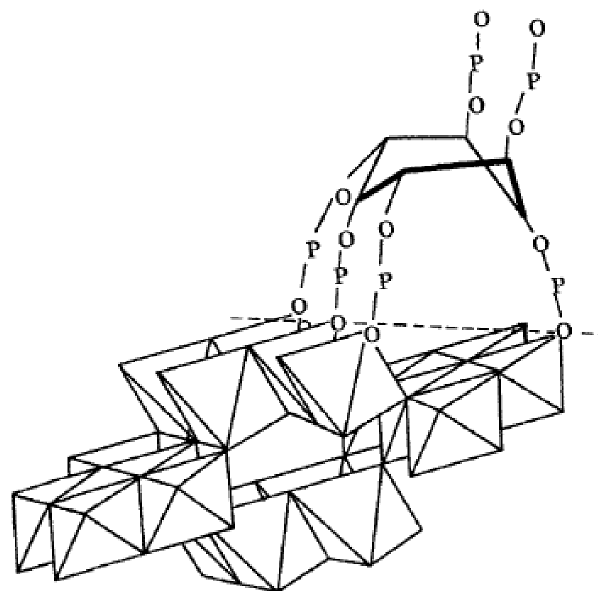




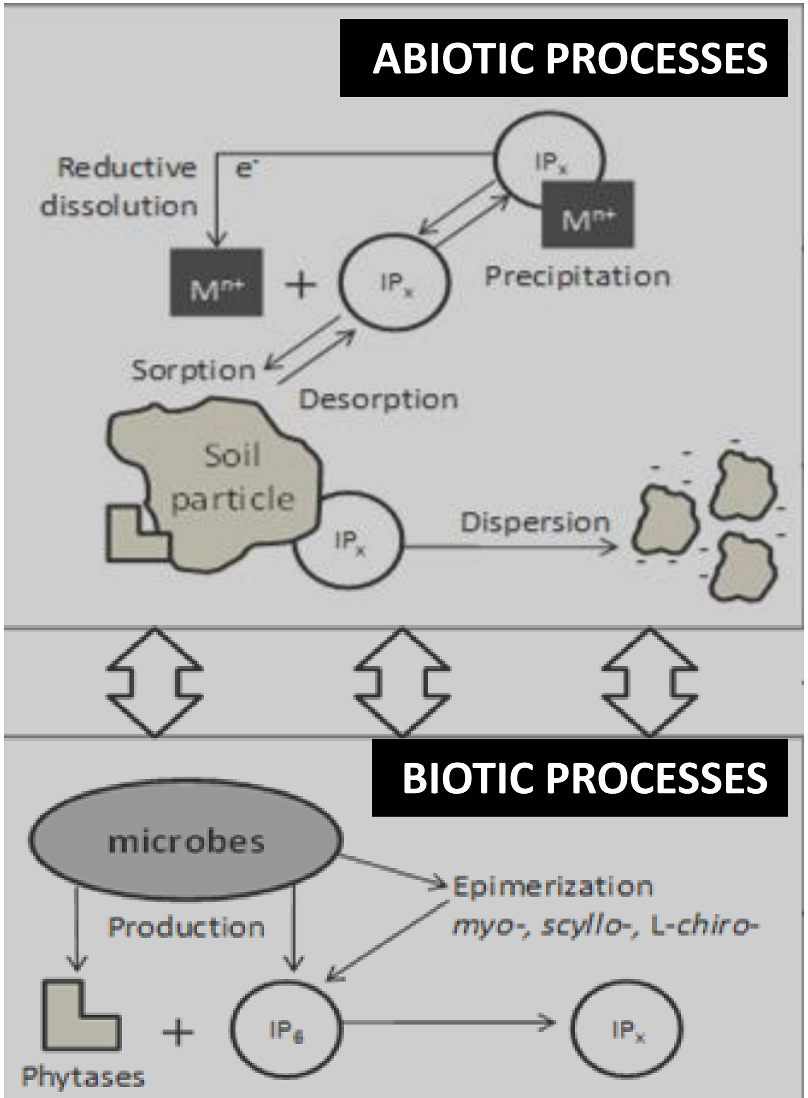


RECAP: Behavior in Soils





RECAP: Behavior in Soils



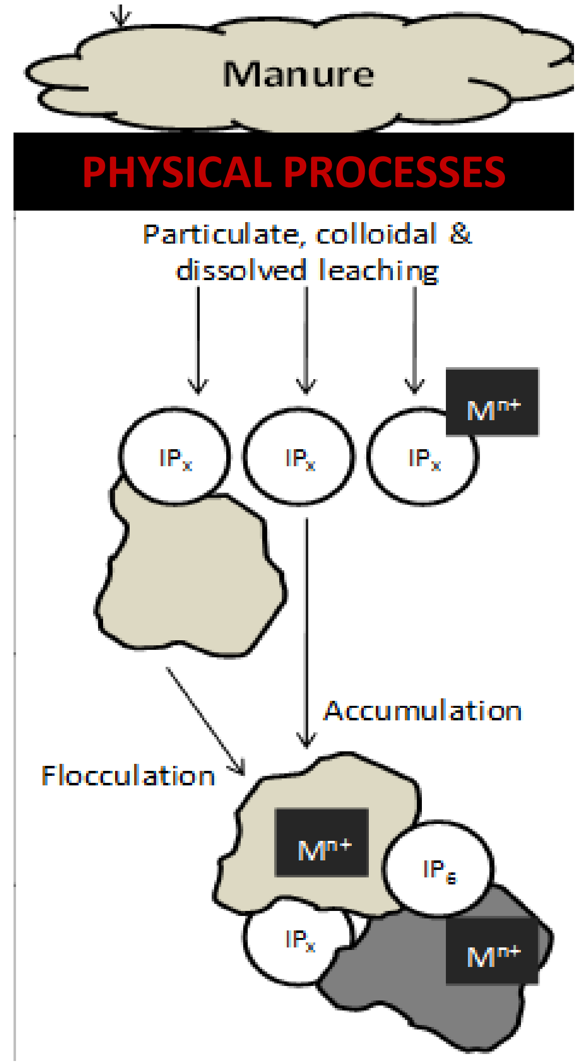
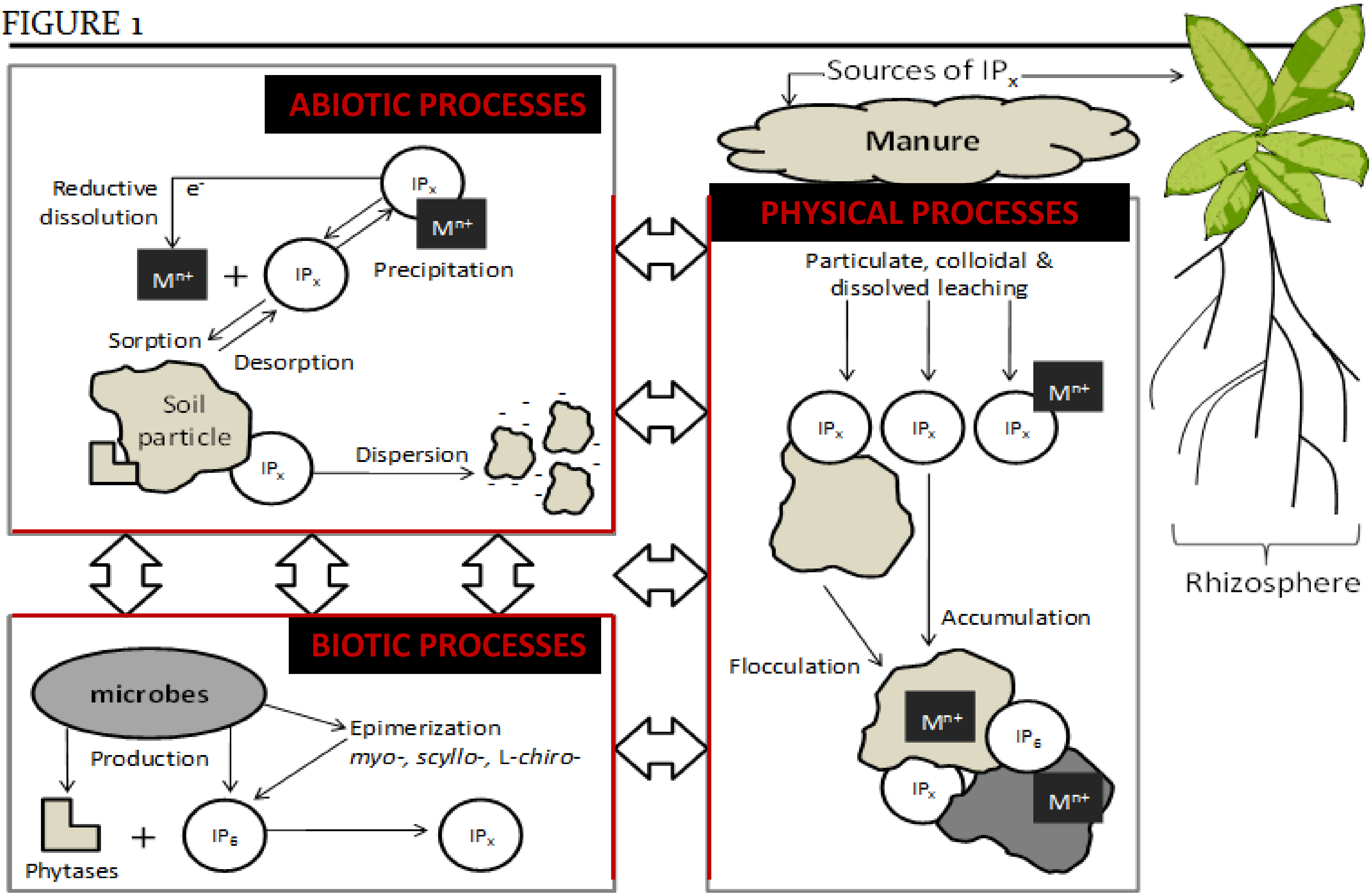


FIGURE 1



ABIOTIC PROCESSES
Reductive dissolution
e-
IPx
Mn+
Mn+
+
IPx
Precipitation
Sorption
Desorption
Soil particle
IPx
Dispersion
BIOTIC PROCESSES
microbes
Epimerization
myo-, scyllo-, L-chiro-
Production
Phytases
+
IP6
IPx
Sources of IPx
Manure
PHYSICAL PROCESSES
Particulate, colloidal & dissolved leaching
IPx
IPx
IPx
Mn+
Accumulation
Flocculation
Mn+
IP6
IPx
Mn+
Rhizosphere

