



# **Phosphorus Availability from Organic Residuals**

**UMass Extension Symposium:  
Managing Phosphorus in Organic Residuals  
Applied to Soils  
November 2, 2016**

Amy L. Shober  
Associate Professor and Extension Specialist  
University of Delaware

# Topics for Discussion

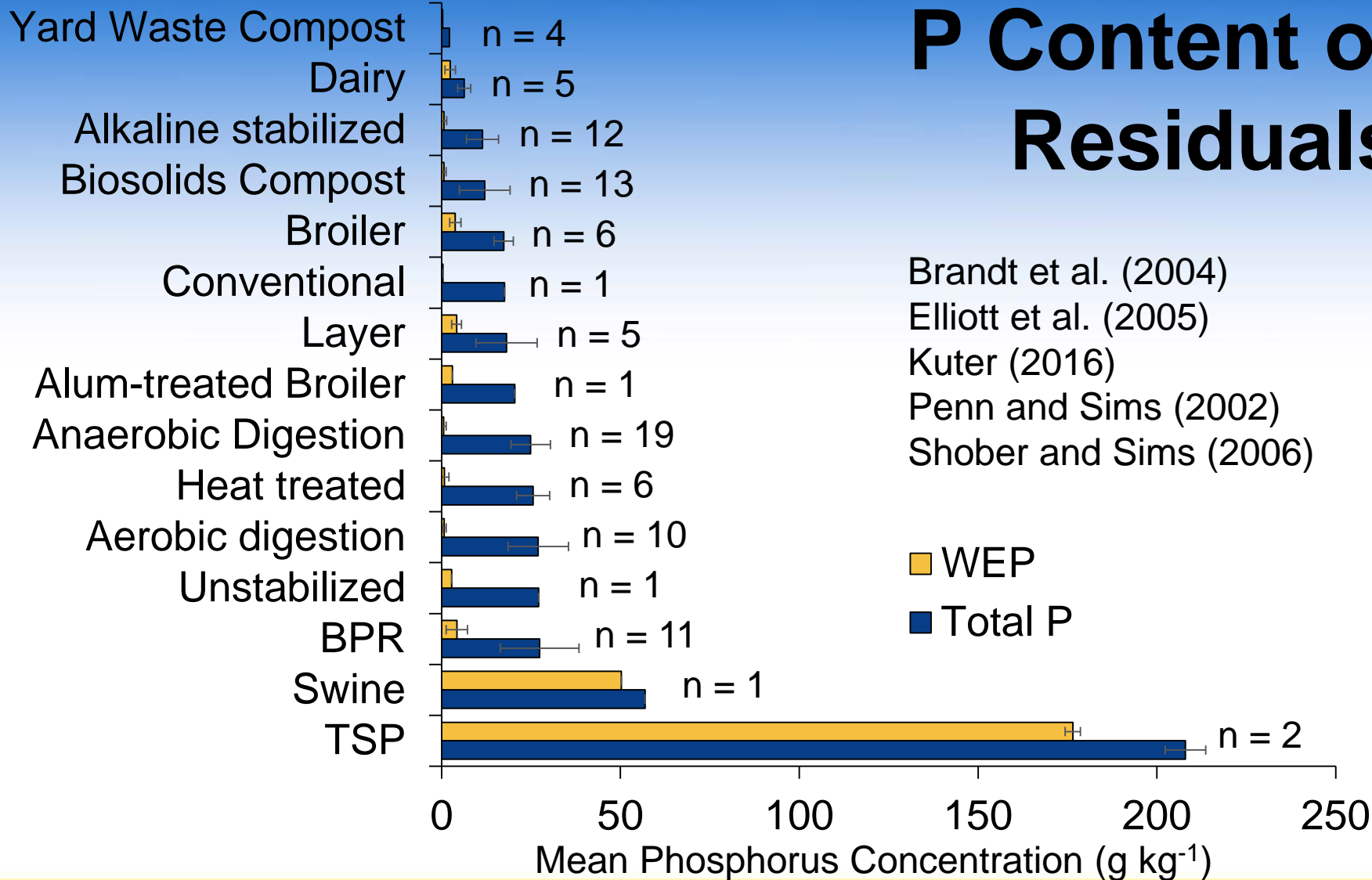
- Survey of P in organic residuals
- Chemical speciation of P in residuals
- Fate of residual P in agricultural soils
  - Surface applied residuals
  - Incorporated/injected residuals
- Phosphorus dynamics following application of residuals

