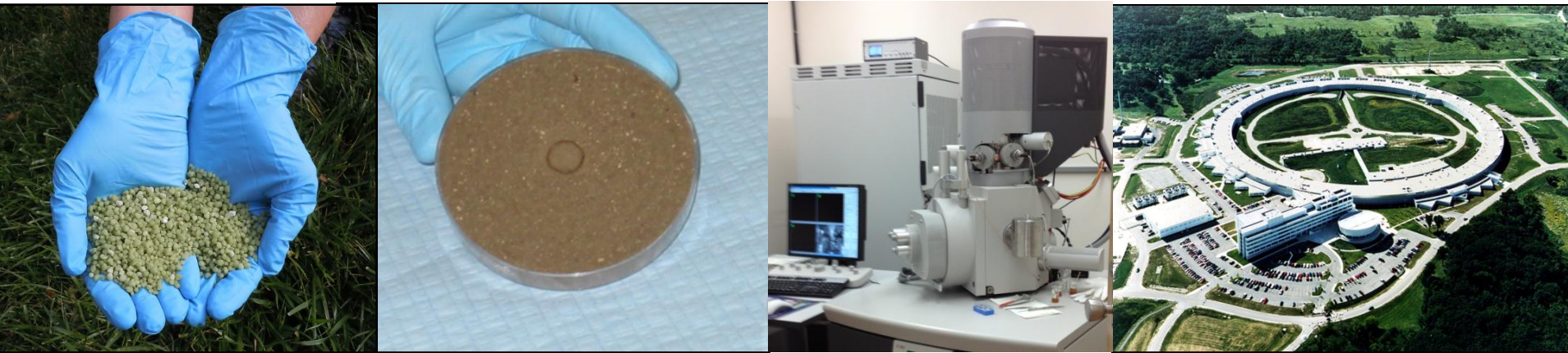


Mobility, Availability and Reaction Products of P from MAP, DAP and APP Fertilizers



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and
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Department of Agronomy
Kansas State University

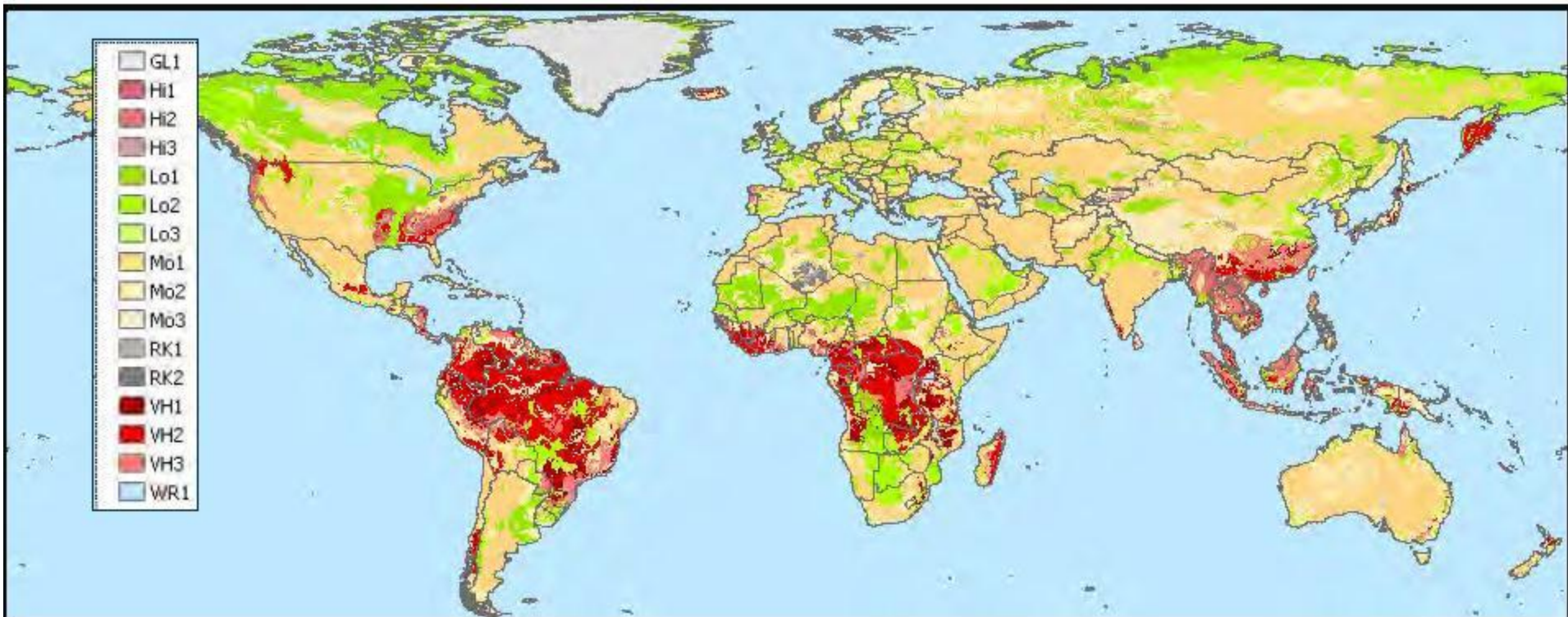
Introduction

- A high proportion of applied P is rapidly converted to insoluble phosphates that plants have virtually no access
- These transformations mainly depend on
 - fertilizer sources
 - type of soil
 - soil moisture conditions
- Understanding major reaction products of fertilizer P in different soil types and their solubility may help designing better suited fertilizer formulations for different soil types

Objectives

- To understand mobility, availability and reactions products of P from MAP, DAP and APP fertilizers in different soils
- To integrate mobility, wet chemical data and reaction products to understand their performance in different soils

How widespread or distributed are soil containing high P fixing capacity?



International Soil Reference and Information Centre, 2011

❖ There is a great need in increasing P availability on these enhanced P fixing soils.

Soils

Six soils

1. Oxisol, Brazil
2. Calcareous soil, Idaho
3. Andisol, Ecuador
4. Calcareous soil, South Australia
5. Ultisol, Sri Lanka
6. Calcareous or acid soil, KS

Methodology

Treatments:

- ❖ Control
- ❖ MAP (11-52-0 N-P₂O₅-K₂O)
- ❖ DAP (18-46-0 N-P₂O₅-K₂O)
- ❖ APP (11-37-0 N-P₂O₅-K₂O)
- ❖ MAP + Fertilizer Enhancement Product (FEP)
- ❖ DAP + FEP
- ❖ APP + FEP



Petri dish size: 87 mm

MAP: 42 mg granules per dish; DAP: 43.4 mg granule; APP: ~40 μ L

N was balanced by Urea

Methodology (cont.)