Today

Soil **Organic P**

Forms/Sources

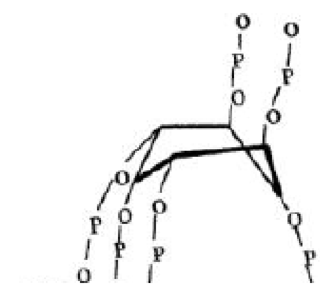
Behavior in Soils

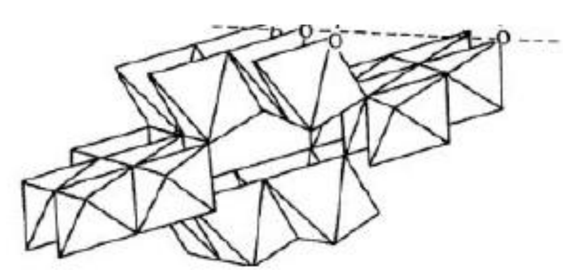
Measurement

DESORPTION (e.g. phytate)

Mechanisms

Kinetics

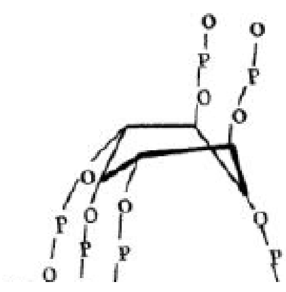


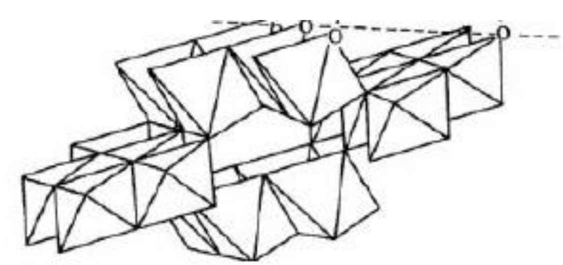


Measurement

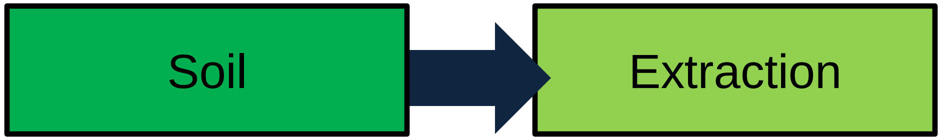
METHODS

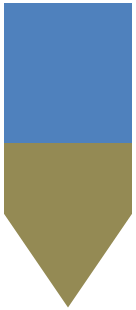
- Aqueous Extraction
- ^{31}P-NMR
- Enzymatic Hydrolysis





Aqueous Extraction





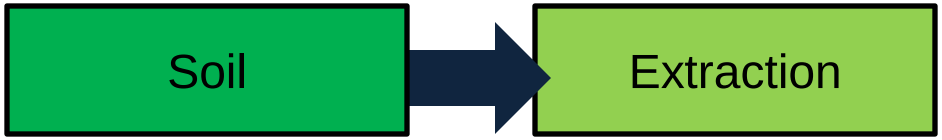
WATER

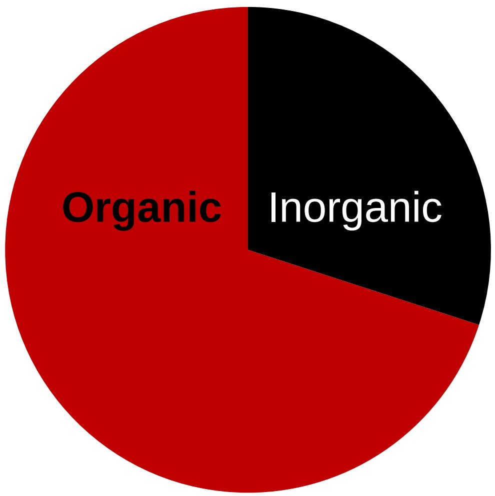
SODIUM BICARBONATE

NaOH EDTA

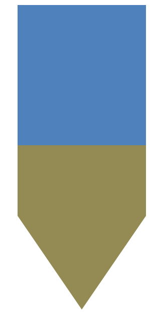
'The Inositol Phosphates in Soils and Manures: Abundance, Cycling, and Measurement'. Giles, CD, BJ Cade-Menun, JE Hill, 2011, Can. J. Soil Sci., *in press*.

Aqueous Extraction





Total Soil P



WATER

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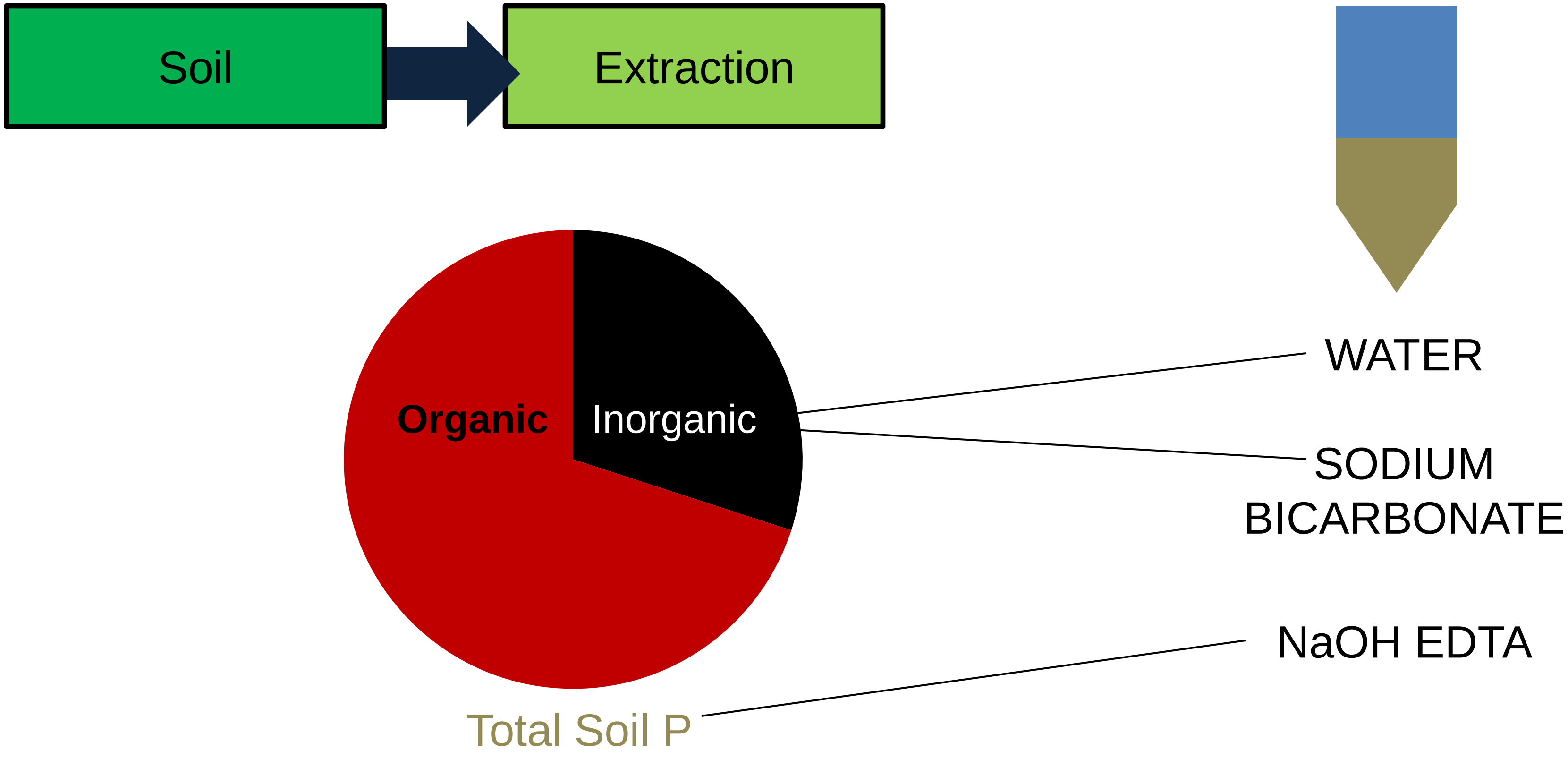
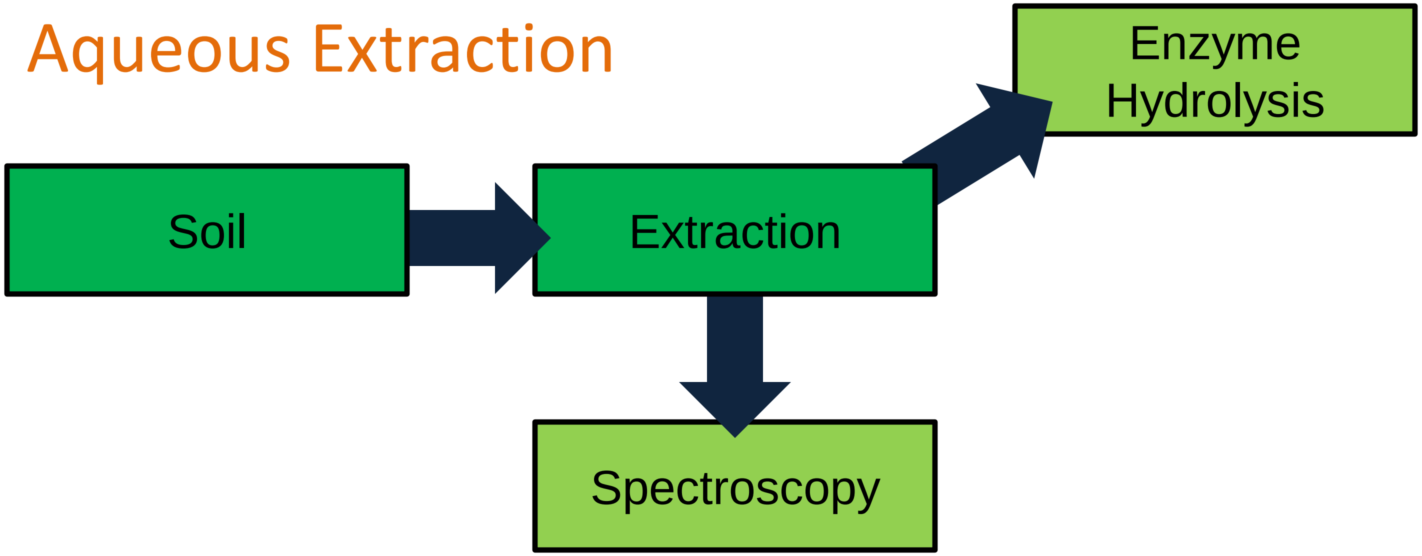
Aqueous Extraction

