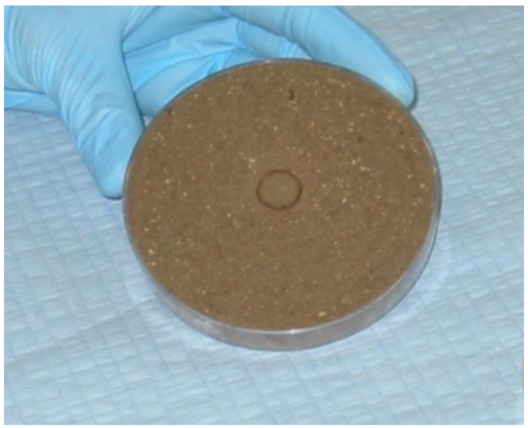
Mobility, Availability and Reaction Products of P from MAP, DAP and APP Fertilizers



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Fluid Fertilizer Forum, February 2012

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
- Efficient fertilizers result agronomic, economic and environmental benefits

Objectives

- To understand mobility and reactions products of P from MAP, DAP and APP fertilizers in different soils
- To understand fate of fertilizer P in soils using P fractionation method
- To integrate mobility, reaction products and wet chemical data to understand their potential performance in different soils

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Soils

Two soils

1. Oxisol, Brazil

2. Calcareous soil, Idaho

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Methodology

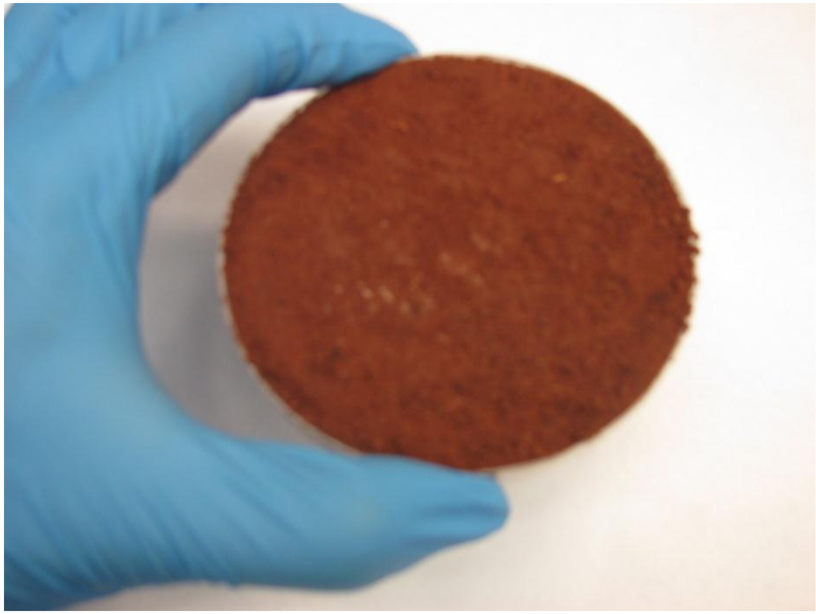
Treatments: (4)

Control

MAP (11-52-0 N-P_2O_5-K_2O)

DAP (18-46-0 N-P_2O_5-K_2O)

APP (11-37-0 N-P_2O_5-K_2O)



Petri dish size: 87mm in diameter

Moisture: 60% MWHC

MAP: 42 mg granules per dish

DAP: 43.4 mg granule

APP: equivalent amount of P

N balanced by Urea

5 + 2 replicates

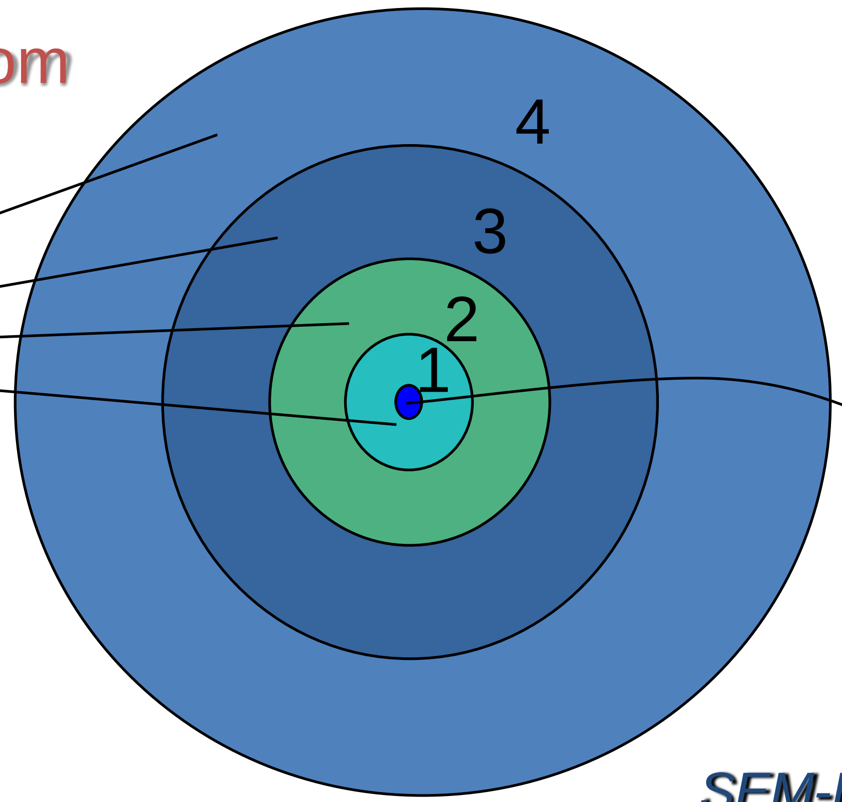
Incubation time: 5 weeks of incubation at 25^o C

Methodology (cont.)
Soil Sampling and Analyses

Diffusion of P from fertilizers

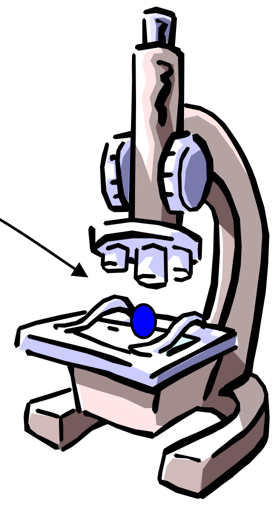
Samples

• *pH*
• *Total P*
• *P fractionation (not completed)*



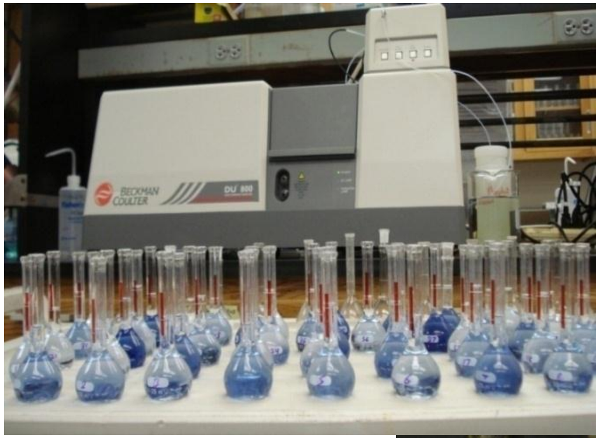
43.5
25
13.75
7.5
mm

Reaction products in granules and soils



SEM-EDX, XANES
• Changes in structure
• *In situ* elemental analyses
• Reaction products

Methodology (cont.)