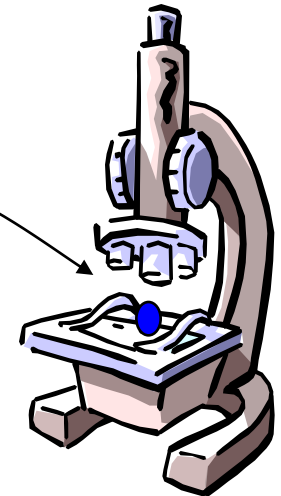
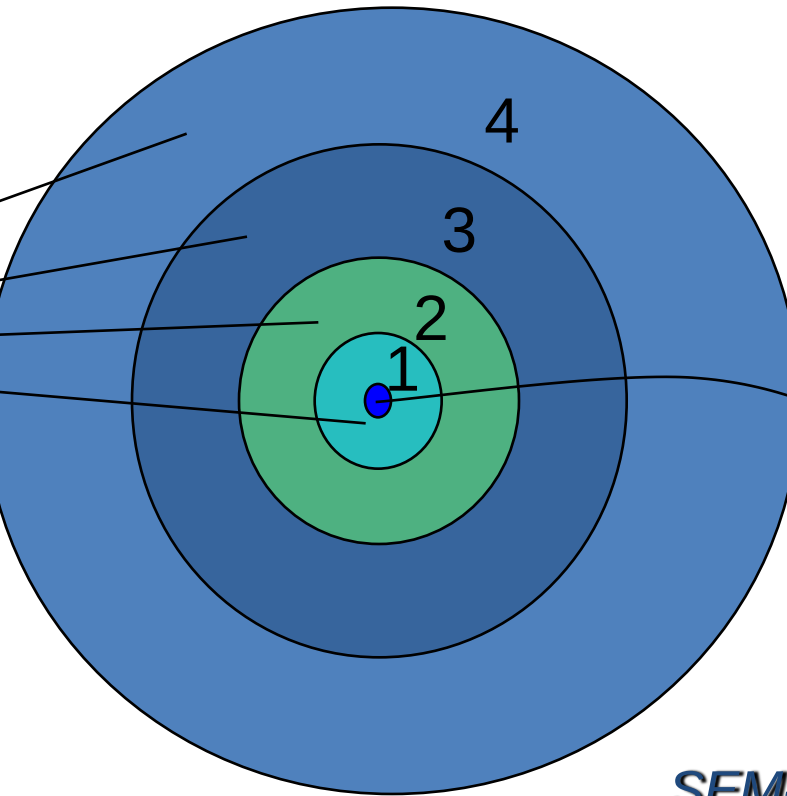
Soil Sampling and Analyses

Diffusion of P from
fertilizers

Reaction products
in granules

Samples

- pH
- Total P
- Resin P
- Reaction products (XANES)



- SEM-EDX and/or XRD
- Changes in structure
 - In situ elemental analyses

43.5 mm

25

13.75

7.5

Methodology (cont.)

Wet chemical based analyses

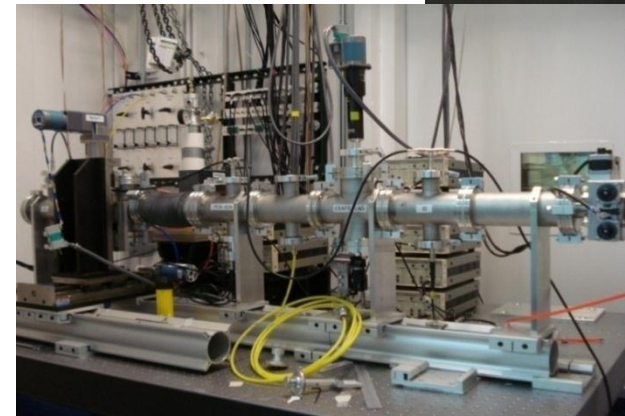
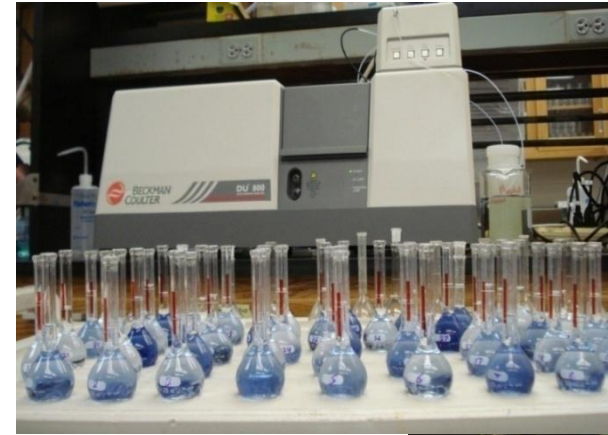
- Soil pH (1:5 soil:water)
- Total P –Aqua-regia digestion
- Resin extractable P

P Speciation and granule observations

- X-ray Absorption Near Edge Structure Spectroscopy (XANES)

Data analysis: Principal Component Analysis (PCA)
followed by Linear combination fitting-LCF