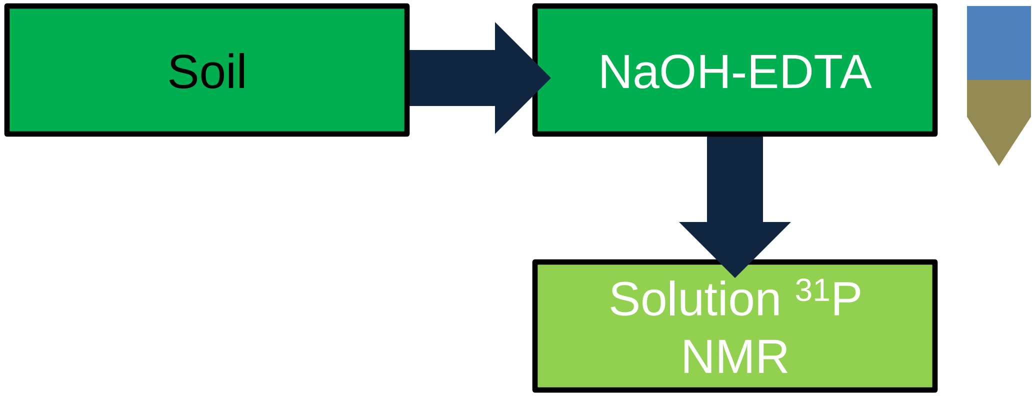


Aqueous Extraction



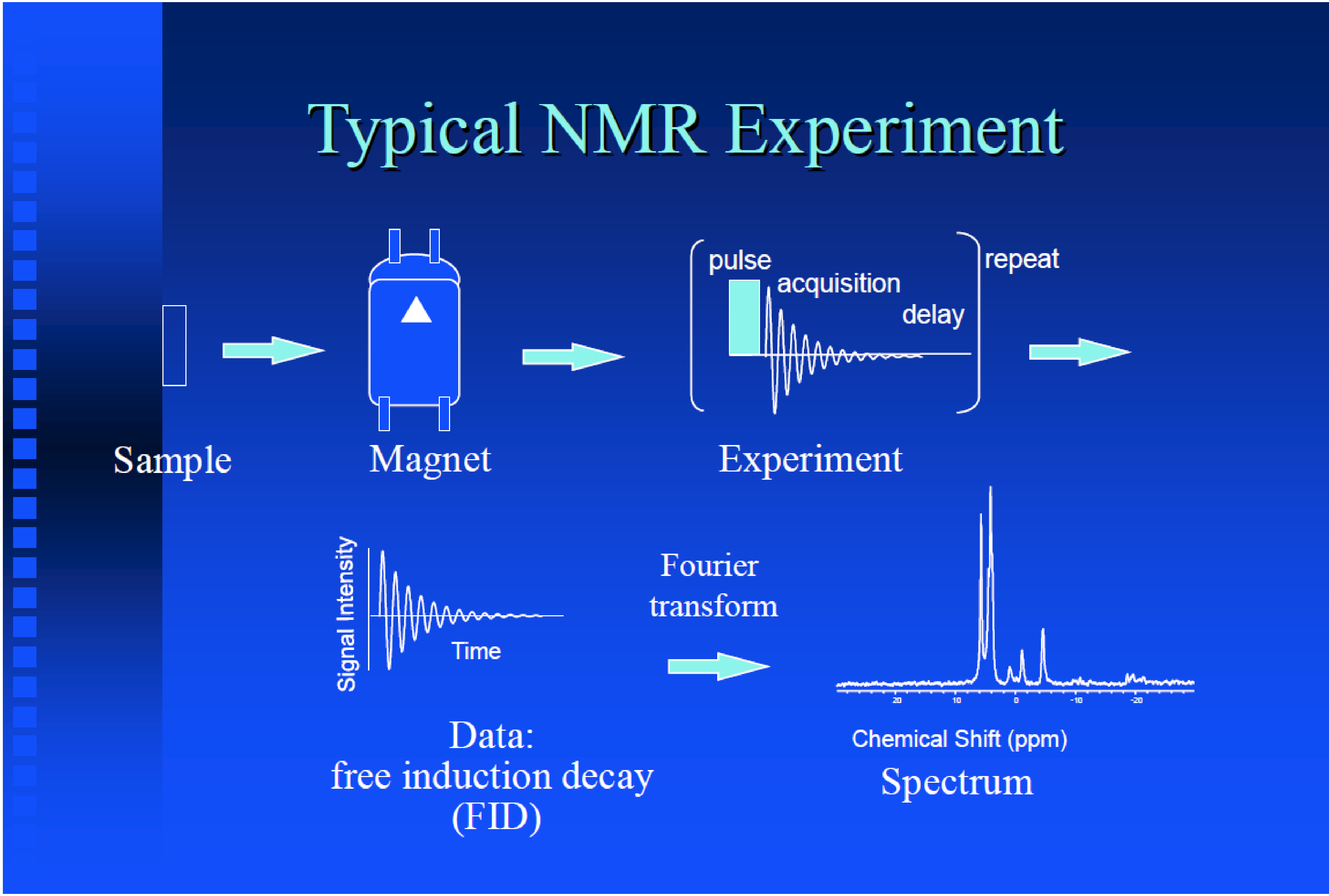
'The Inositol Phosphates in Soils and Manures: Abundance, Cycling, and Measurement'. Giles, CD, BJ Cade-Menun, JE Hill, 2011, Can. J. Soil Sci., *in press*.

Solution ^{31}P **N**uclear **M**agnetic **R**esonance Spectroscopy



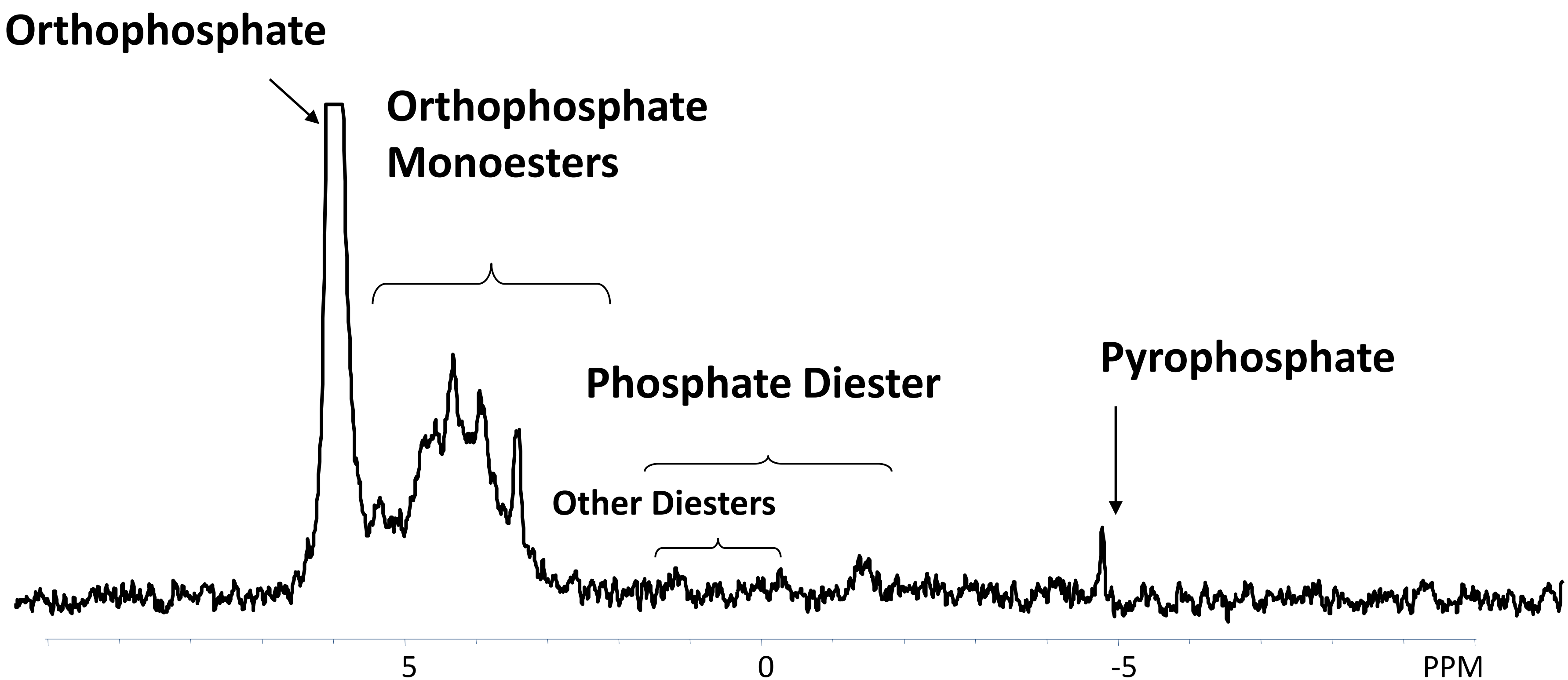
'The Inositol Phosphates in Soils and Manures: Abundance, Cycling, and Measurement'. Giles, CD, BJ Cade-Menun, JE Hill, 2011, Can. J. Soil Sci., *in press*.

Solution ^{31}P Nuclear Magnetic Resonance Spectroscopy



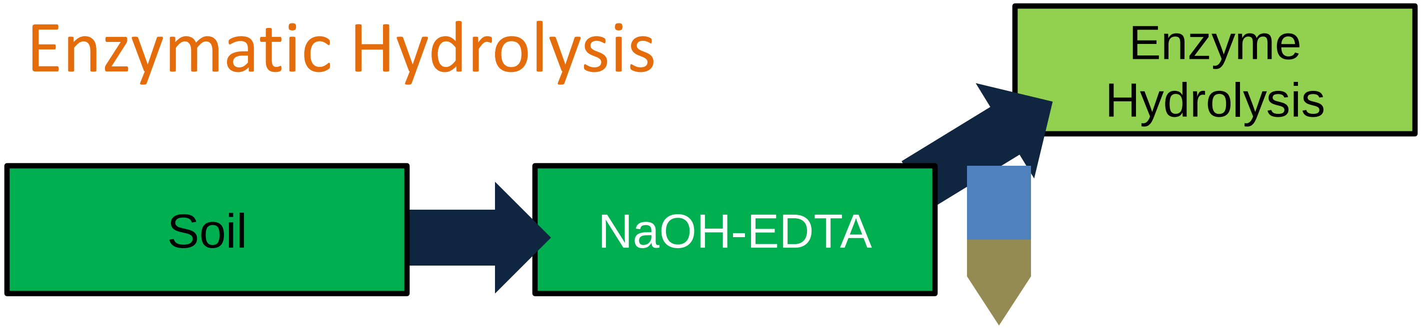
Barbara J. Cade-Menun 2007

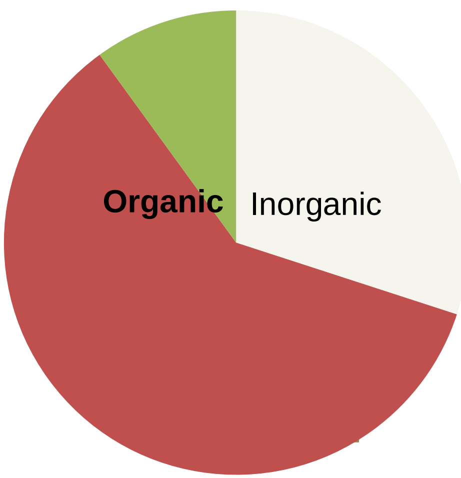
Solution ^{31}P **N**uclear **M**agnetic **R**esonance Spectroscopy



'The Inositol Phosphates in Soils and Manures: Abundance, Cycling, and Measurement'. Giles, CD, BJ Cade-Menun, JE Hill, 2011, Can. J. Soil Sci., *in press*.