Managing Phosphorus in Organic Residuals Applied to Soils

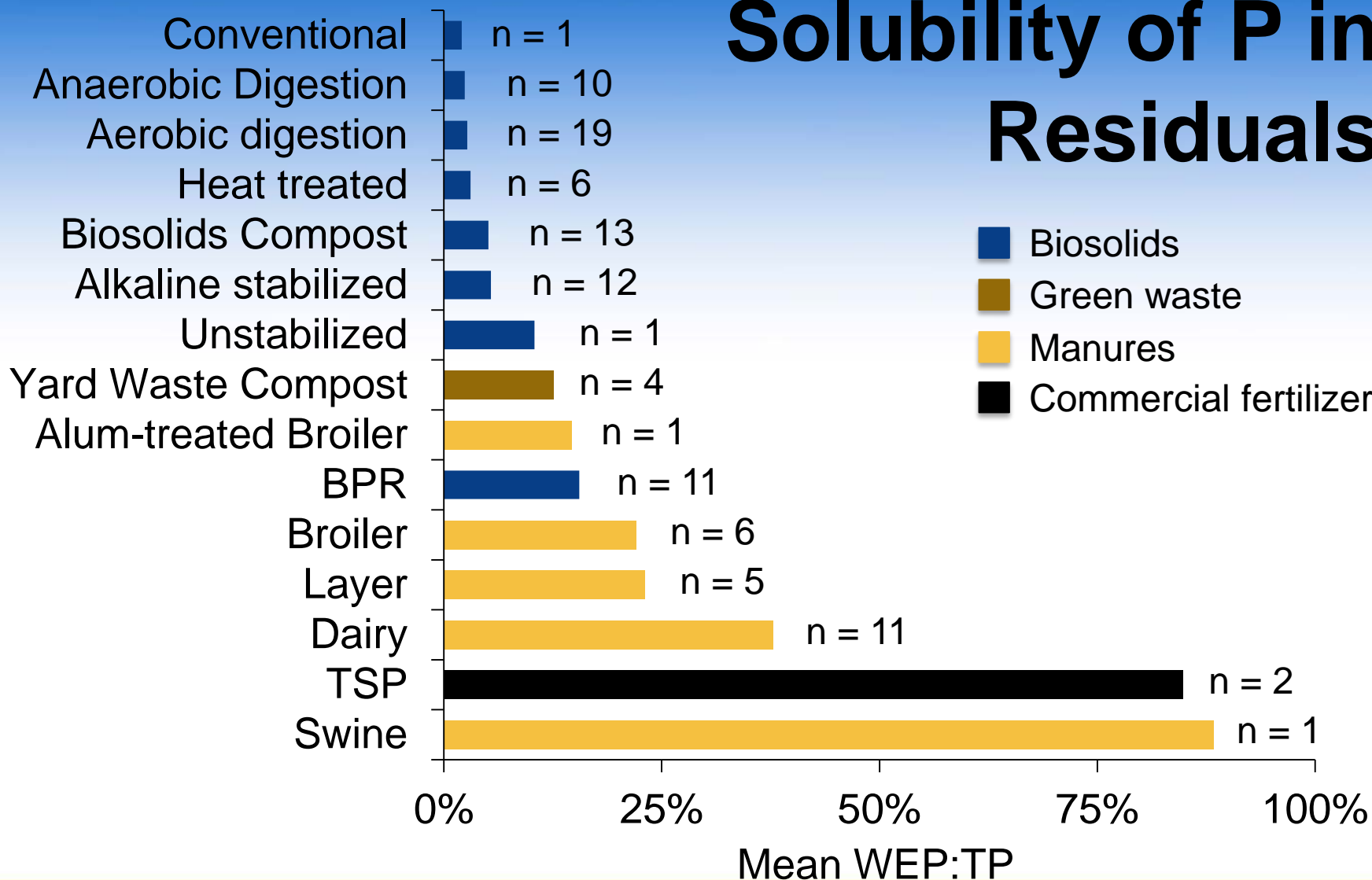
# **SURVEY OF PHOSPHORUS IN RESIDUALS**

# What Do We Know About Phosphorus in Residuals?

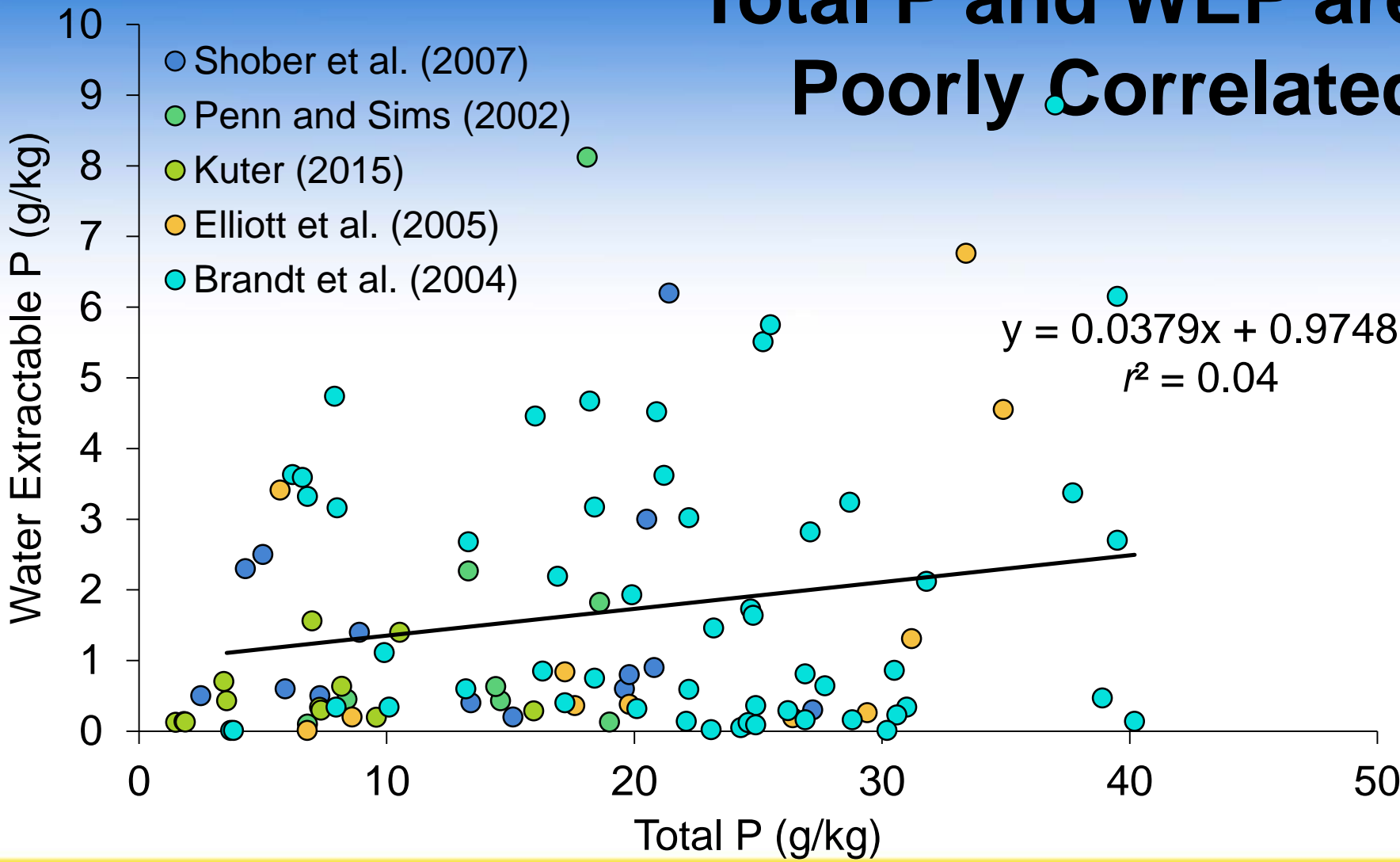
- Wet chemical analysis provide some evidence of chemical “forms”
  - Examples:
    - EPA 3050 digestion (“Total” elements)
    - Water extractable P (WEP)
    - Sequential chemical fractionation (Operational fractions)
- Requires sample destruction



# Solubility of P in Residuals



# Total P and WEP are Poorly Correlated



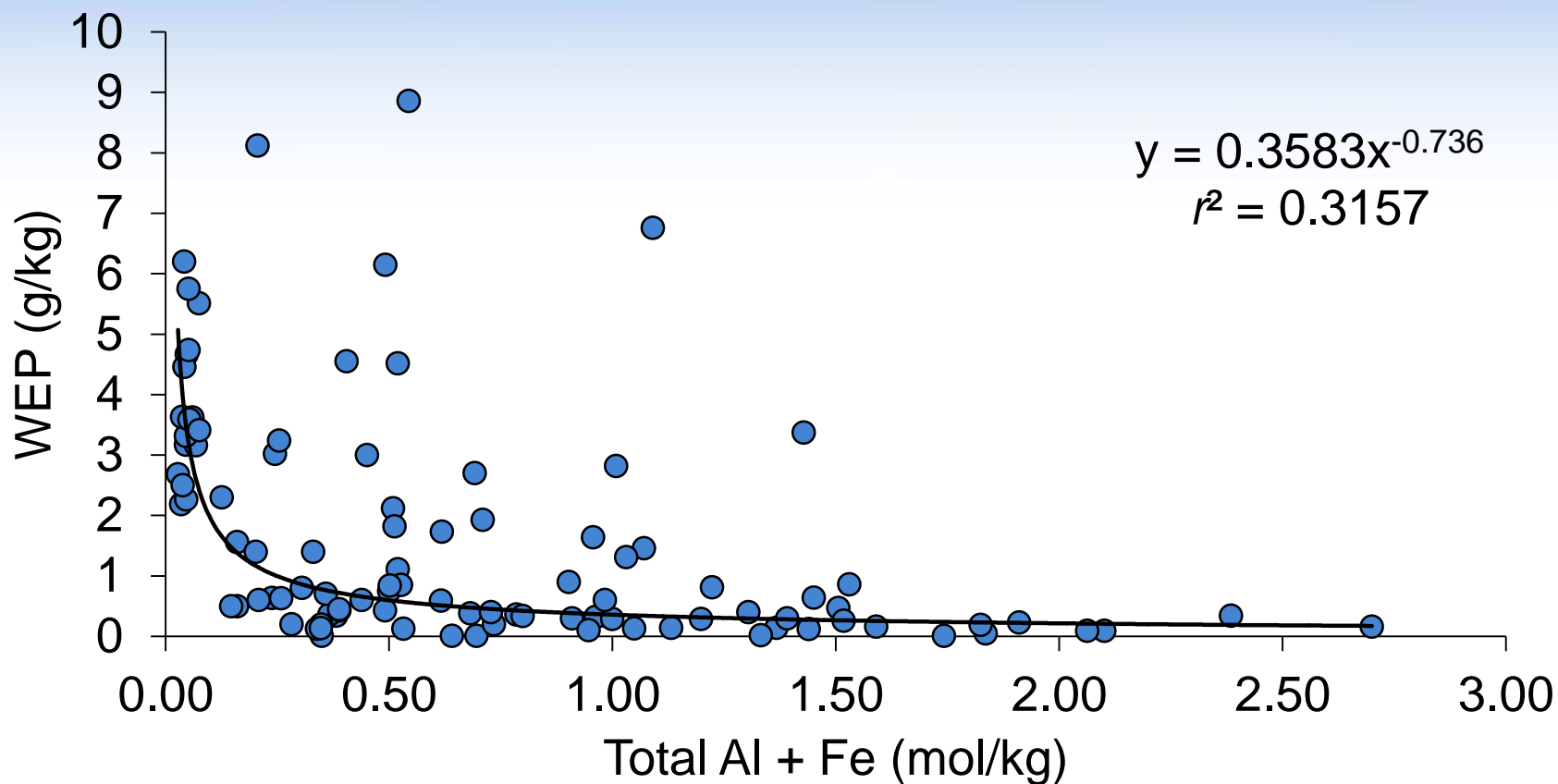
# What Factors Affect P Solubility?

1. Chemical composition and treatment
2. Animal type and diet modification
3. Storage of materials (wet vs. dry)





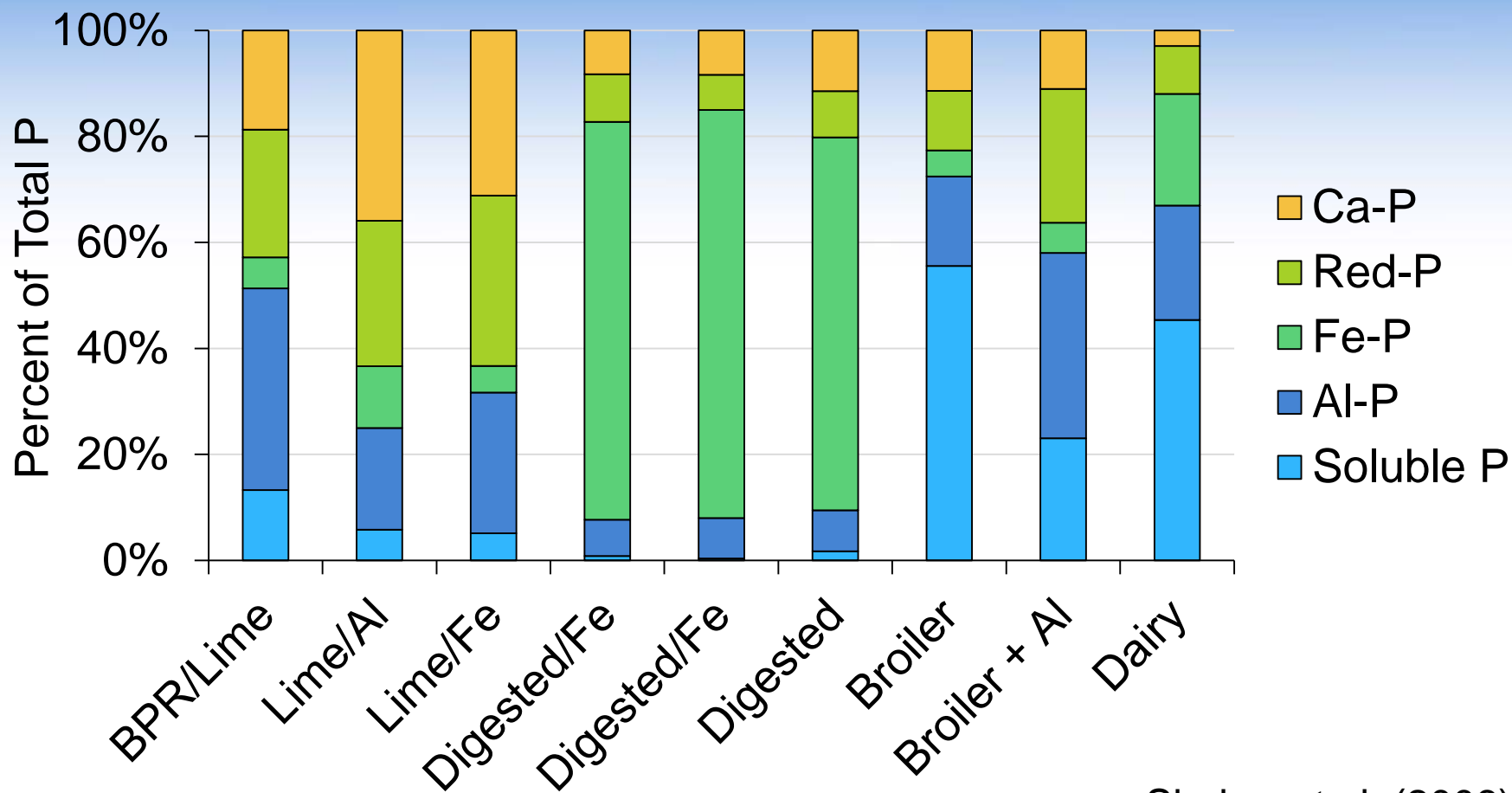
# Other Chemical Properties Control Phosphorus Solubility



