Behavior of Organic Sources of Phosphorus in Agricultural Systems

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Plant Available Phosphorus

- Inorganic orthophosphates
  - $H_2PO_4^-$
  - $HPO_4^{2-}$
Organic Phosphorus

- Surface Soils (75% of Total P)
- Average C:N:P ratio 140:10:1.3
- C:P range
  - 67 - 311:1 Virgin Soils
  - 141 - 526:1 Cultivated Soils
Factors Influencing C:P Ratio

- P Supply
- Parent Materials
- Texture
- Climate
- pH
- Depth of Soil
Mineralization of Organic P

- Organic P → Inorganic P
- C:P <200: Mineralization (P gain)
- C:P 200-300: No Change
- C:P >300: Immobilization (P loss)
Factors Controlling Mineralization of P

- Chemical form of organic P
- pH
- Temperature
- Soil Moisture
- Soil Microbial Communities
- Soil Enzymes
Phospholipids

- Parts of Cell Membranes
- Ill defined Group
- Estimates 1-3% of Soil Organic Matter
- Underestimated
- Strongly associated with soil mineral fractions
Nucleic Acids

- Present in all Cells
- Backbone of Nucleic acids
- Easily Decomposed
- Less than 3% of Soil Organic Phosphorus
Phytic Acid (Inositol Hexaphosphate)

- Mixed with Ca
- Cereal Grains
- Insoluble complexes
- Slow Decomposition
- High Stability
- Limited Phytase in Soils
- Synthesized in Soils
Mineralization of Organic Phosphorus

- Plant and Animal Remains
  - Phytin
    - Inositol: Rapid decomposition
    - Slow Decomposition
  - Nucleic Acids
  - Phospholipids

- Inorganic Phosphorus
  - Microbial Phosphorus
## Distribution of Inositol P in Soils

<table>
<thead>
<tr>
<th>Form</th>
<th>% of Soil Organic P</th>
<th>Percentage of IP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mono</td>
<td>1 -6</td>
<td>1-11</td>
</tr>
<tr>
<td>Di and Tri</td>
<td>4-11</td>
<td>6-15</td>
</tr>
<tr>
<td>Tetra</td>
<td>5-18</td>
<td>8-30</td>
</tr>
<tr>
<td>Penta</td>
<td>15-27</td>
<td>15-30</td>
</tr>
<tr>
<td>Hexa</td>
<td>20-66</td>
<td>20-66</td>
</tr>
</tbody>
</table>
## Recovery of Organic P

<table>
<thead>
<tr>
<th>Soil</th>
<th>Organic P ppm</th>
<th>IHP %</th>
<th>Phospholipids %</th>
<th>Nucleic Acids %</th>
<th>Total %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>39</td>
<td>44</td>
<td>7</td>
<td>2</td>
<td>54</td>
</tr>
<tr>
<td>2</td>
<td>187</td>
<td>66</td>
<td>2</td>
<td>0.2</td>
<td>68</td>
</tr>
<tr>
<td>3</td>
<td>250</td>
<td>60</td>
<td>1</td>
<td>0.5</td>
<td>61</td>
</tr>
</tbody>
</table>
## Water Soluble Organic P

<table>
<thead>
<tr>
<th>P form</th>
<th>P Faction</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Organic P</td>
<td>779</td>
<td>100</td>
</tr>
<tr>
<td>Monoester P</td>
<td>55</td>
<td>7</td>
</tr>
<tr>
<td>Inositol P</td>
<td>302</td>
<td>40</td>
</tr>
<tr>
<td>Nucleic Acids</td>
<td>43</td>
<td>6</td>
</tr>
<tr>
<td>Unreleased</td>
<td>377</td>
<td>48</td>
</tr>
</tbody>
</table>
**NaHCO₃ Extractable Organic P in Manure**

<table>
<thead>
<tr>
<th>P form</th>
<th>P Faction</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Organic P</td>
<td>426</td>
<td>100</td>
</tr>
<tr>
<td>Monoester P</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Inositol P</td>
<td>14</td>
<td>3</td>
</tr>
<tr>
<td>Nucleic Acids</td>
<td>5</td>
<td>1.1</td>
</tr>
<tr>
<td>Unreleased</td>
<td>48</td>
<td>86</td>
</tr>
</tbody>
</table>
Mode Of Organic P Loss

- Two forms: soluble P and particulate P.
  - Soluble P:
    - Inositol hexaphosphate
    - Subsurface flow in tile drainage systems;
    - Not directly available to algae.
Modes Of P Loss (Contd.)

- Particulate P (Sediment P):
  - rides fine-sized particles;
  - less available;
  - forms better part of total P loss.
Lack Of Control Of Dissolved P

Most of the management practices, namely, riparian buffer strips, conservation tillage, terracing, contour plowing, impoundments, etc., effective in controlling particulate P, but do not reduce soluble P levels adequately.
Loss Of Dissolved P: relation Between Soil Test P And Water Soluble P

- With increase in soil test P (STP), water soluble P (or the propensity of the soil to release P) in the runoff increases.
- Release explained by two linear relations of significantly different slopes on either side of a point, called change-point;
Change-point
Slow crop removal (McCollum, 1991)

0 = After 8 yr buildup
Crop removal of residual P doesn’t have adequate effect
THEREFORE, NEED TO CONTROL DISSOLVED P

How ??