Enzymatic Hydrolysis





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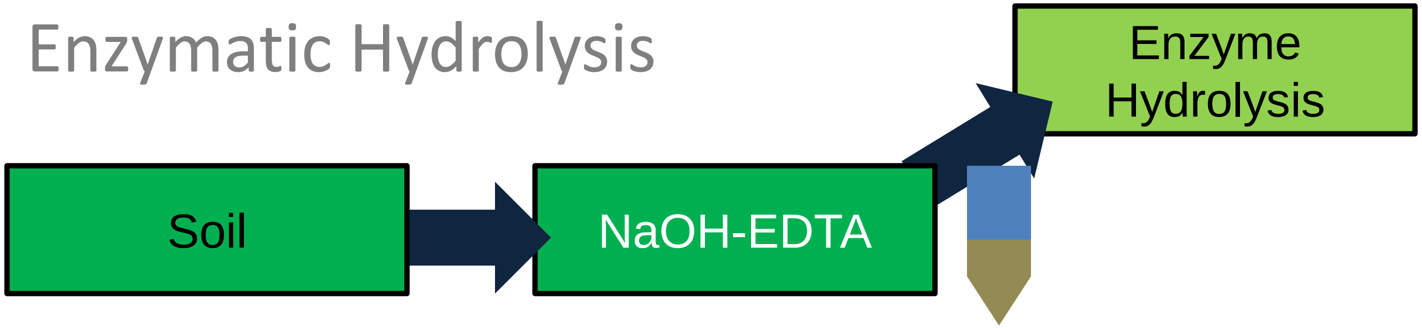
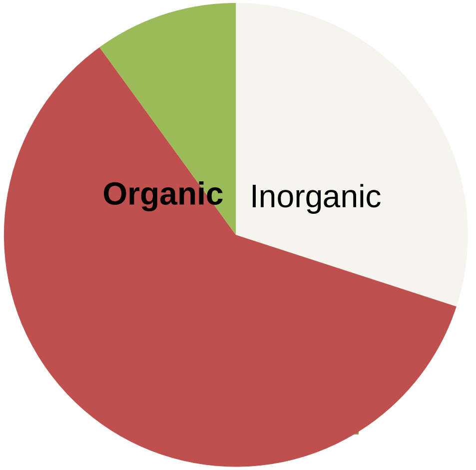
Enzymatic Hydrolysis



PHOSPHATASES



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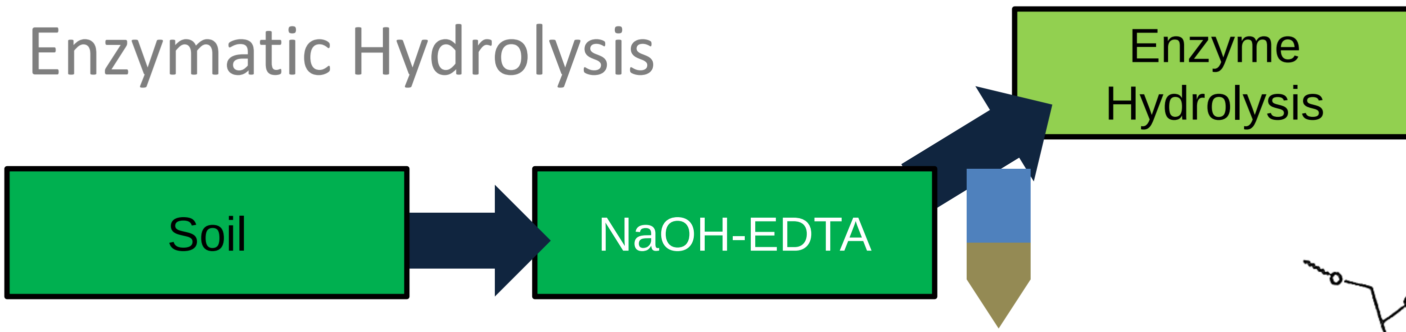
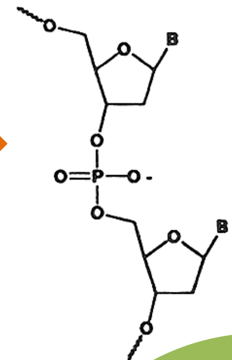
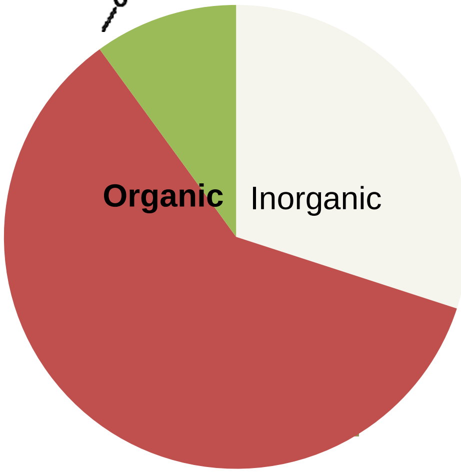
Enzymatic Hydrolysis



PHOSPHATASES

Diesterases →





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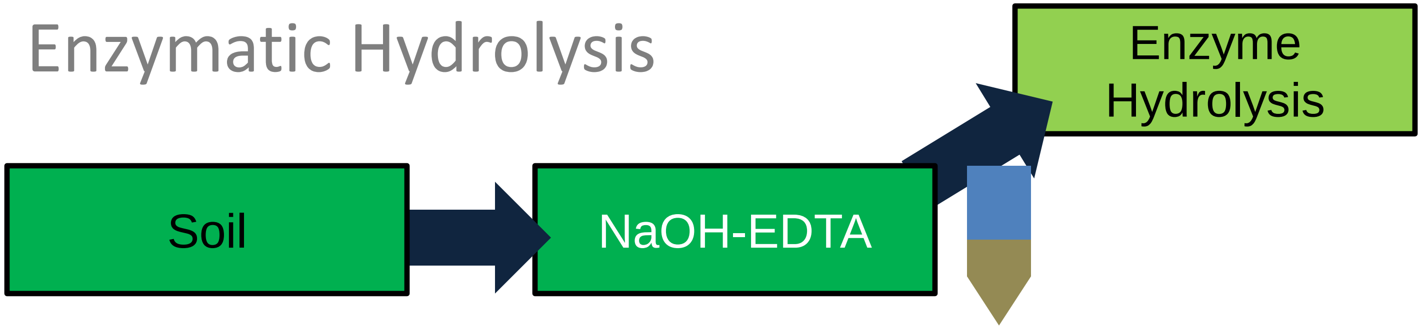
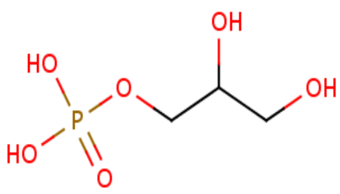
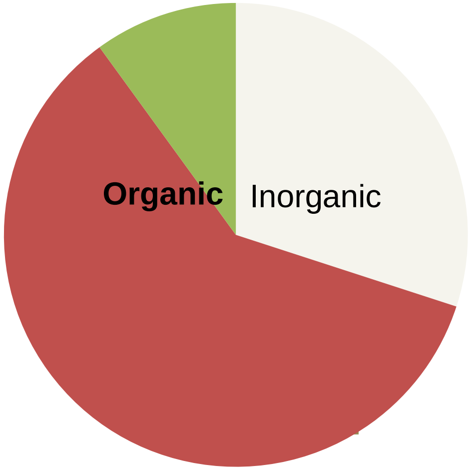
Enzymatic Hydrolysis



PHOSPHATASES

Monoesterases →





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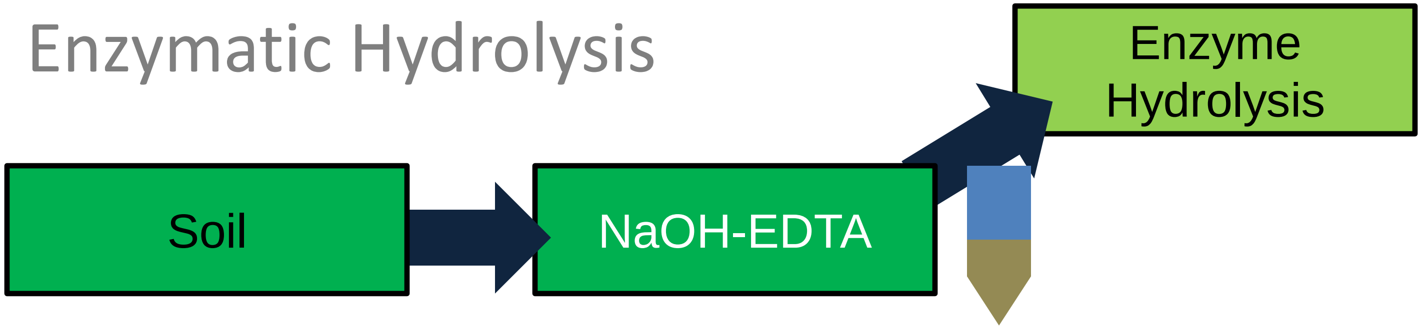
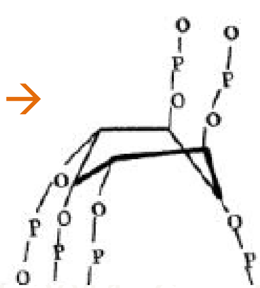
Enzymatic Hydrolysis

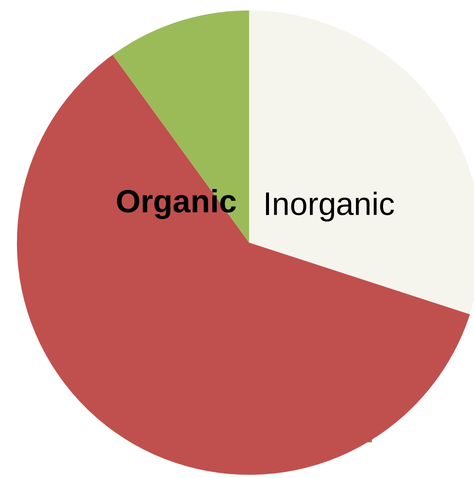


PHOSPHATASES

Monoesterases →

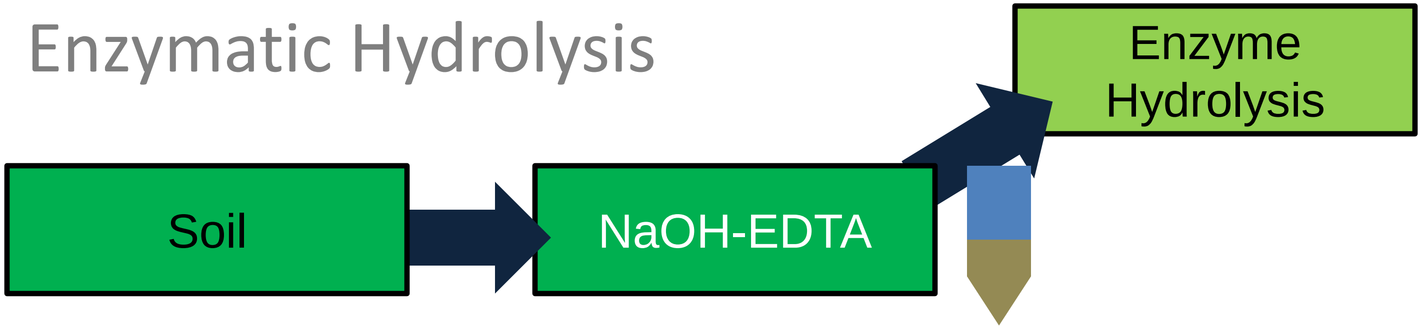
Phytases →





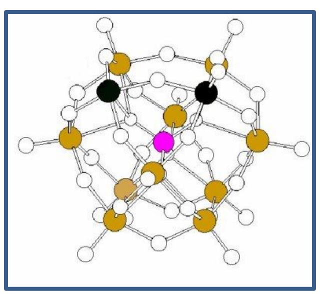
'The Inositol Phosphates in Soils and Manures: … **ng, and Measurement'**. Giles, CD, BJ Cade-Menun, JE Hill, 2011, Can. J. Soil Sci., *in press*.