<u>Wet chemical based analyses</u>

- Soil pH (1:5 soil:water)
- Total P –Salicylic sulfuric acid digestion (Bremner et al., 1982)
- P fractionation (modified Hedley et al., 1982)

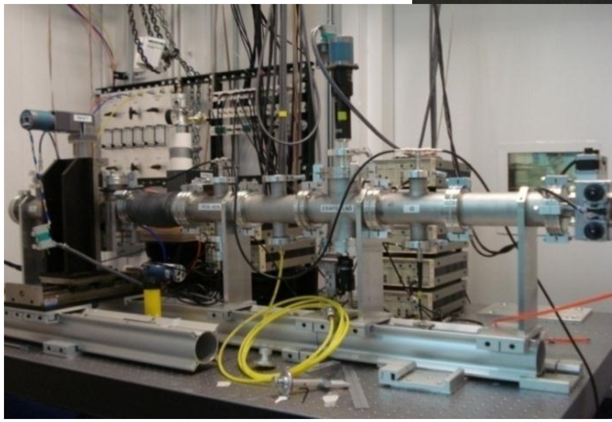
<u>P Speciation and granule observations</u>

- 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	Ext. Ca	CEC	OM	Ext. Fe	Ext. Mn	Ext. Al	Total N	Total P
	(H_2O)	mg/kg	meq/100g	%	---------------- mg/kg ------------------				
Brazil soil	4.3	49	12.4	3.7	52.9	2.2	79.5	1243	237
Idaho soil*	8.0	3376	19.6	0.6	2.4	3.6	n.d.	403	468

* $CaCO_3$ = 7.4%

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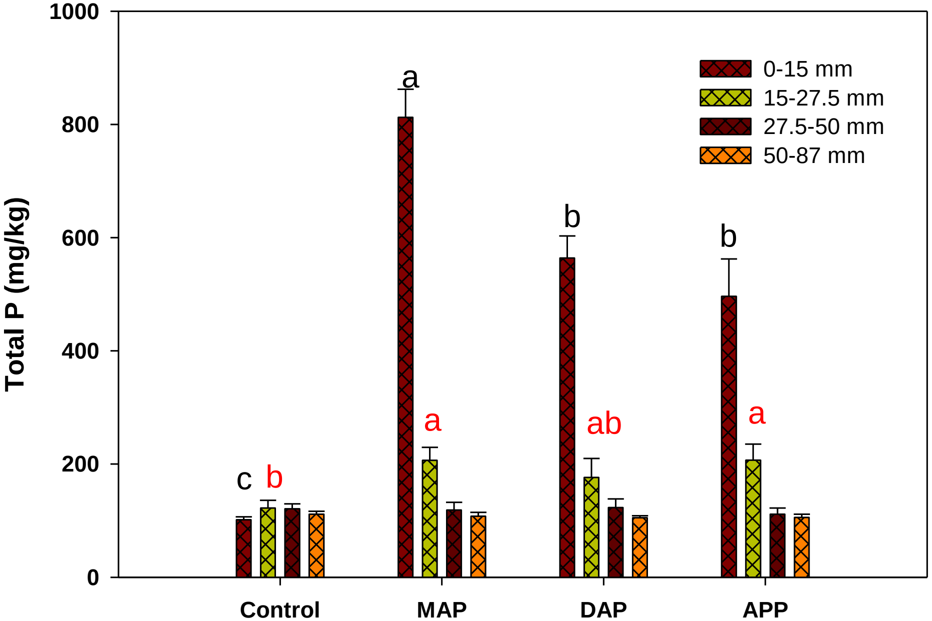
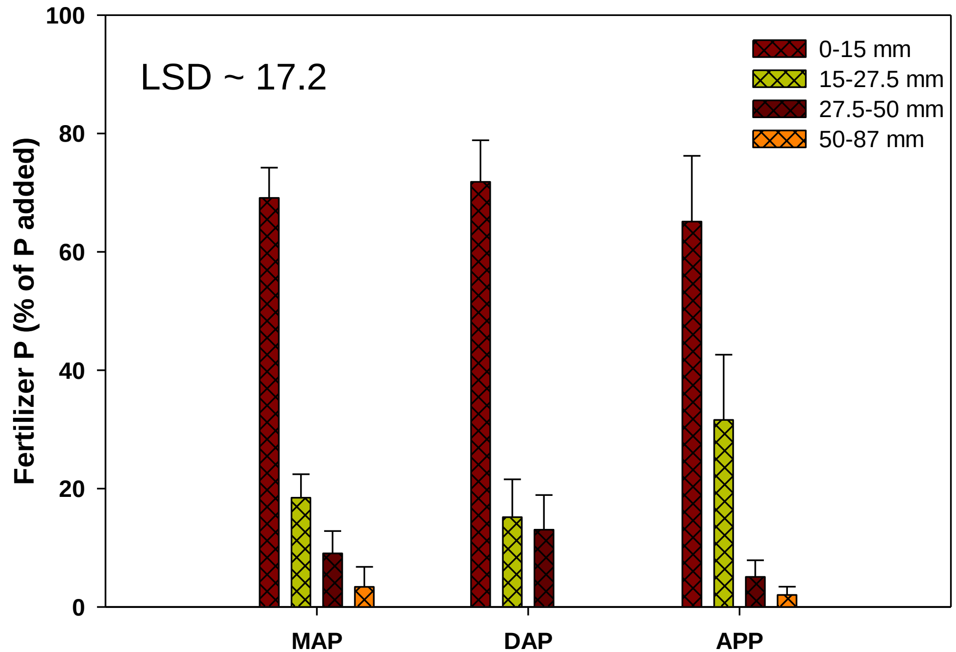
Fertilizer P Distribution- Brazil Acid Soil