- Reducing dissolved P content in manures.
- Increasing P sorption capacity (or decreasing degree of phosphorus saturation) of the soil or border strips.
Iron And Aluminum Oxides

- Have great affinity for dissolved P.
- Several industrial and mining wastes are rich in these oxides.
- Acid mine drainage floc is one.
Use Of Industrial And Mining Wastes

- Peacock and Rimmer (2000) examined the suitability of an iron oxide-rich gypsum byproduct as a soil amendment.
- Red gypsum: a byproduct of titanium oxide pigment manufacturing industry; contains about 35% iron oxides.
- $P$ sorption characteristics of red gypsum compared with those of pure gypsum and iron oxides isolated from the red gypsum.
So, other readily available iron oxide-rich mining wastes should be evaluated for their ability to attenuate P in runoff and leachates from soils.
Fig. 2. Initial drying stage of acid mine drainage floc (5% solids)
Objectives

Study of effectiveness of border strips treated with acid mine drainage (AMD) floc in controlling runoff P loss; and

❖ Study of P sorption onto AMD floc.
Sorption of P onto acid mine drainage floc

• Objectives:
  – To assess P remediation potential of various AMD flocs.
  – To investigate implications of P sorption on various AMD flocs in determining environmental thresholds of P for soils in which amorphous Fe and Al oxides are the main controllers of P movement.
Materials and Methods

• AMD collected from Omega mine in Monongalia county of WV.
• One part of AMD collected and titrated at the site of discharge with 1.0M ammonium hydroxide to pH 7.
• Similarly, the other part titrated with 1.0M NaOH.
• The third type of floc was lime-treated.
Materials and Methods (contd.)

• Similarly, another set equilibrated with inositol hexaphosphate (IHP)-P.
• Three replicates.
• Measurements for inorganic P, IHP-P and metals on ICP-AES.
Elemental composition and P sorption capacity of the flocs

- >99% of total Fe amorphous.
- > 98% of total Al amorphous.
Sorption of inorganic-P on various acid mine drainage flocs

Equilibrium solution concentration (µMol L⁻¹)

P sorbed (µMol g⁻¹)

- Ammonia
- Lime
- NaOH
Sorption of inositol hexaphosphate (IHP)-P on various acid mine drainage flocs.
Ratio of inositol hexaphosphate (IHP)-P and inorganic P sorbed onto various acid mine drainage flocs.
Conclusions

• Various AMD flocs can sorb substantial amounts of P.
• Far greater amounts of IHP-P than inorganic-P sorbed.
Hydrolysis of inositol hexaphosphate (IHP) by AMD floc

- Inositol hexaphosphate (IHP) or phytate sorbs strongly onto Fe and Al oxides.
- Some studies: metal oxides facilitate hydrolysis of organic compounds.
Consequences of hydrolysis

- Hypothesis: P retained, organic moiety released.
- Then, P attenuation capacity of flocs impaired.
- If IHP hydrolyzed first, P ions take more sites.
Diagnosis for hydrolysis

- Carbon: Phosphorus ratio in equilibrium solution (with AMD floc).
- If ratio more than that in blank, IHP-P sorbed after hydrolysis.
- If ratio same: sorbed as it is.
Carbon: Phosphorus ratio of IHP-P solutions equilibrated with or without AMD flocs.

![Graph showing Carbon: Phosphorus ratio vs pH with different treatments: Control, Ammonia, Lime, NaOH.](image-url)
Orthophosphate-P concentrations of 200mg L⁻¹ IHP-P solution at various pH levels
Conclusions

- IHP sorbed *as such*.
- No appreciable effect of pH.
- AMD floc attenuates much more IHP-P than inorganic P.
Effectiveness Of Border Strips Treated With AMD Floc In Controlling Runoff P Loss

- Rainfall simulation experiment:
  - runoff plots set up at three different locations in Grant and Pendleton counties (WV).
  - 0, 20, 40, and 60 per cent of the area covered by slurry of AMD floc.
  - USDA-ARS rainfall simulator.
  - Four rainfall events
Runoff Plots
Rainfall Simulator
Degree of phosphorus saturation(%)
Fig. 8. Effect of acid mine drainage floc additions on Mehlich-1 P.
Fig. 10. Effect of acid mine drainage floc additions on degree of phosphorus saturation.
Border Strips
Fig. 13. Effect of acid mine drainage floc buffer strips on dissolved P in runoff from site 1.
Fig. 14. Effect of acid mine drainage floc buffer strips on dissolved P in runoff at Site 2.
Fig. 15. Effect of acid mine drainage floc buffer strips on dissolved P in runoff at Site 3.
Manure Storage Areas
Total Dissolved Phosphorus In Runoff At 2% Slope

TDP (ppm)

Minutes

20%
40%
CONTROL
Total Dissolved Phosphorus In Runoff At 8% Slope

TDP (ppm)

Minute

20%  40%  CONTROL

0  5  10  15

0  10  20  30  40

Total Dissolved Phosphorus In Runoff At 16% Slope

TDP (ppm)

Minute

20%  40%  CONTROL
Conclusions

Acid mine drainage floc has very high capacity to fix P
High amounts of phytic acid phosphate is fixed by AMD flocs
Border strips treated with AMD floc reduce dissolved P
AMD floc reduces dissolved P from temporary manure storage areas
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