Enzymatic Hydrolysis

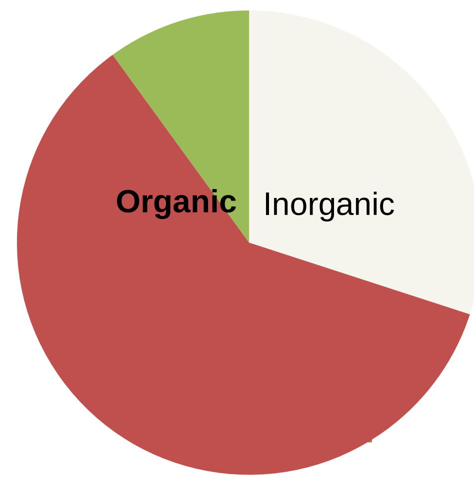


Diesterases → P

PHOSPHATASES



Monoesterases → P



Phytases → P

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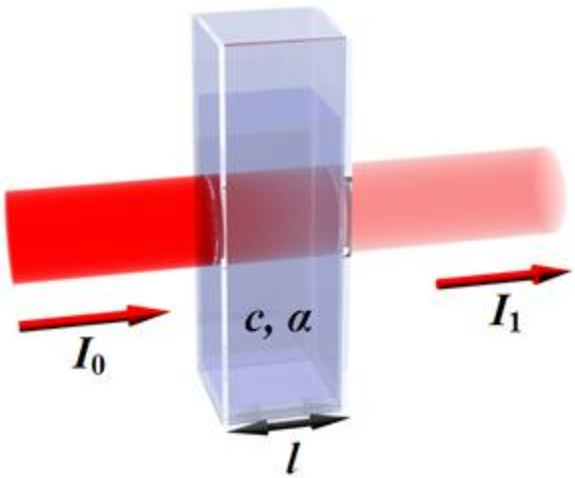
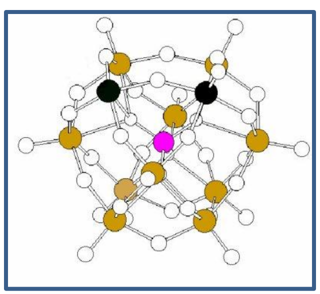
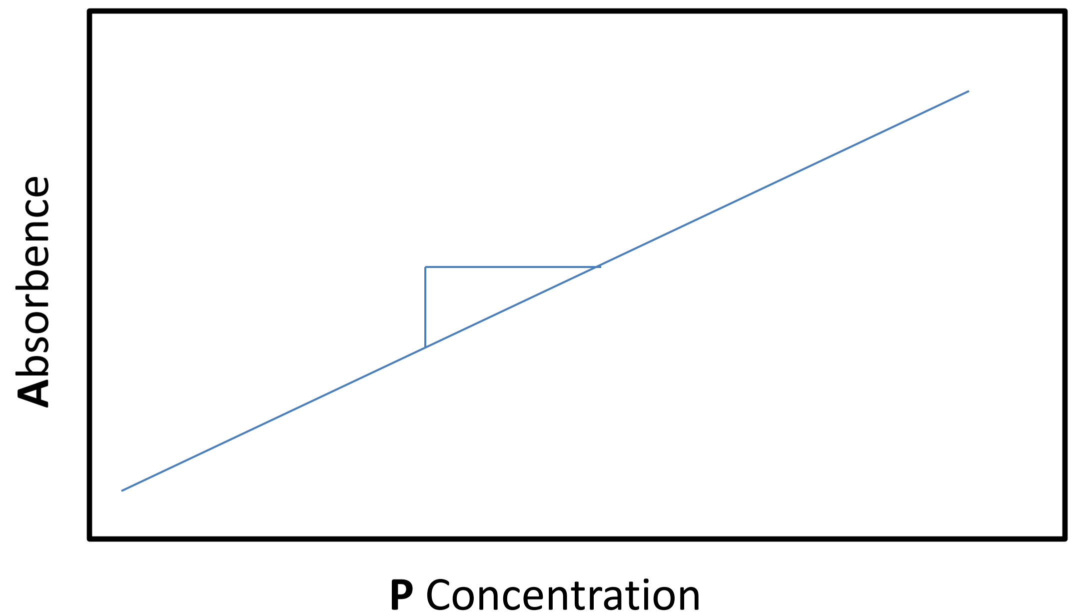
Enzymatic Hydrolysis



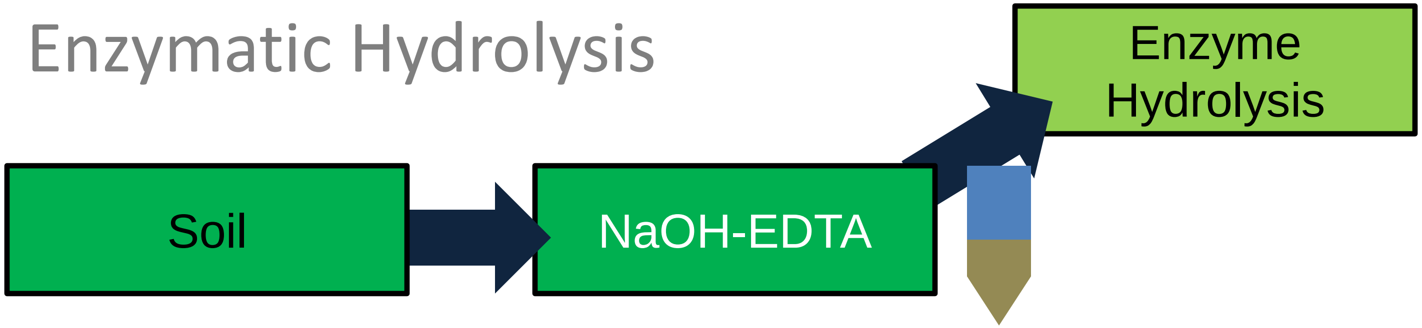


Beer-Lambert

A = ε l c

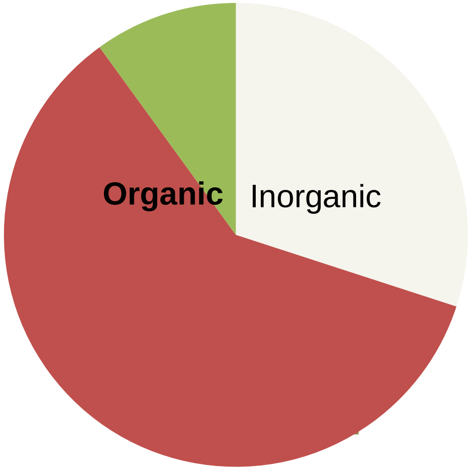


Enzymatic Hydrolysis



ESTIMATES Enzyme-Labile P

→ MEASURES Specific P classes



Today

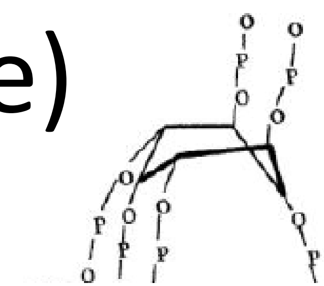
Soil **Organic P**

Forms/Sources

Behavior in Soils

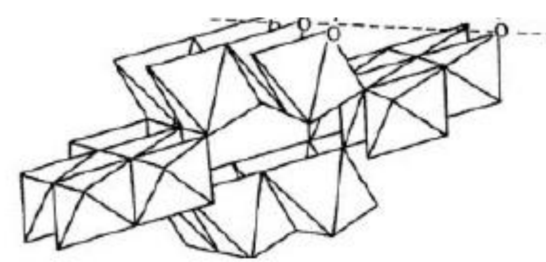
Measurement

DESORPTION (e.g. phytate)

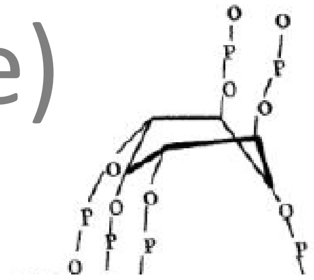


Mechanisms

Kinetics

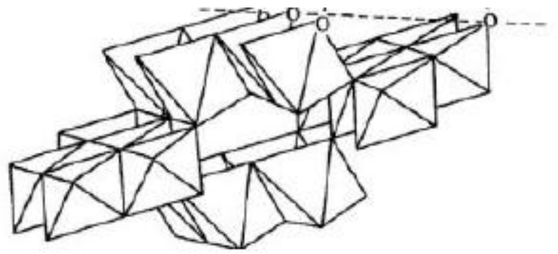


DESORPTION (e.g. phytate)

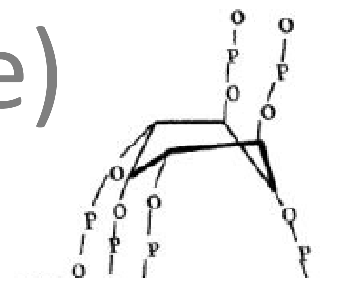


☹

Negligible under environmental conditions…

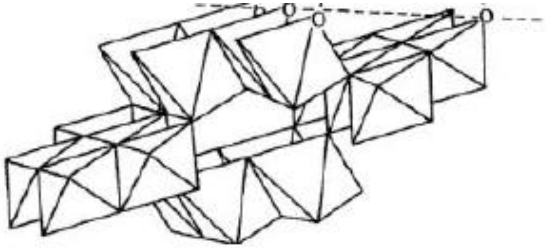


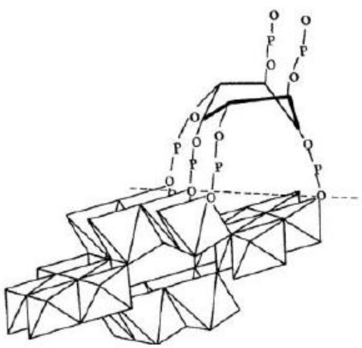
DESORPTION (e.g. phytate)



☺

Possible with **Organic Anions/**Siderophores**…**



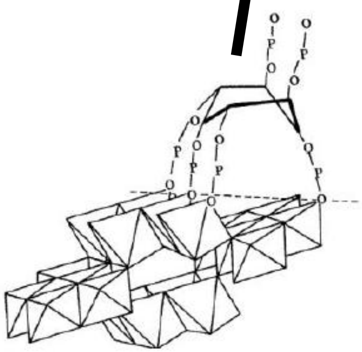


Mechanisms….

