Mobility, Availability and Reaction Products of Different P Fertilizer Sources in Soils: Influence of P Management Practices

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Introduction

- Reduced or no tillage seedbed preparation methods coupled with broadcast P applications
  - leads to an accumulation of available P on the surface (nutrient stratification)
  - depletion of available P deeper in the profile

(Schwab et al., 2006)

Introduction (cont.)

- Increasing efficiency of soil and fertilizer P use in agriculture becoming increasingly important
  - ↑ Fertilizer prices
  - Environmental concerns related to P in surface waters

Introduction (cont.)

- Advances in molecular spectroscopy provides scientists with increasingly powerful tools to probe the chemical speciation of nutrients in environmental samples
- Developing relationships between different P reaction products and P availability and/or mobility will be helpful in designing
  - Better and efficient P fertilizers
  - P management practices

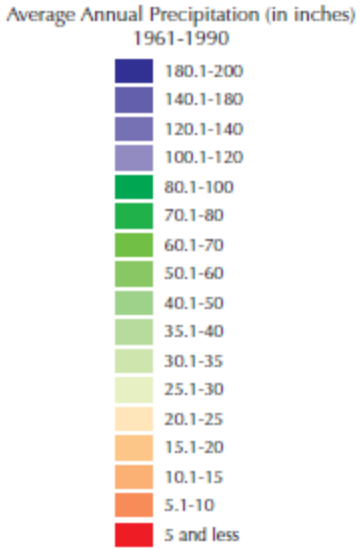
Objectives

- To study fertilizer placement (broadcast vs. deep placed/banded); and source (granular vs. liquid) effect on reaction products of P at different time periods (5wk and/or 6 months)
- To study availability of P at different distances from the point of fertilizer application and linking that to soil P chemistry

Site/Soil Selection and Approach

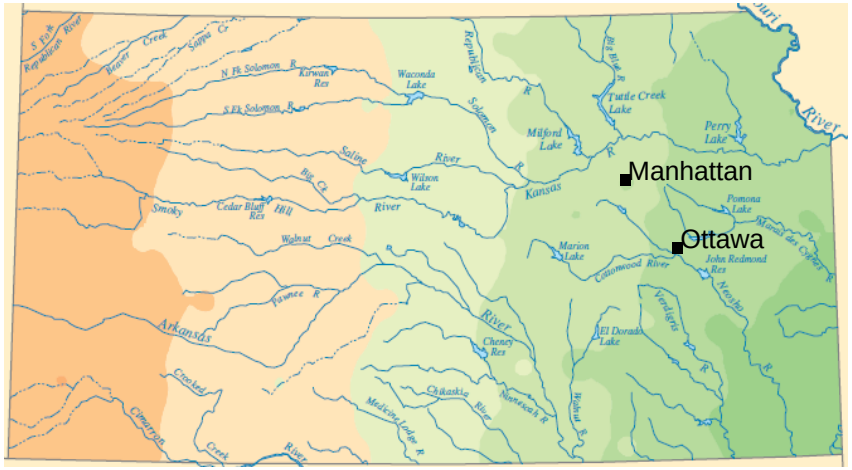
Site selection:

1) Agronomy North Farm, Manhattan (high soil test P)
2) East Central Experiment Field, Ottawa (low soil test P)



Experimental Approach:

- Field incubation experiments
  - North Farm
- Column experiments (greenhouse)
  - North farm
  - Ottawa



Field study: Methodology

Location: Agronomy North Farm, Manhattan, KS

Design: RCBD with five replications

Treatments:

Control (Broadcast)	Control(Deepband)
MAP Broadcast	MAP Deepband
TGMAP Broadcast	TGMAP Deepband

MAP = Monoammonium Phosphate (Granular)

TGMAP = Technical Grade MAP (Liquid)

Plot size: 5’ by 8’ with a 3’ alley.

Fertilizer rate : P @75 kg/ha, and N @200 kg/ha.

Urea was added to all treatments to balance N rate

Soil Sampling: 0-2.5, 2.5-5, 5-7.5,……. 27.5-30 cm

Statistical Analysis: *proc mixed*, pairwise comparision, Bonferroni test (α=0.05) (SAS 9.1)

Methodology (cont.)

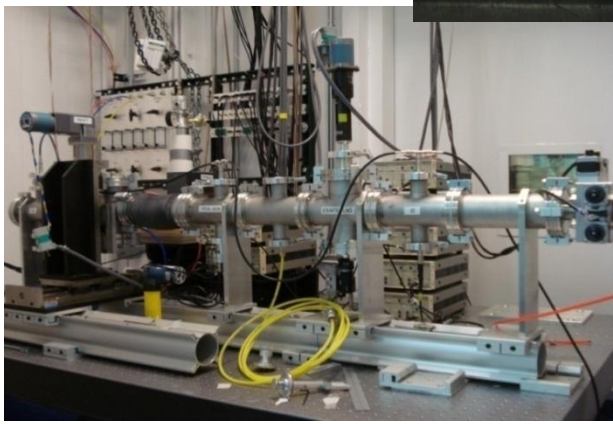
Wet chemical based analyses

- Soil pH (1:5 soil:water)
- Total P –Salicylic sulfuric acid digestion (Bremner et al., 1982)
- Resin Extractable P (Myers et al.,2005)

P Speciation

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

Beamline: 9 BM-B, Advanced Photon Source, ANL



Data analysis:

Linear combination fitting (LCF) using Athena software (v0.8.061)

First derivative: -5 eV below and 30 eV

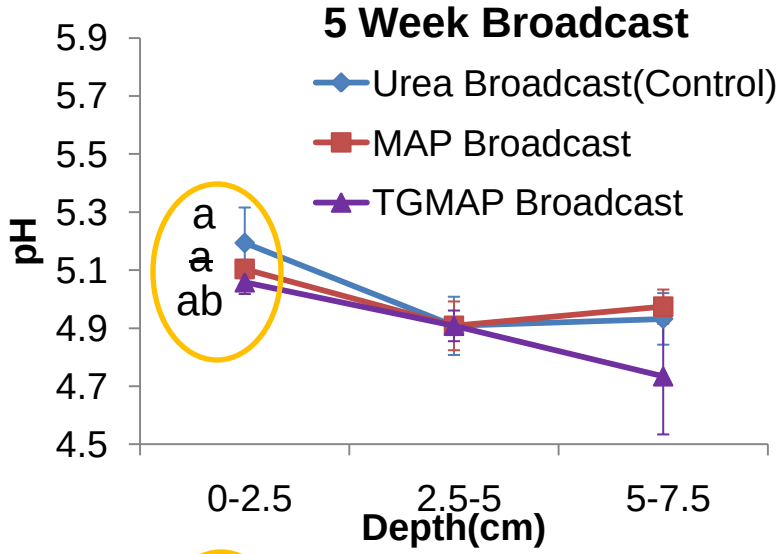
Selected soil properties

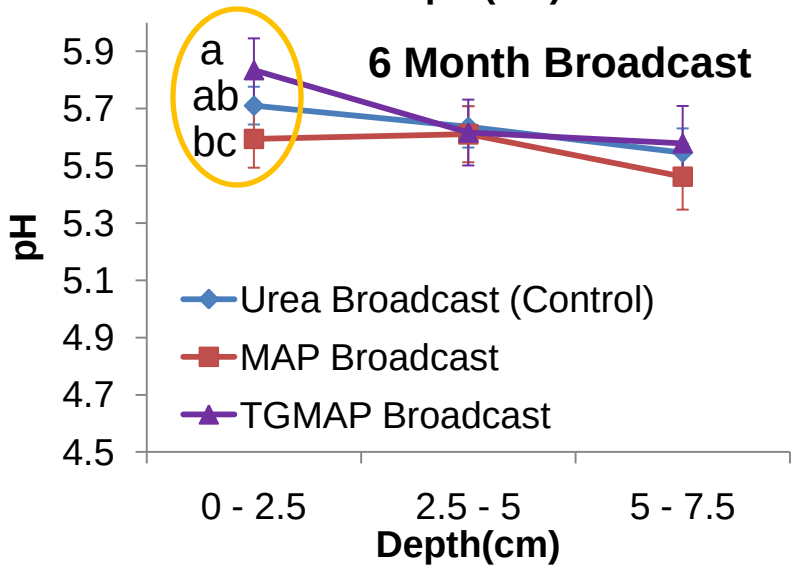
Soil Type :
Smolan silt loam (fine, smectitic, mesic Pachic Argiusdolls)