- Scanning Electron Microscopy- Energy Dispersive X-ray Analysis

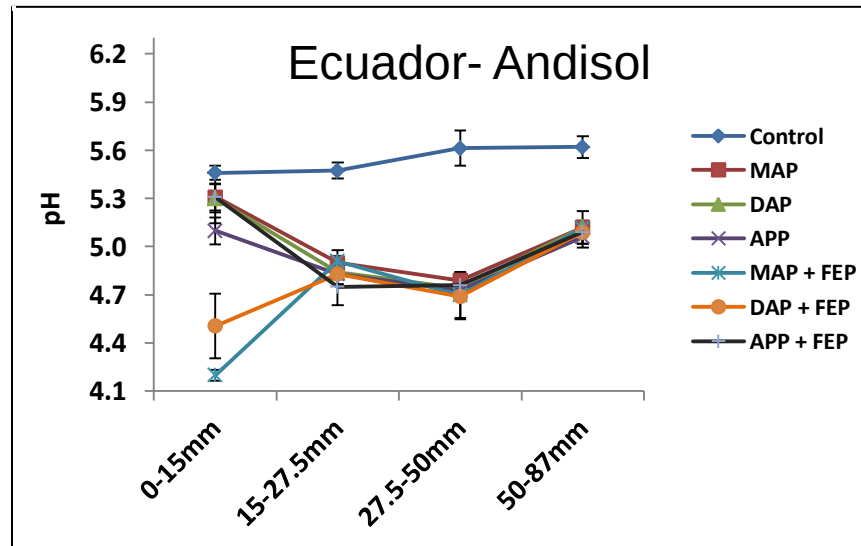
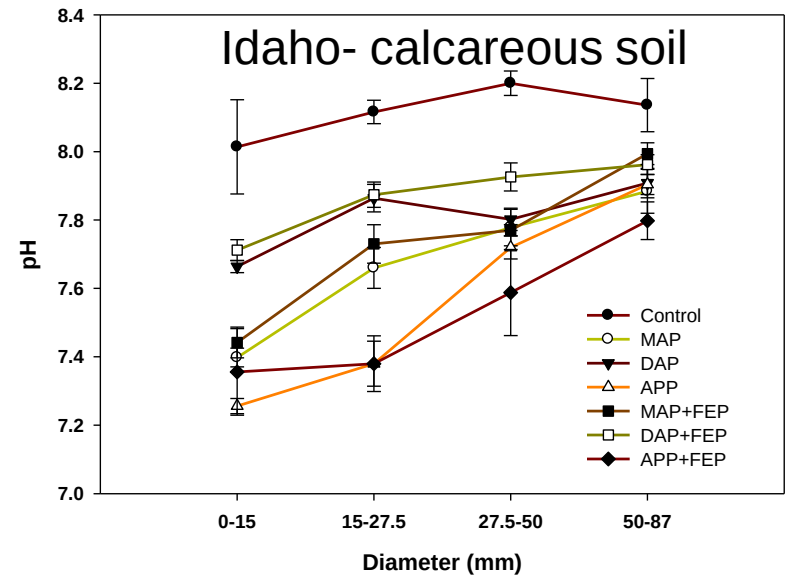
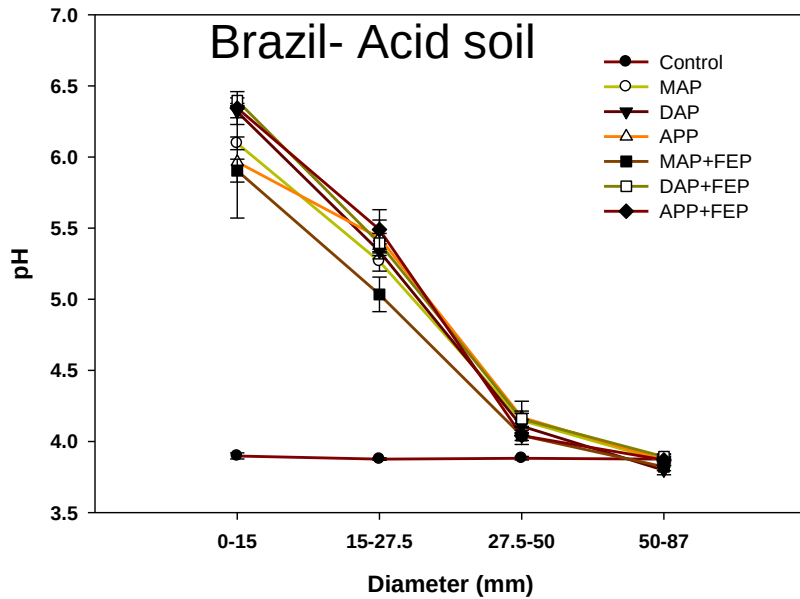


Selected Soil Properties

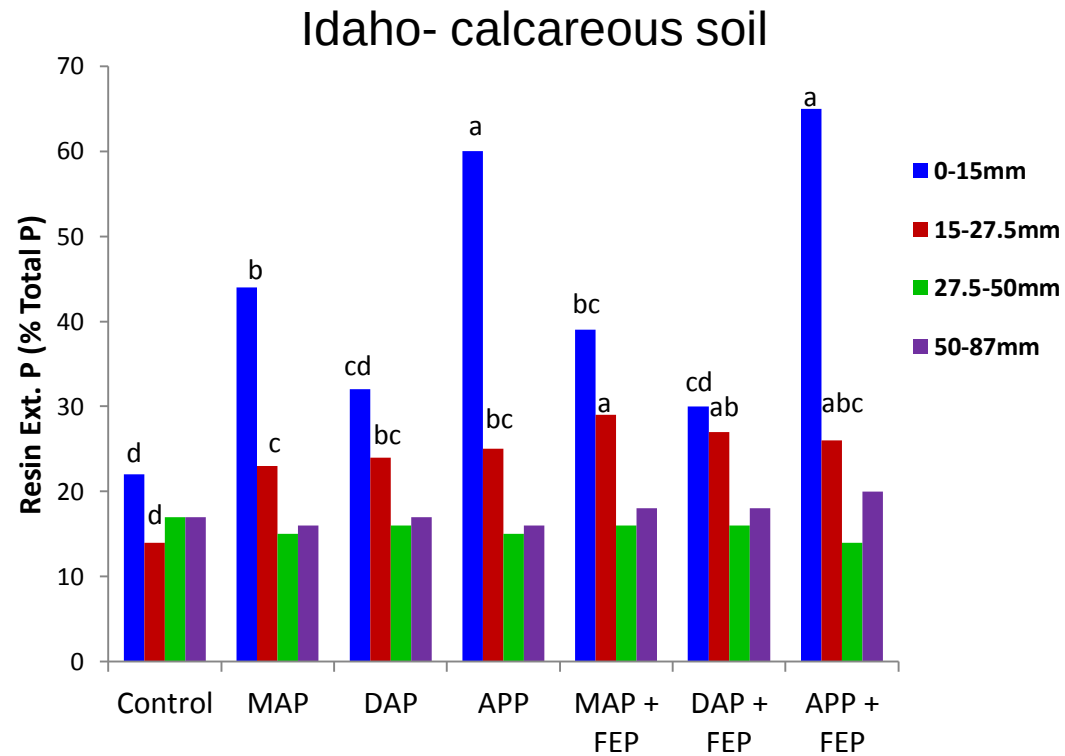
Sample ID	pH	CEC	OM	Ext. Ca	Ext. Fe	Ext. Al	Total P
	(H ₂ O)	cmol _c /kg	%	----- mg/kg -----			
Brazil soil	4.3	12.4	3.7	49	52.9	79.5	237
Idaho soil*	8.0	19.6	0.6	3376	2.4	n.d.	468
Ecuador soil	5.5	16.5	5.4	565	37.6	6.5	447