# Chemical Properties of Residuals

Source	Treatment	Solids	WEP	P	Al	Ca	Fe
		%		-----g kg <sup>-1</sup> -----			
<u>Biosolids</u>							
BPR	Lime	31	0.82	17.8	5.84	78.5	4.12
Alkaline stabilization	Al	21	0.21	12.6	9.78	196	19.0
Alkaline stabilization	Fe	30	0.42	13.7	5.11	126	36.3
Anaerobic digestion	Fe	20	0.58	30.1	13.7	14.5	56.0
Anaerobic digestion	Fe	19	0.27	30.3	15.8	22.5	57.6
Anaerobic digestion	None	26	0.94	21.7	11.9	19	29.7
<u>Manures</u>							
Broiler	None	77	6.24	21.4	0.71	30.8	0.99
Broiler + Alum	Al	76	3.01	20.5	12.1	24.7	1.25
Dairy	None	18	2.32	4.30	0.87	73.6	2.12
Dairy	None	16	4.88	8.10	2.87	21.3	10.3

# Fractionation of P in Residuals

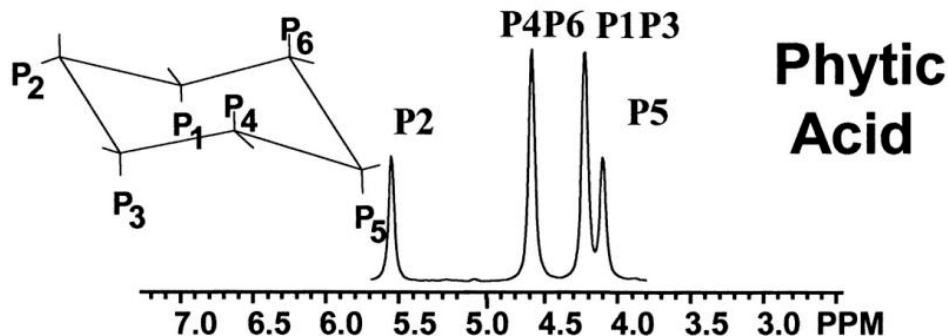
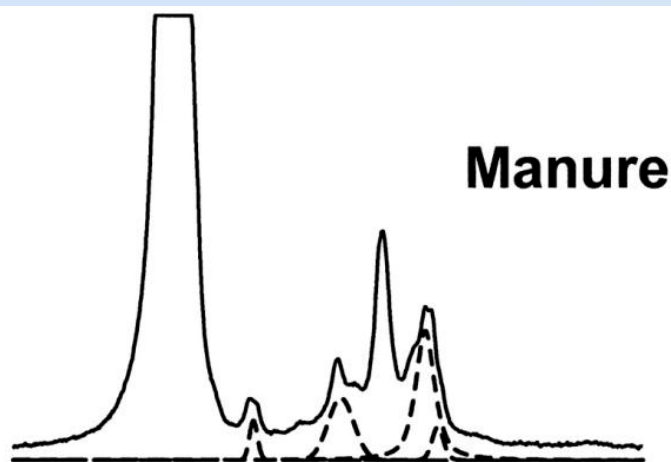


Shober et al. (2006)

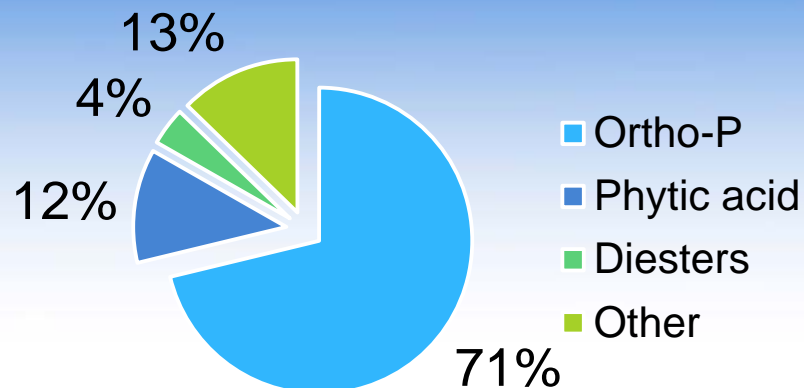
# Direct Speciation Techniques

- **X-ray Diffraction (XRD):** ID crystalline minerals
- **Scanning Electron Microscopy (SEM) with X-ray elemental spectrometry (EDXS):** Mapping of elemental components
- **$^{31}\text{P}$ -Nuclear Magnetic Resonance (P-NMR):** No ID of Fe-P species due to interference
- **X-ray Absorption Near Edge Structure Spectroscopy (XANES):** Limited access to facilities

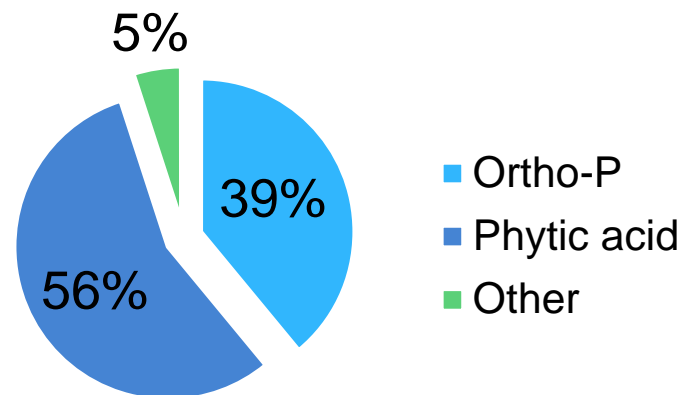
# $^{31}\text{P}$ -NMR Analysis of Manure