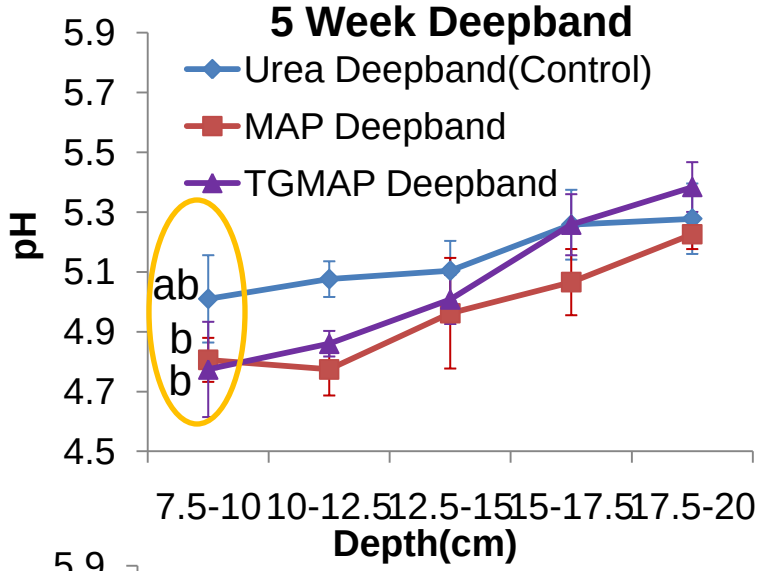
Depth(cm)	Total		NH_4-Oxa-Ext		Na-Act-Ext	Total			
	C	N	Fe	Al	Ca	Clay	Silt	Sand	CEC
	(----------%----------)				cmol(+)kg^{-1}	(--------% ---------)			cmol(+)kg^{-1}
0-13	1.14	0.14	0.18	0.12	31.6	33.0	56.2	10.8	34.4
13-29	0.86	0.11	0.17	0.13	19.3	38.3	51.8	27.8	23.9

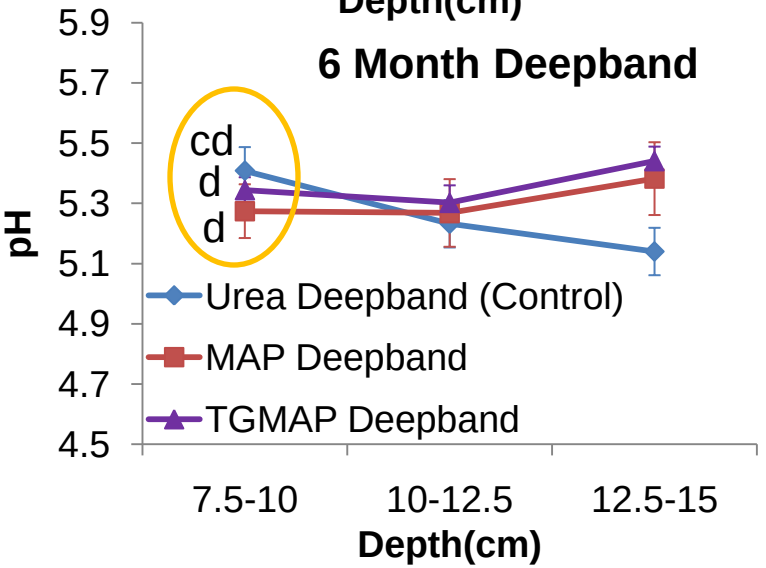
http://ssldata.nrcs.usda.gov/

Results: pH

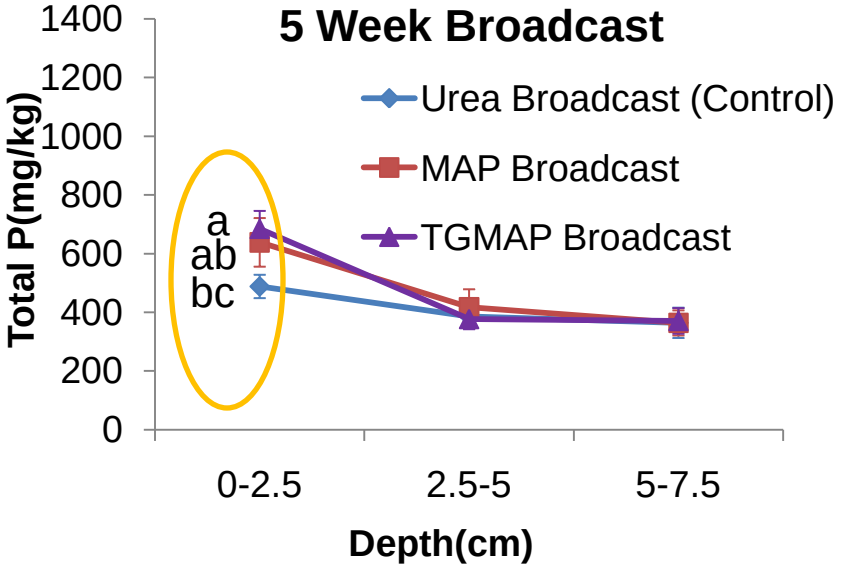

5 Week Broadcast
Urea Broadcast(Control)
MAP Broadcast
TGMAP Broadcast
pH
5.9
5.7
5.5
5.3
5.1
4.9
4.7
4.5
a
a
ab
0-2.5
2.5-5
5-7.5
Depth(cm)

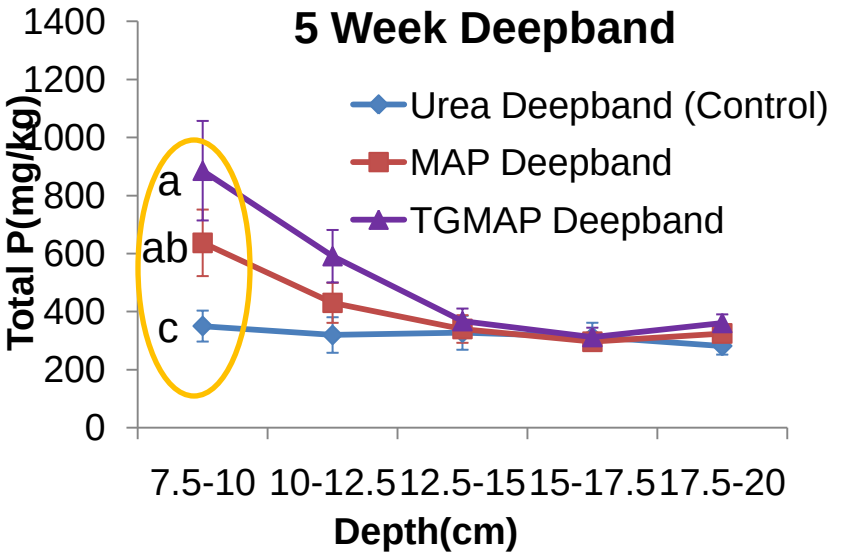

6 Month Broadcast
pH
5.9
5.7
5.5
5.3
5.1
4.9
4.7
4.5
a
ab
bc
Urea Broadcast (Control)
MAP Broadcast
TGMAP Broadcast
0 - 2.5
2.5 - 5
5 - 7.5
Depth(cm)

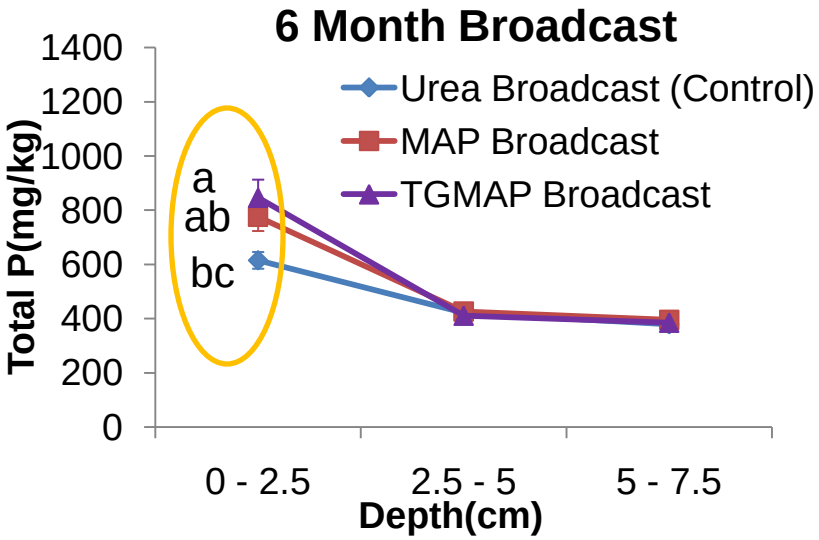

5 Week Deepband
Urea Deepband(Control)
MAP Deepband
TGMAP Deepband
pH
5.9
5.7
5.5
5.3
5.1
4.9
4.7
4.5
ab
b
b
7.5-10
10-12.5
12.5-15
15-17.5
17.5-20
Depth(cm)

