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
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
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 comparison, Bonferroni test ($\alpha=0.05$) (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)

<table>
<thead>
<tr>
<th>Depth(cm)</th>
<th>Total C (%)</th>
<th>Total N (%)</th>
<th>Total Fe (%)</th>
<th>Total Al (%)</th>
<th>Total Ca cmol(+)/kg⁻¹</th>
<th>Total Clay %</th>
<th>Total Silt %</th>
<th>Total Sand %</th>
<th>Total CEC cmol(+)/kg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-13</td>
<td>1.14</td>
<td>0.14</td>
<td>0.18</td>
<td>0.12</td>
<td>31.6 cmol(+)/kg⁻¹</td>
<td>33.0</td>
<td>56.2</td>
<td>10.8</td>
<td>34.4 cmol(+)/kg⁻¹</td>
</tr>
<tr>
<td>13-29</td>
<td>0.86</td>
<td>0.11</td>
<td>0.17</td>
<td>0.13</td>
<td>19.3 cmol(+)/kg⁻¹</td>
<td>38.3</td>
<td>51.8</td>
<td>27.8</td>
<td>23.9 cmol(+)/kg⁻¹</td>
</tr>
</tbody>
</table>

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

5 Week Broadcast
- Urea Broadcast (Control)
- MAP Broadcast
- TGMAP Broadcast

5 Week Deepband
- Urea Deepband (Control)
- MAP Deepband
- TGMAP Deepband

6 Month Broadcast
- Urea Broadcast (Control)
- MAP Broadcast
- TGMAP Broadcast

6 Month Deepband
- Urea Deepband (Control)
- MAP Deepband
- TGMAP Deepband
Total P

5 Week Broadcast
- Urea Broadcast (Control)
- MAP Broadcast
- TGMAP Broadcast

5 Week Deepband
- Urea Deepband (Control)
- MAP Deepband
- TGMAP Deepband

6 Month Broadcast
- Urea Broadcast (Control)
- MAP Broadcast
- TGMAP Broadcast

6 Month Deepband
- Urea Deepband (Control)
- MAP Deepband
- TGMAP Deepband
Resin P

**5 Week Broadcast**
- Resin Extractable P (mg/kg)
  - Control
  - MAP Broadcast
  - TGMAP Broadcast
- Depth (cm): 0-2.5, 2.5-5, 5-7.5

**5 Week Deepband**
- Resin Extractable P (mg/kg)
  - Control
  - Map Deepband
  - TGMAP Deepband
- Depth (cm): 5-7.5, 7.5-10, 10-12.5, 12.5-15

**6 Month Broadcast**
- Resin Extractable P (mg/kg)
  - Control
  - MAP Broadcast
  - TGMAP Broadcast
- Depth (cm): 0-2.5, 2.5-5, 5-7.5

**6 Month Deepband**
- Resin Extractable P (mg/kg)
  - Control
  - MAP Deepband
  - TGMAP Deepband
- Depth (cm): 5-7.5, 7.5-10, 10-12.5, 12.5-15

Legend:
- b, c
- b, c
- a

Legend:**
- b, c
- b, c
- a

Legend:**
- b, c
- b, c
- a
Resin Extractable P (%Total P)

Field Samples 5 wk Resin Extractable P (% Total P)

Field Samples 6 Months Resin Extractable P (% Total P)

Field Samples 5 wk Resin Extractable P (% Total P)

Field Samples 6 Months Resin Extractable P (% Total P)

LaSD=1.87

LaSD=7.36

LaSD=0.96

LaSD=3.32
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

**MAP Broadcast**

- Sample Data
- LC fitting

**MAP Deepband**

- Sample Data
- LC fitting

**TGMAP Broadcast**

- Sample Data
- LC fitting

**TGMAP Deepband**

- Sample Data
- LC fitting
## XANES Speciation Results

### 5 Week

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Al-Phosphates</th>
<th>Ca-Phosphates</th>
<th>Fe(III) Phosphate</th>
<th>Fe(II) Phosphate</th>
<th>Adsorbed P</th>
<th>Red. $\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea Broadcast (C)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>57.9</td>
<td>42.1</td>
<td>0.062</td>
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<tr>
<td>MAP Broadcast</td>
<td>11.3</td>
<td>-</td>
<td>-</td>
<td>69.2</td>
<td>19.5</td>
<td>0.003</td>
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<tr>
<td>TGMAP Broadcast</td>
<td>-</td>
<td>17.7</td>
<td>38.9</td>
<td>-</td>
<td>43.4</td>
<td>0.058</td>
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<tr>
<td>Urea Deepband (C)</td>
<td>40.5</td>
<td>47</td>
<td>-</td>
<td>-</td>
<td>12.5</td>
<td>0.007</td>
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<tr>
<td>MAP Deepband</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>64.5</td>
<td>33.5</td>
<td>0.120</td>
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<tr>
<td>TGMAP Deepband</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>46.7</td>
<td>53.4</td>
<td>0.003</td>
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</tbody>
</table>