Total P distribution



Fertlilizer P as % of total applied P



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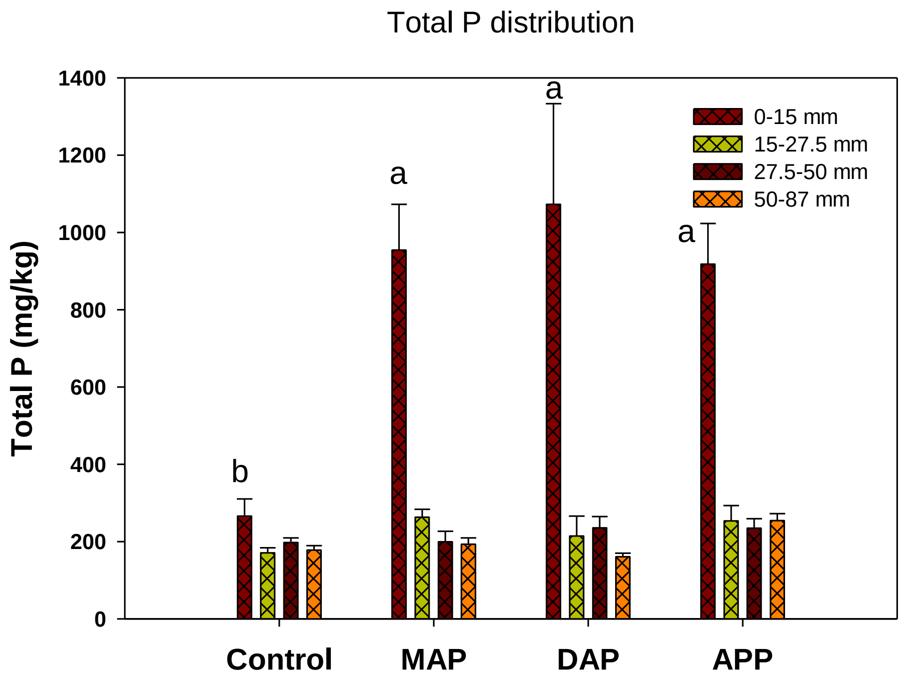
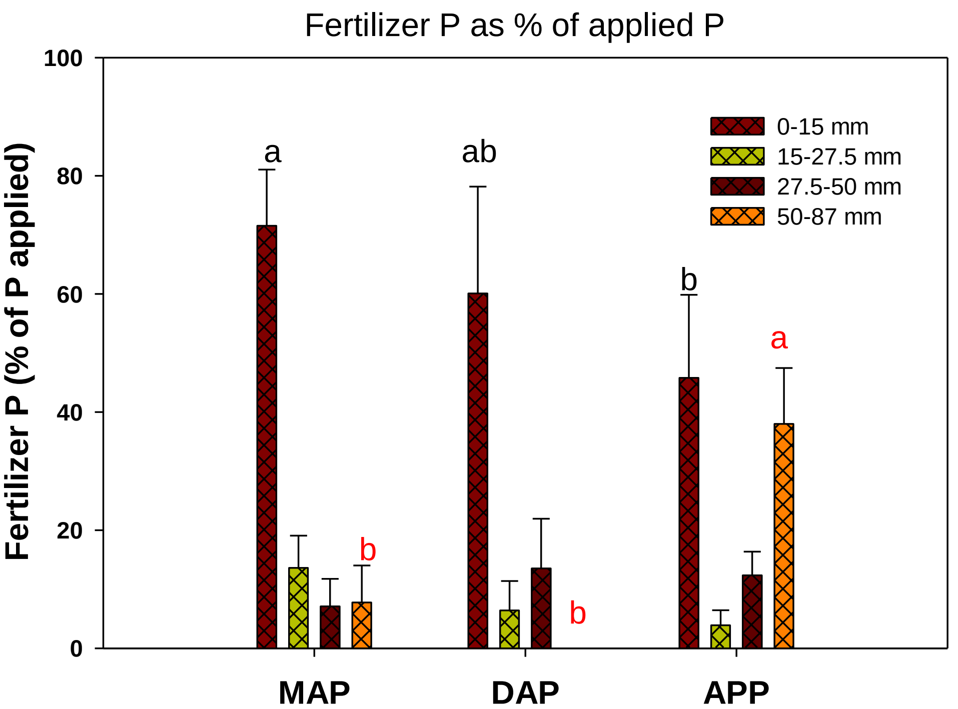
Fertilizer P Distribution- Idaho Calc. Soil