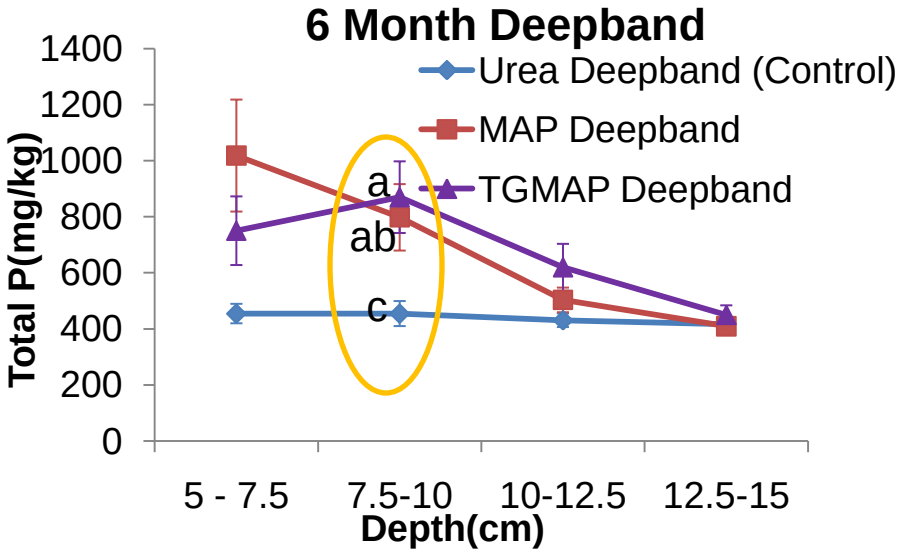

6 Month Deepband
pH
5.9
5.7
5.5
5.3
5.1
4.9
4.7
4.5
cd
d
d
Urea Deepband (Control)
MAP Deepband
TGMAP Deepband
7.5-10
10-12.5
12.5-15
Depth(cm)

Total P

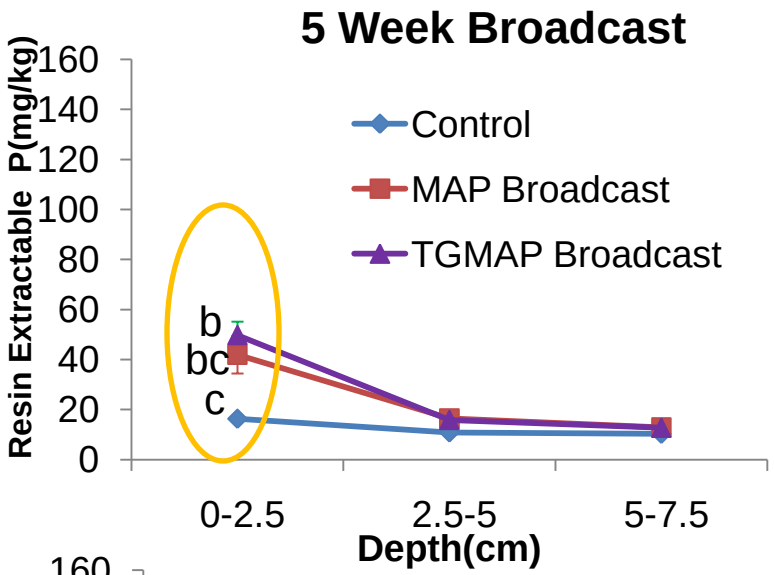

5 Week Broadcast
Urea Broadcast (Control)
MAP Broadcast
TGMAP Broadcast
Total P(mg/kg)
1400
1200
1000
800
600
400
200
0
a
ab
bc
0-2.5
2.5-5
5-7.5
Depth(cm)

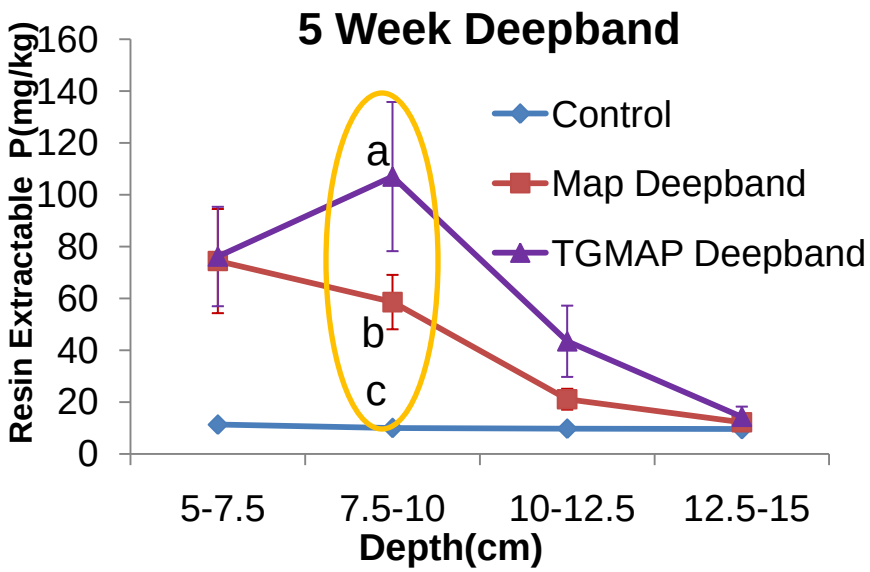

5 Week Deepband
Urea Deepband (Control)
MAP Deepband
TGMAP Deepband
Total P(mg/kg)
1400
1200
1000
800
600
400
200
0
a
ab
c
7.5-10
10-12.5
12.5-15
15-17.5
17.5-20
Depth(cm)

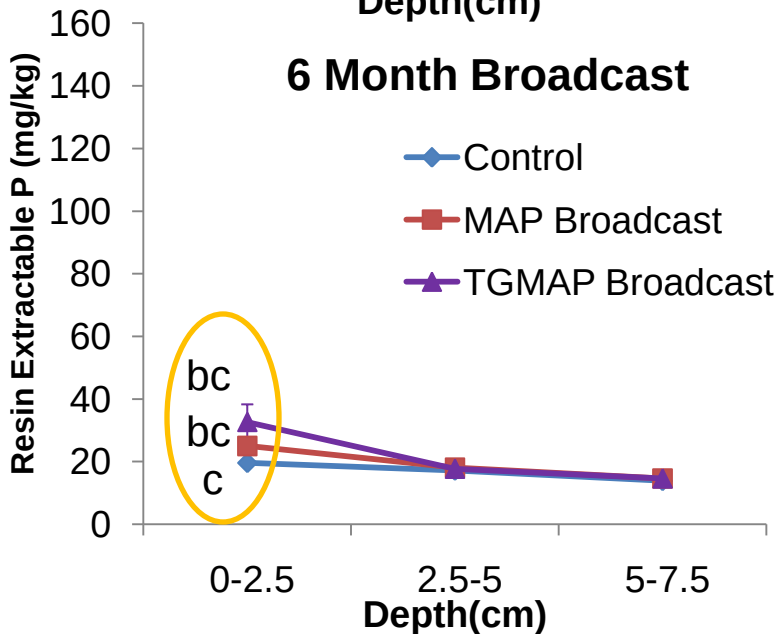

6 Month Broadcast
Urea Broadcast (Control)
MAP Broadcast
TGMAP Broadcast
Total P(mg/kg)
1400
1200
1000
800
600
400
200
0
a
ab
bc
0 - 2.5
2.5 - 5
5 - 7.5
Depth(cm)

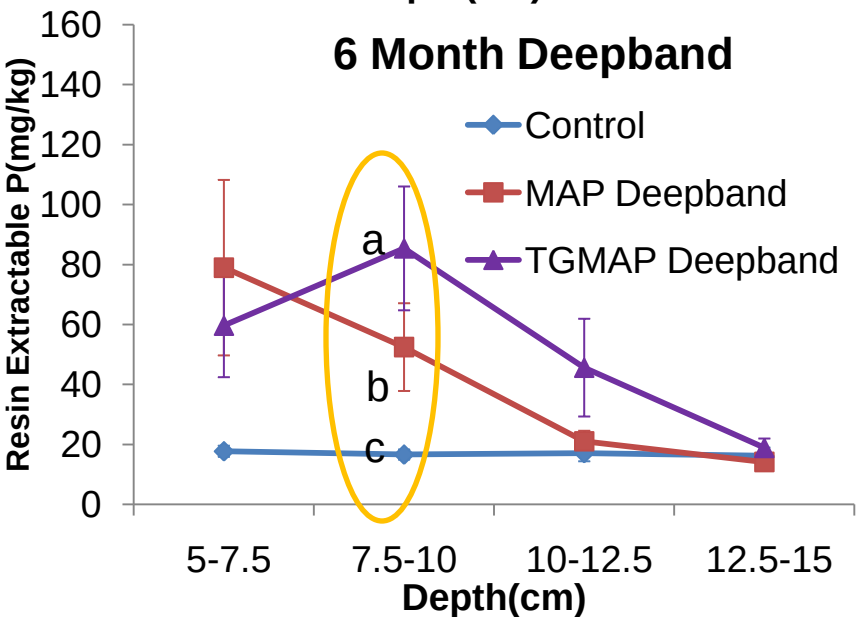

6 Month Deepband
Urea Deepband (Control)
MAP Deepband
TGMAP Deepband
Total P(mg/kg)
1400
1200
1000
800
600
400
200
0
a
ab
c
5 - 7.5
7.5-10
10-12.5
12.5-15
Depth(cm)