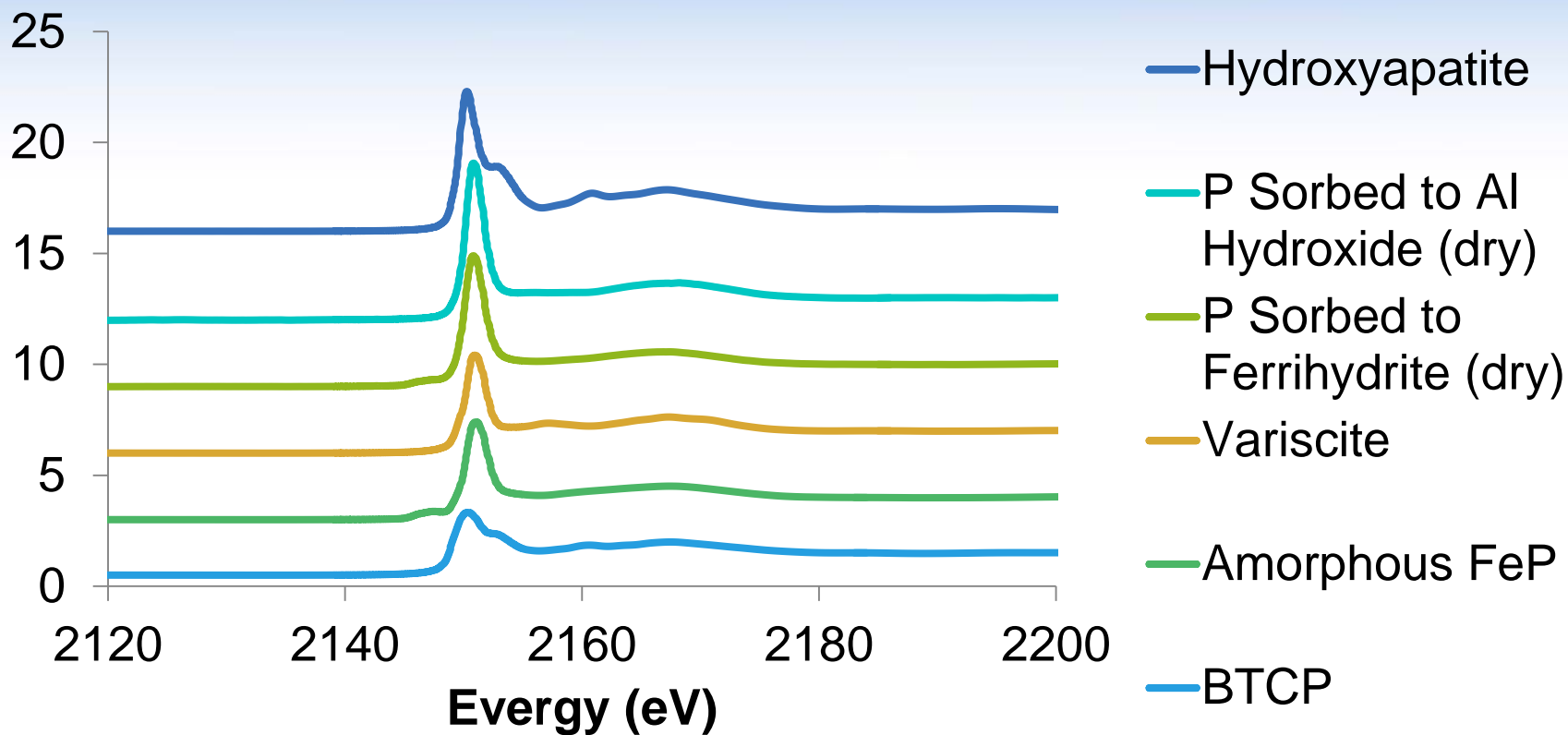
Dairy manure – Toor et al. (2005)



Broiler litter – McGrath et al. (2005)



# XANES Linear Combination Fitting With Known Standards

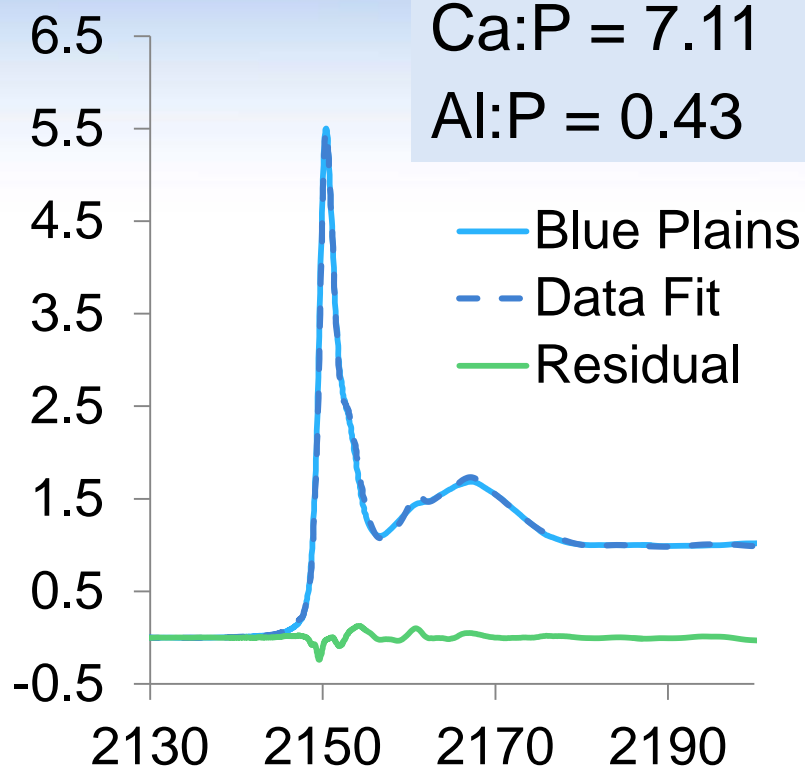


# XANES Speciation of Biosolids P

Fe:P = 1.47

Ca:P = 7.11

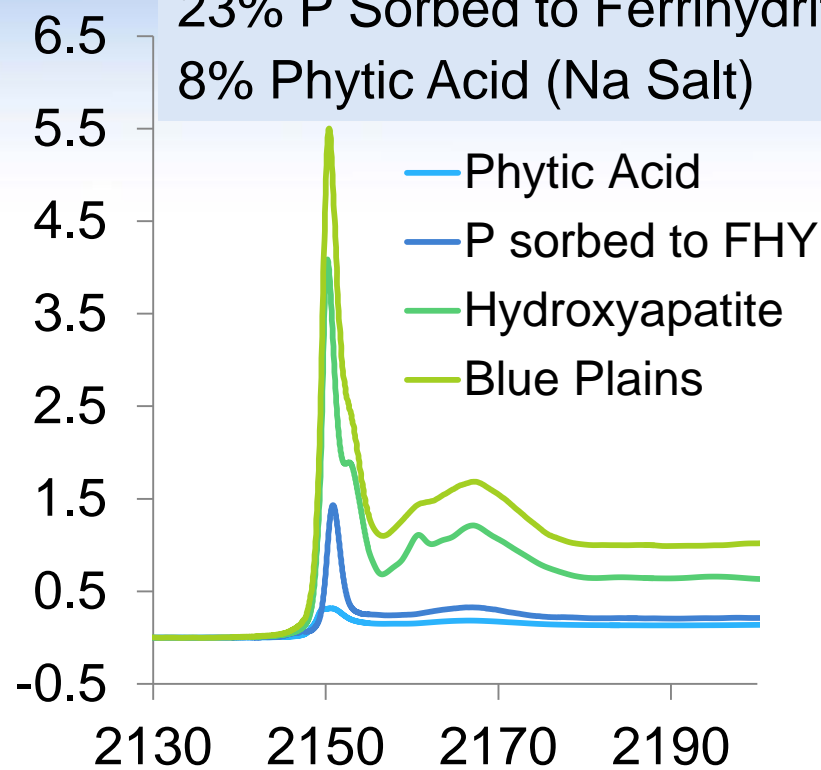
Al:P = 0.43



61% Hydroxylapatite

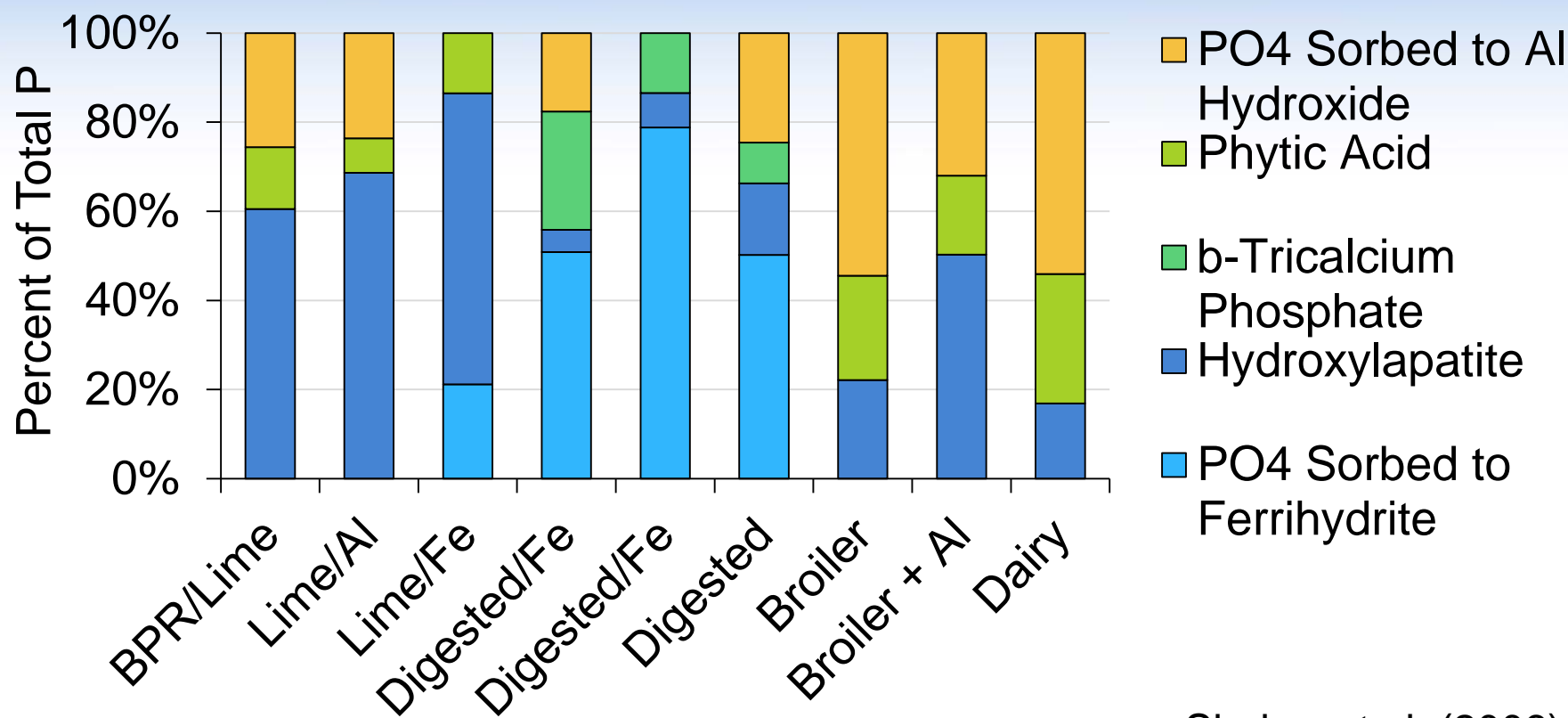
23% P Sorbed to Ferrihydrite

8% Phytic Acid (Na Salt)