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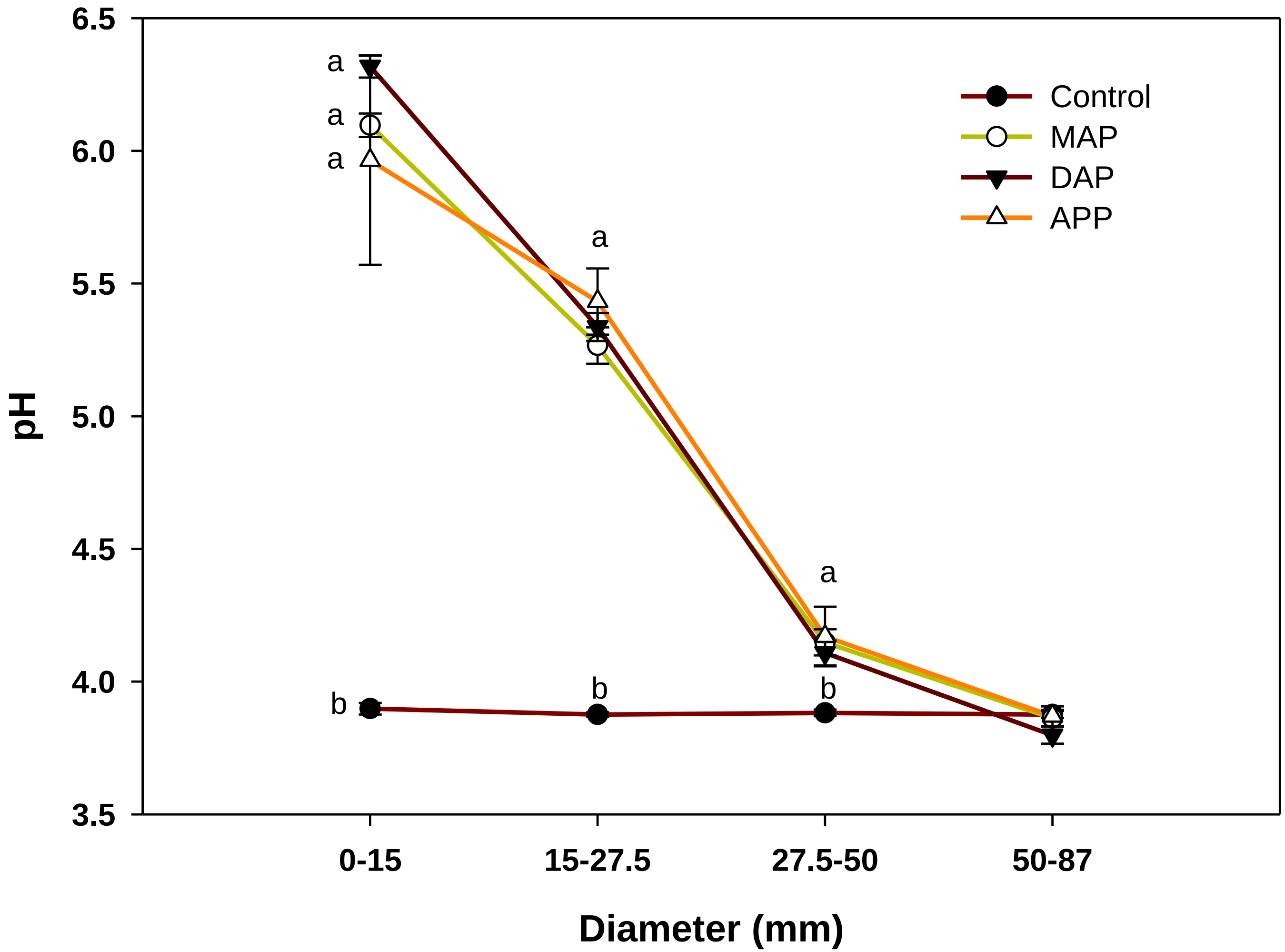
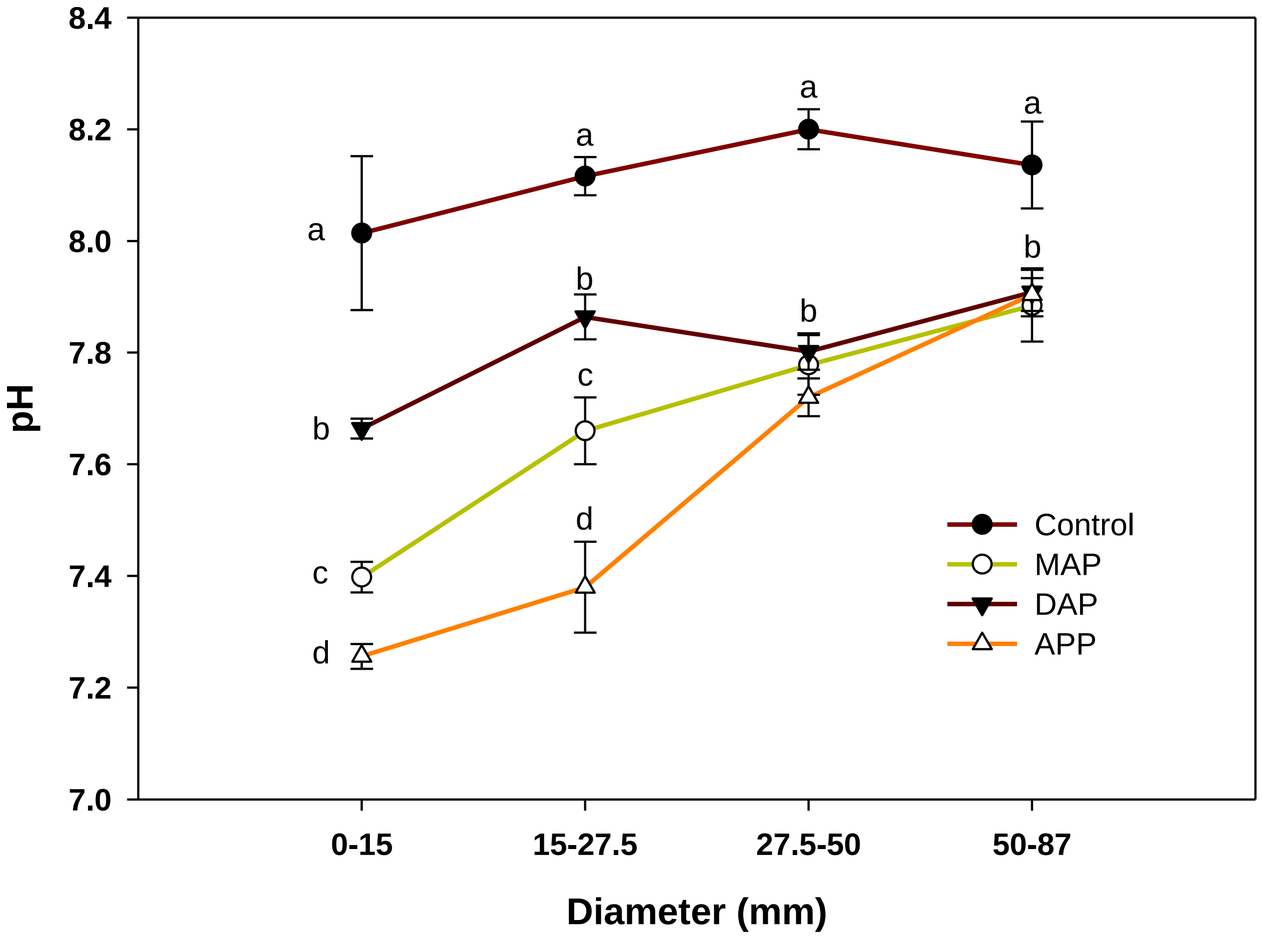
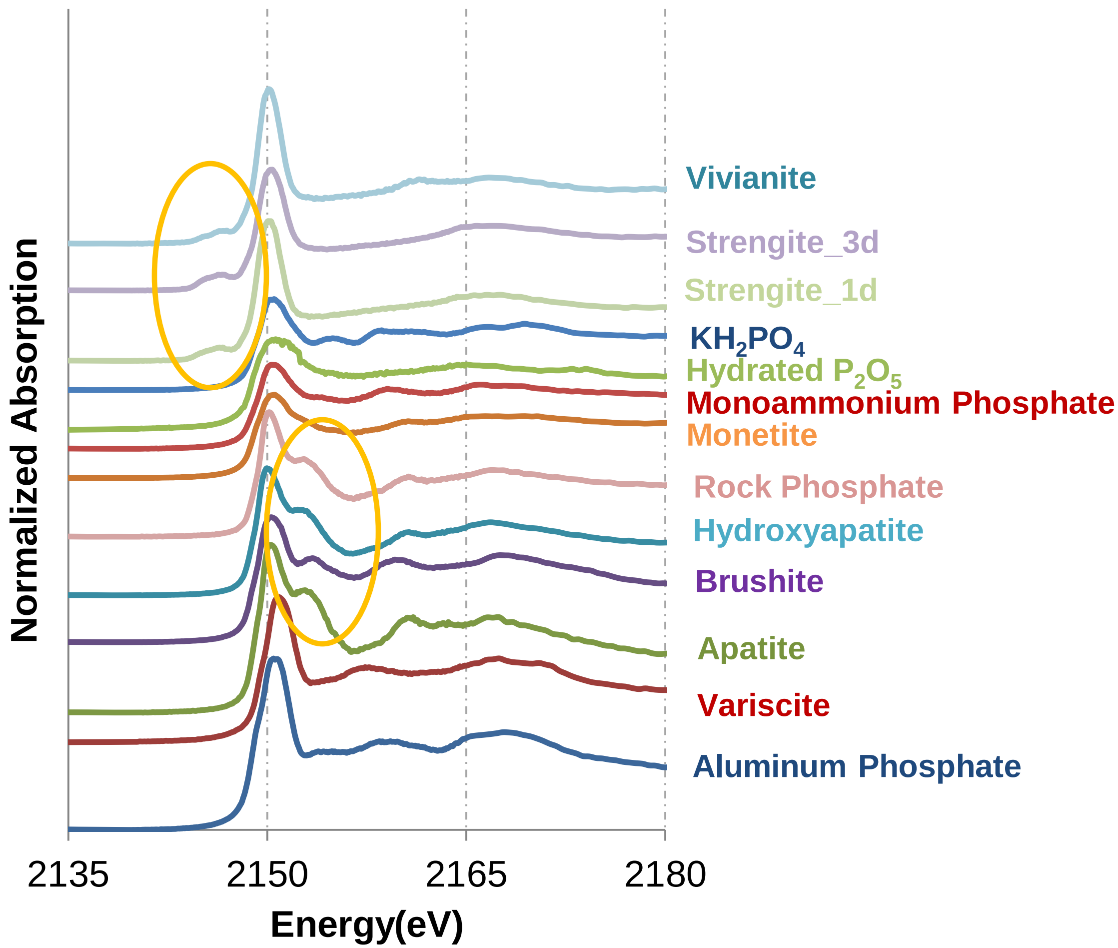
Soil pH- Brazil Acid Soil