Resin P

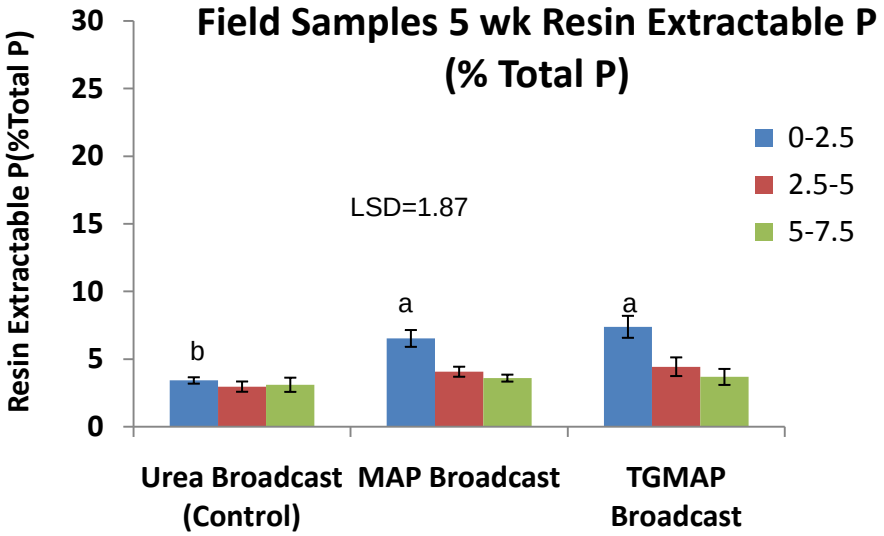

5 Week Broadcast
Resin Extractable P(mg/kg)
160
140
120
100
80
60
40
20
0
Control
MAP Broadcast
TGMAP Broadcast
b
bc
c
0-2.5
2.5-5
5-7.5
Depth(cm)

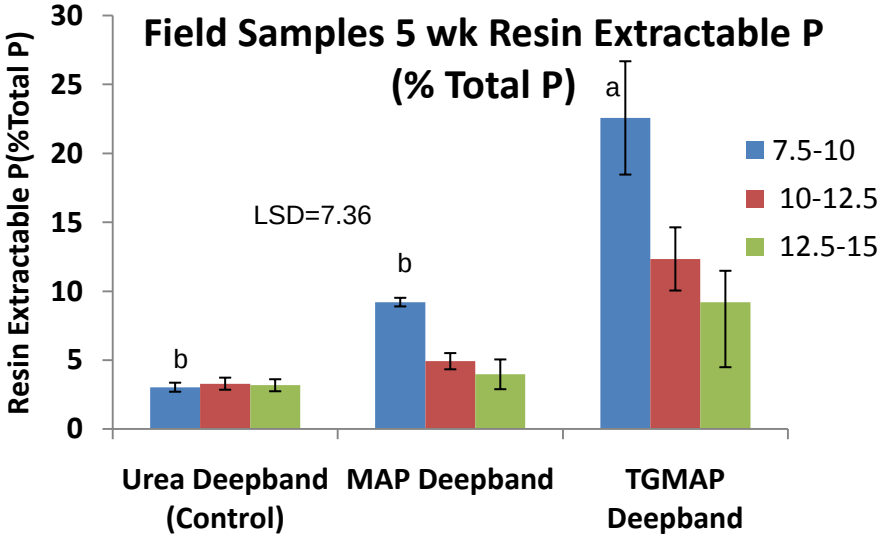

5 Week Deepband
Resin Extractable P(mg/kg)
160
140
120
100
80
60
40
20
0
Control
Map Deepband
TGMAP Deepband
a
b
c
5-7.5
7.5-10
10-12.5
12.5-15
Depth(cm)

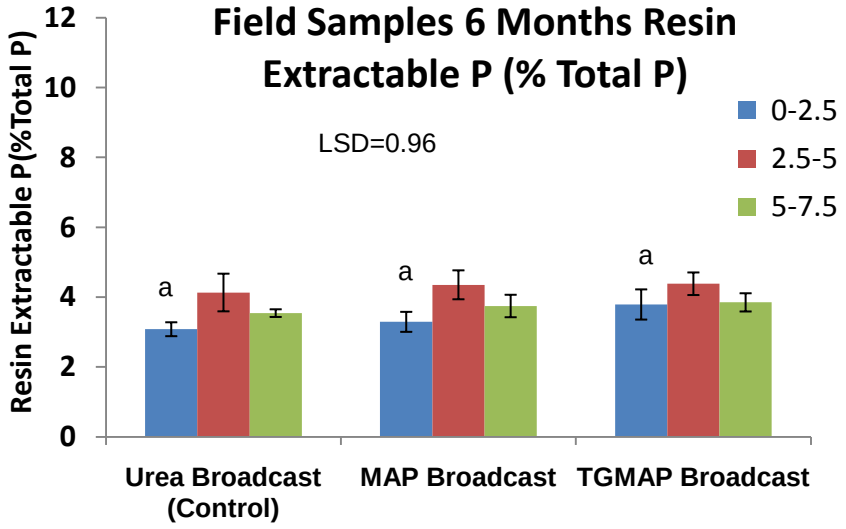

6 Month Broadcast
Resin Extractable P (mg/kg)
160
140
120
100
80
60
40
20
0
Control
MAP Broadcast
TGMAP Broadcast
bc
bc
c
0-2.5
2.5-5
5-7.5
Depth(cm)

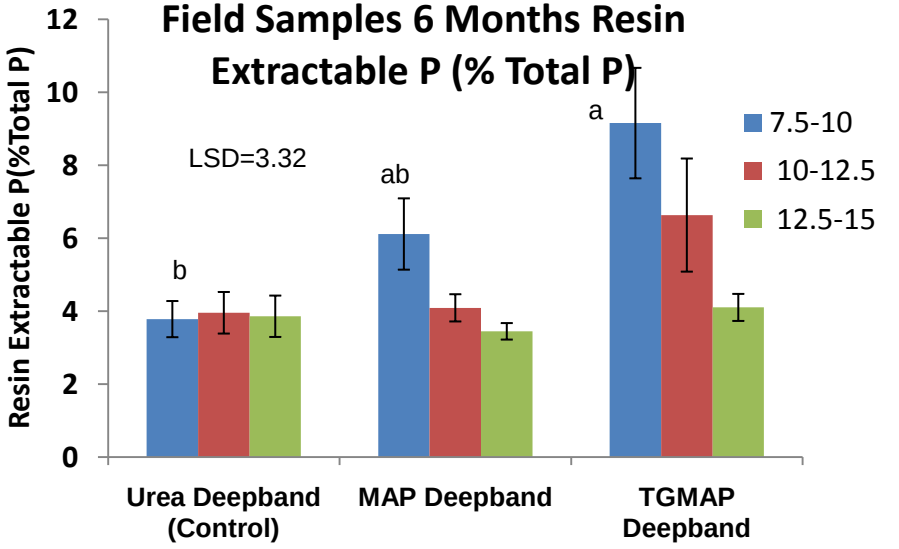

6 Month Deepband
Resin Extractable P(mg/kg)
160
140
120
100
80
60
40
20
0
Control
MAP Deepband
TGMAP Deepband
a
b
c
5-7.5
7.5-10
10-12.5
12.5-15
Depth(cm)

Resin Extractable P (%Total P)