Energy (eV)

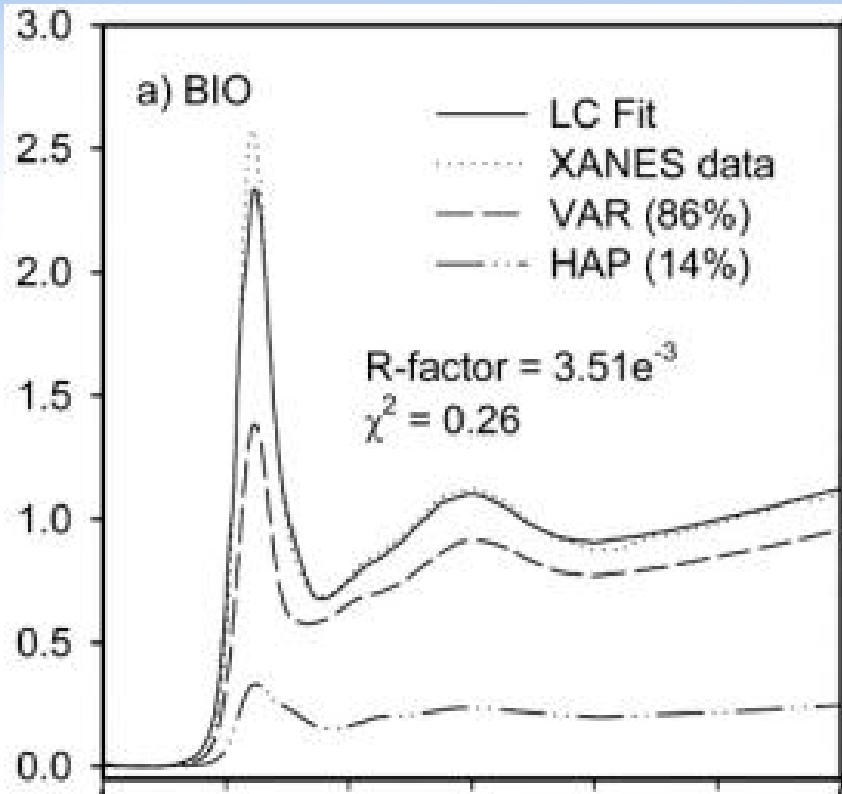
# XANES Speciation of Phosphorus



Shober et al. (2006)



# Other XANES Speciation Work



## Digested biosolids - Ajiboye et al. (2007)

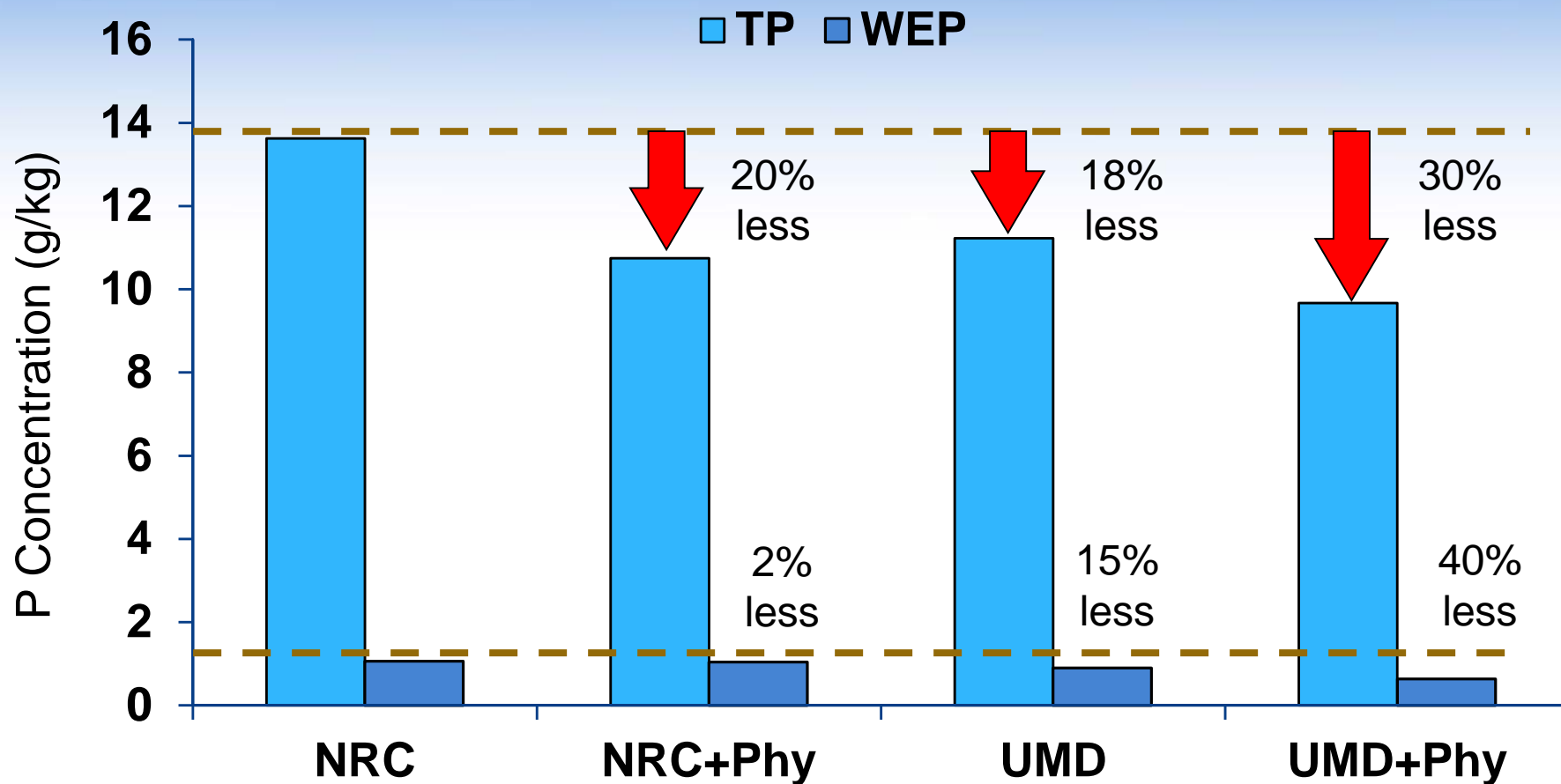
- 86% Variscite (Al-P)
- 14% Hydroxyapatite (Ca-P)