P

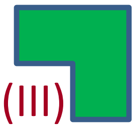
Fe (III)

Chelation

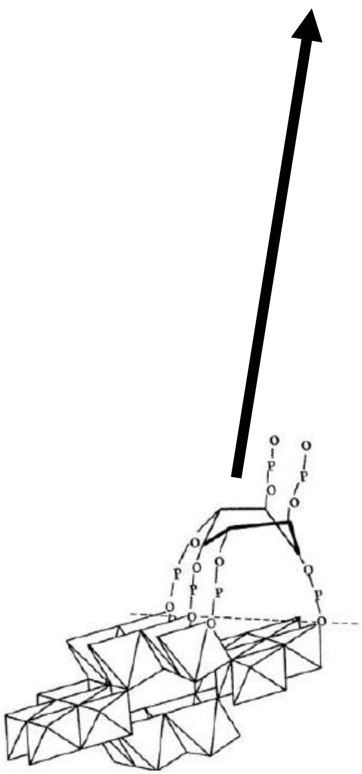


Mechanisms….

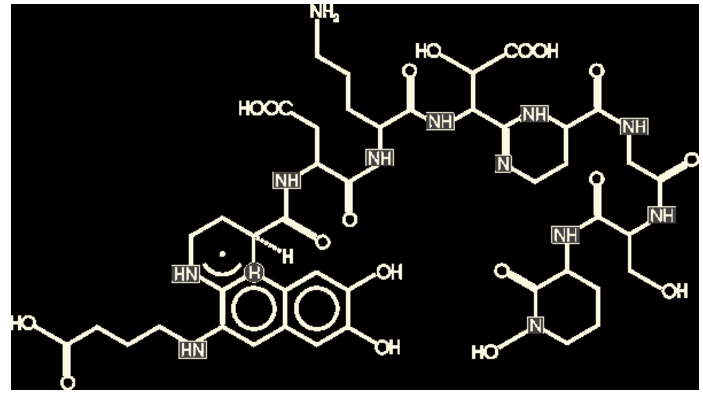
P

Fe (III) 

Chelation

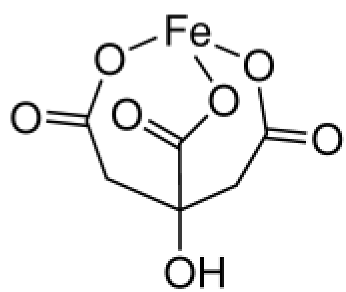


Mechanisms….

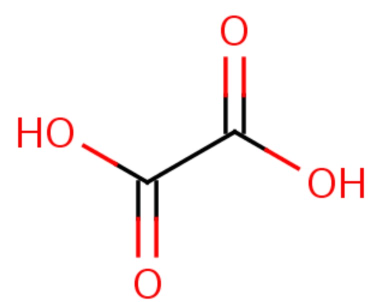


- Bacterial **Siderophores**

- **Citrate**

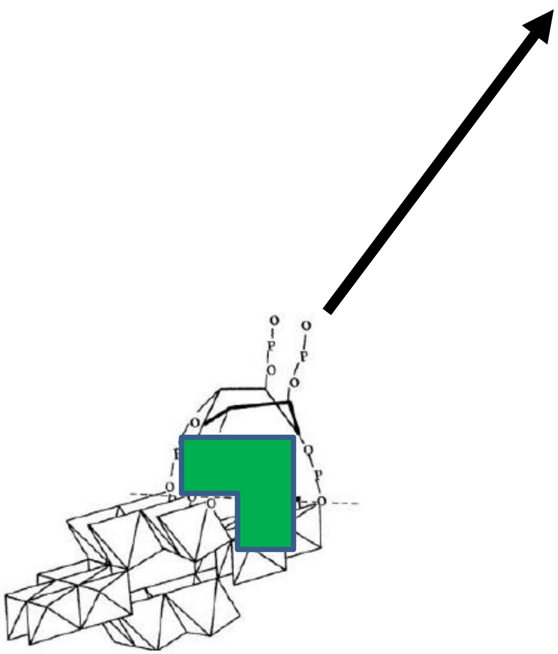


- **Oxalate**



P

Competitive Displacement



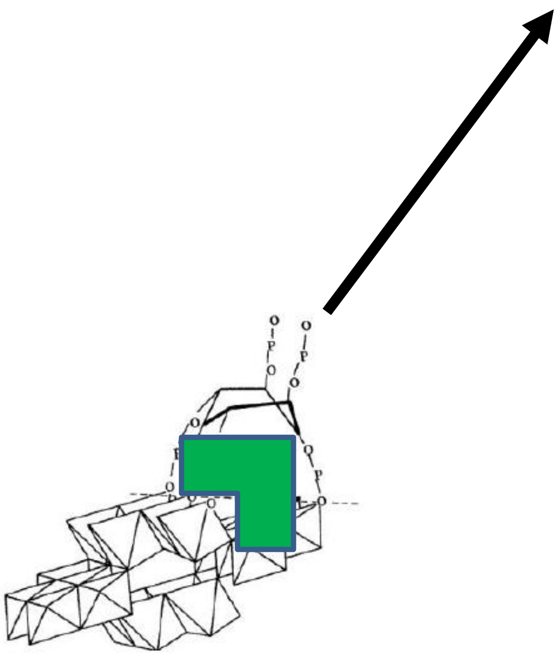
Mechanisms….

P

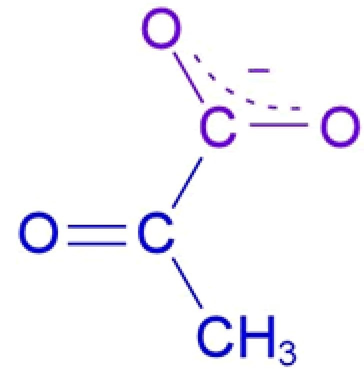
Competitive Displacement

Depends on the **DISSOCIATION CONSTANTS (*K*)**

metal-**organic anion**
metal-**siderophore**



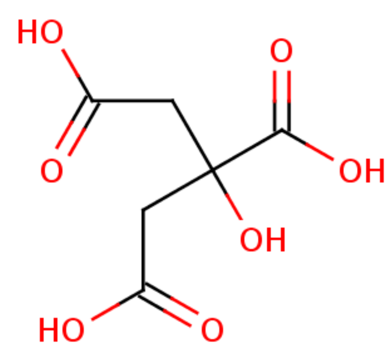
Mechanisms….



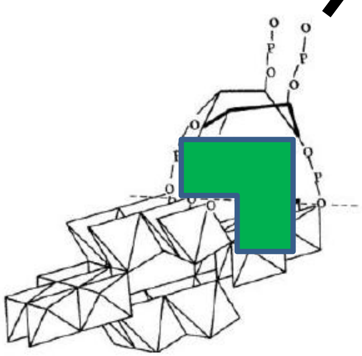
pyruvate

P

Competitive Displacement



Citrate

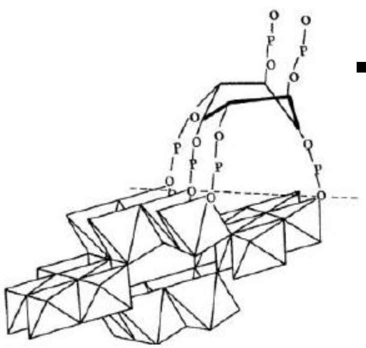


Mechanisms….

Electron Donor

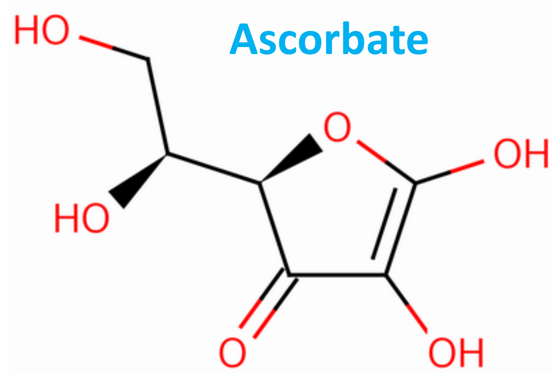
P

Fe (III) → Fe (II)

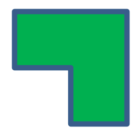


Reductive Dissolution

Mechanisms….