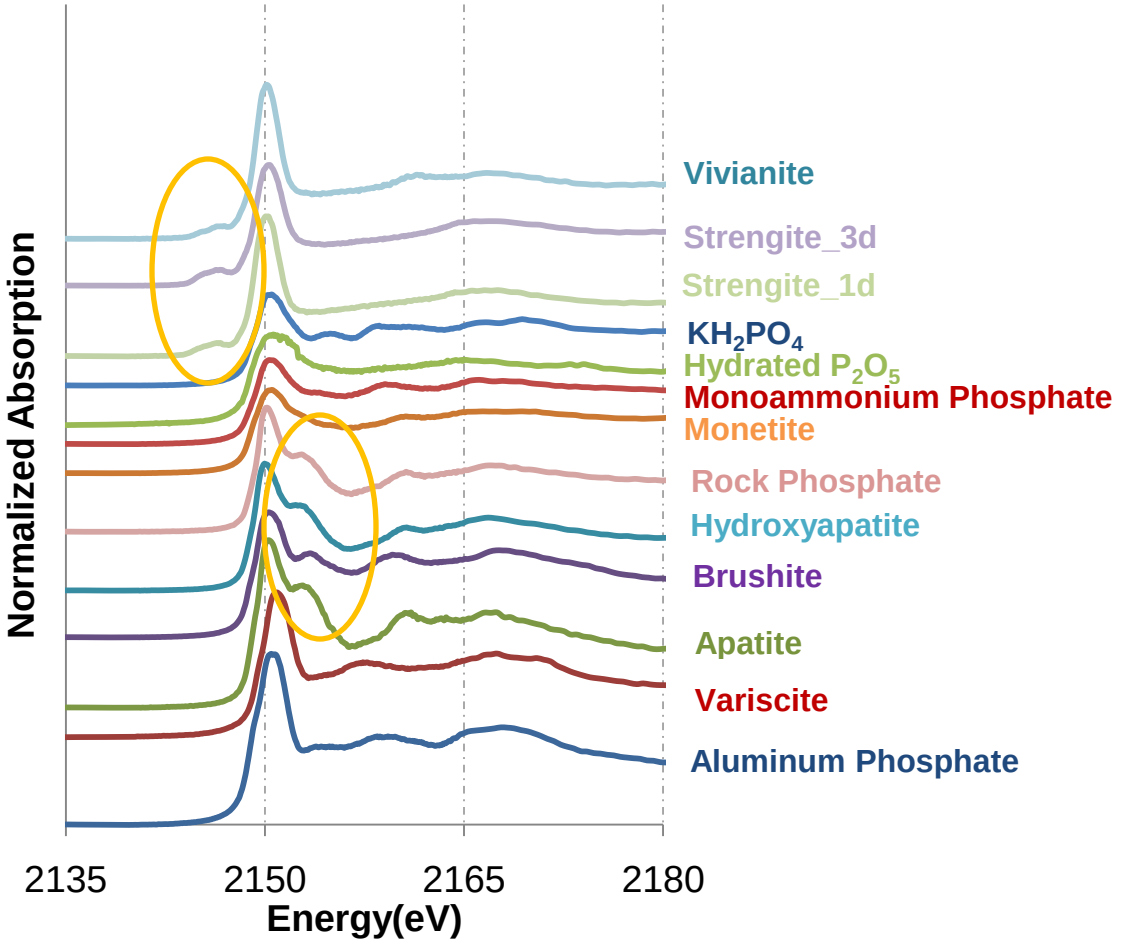


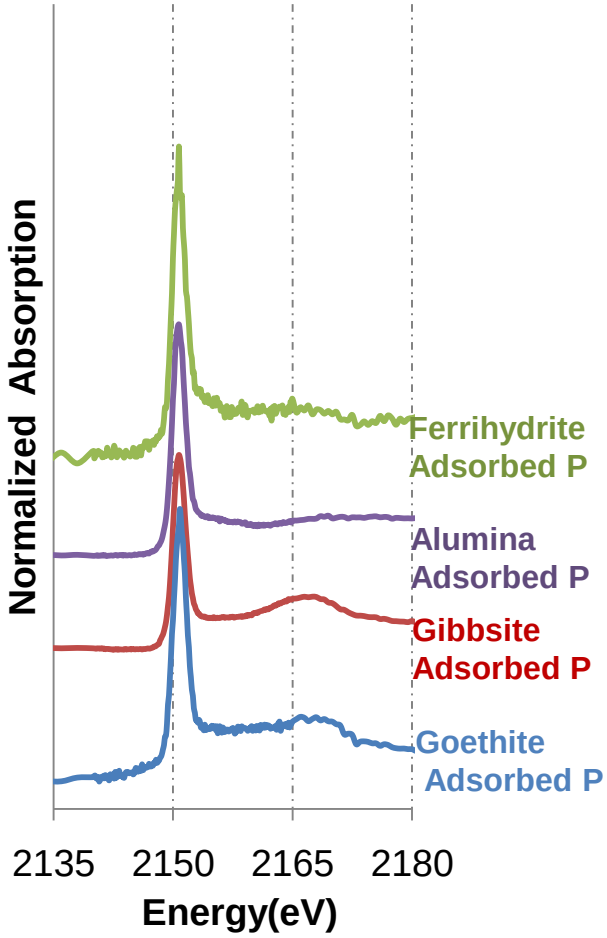






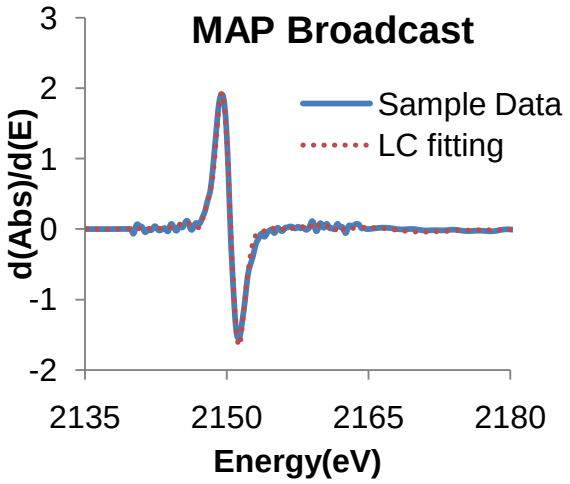
XANES Analysis

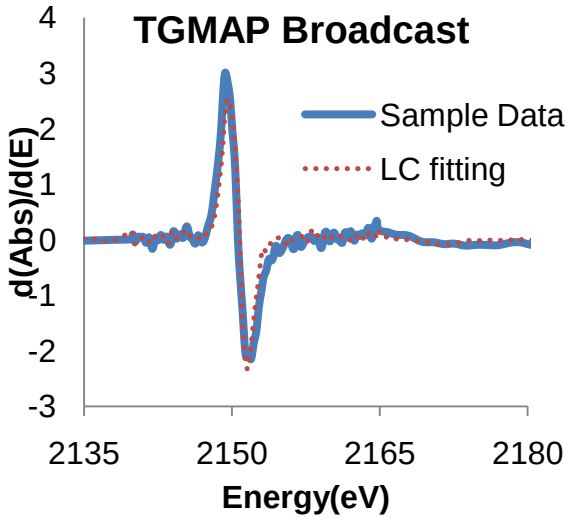


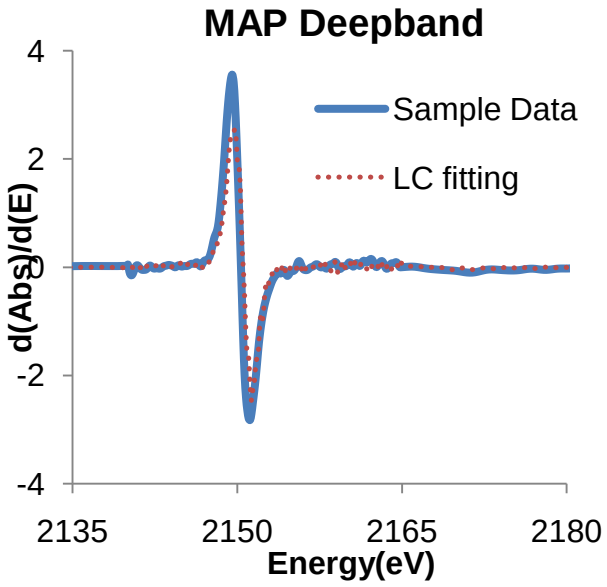


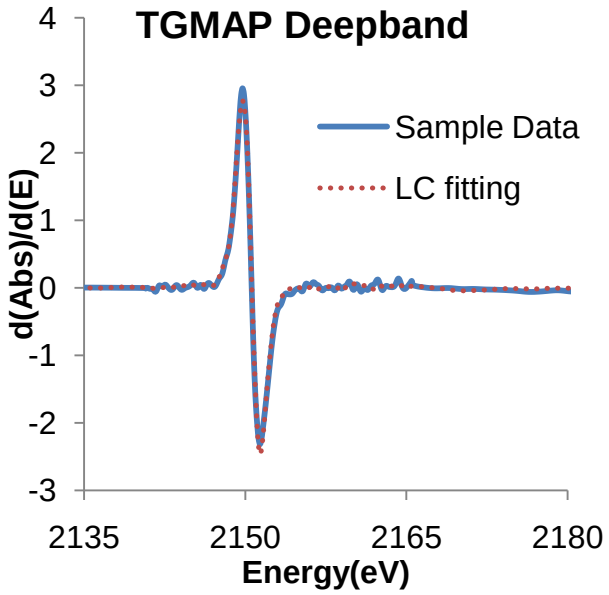
Normalized P K-XANES spectra of standards used for LCF fitting

The first derivative of the sample XANES spectra and the LC fits of selected treatments









XANES Speciation Results

5 Week

Treatment	Al-Phosphates	Ca-Phosphates	Fe(III) Phosphate	Fe(II) Phosphate	Adsorbed P	Red. χ^2
Urea Broadcast (C)	-	-	-	57.9	42.1	0.062
MAP Broadcast	11.3	-	-	69.2	19.5	0.003
TGMAP Broadcast	-	17.7	38.9	-	43.4	0.058
Urea Deepband (C)	40.5	47	-	-	12.5	0.007
MAP Deepband	-	-	-	64.5	33.5	0.120
TGMAP Deepband	-	-	-	46.7	53.4	0.003

6 Month

Treatment	Al-Phosphates	Ca-Phosphates	Fe(III) Phosphate	Fe(II) Phosphate	Adsorbed P	Red. χ^2
Urea Broadcast (C)	60.4	-	-	39.6	-	0.411
MAP Broadcast	-	100	-	-	-	1.130
TGMAP Broadcast	-	100	-	-	-	1.130
Urea Deepband (C)	-	53	-	47	-	6.600
MAP Deepband	-	51.6	-	-	48.4	1.470
TGMAP Deepband	-	19.8	-	-	80.3	0.010