## Broiler litter - Toor et al. (2005)

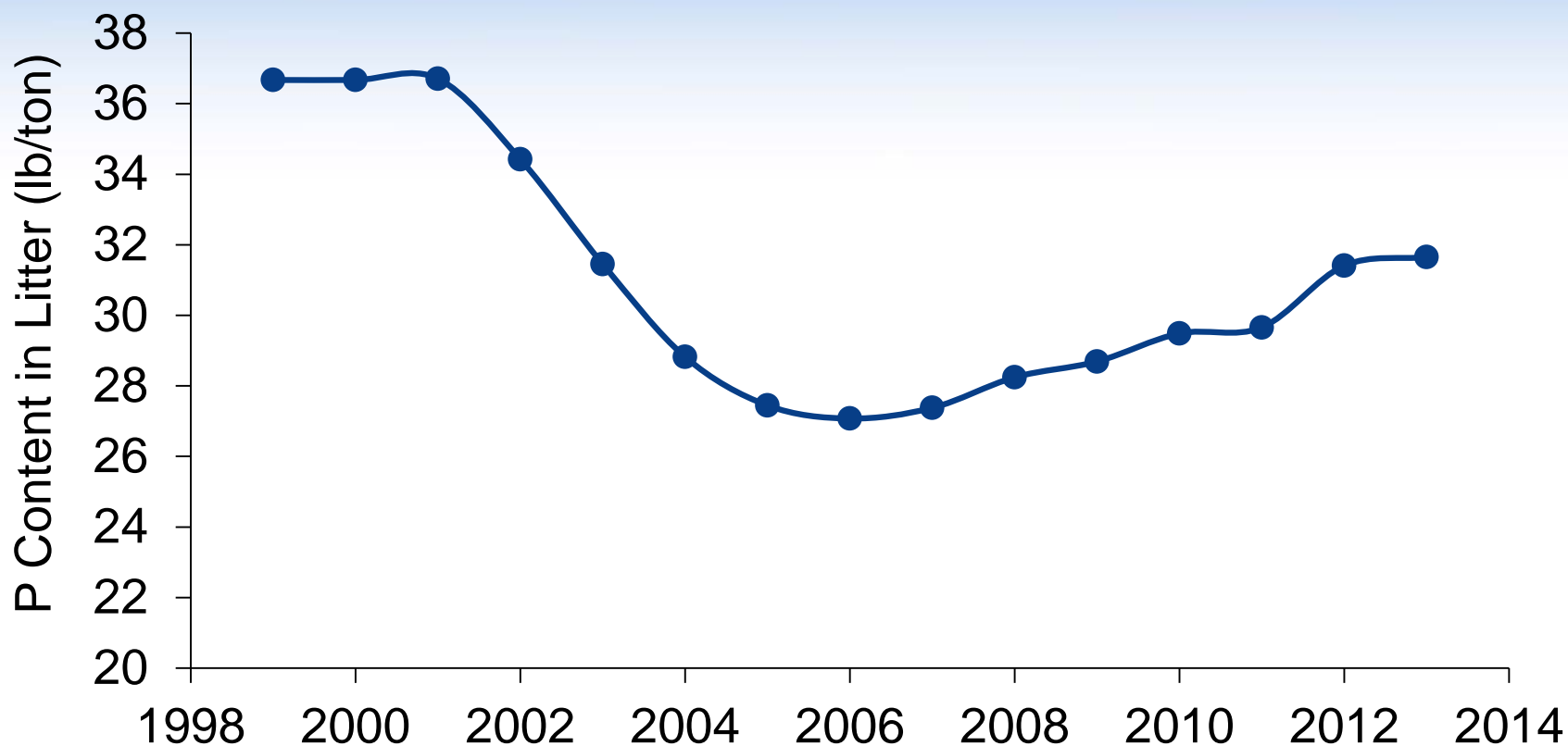
Add phytase to diet

- 15% aqueous P 13%
- 20% phytic acid 7%
- 65% dicalcium phosphate 80%

# Diet Affects Total P in Broiler Litter



# Industry Adoption of Phytase Reduced Manure P Load

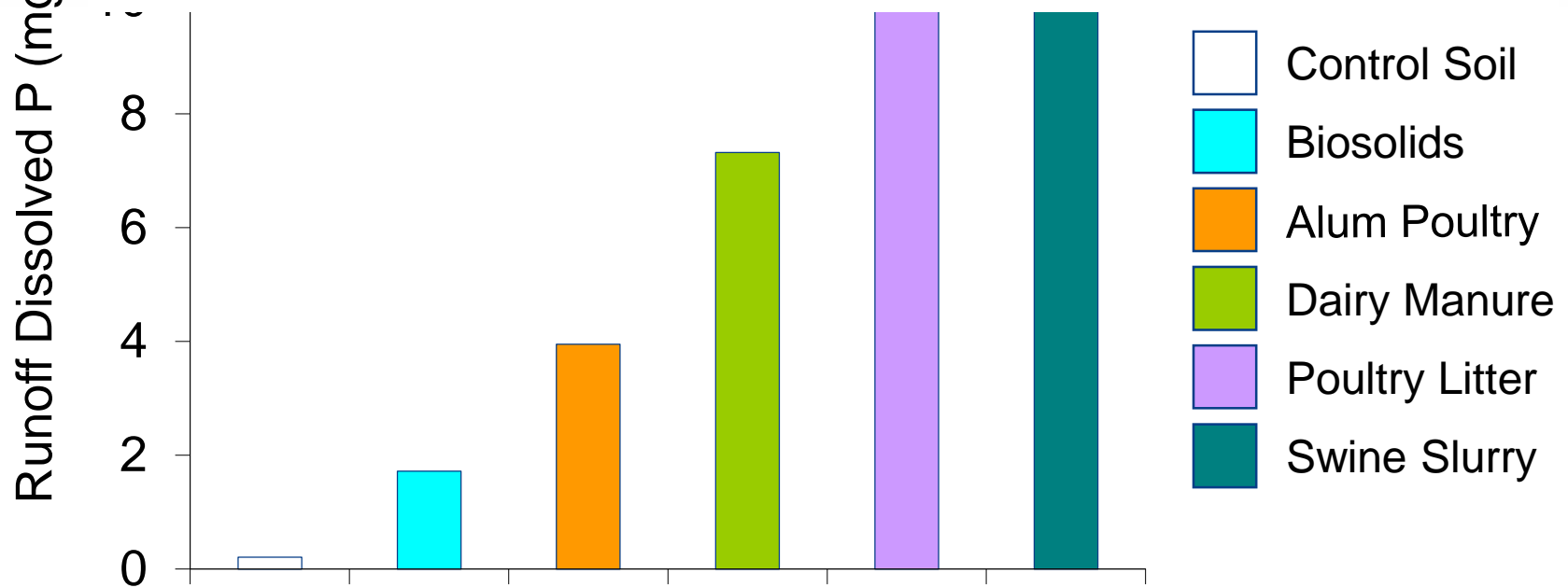


Managing Phosphorus in Organic Residuals Applied to Soils

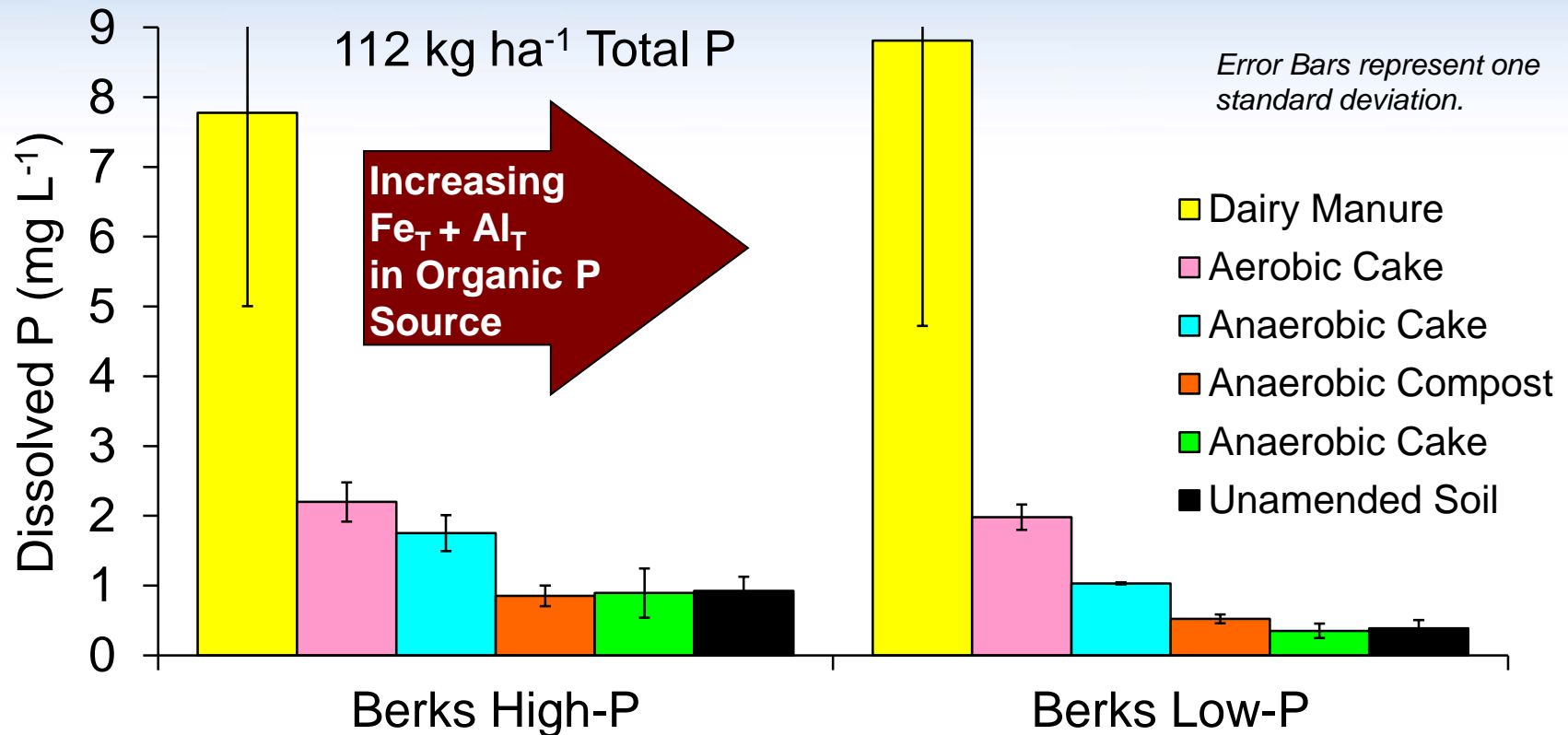
# **BEHAVIOR OF P IN RESIDUALS-AMENDED SOILS**