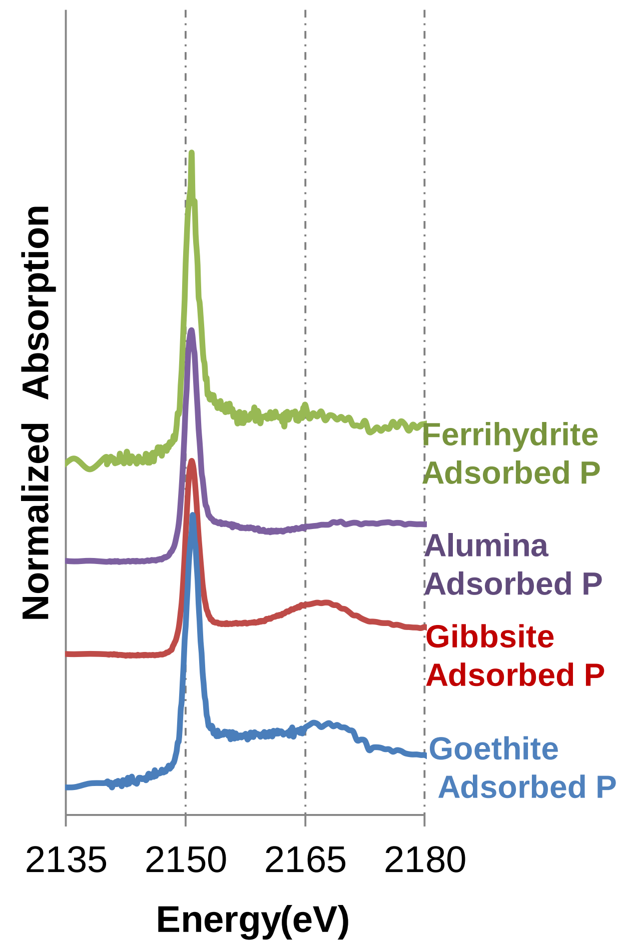


Soil pH- Idaho Calcareous Soil



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





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

P XANES Data- Brazil Acid Soil

Soil P species (%)

Section I- 0 to 15 mm diameter- innermost section

Treatment	Aluminum Phosphate	Alumina Adsorbed P	Ferrihydrite Adsorbed P	Vivianite (Fe(II) 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

The total percentage was constrained to be 100% in all fits. Typical uncertainties in the percentages listed for each standard component are 5%.

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P XANES Data- Idaho Calc. Soil

Soil P species (%)

Section I- 0 to 15 mm diameter- innermost section

Treatment	Apatite	Hydroxy apatite	Ferrihydrite Adsorbed P	Vivianite (Fe(II) phosphate)	Red. Chi Square
Control	20.4	48.2	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

The total percentage was constrained to be 100% in all fits. Typical uncertainties in the percentages listed for each standard component are 5%.

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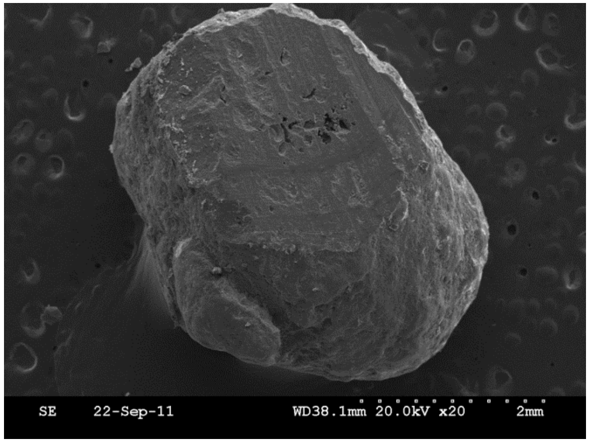
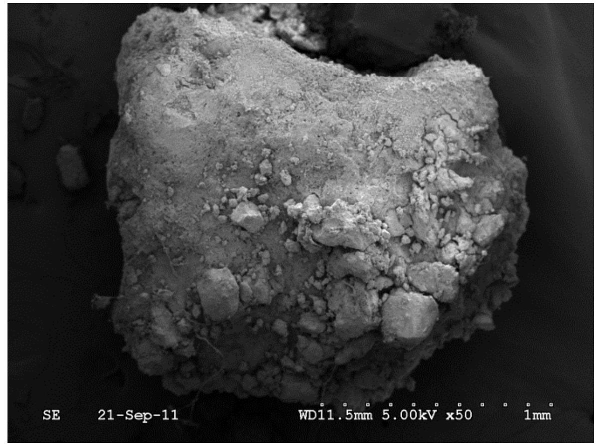
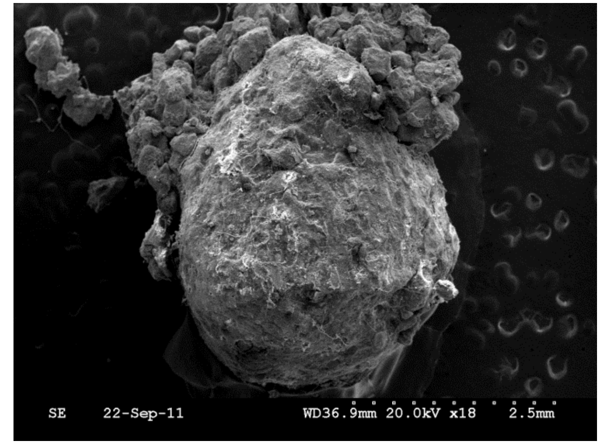
SEM Images of Granules