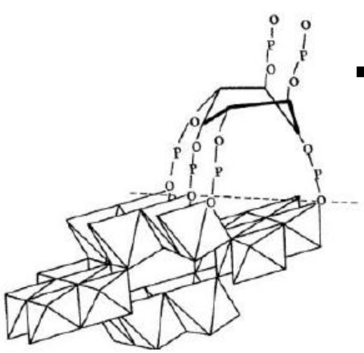


Electron Donor



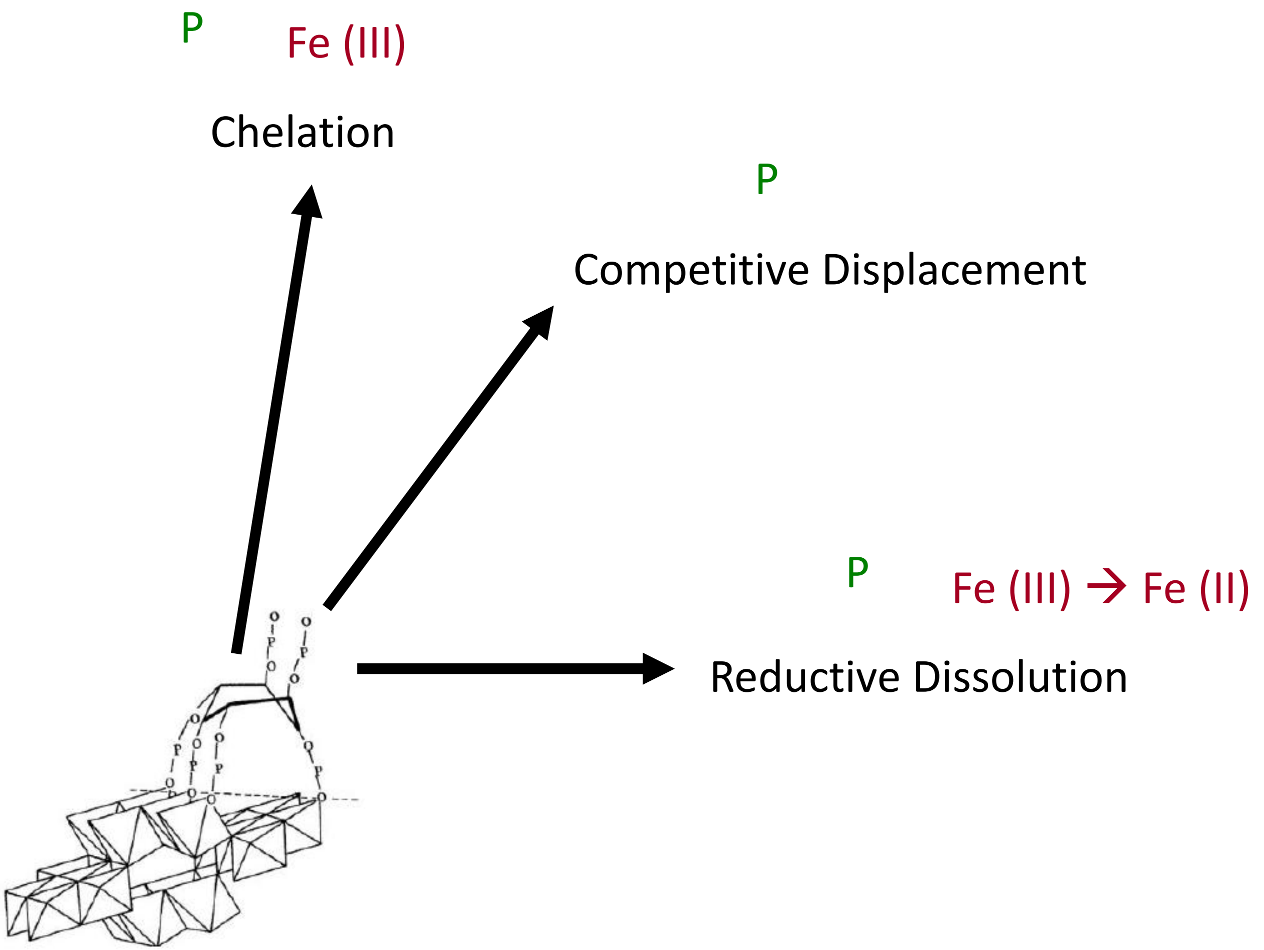
P

Fe (III) → Fe (II)



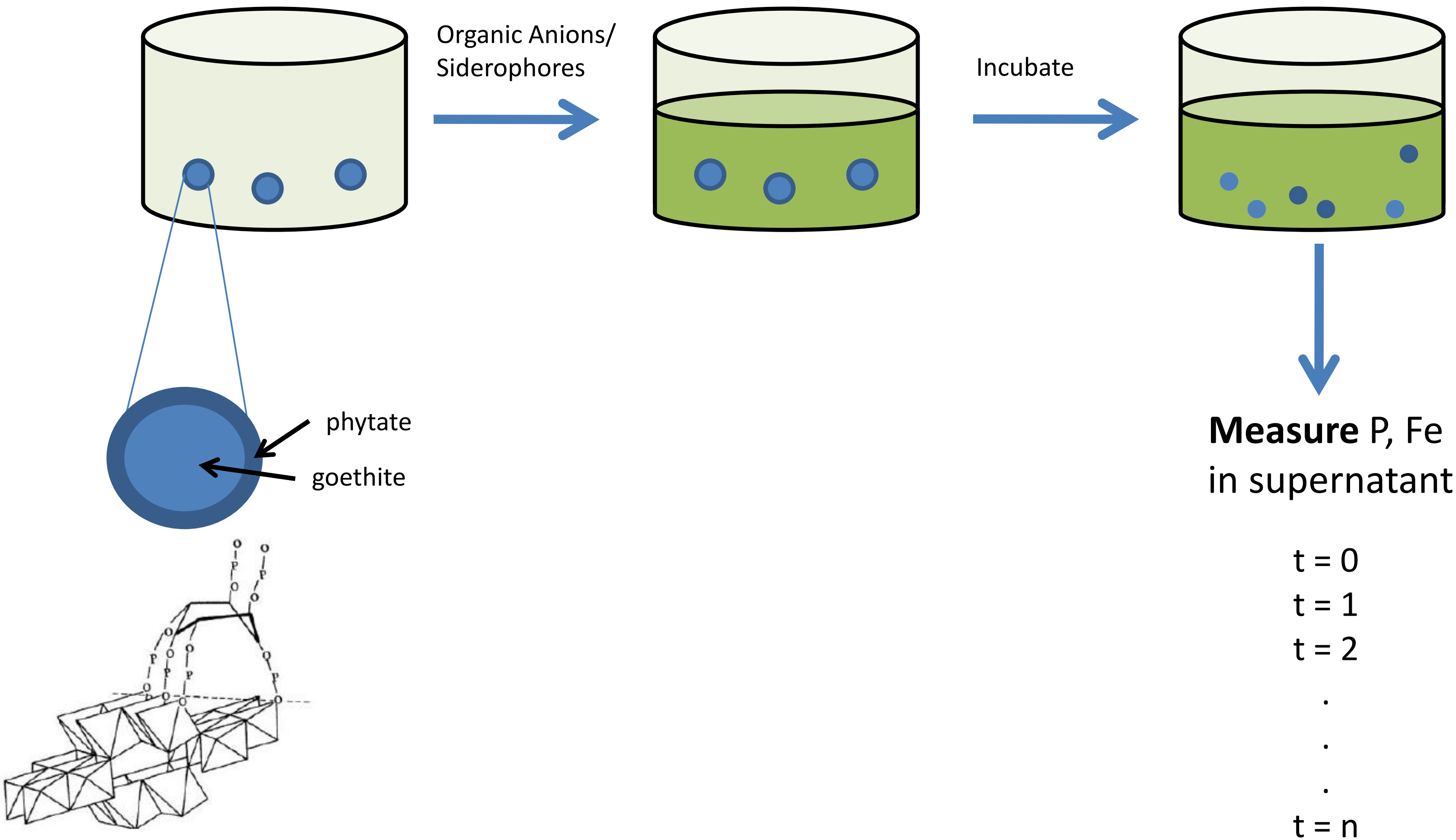
Reductive Dissolution

Mechanisms….


P
Fe (III)
Chelation
P
Competitive Displacement
P
Fe (III) → Fe (II)
Reductive Dissolution

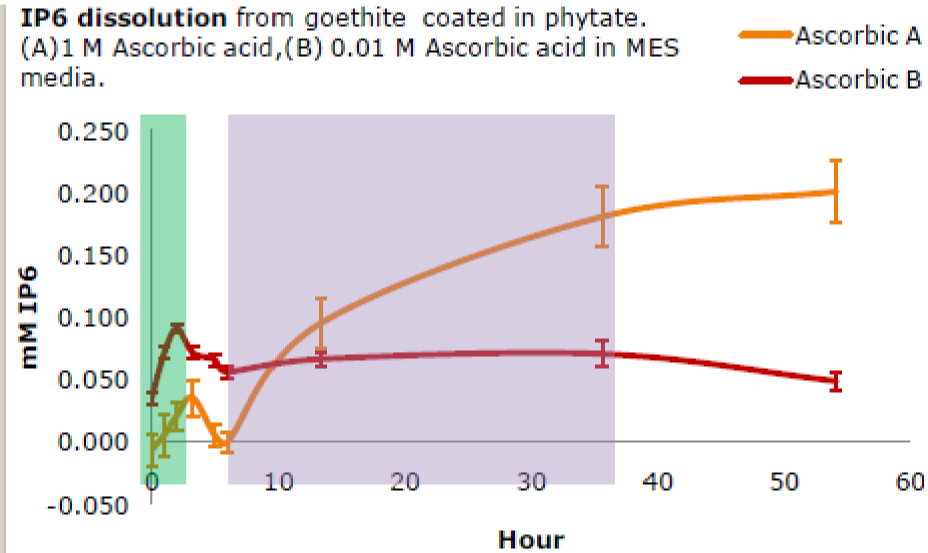
Mechanisms….

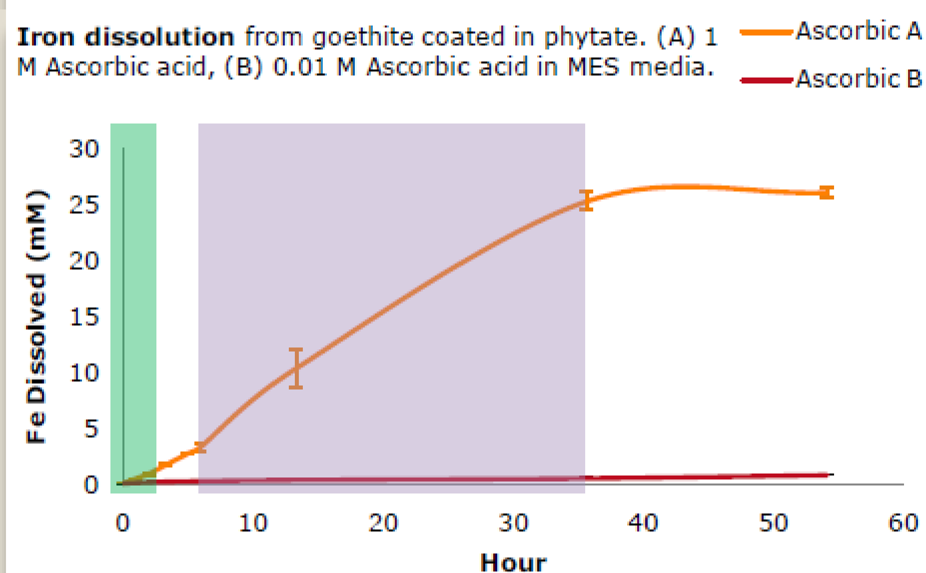
Desorption Kinetics



Methods….