* CaCO₃ = 7.4%

Soil pH

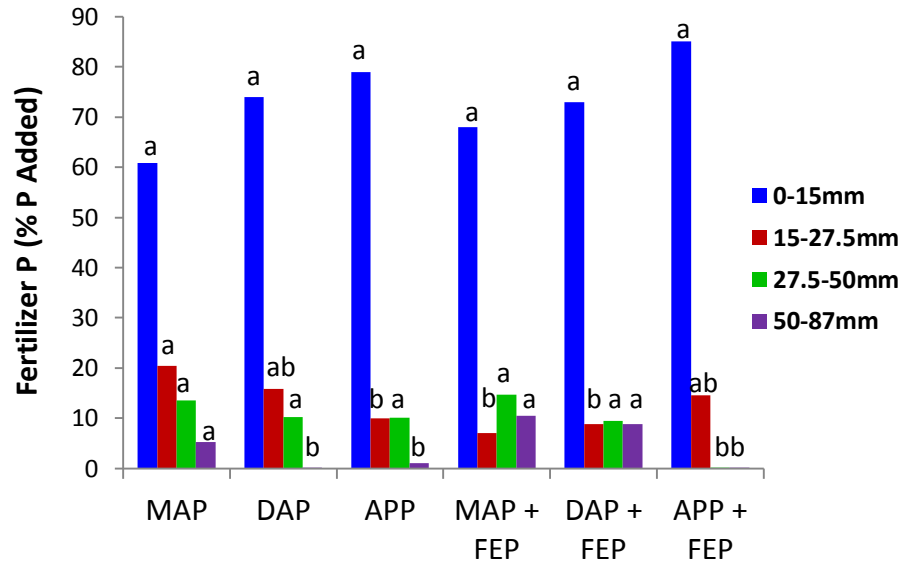


Resin P

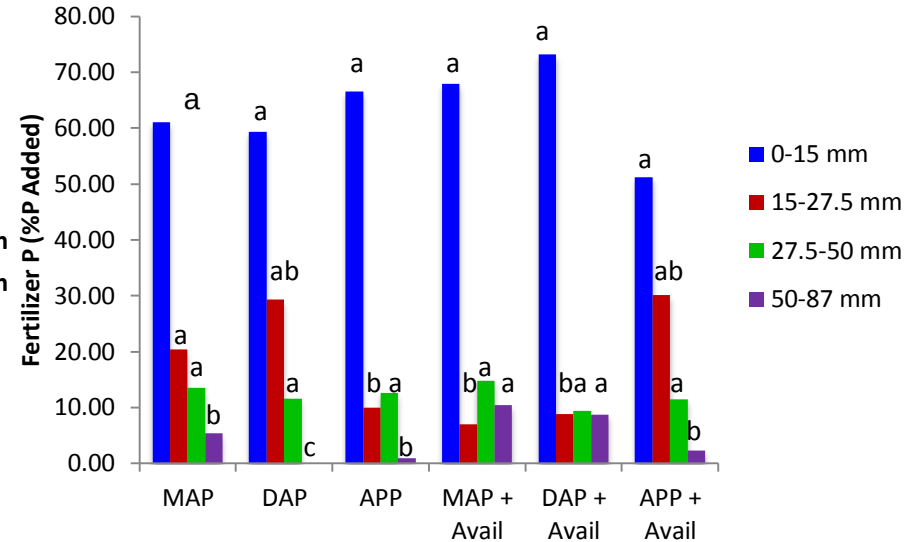


Fertilizer P Distribution

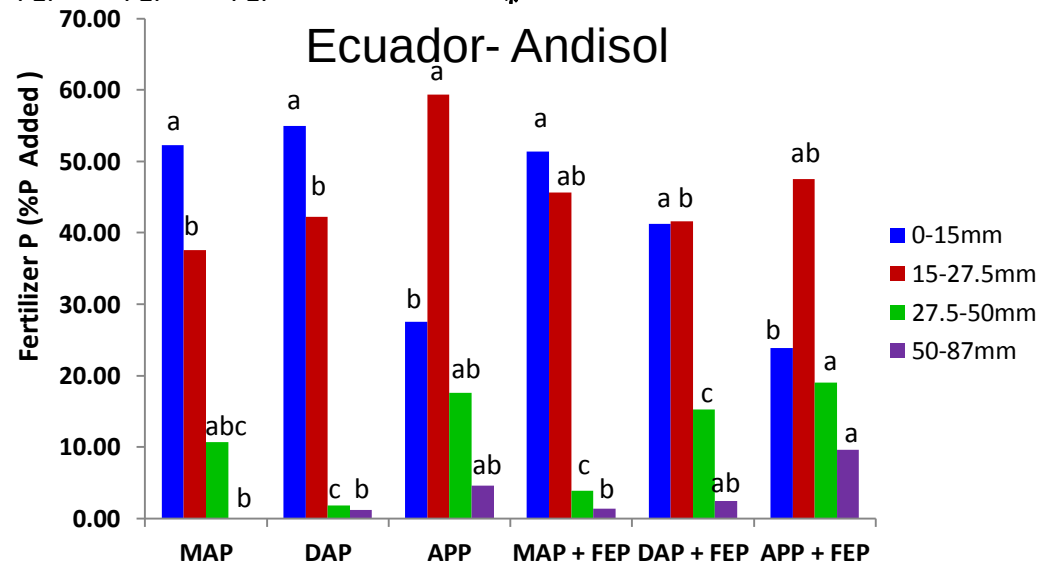
Brazil- Acid soil



Idaho- calcareous soil



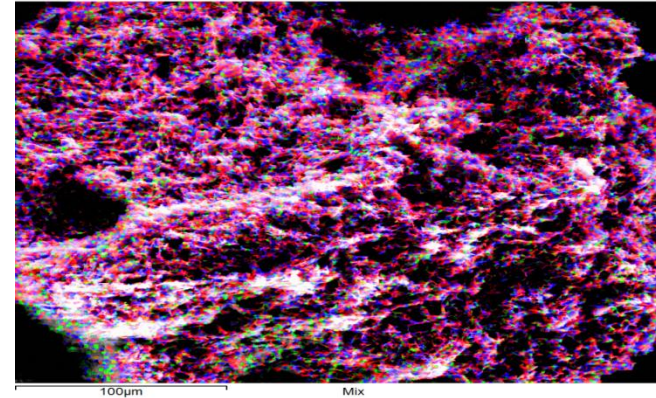
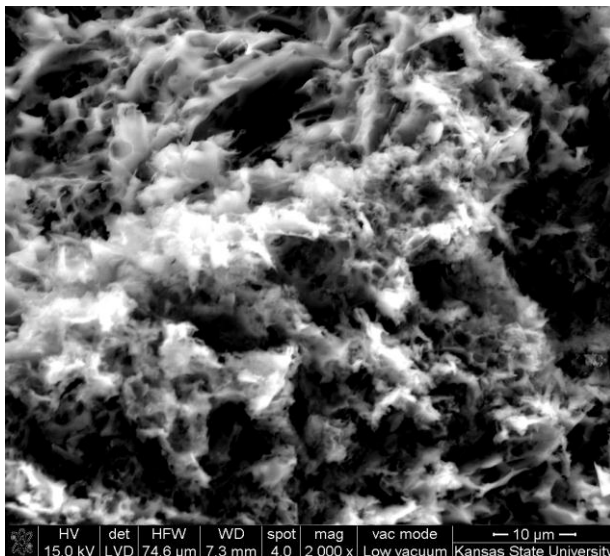
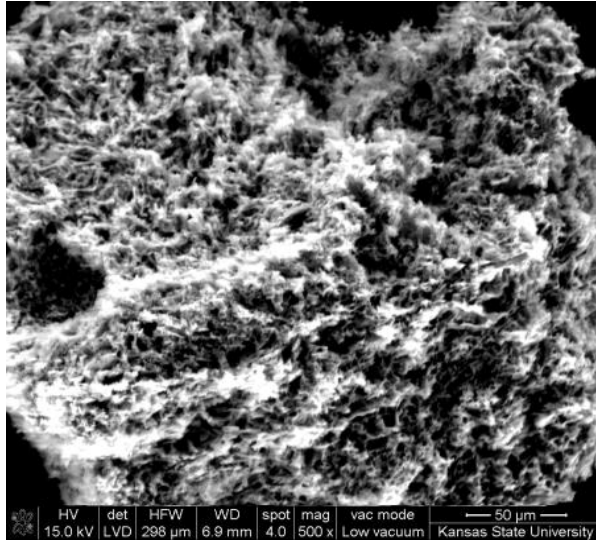
Ecuador- Andisol