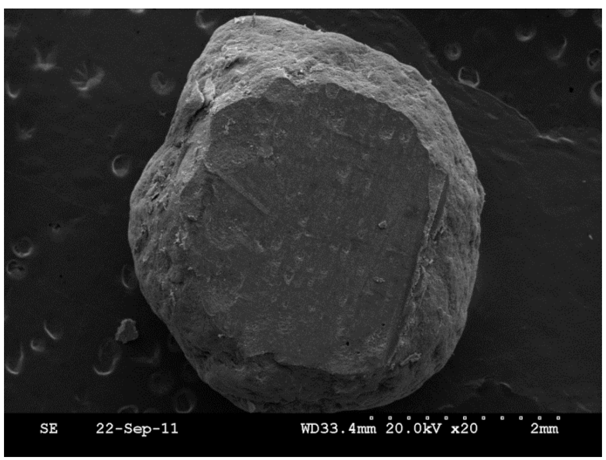
Original MAP granule



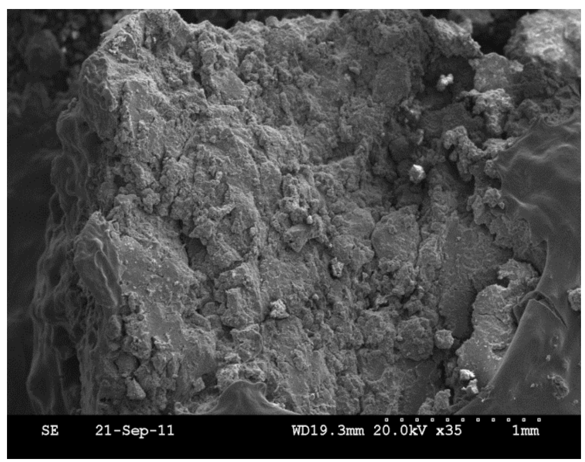
Incubated MAP granule- Brazil soil



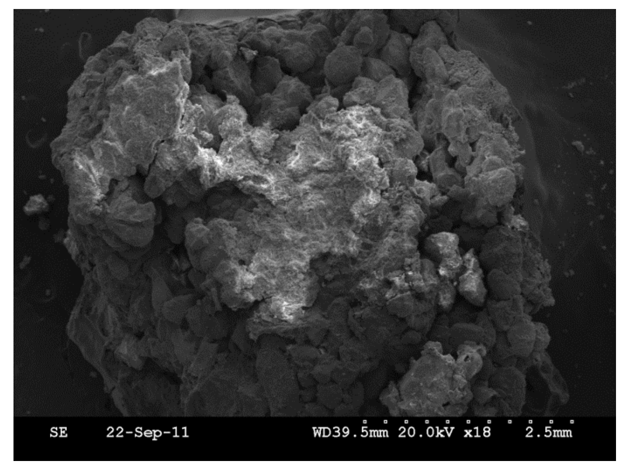
Incubated MAP granule- Idaho soil



Original DAP granule



Incubated DAP granule- Brazil soil



Incubated DAP granule- Idaho soil

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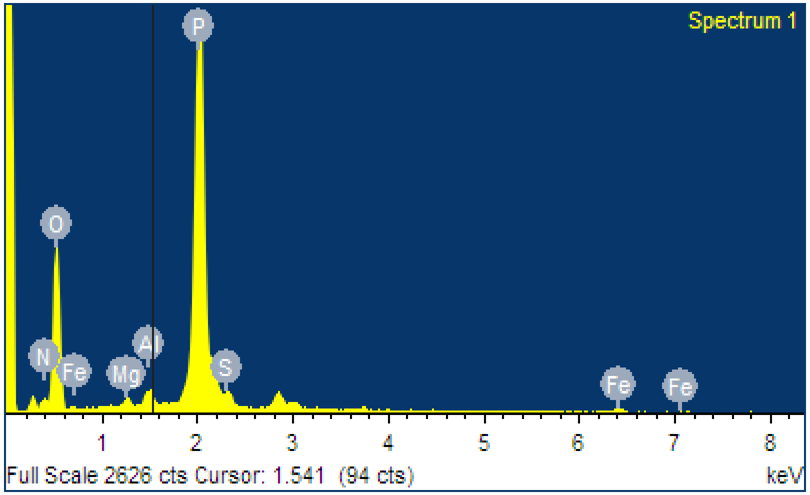
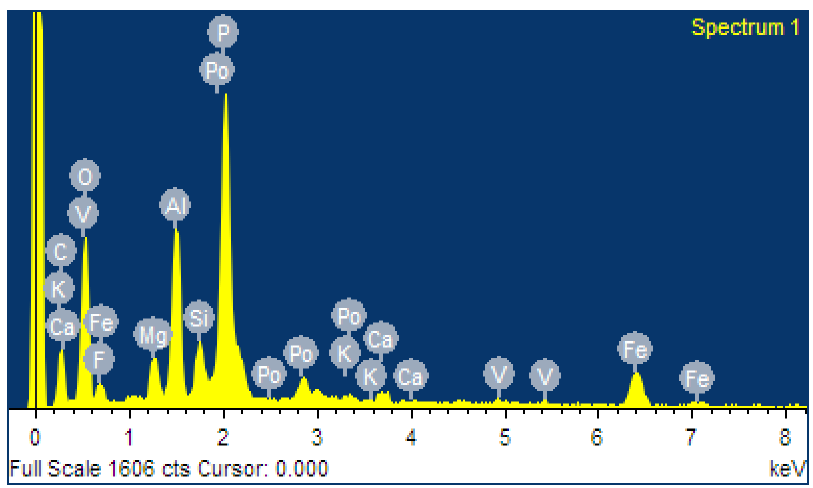
EDXA- Brazil Acid Soil- MAP



Original MAP granule

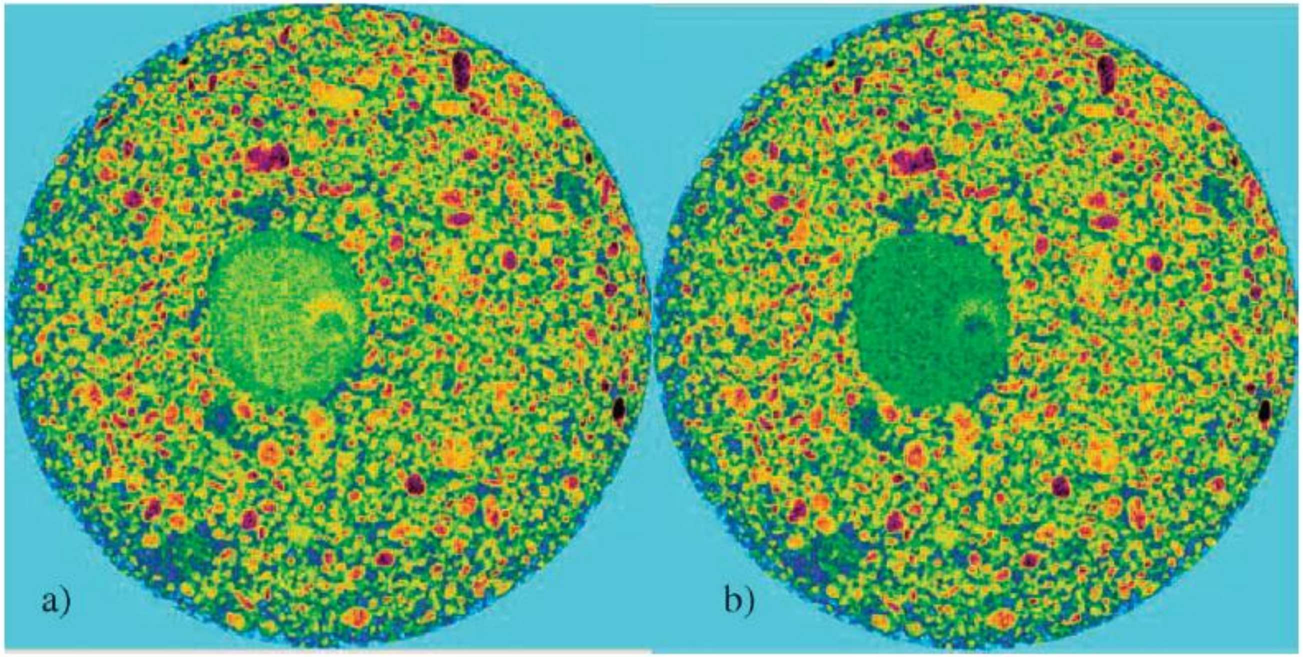
Element	Weight%
N	10.7
O	53.5
Mg	0.8
Al	1.1
P	31.8
S	1.0
Fe	1.1
Totals	100.0