# Runoff Losses from Surface Applied Residuals

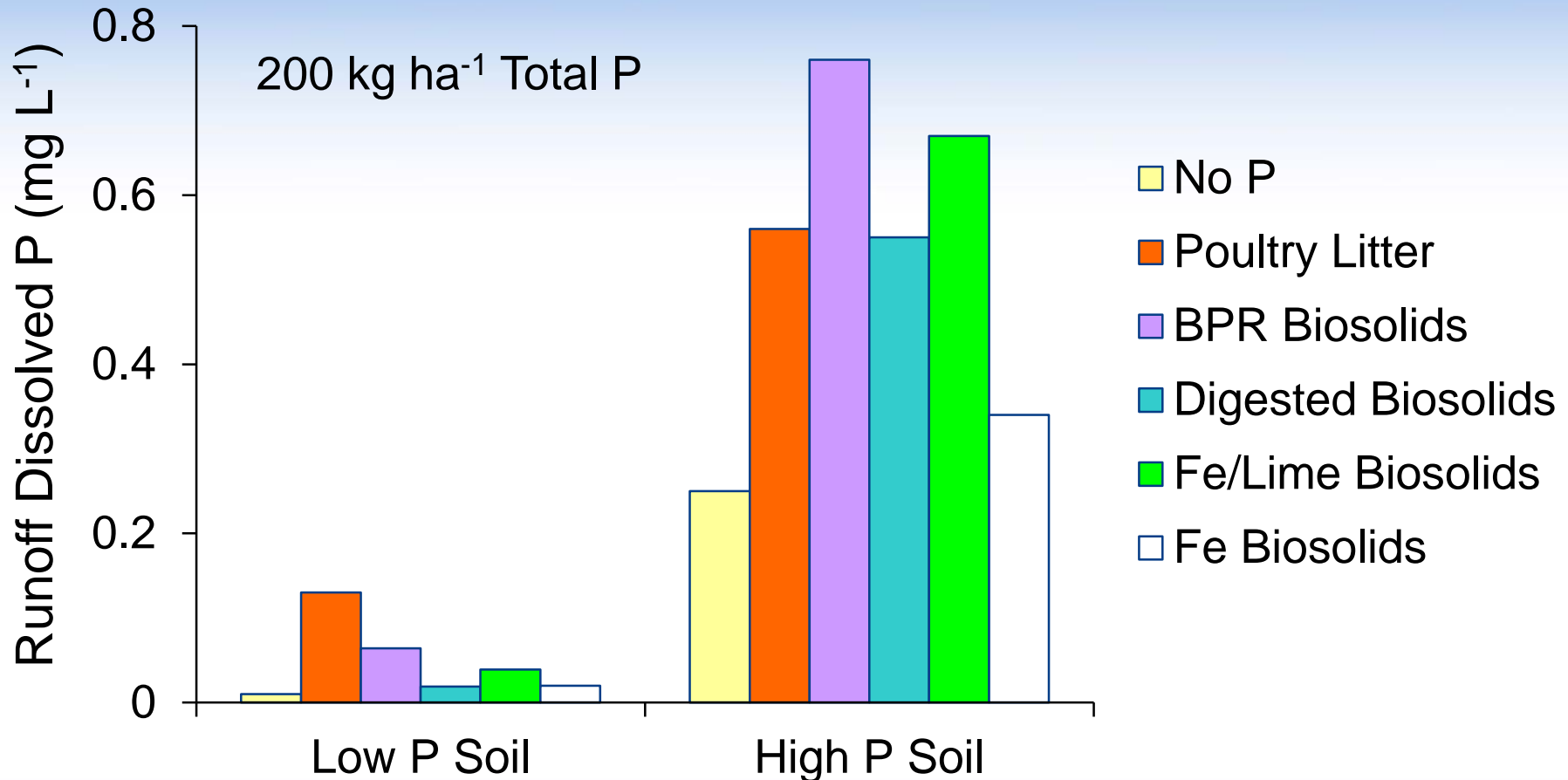
Higher solubility of P in residuals increases the risk of P loss in runoff.



# Soil Properties Runoff P from Surface Applied Residuals



# P in Runoff Incorporated Residuals is Affected by Soil and Source



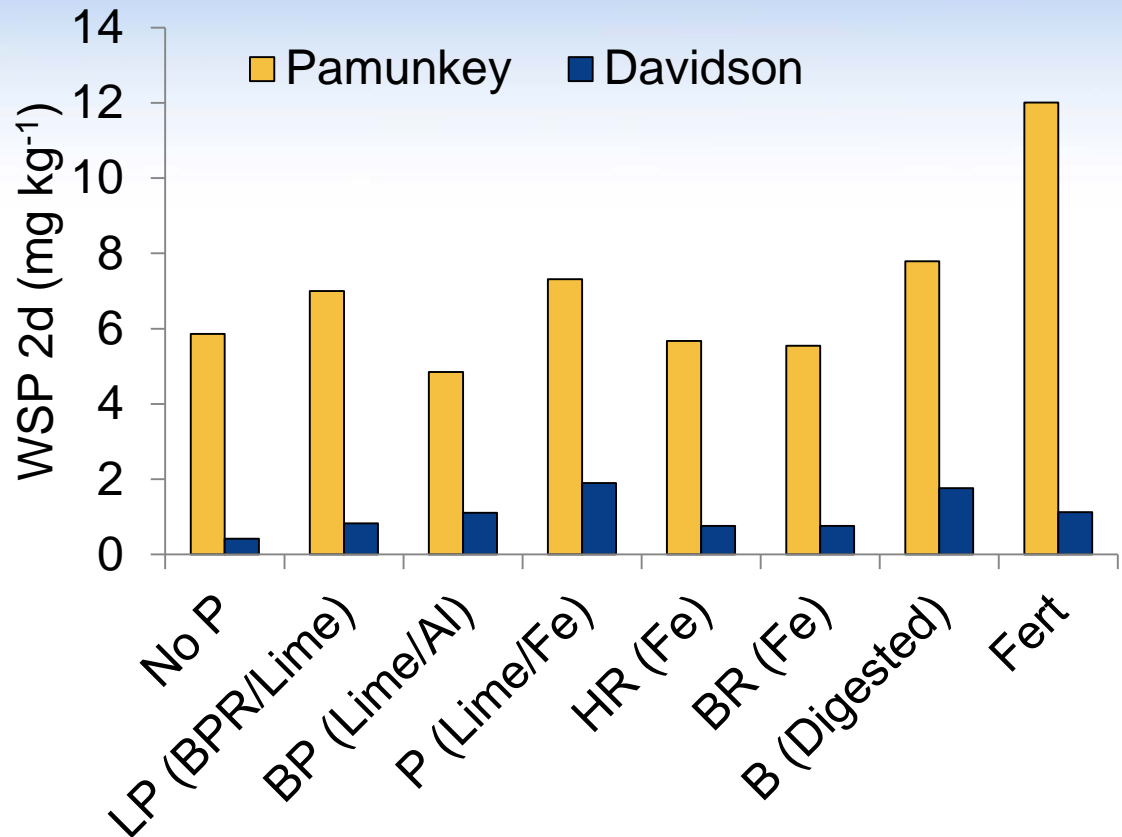
# Soil P Solubility Following Incorporation of Biosolids

## Davidson clay

- Soil Test P = 27 mg kg<sup>-1</sup> (Mehlich 3)
- P Saturation = 0.02

## Pamunkey sand

- Soil Test P = 134 mg kg<sup>-1</sup>
  - P Saturation = 0.18
- P Rate = 135 kg total P ha<sup>-1</sup>**





# Predicting Short-term Solubility from Incorporated Biosolids

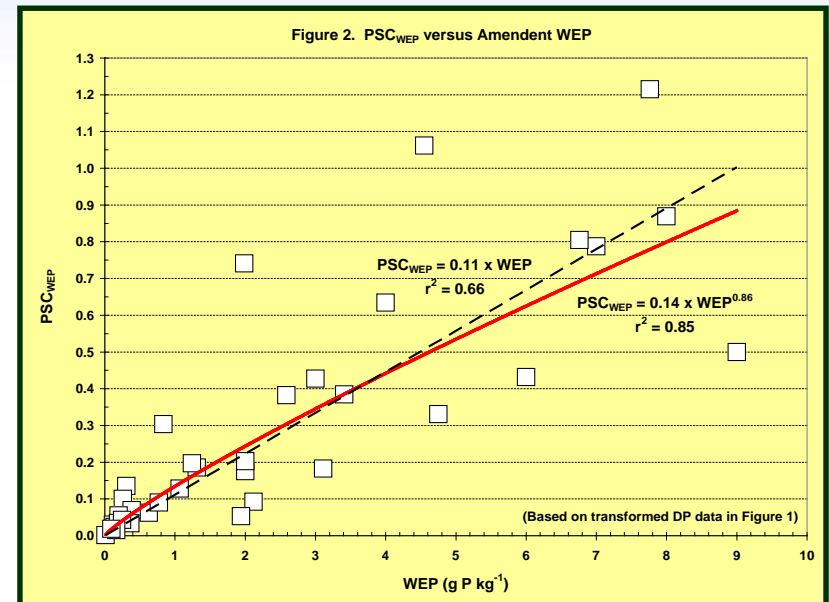
Soil Property	P Source Property	$r^2$ ( $P < 0.01$ )		
		2 d	30 d	180 d
DPS	None	0.69	0.77	0.79
M3-PSR	None	0.65	0.74	0.74
M3-P	None	0.54	0.62	0.57
None	WEP	0.41	0.38	0.21
None	WEP/TP ratio	0.49	0.34	0.21
DPS	WEP	0.64	0.73	0.66
M3-PSR	WEP	0.59	0.68	0.59
M3-PSR	WEP/TP ratio	0.68	0.66	0.61