P Fertilizer Treatment

MAP Granule- Incubated 3 days

Ecuador Soil

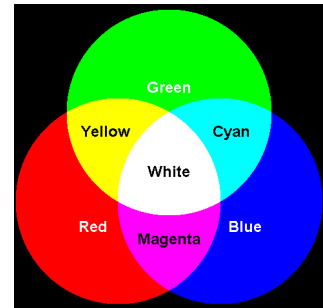


Elemental map-EDS

P=Red

Al=blue

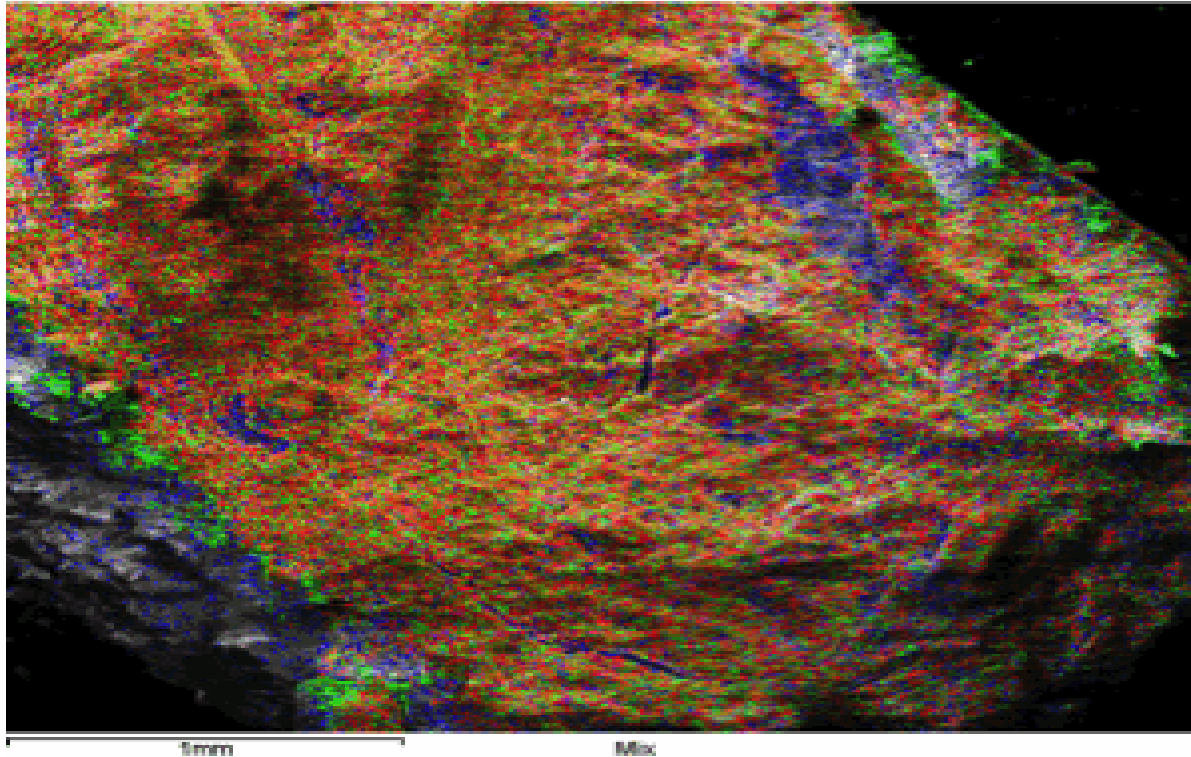
Fe=Green



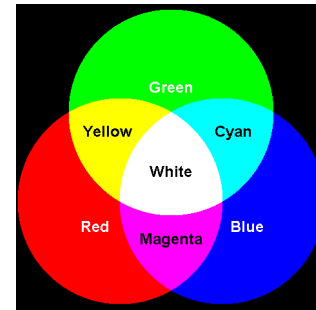
Element- Wt %

N	-----
Al	4.07
P	12.51
Fe	3.86

MAP Granule- Incubated 5 wk Ecuador Soil



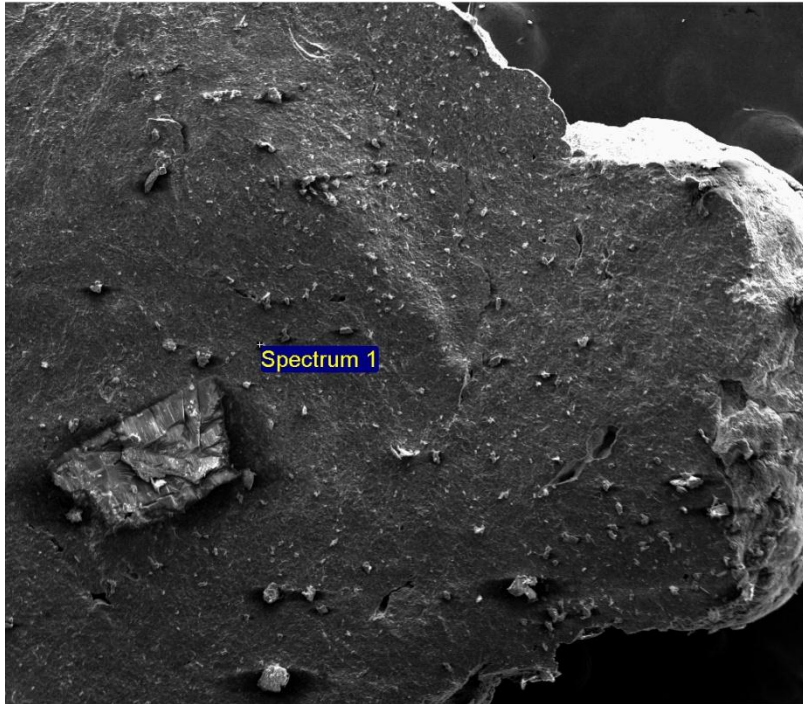
Elemental map-EDS
P=Red
Al=Green
Fe=Blue