Original
MAP ~ 22% P

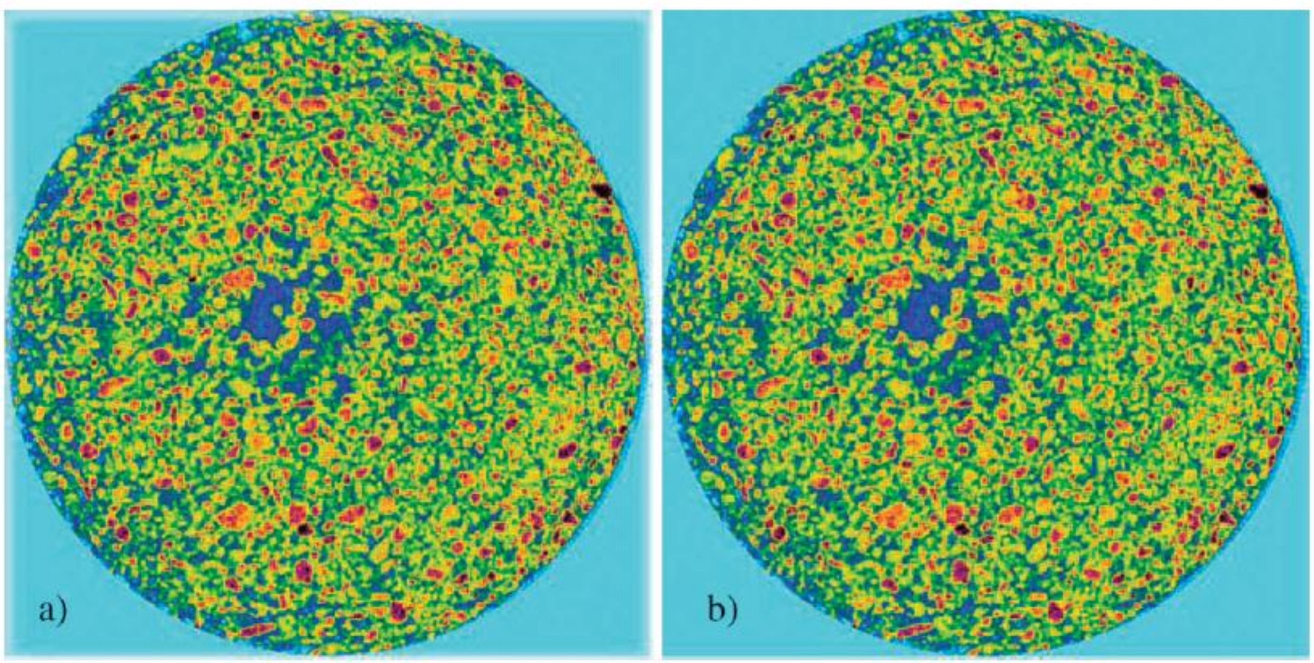


Incubated MAP granule

Element	Weight%
C	25.7
O	33.7
F	6.0
Mg	2.1
Al	7.3
Si	2.0
P	14.2
K	0.4
Ca	0.8
V	0.5
Fe	6.5
Po	0.9
Totals	100.0



Granule MAP



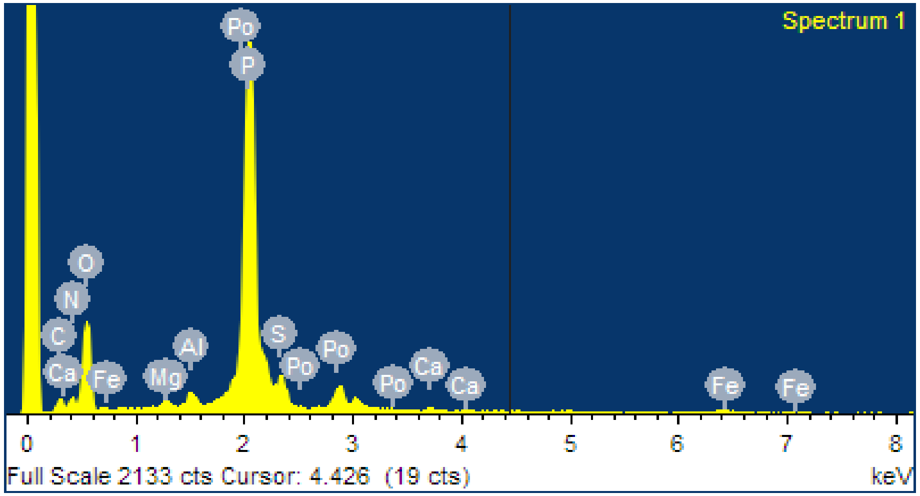
Fluid MAP

Hettiarachchi et al., 2006. SSSAJ

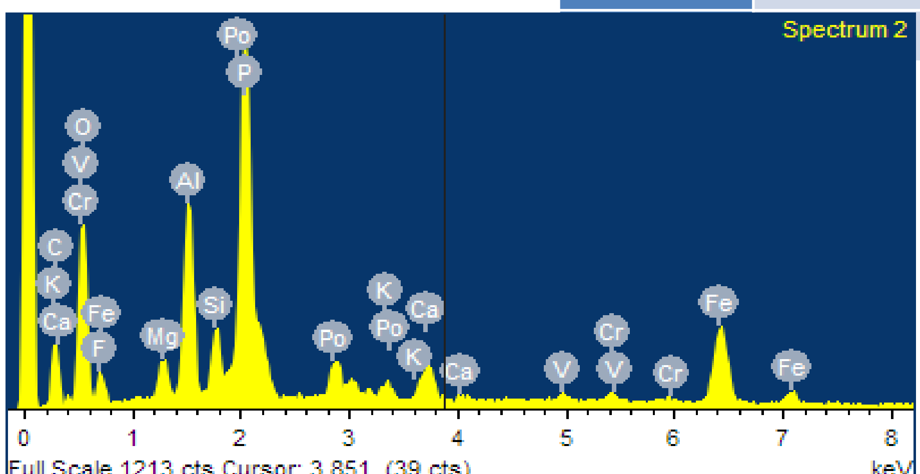
EDXA- Brazil Acid Soil- DAP

Element	Weight%
C	13.1
N	14.0
O	40.1
Mg	0.5
Al	0.9
P	26.6
S	2.1
Ca	0.4
Fe	1.0
Po	1.3