**One year samples data just collected at APS*

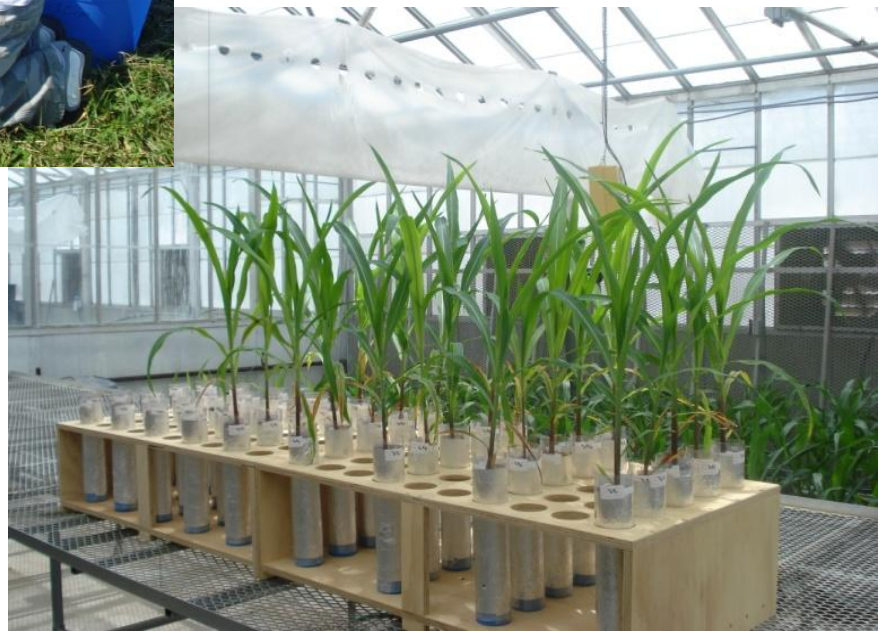
Conclusions- Field study

- The deep placement resulted greater resin extractable P in P applied zone compared to the broadcast treatment
- Deep placed liquid fertilizer P gave greater resin extractable P both at 5 wk and 6 month after application
- Speciation results showed that at 5 wk granular-P fertilizers tended to form Fe-Phosphate like products whereas liquid forms found to remain in adsorbed-P like forms in soil

Conclusions- Field study (cont.)

- With time reaction products of broadcast-granular and liquid P fertilizers transformed to Ca phosphate-like forms while deep placed fertilizers continued to remain in adsorbed-P like forms

Greenhouse- Plant Study



Methodology- Greenhouse study

- **Pre Study Sampling :** 0-7, 7-15 and 15-30 cm
  Column size: 2.75 inch diameter, 13.8 inch long
  Plant: Corn (DKC 64-79 a VT3 hybrid)

Experimental Design: RCBD (5 reps/blocks)
Treatments:

Control (Broadcast)	Control(Deepband)
MAP Broadcast	MAP Deepband
TGMAP Broadcast	TGMAP Deepband

Fertilizer Rate: P @75 kg/ha, N @200 kg/ha
Soil Moisture Level: 80% of WHC

- **Post Study Sampling**

For wet chemical analyses: 0-2.5, 2.5-5, 5-7.5,……. 27.5-30 cm
For synchrotron x-ray based and electron microscopic analyses:
Broadcast and control treatments: 0-0.5,0.5-1, 1-2.5 cm
Deep band treatments: 14-14.5, 14.5-15, 15-15.5, 15.5-16 cm

Methodology (cont.)

Plant Parameters:

Plant Biomass

Total P(H_2SO_4/H_2O_2 digestion)

Plant P uptake

Soil Parameters:

Wet chemical based analyses

Soil pH(1:5 soil to water ratio)

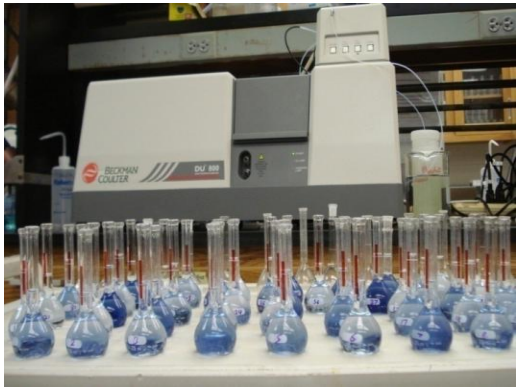
Total P (Bremner et al., 1982)

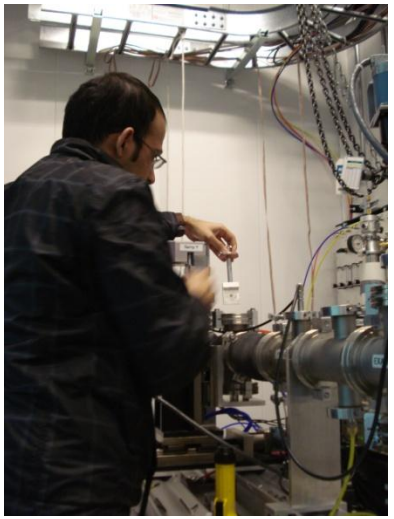
Resin Extractable P (Myers et al.,2005)

Speciation of P using synchrotron x-ray based and electron microscopic techniques

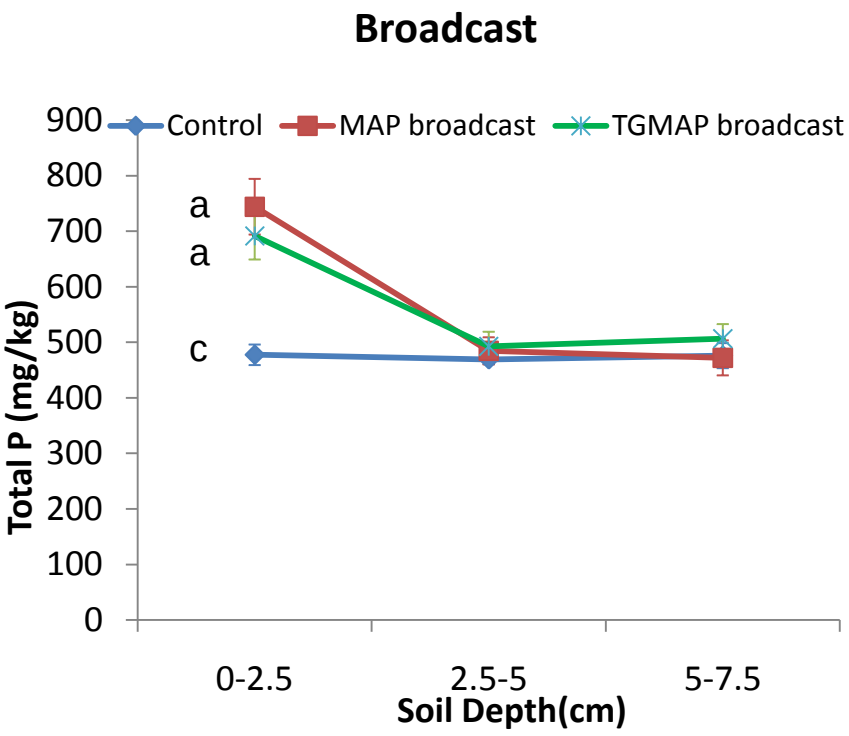
X-ray absorption near edge structure (XANES) spectroscopy

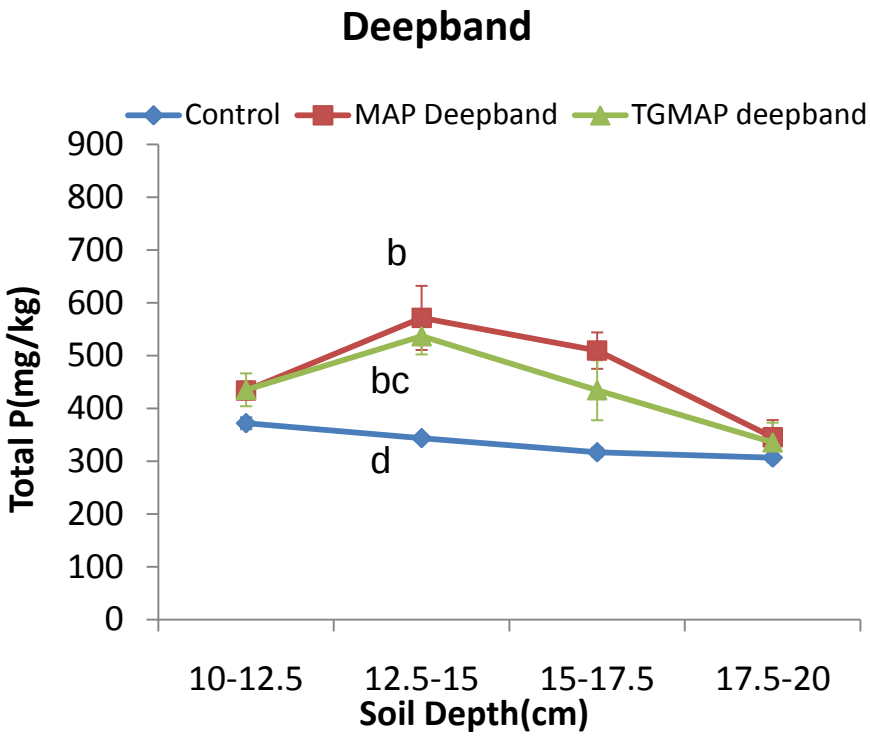
Scanning electron microscopy with energy dispersive X-ray (SEM-EDX) analyzer