Element- Wt %	
N	-----
Al	4.55
P	11.81
Fe	4.54

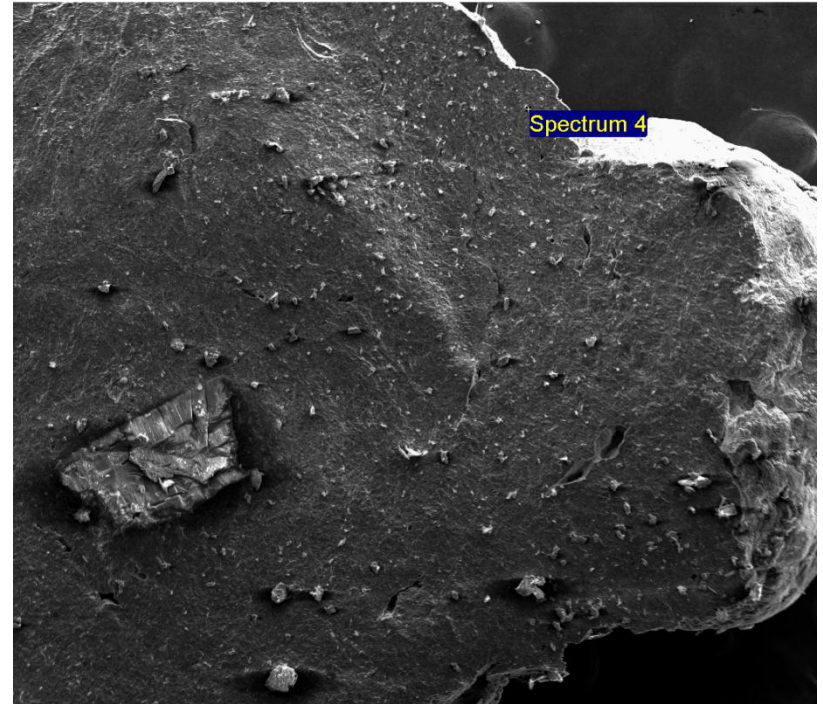
Zn, Re, Mg
~ 1- 1.5 %

DAP Granule- Original



1mm

Electron Image 1



1mm

Electron Image 1

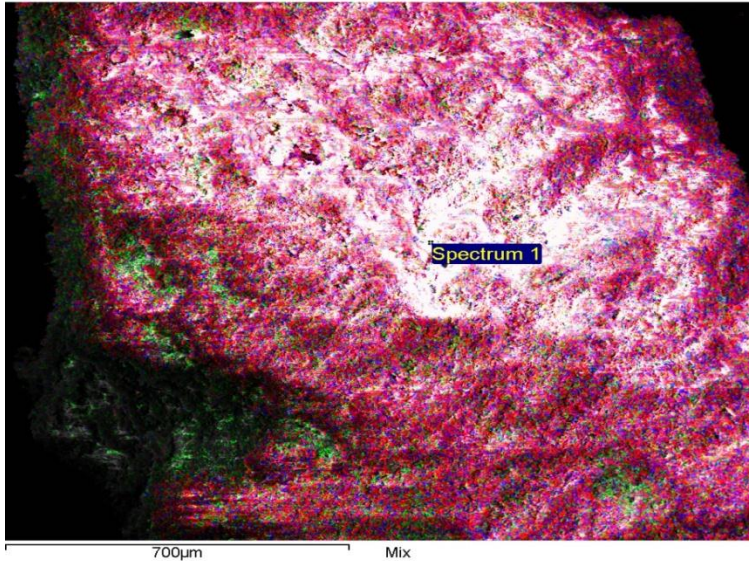
Element/Wt %

N	14.9
Al	0.8
P	21.7
Fe	0.5
Ca	0.2

Element/Wt %

N	13.3
Al	0.6
P	19.2
Fe	0.3
Ca	0.1

DAP Granule- Incubated 5 wk Ecuador Soil



Elemental map-EDS

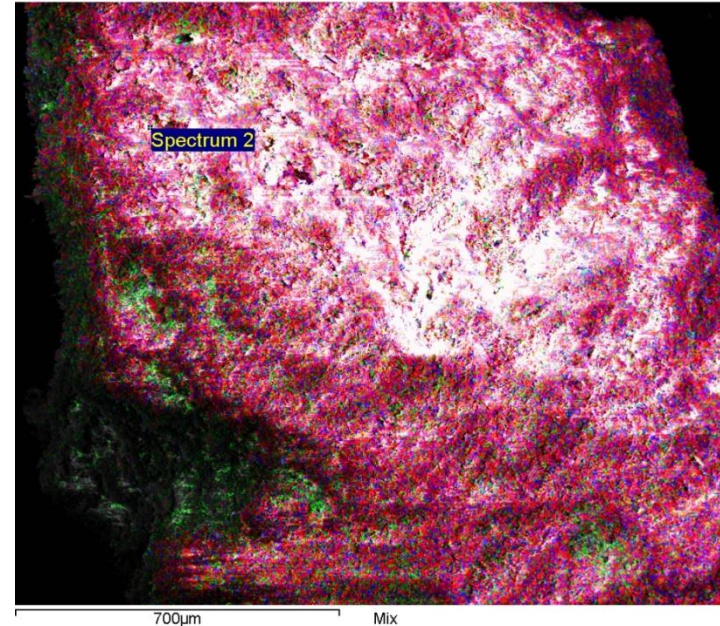
P=Red

Al=Blue

Fe=Green

Element-Wt %

N	-----
Al	5.5
P	12.9
Fe	4.9
Ca	5.3



Elemental map-EDS

P=Red

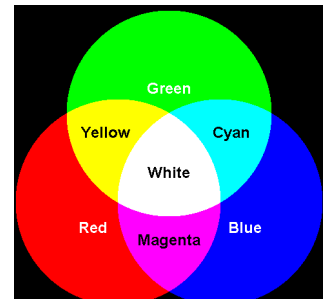
Al=Blue

Fe=Green

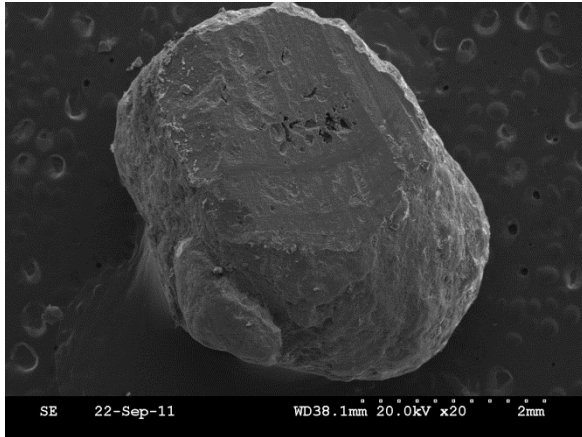
Element-Wt %

N	-----
Al	5.8
P	13.3
Fe	4.3
Ca	4.9

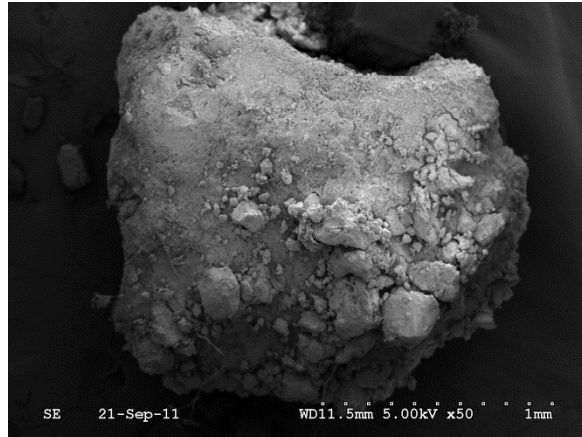
Zn, Re, Mg
~ 1%



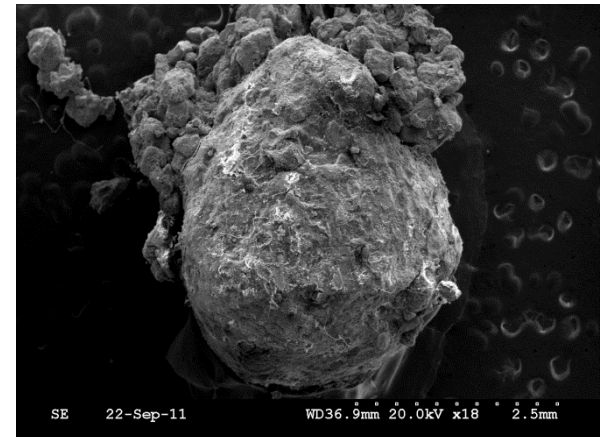
SEM Images of Granules



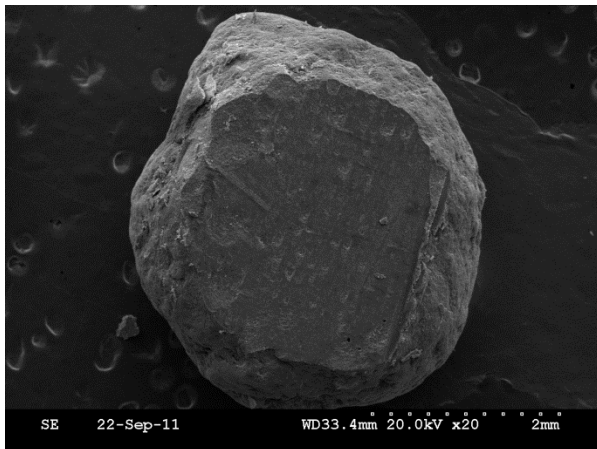
Original MAP granule



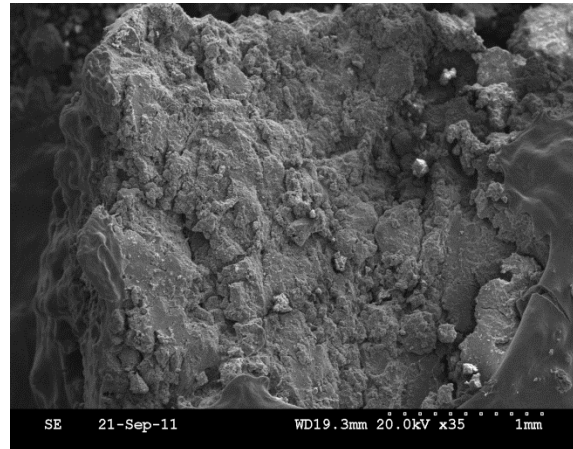
Incubated MAP granule- Brazil soil



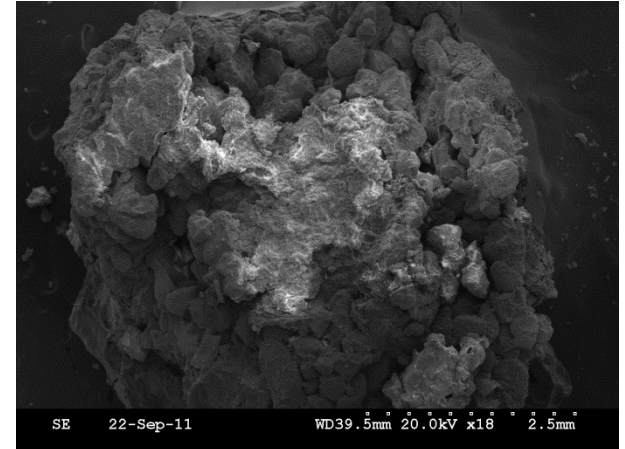
Incubated MAP granule- Idaho soil



Original DAP granule



Incubated DAP granule- Brazil soil



Incubated DAP granule- Idaho soil

Brazil Acid Soil

----- % by weight -----

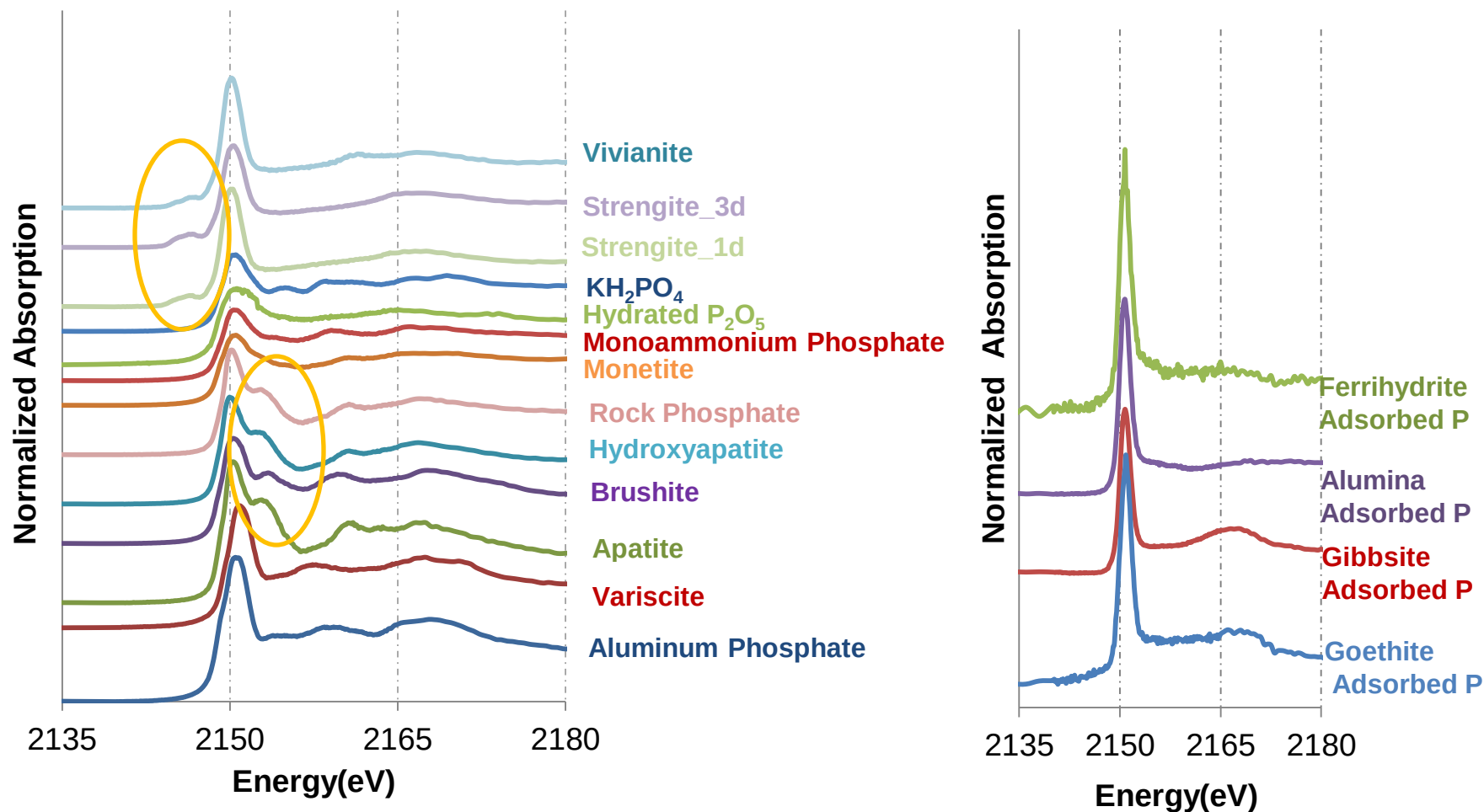