Desorption Kinetics



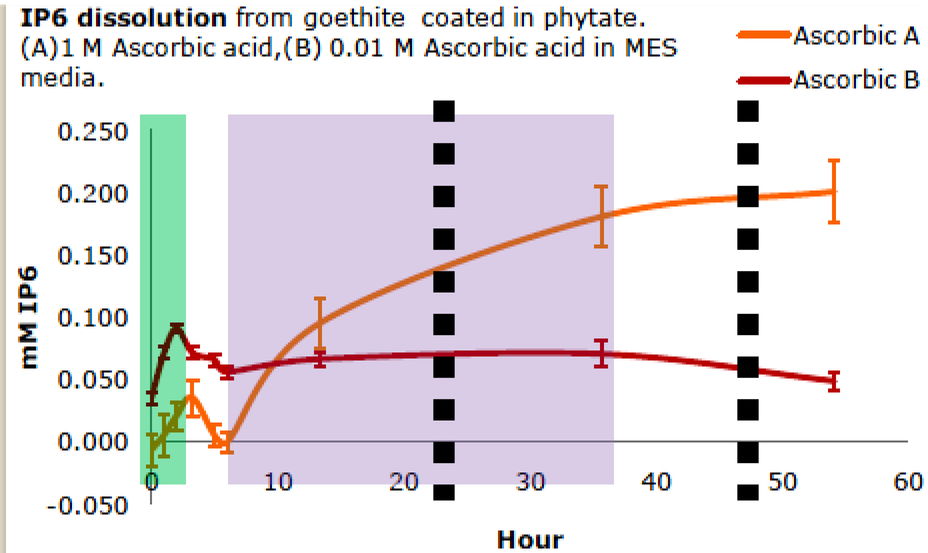


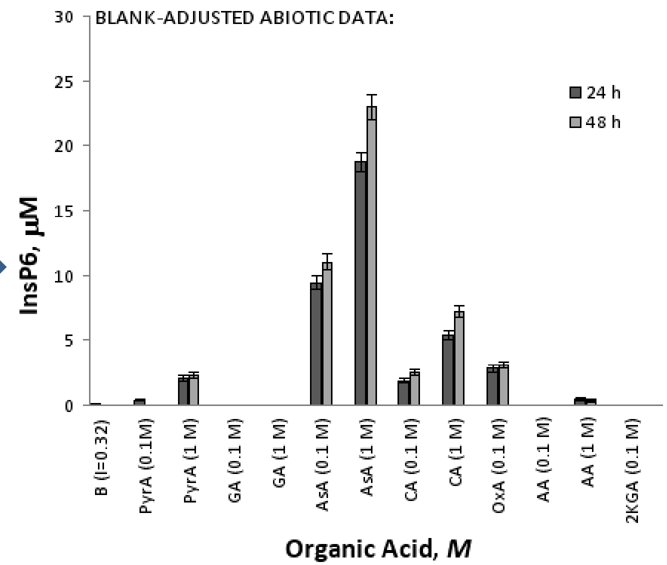
Average Rate of Desorption in **0-4 h** **(mmol L^{-1} h^{-1})**	
InsP6	0.01
Fe	0.49

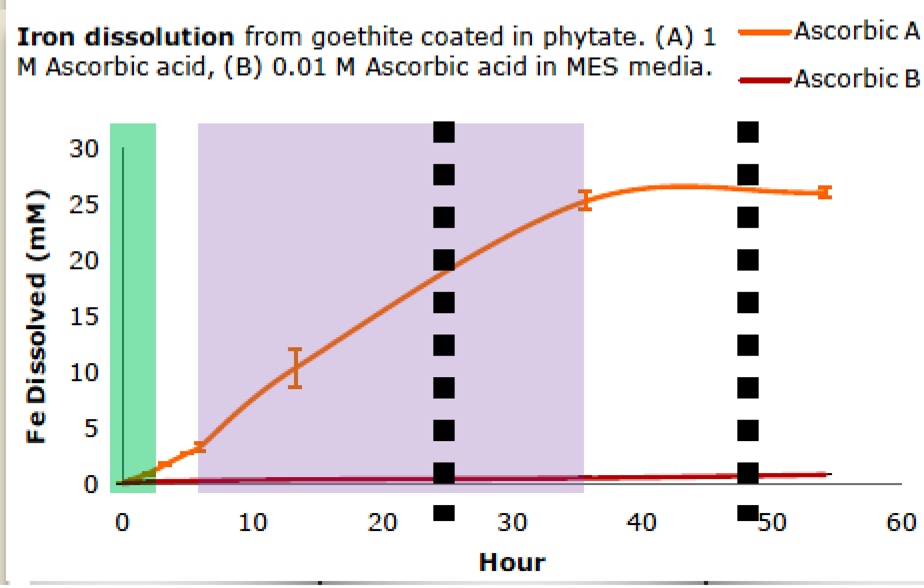
Average Rate of Desorption in **6-37 h** **(mmol L^{-1} h^{-1})**	
InsP6	0.004
Fe	0.74

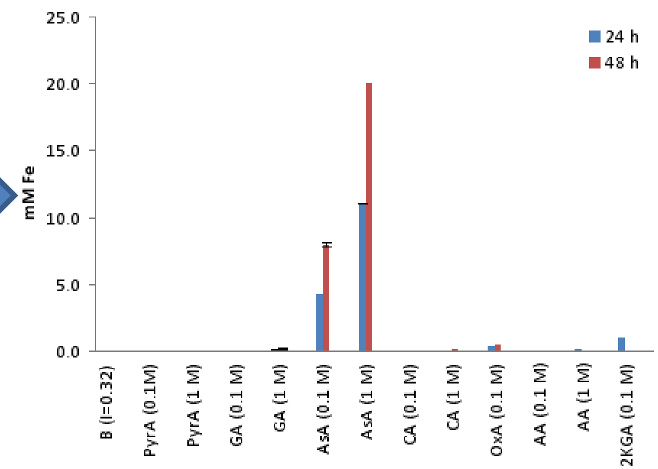
Ascorbate Example….

Desorption Kinetics



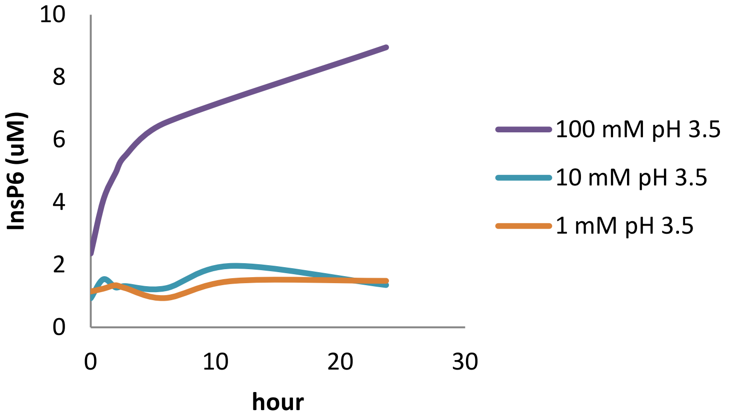


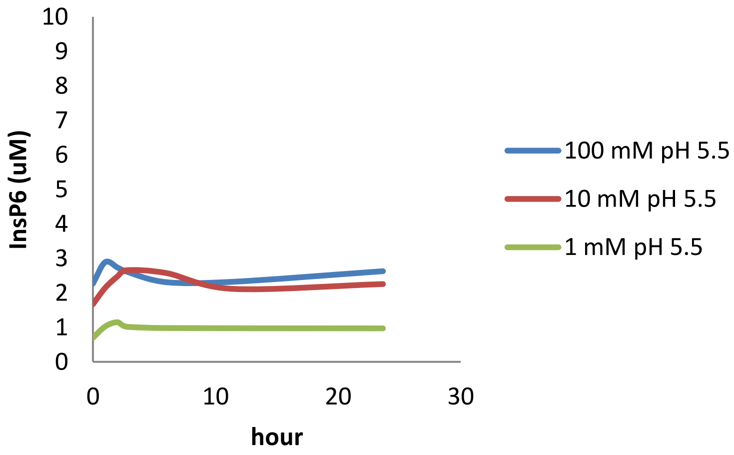




Ascorbate Example….

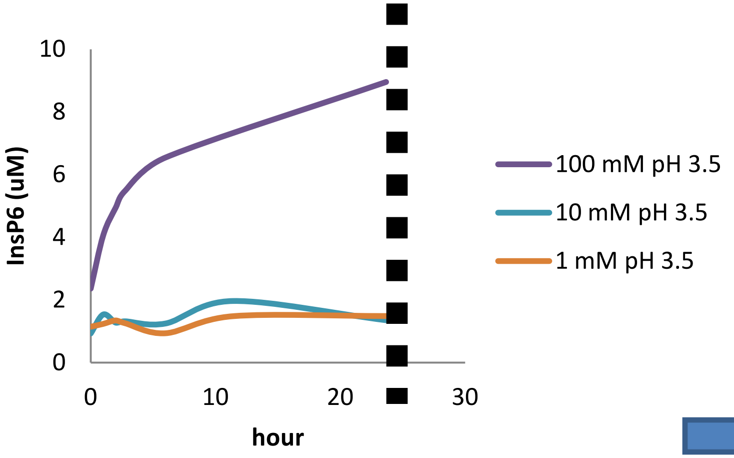
Influence of pH and Oxalate Concentration

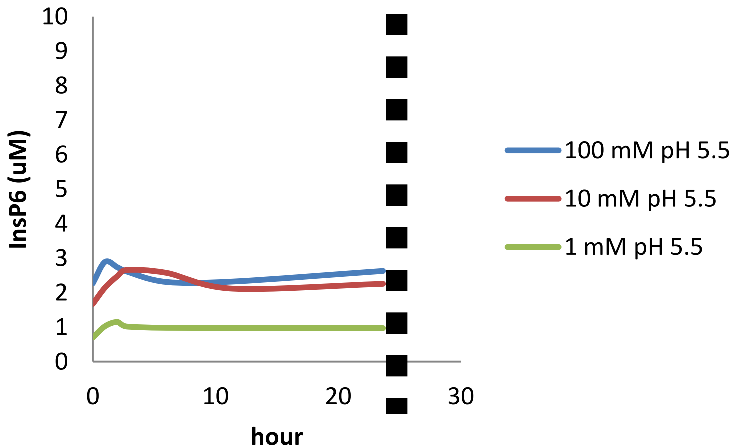


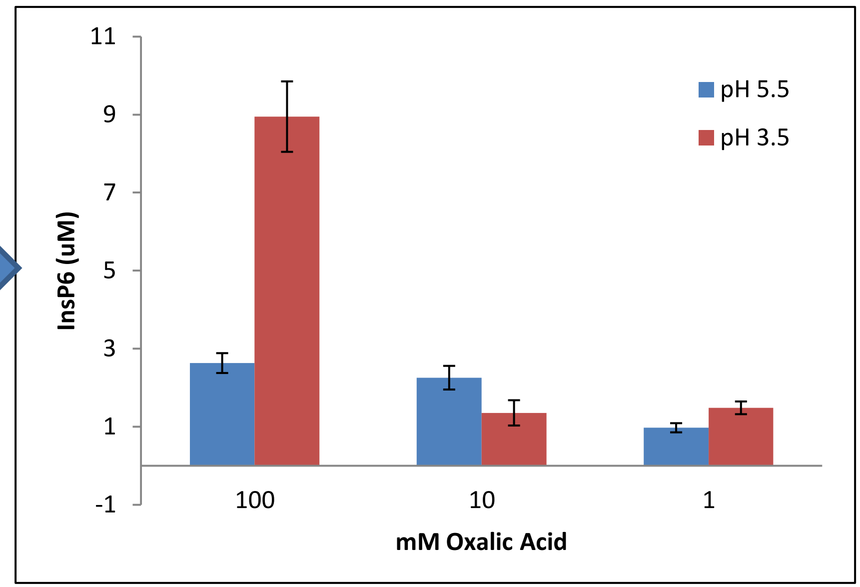


Oxalate Example….

Influence of pH and Oxalate Concentration

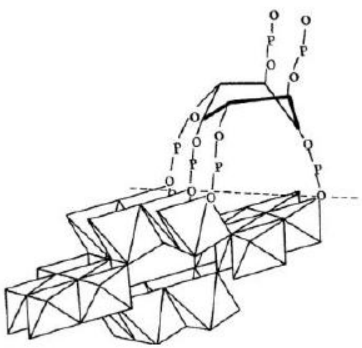






Oxalate Example….

cdgiles@uvm.edu
Perkins 203



Questions? Comments? Concerns?