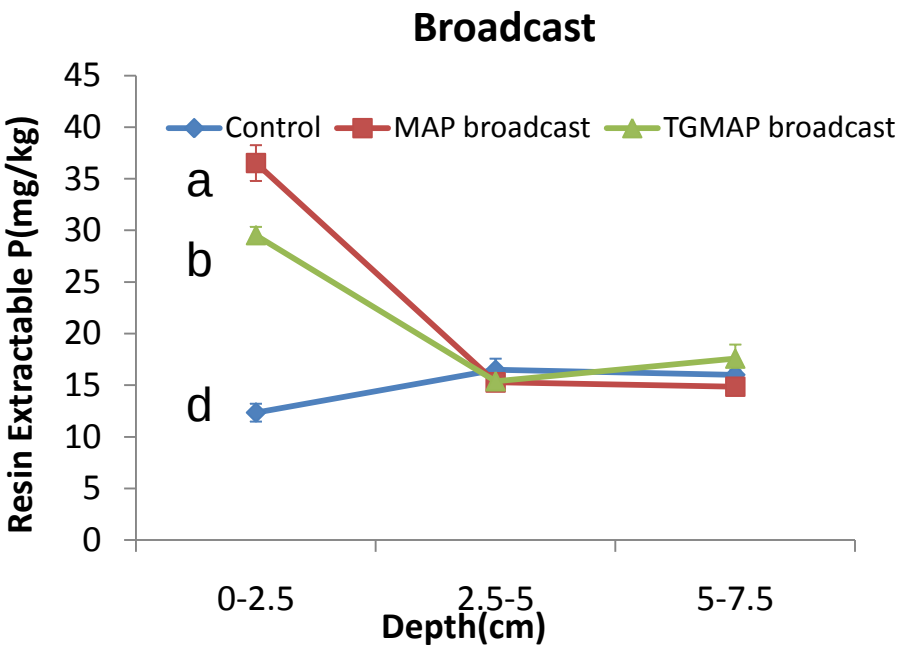


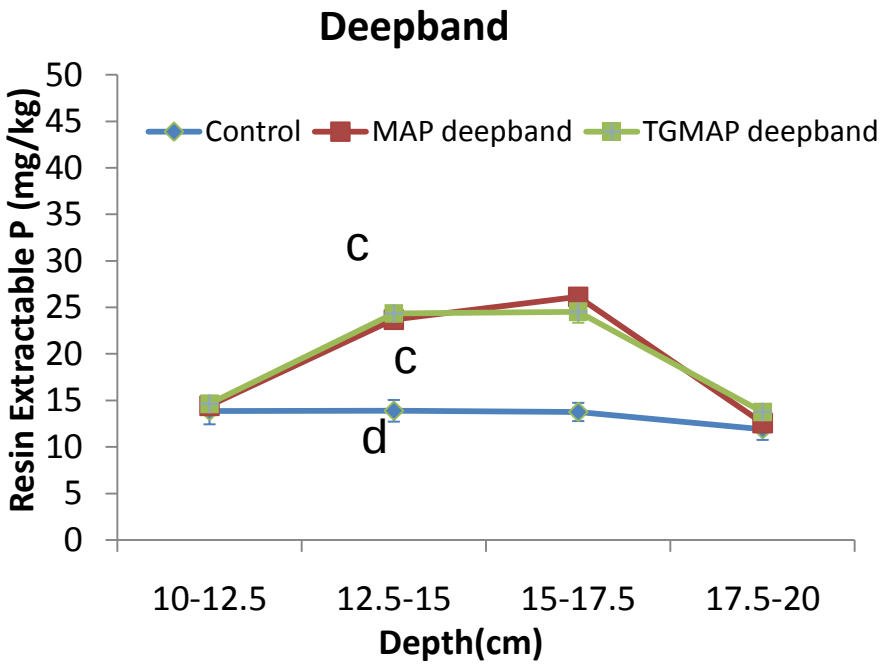
Results: Total P



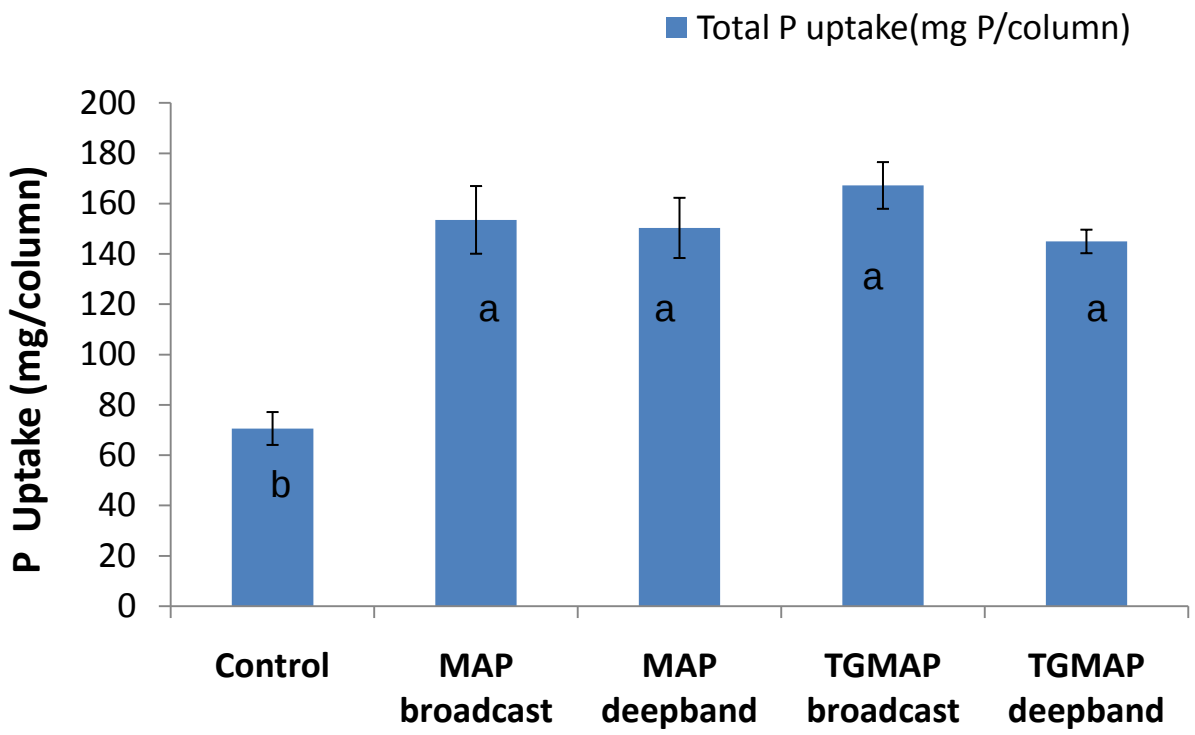


Resin Extractable P

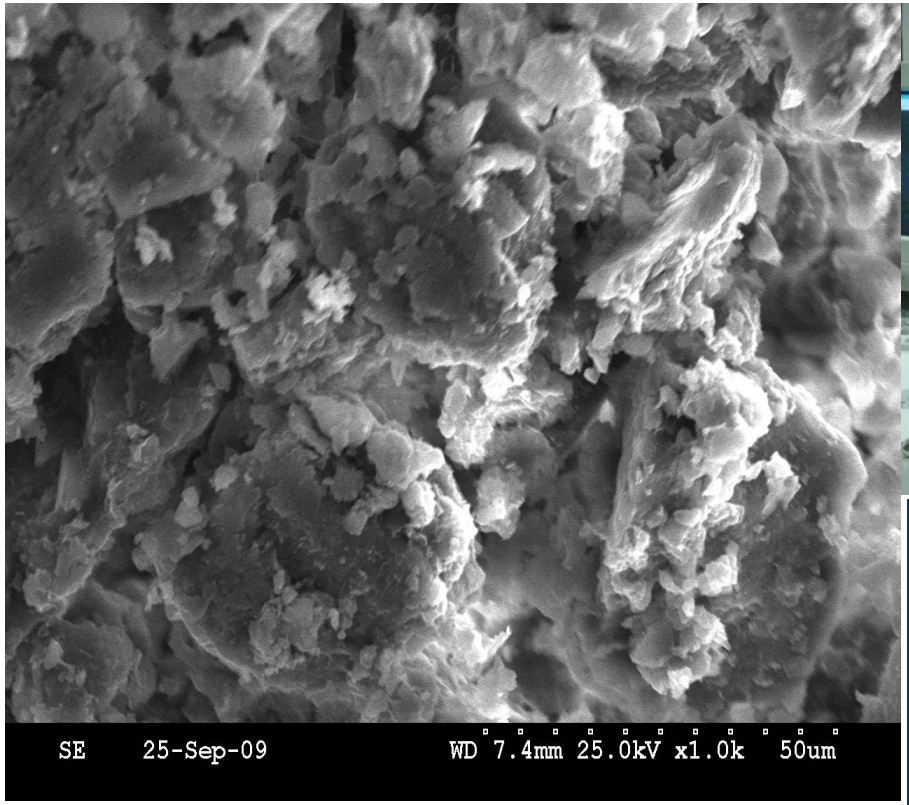




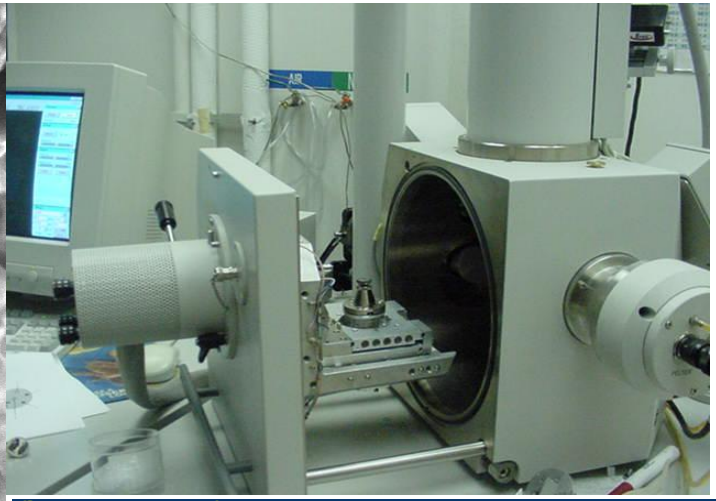
P Uptake

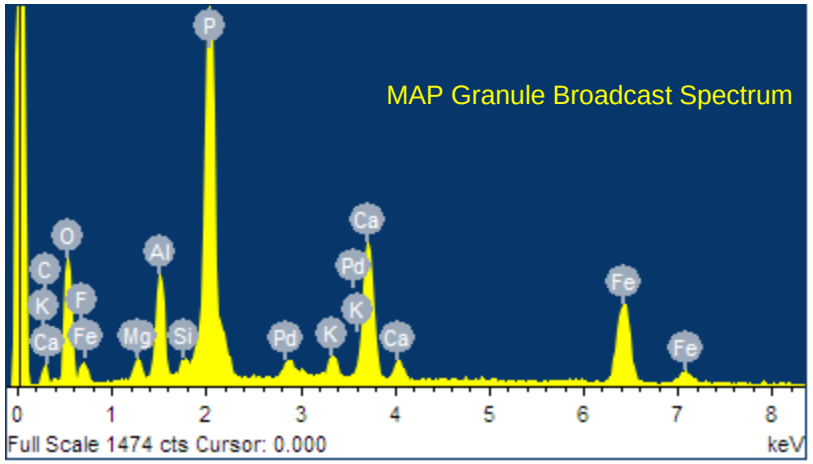

Total P uptake(mg P/column)
P Uptake (mg/column)
200
180
160
140
120
100
80
60
40
20
0
a
a
a
a
b
Control
MAP broadcast
MAP deepband
TGMAP broadcast
TGMAP deepband

SEM-EDX



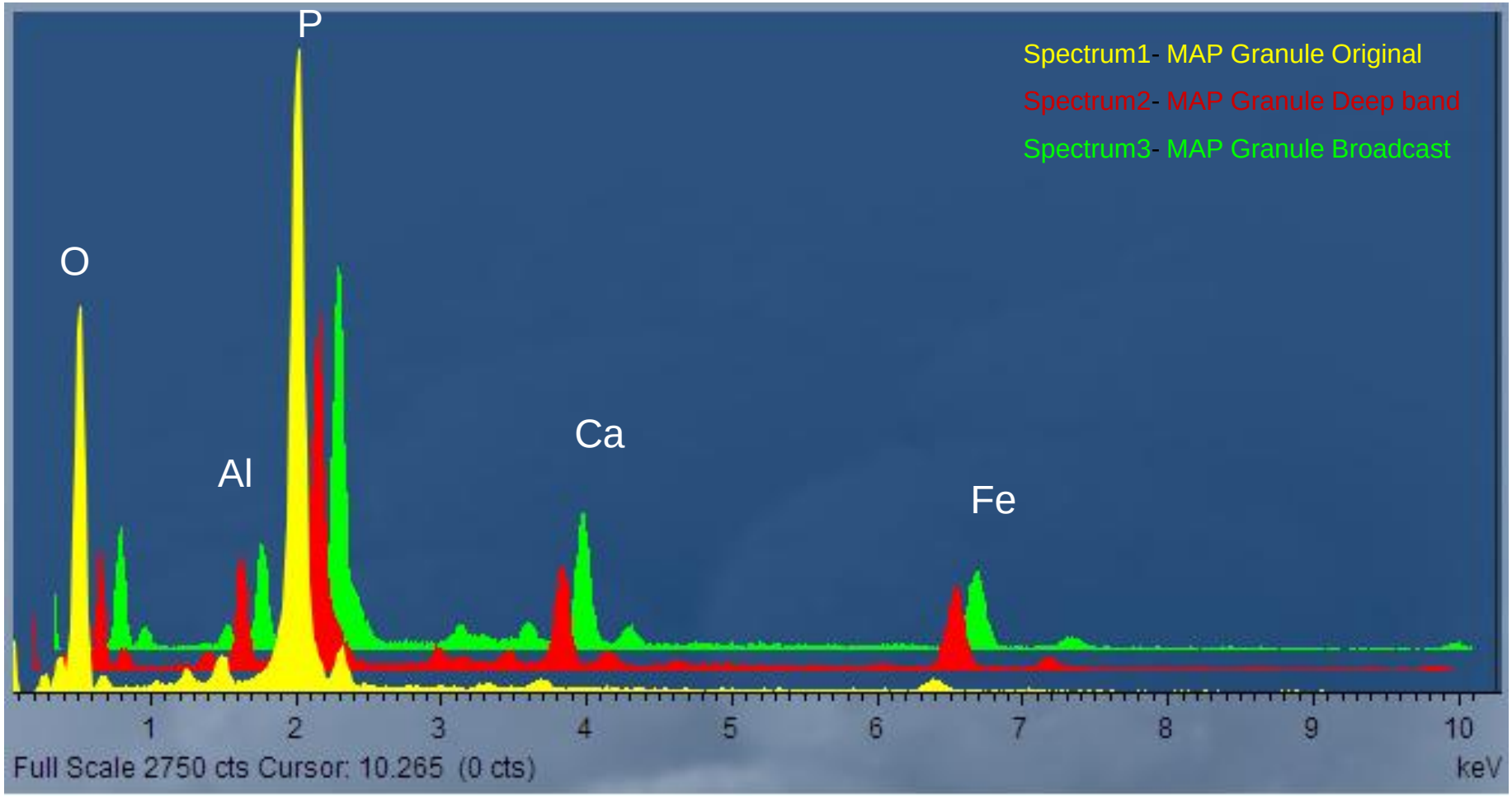
MAP Granule Broadcast Scattered Electron Image





MAP Granule Broadcast Spectrum

SEM-EDX (Spectrum Analysis)



SEM-EDXA (Elemental Analysis)

MAP Granule Original		MAP Granule Broadcast		MAP Granule Deep Band	
Element	Weight%	Element	Weight%	Element	Weight%
Mg	0.5	Mg	1.0	Mg	0.9
Al	**0.9**	**Al**	**3.9**	**Al**	**5.5**
Si	-	Si	0.3	Si	0.4
P	**19.9**	**P**	**15.3**	**P**	**17.7**
S	1.4	S	-	S	-
K	0.2	K	1.1	K	1.0
Ca	**0.4**	**Ca**	**8.0**	**Ca**	**7.9**
Fe	**1.5**	**Fe**	**12.9**	**Fe**	**16.7**

XANES Speciation Results

Treatment	Monetite $CaHPO_4$	Adsorbed P	Strengite $Fe(III)_3PO_4 \cdot 2H_2O$	Vivianite $Fe(II)_3(PO_4)_2 \cdot 8H_2O$	Red. χ^2
Control	-	24.8	75.2	-	0.074
MAP Broadcast	-	30.3	-	69.7	0.009
TGMAP Broadcast	-	24.6	-	75.5	0.006
MAP Deepband	50.2	10.7	-	38.4	0.005
TGMAP Deepband	-	22.5	-	77.5	0.009

Results of the Fits (%) Performed in First-Derivative Space, Energy Range between -5 to 30 eV

Conclusions

- Plant P uptake data (at 5 wk) indicated there was no significant source or placement effect
- Resin extractable P did not indicate any significant source or placement effect
- Speciation results indicated that Fe, Ca and/or Al are major cations responsible for P “fixation” in this acidic soil

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