Original
MAP ~ 20% P



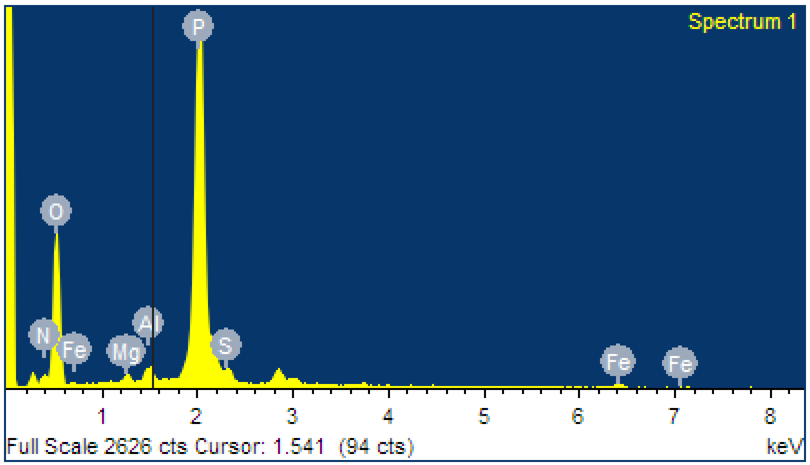
Original DAP granule



Incubated DAP granule

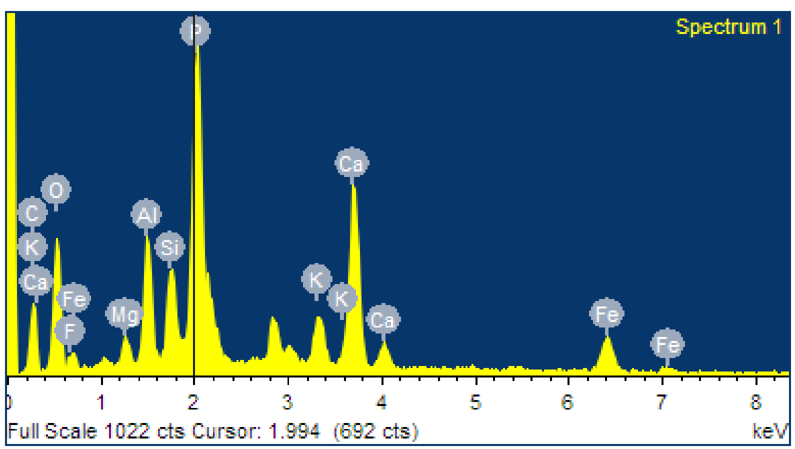
Element	Weight%
C	26.3
O	30.1
F	5.5
Mg	1.6
Al	6.4
Si	2.0
P	12.6
K	0.7
Ca	1.8
V	0.6
Cr	0.6
Fe	11.2
Po	0.8
Totals	100.0

EDXA- Idaho Calcareous Soil



Original MAP granule

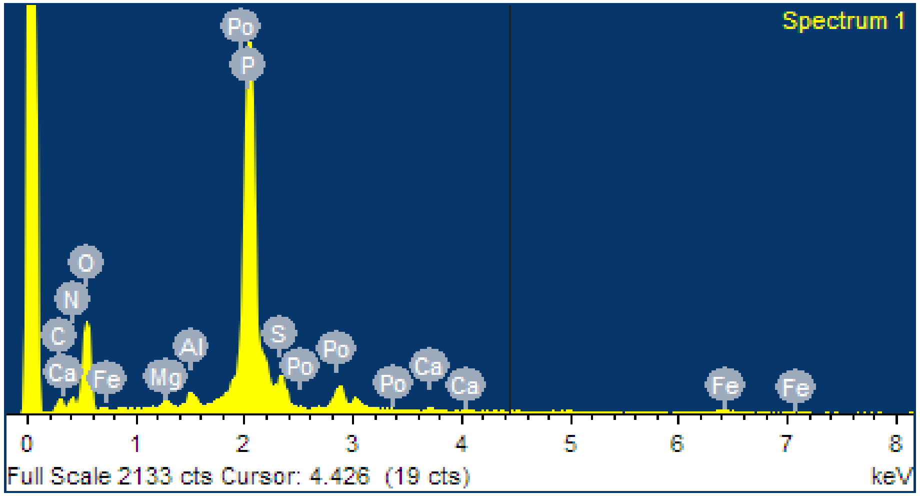
Element	Weight%
N	10.7
O	53.5
Mg	0.8
Al	1.1
P	31.8
S	1.0
Fe	1.1
Totals	100.0



Incubated MAP granule

Element	Weight%
C	26.4
O	31.0
F	3.6
Mg	1.3
Al	4.1
Si	3.1
P	11.5
K	2.2
Ca	10.2
Fe	5.5
Totals	100.00

EDXA- Idaho Calcareous Soil

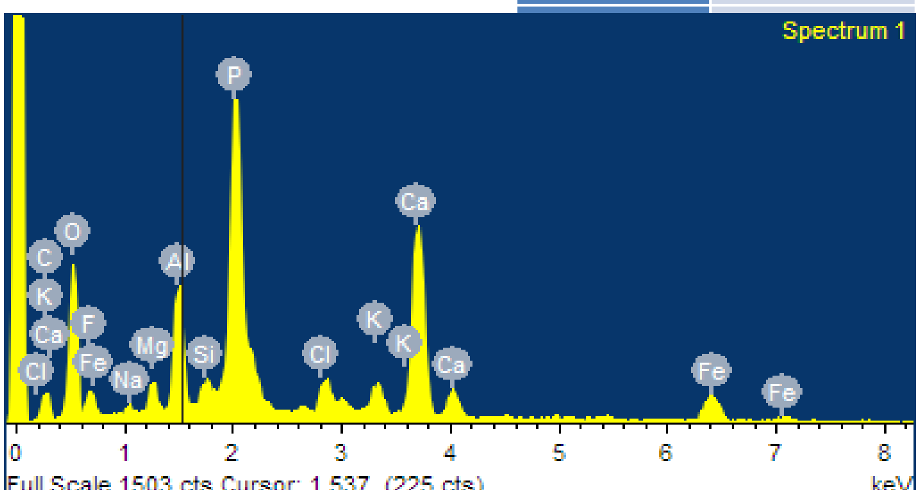


Original DAP granule

Element	Weight%
C	13.1
N	14.0
O	40.1
Mg	0.5
Al	0.9
P	26.6
S	2.1
Ca	0.4
Fe	1.0
Po	1.3

Highest pH

Appeared to have more Ca and P compared to MAP



Incubated DAP granule

Element	Weight%
C	13.8
O	35.8
F	7.5
Na	0.6
Mg	1.4
Al	5.3
Si	0.9
P	13.8
Cl	0.7
K	1.8
Ca	13.5
Fe	4.9
Totals	100.0

Summary

- Soil acidification or resistance to acid neutralization effects of P fertilizers followed the order of APP > MAP > DAP
- Diffusion of P from APP appeared to be greater than the granular MAP or DAP in this calcareous soil
- Greater acidification and enhanced diffusion of APP could be the reasoning for reduced Ca-P species observed in the zones immediately surrounding the point of P application in calcareous soils

Summary (cont.)

- Diffusion of P appears to be low in this acid soil
- Use of DAP maybe beneficial for high Al and Fe containing acid soils as *“acid* neutralizing *effects”* of DAP is greater than the MAP or APP
- P reaction products of MAP applied acid soil had less Al-P forms and more Fe-P forms while the opposite was true for the DAP and APP
- Results need to be integrated with P fractionation data to better understand their implications on potential P availability

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