DAP Control	14.0	0.5	26.6	0.4	0.9	1.0
DAP Incubated	3.0	1.6	12.6	1.8	6.4	11.2
MAP Control	10.7	0.8	31.8	1.1	1.1	0
MAP Incubated	0	2.3	15.3	0.8	6.4	6.0

Idaho Calcareous Soil

----- % by weight -----

DAP Control	14.0	0.5	26.6	0.4	0.9	1.0
DAP Incubated	0	1.4	13.8	13.5	5.3	4.9
MAP Control	10.7	0.8	31.8	1.1	1.1	0
MAP Incubated	0	1.3	11.5	10.2	4.1	5.5

X-ray absorption near-edge structure (XANES) spectroscopy analysis



Normalized P K-XANES spectra of standards used for LCF fitting

XANES Data- Brazil acid soil

P species in soil (%)

Section I- 0 to 7.5 mm

Treatment	Aluminum Phosphate	Alumina Adsorbed P	Ferrihydrite Adsorbed P	Iron Phosphate	Red. Chi Square
Control	13.9	-	64.1	21.9	0.27
MAP	-	-	72.1	27.9	0.32
DAP	-	47.3	-	52.7	0.04
APP	-	43.6	-	56.4	0.02
MAP + FEP	-		24.1	75.9	0.02
DAP + FEP	-	33.7	-	66.3	0.01
APP + FEP	-	21.4	-	78.6	0.00

Is Al-P less available compared to Fe-P in acid soils?

XANES Data- Idaho Calcareous soil

P species in soils (%)

Section I- 0 to 7.5 mm

Treatment	Calcium Phosphate	Aluminum Phosphate	Ferrihydrite Adsorbed P	Vivianite	Red. Chi Square
Control	68.6	-	31.4	-	0.06
MAP	59.2	-	31.0	9.8	0.02
DAP	64.1	-	35.9	-	0.04
APP	27.8	-	48.2	24.0	0.04
MAP + FEP	43.2	-	36.6	20.2	0.06
DAP + FEP	57.1	-	42.9	-	0.06
APP + FEP	32.0	7.1	61.0	-	0.16

APP and APP+FEP: Less Ca-P and/or more ferrihydrite sorbed P

Summary

- Most of the fertilizer P remained within the first two rings of the Petri dishes
- Enhanced P diffusion was observed for both APP and APP-FEP treatments
- Soil pH measurements at 5 wk alone do not provide explanations for enhanced P diffusion in some soils
- Osmotic effects of fluid fertilizer may not be detrimental to outward movement of P- thereby reducing chances of P precipitation

Summary (cont.)

- In calcareous soil, a possible explanation for increased resin extractability for the APP, APP-FEP treatments- increase in acidification immediately around fertilizer application point which resulted in decrease in calcium-P species

Acknowledgements

- Kansas State University- P Fellowship Consortium of International Plant Nutrition Institute; Mosaic, Agrium, Potash Corp., and JR Simplot, and Fluid Fertilizer Foundation for funding
- E. Francisco, L. Prochnow and T. Tindall for providing soils
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- Beamline 9-BM-B, Advanced Photon Source, Argonne National Laboratory