### 6 Month

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Al-Phosphates</th>
<th>Ca-Phosphates</th>
<th>Fe(III) Phosphate</th>
<th>Fe(II) Phosphate</th>
<th>Adsorbed P</th>
<th>Red. $\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea Broadcast (C)</td>
<td>60.4</td>
<td>-</td>
<td>-</td>
<td>39.6</td>
<td>-</td>
<td>0.411</td>
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<tr>
<td>MAP Broadcast</td>
<td>-</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.130</td>
</tr>
<tr>
<td>TGMAP Broadcast</td>
<td>-</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.130</td>
</tr>
<tr>
<td>Urea Deepband (C)</td>
<td>-</td>
<td>53</td>
<td>-</td>
<td>47</td>
<td>-</td>
<td>6.600</td>
</tr>
<tr>
<td>MAP Deepband</td>
<td>-</td>
<td>51.6</td>
<td>-</td>
<td>-</td>
<td>48.4</td>
<td>1.470</td>
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<tr>
<td>TGMAP Deepband</td>
<td>-</td>
<td>19.8</td>
<td>-</td>
<td>-</td>
<td>80.3</td>
<td>0.010</td>
</tr>
</tbody>
</table>

*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$_2$SO$_4$/H$_2$O$_2$ 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

Broadcast

Deepband

Soil Depth (cm)

Soil Depth (cm)

Total P (mg/kg)

Total P (mg/kg)
Resin Extractable P

Broadcast

Deepband

Resin Extractable P (mg/kg)

Depth (cm)

0-2.5
2.5-5
5-7.5
10-12.5
12.5-15
15-17.5
17.5-20

Control
MAP broadcast
TGMAP broadcast

Control
MAP deepband
TGMAP deepband

a
b
d
c
c
d
P Uptake

![Bar graph showing P uptake (mg/column) for different treatments: Control, MAP broadcast, MAP deepband, TGMAP broadcast, TGMAP deepband. The graph indicates that TGMAP treatments result in higher P uptake compared to the control and other treatments.](image)
SEM-EDX

MAP Granule Broadcast Scattered Electron Image

MAP Granule Broadcast Spectrum
SEM-EDX (Spectrum Analysis)

Spectrum1 - MAP Granule Original
Spectrum2 - MAP Granule Deep band
Spectrum3 - MAP Granule Broadcast

Full Scale 2750 cts Cursor: 10.265 (0 cts)

Elements identified: O, Al, Ca, Fe, P
### SEM-EDXRA (Elemental Analysis)

<table>
<thead>
<tr>
<th>Element</th>
<th>MAP Granule Original</th>
<th></th>
<th>Element</th>
<th>Weight%</th>
<th>Element</th>
<th>Weight%</th>
<th>Element</th>
<th>Weight%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>0.5</td>
<td></td>
<td>Mg</td>
<td>1.0</td>
<td>Mg</td>
<td>0.9</td>
<td></td>
<td></td>
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<tr>
<td>Al</td>
<td>0.9</td>
<td></td>
<td>Al</td>
<td>3.9</td>
<td>Al</td>
<td>5.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td></td>
<td></td>
<td>Si</td>
<td>0.3</td>
<td>Si</td>
<td>0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>19.9</td>
<td></td>
<td>P</td>
<td>15.3</td>
<td>P</td>
<td>17.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>1.4</td>
<td></td>
<td>S</td>
<td></td>
<td>S</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>0.2</td>
<td></td>
<td>K</td>
<td>1.1</td>
<td>K</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>0.4</td>
<td></td>
<td>Ca</td>
<td>8.0</td>
<td>Ca</td>
<td>7.9</td>
<td></td>
<td></td>
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<tr>
<td>Fe</td>
<td>1.5</td>
<td></td>
<td>Fe</td>
<td>12.9</td>
<td>Fe</td>
<td>16.7</td>
<td></td>
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</table>
# XANES Speciation Results

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Monetite CaHPO$_4$</th>
<th>Adsorbed P Fe(III)$_3$PO$_4$ • 2H$_2$O</th>
<th>Strengite Fe(II)$_3$(PO$_4$)$_2$ • 8H$_2$O</th>
<th>Vivianite Fe(II)$_3$(PO$_4$)$_2$ • 8H$_2$O</th>
<th>Red. $\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>-</td>
<td>24.8</td>
<td>75.2</td>
<td>-</td>
<td>0.074</td>
</tr>
<tr>
<td>MAP Broadcast</td>
<td>-</td>
<td>30.3</td>
<td>-</td>
<td>69.7</td>
<td>0.009</td>
</tr>
<tr>
<td>TGMAP Broadcast</td>
<td>-</td>
<td>24.6</td>
<td>-</td>
<td>75.5</td>
<td>0.006</td>
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<tr>
<td>MAP Deepband</td>
<td>50.2</td>
<td>10.7</td>
<td>-</td>
<td>38.4</td>
<td>0.005</td>
</tr>
<tr>
<td>TGMAP Deepband</td>
<td>-</td>
<td>22.5</td>
<td>-</td>
<td>77.5</td>
<td>0.009</td>
</tr>
</tbody>
</table>

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
Contributors

- Raju Khatiwada, Department of Agronomy, KSU
- Dave Mengel, Department of Agronomy, KSU
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