# Phosphorus Source Coefficients

## Regional Default Values

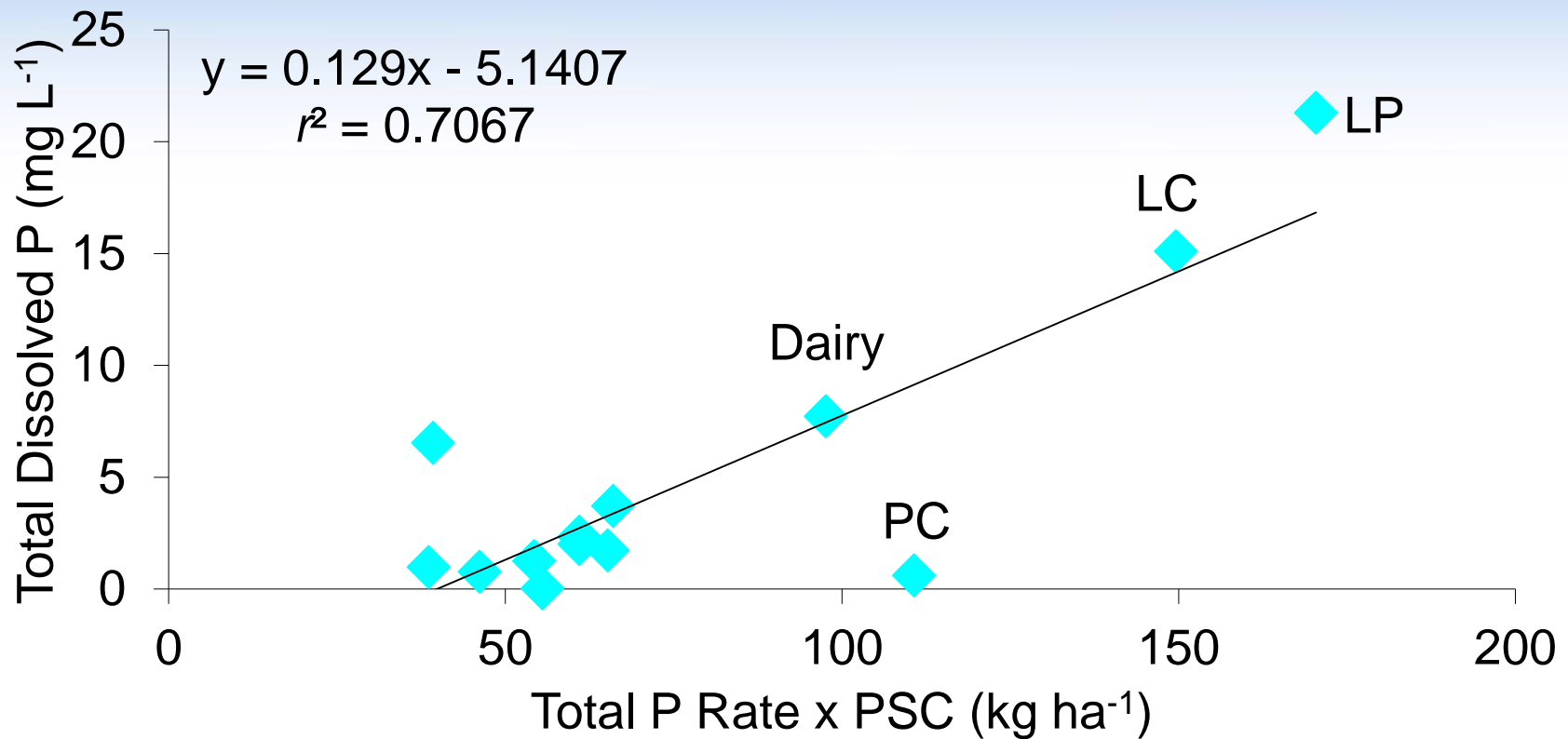
Organic P Source	PSC
Inorganic P fertilizer	1.0
Swine slurry	1.0
Non-stabilized beef, dairy, poultry and other manures	0.8
Biological nutrient removal biosolids	0.8
Alum-treated poultry litters	0.5
Biosolids (except BNR)	0.4

## Source Specific Values



$$\mathbf{PSC = 1.17 \times WEP (\%)}$$

# Surface Applications and P Source Coefficients



# Subsurface Application – Benefits of Incorporation with Low Disturbance



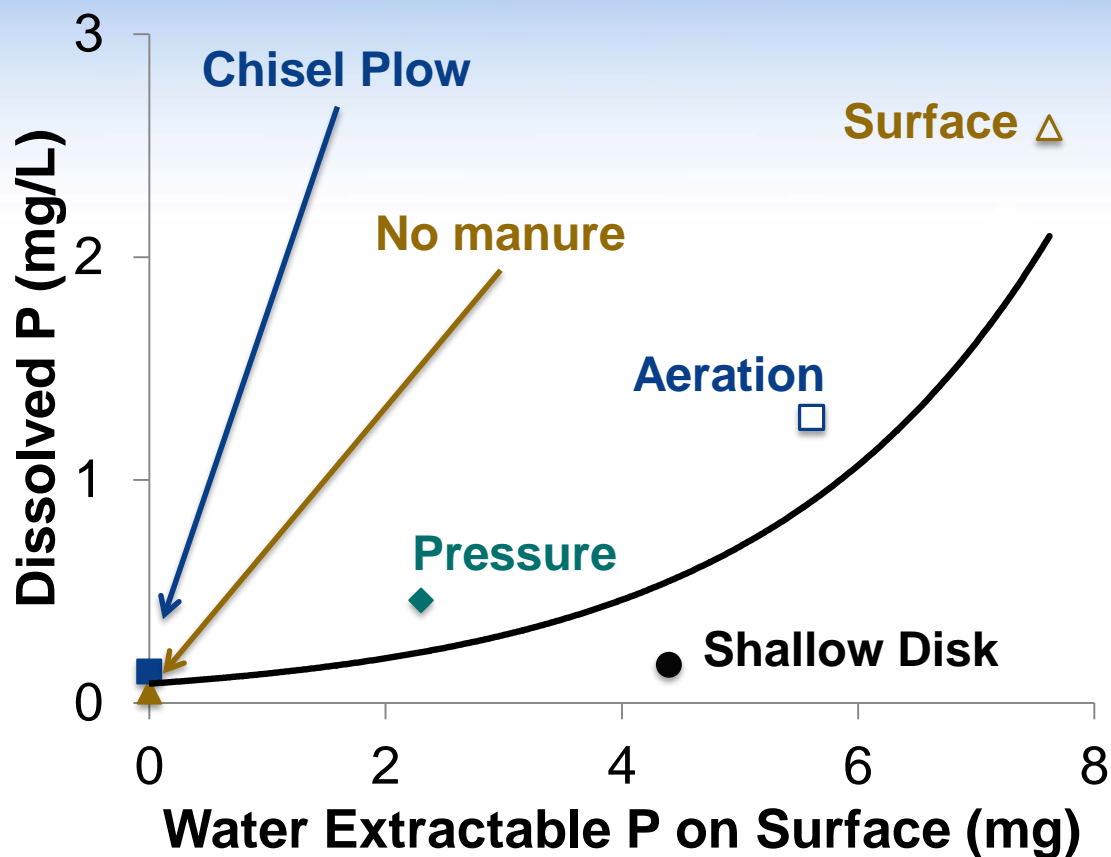
**Heavy Cover Crop**



**Permanent Pasture**

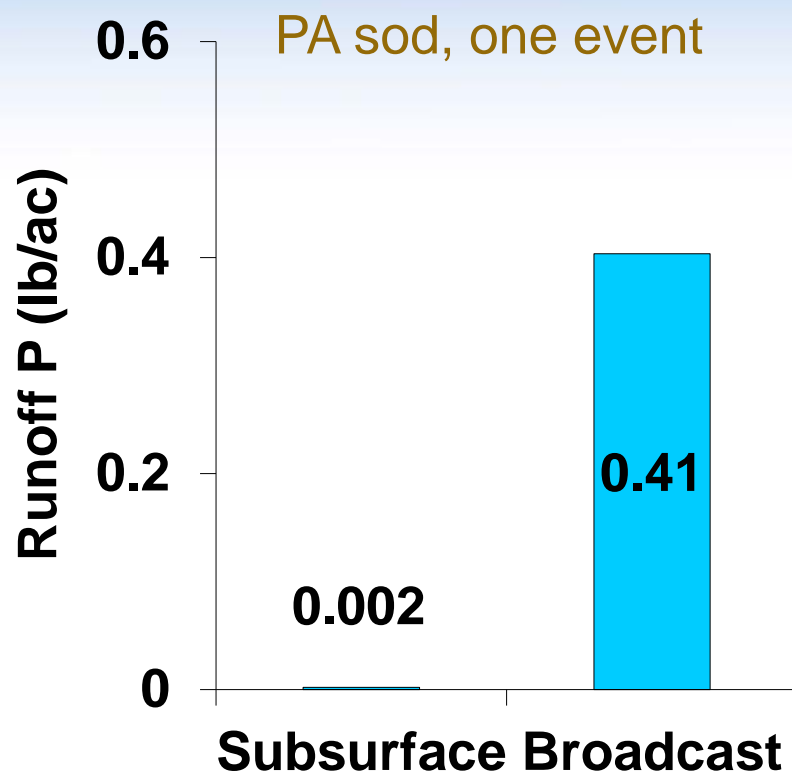


# Manure Application Method Affects Phosphorus Loss



More P at surface =  
More P in runoff

# Subsurface Application of Solid Manures in No-Till/Pasture



Managing Phosphorus in Organic Residuals Applied to Soils

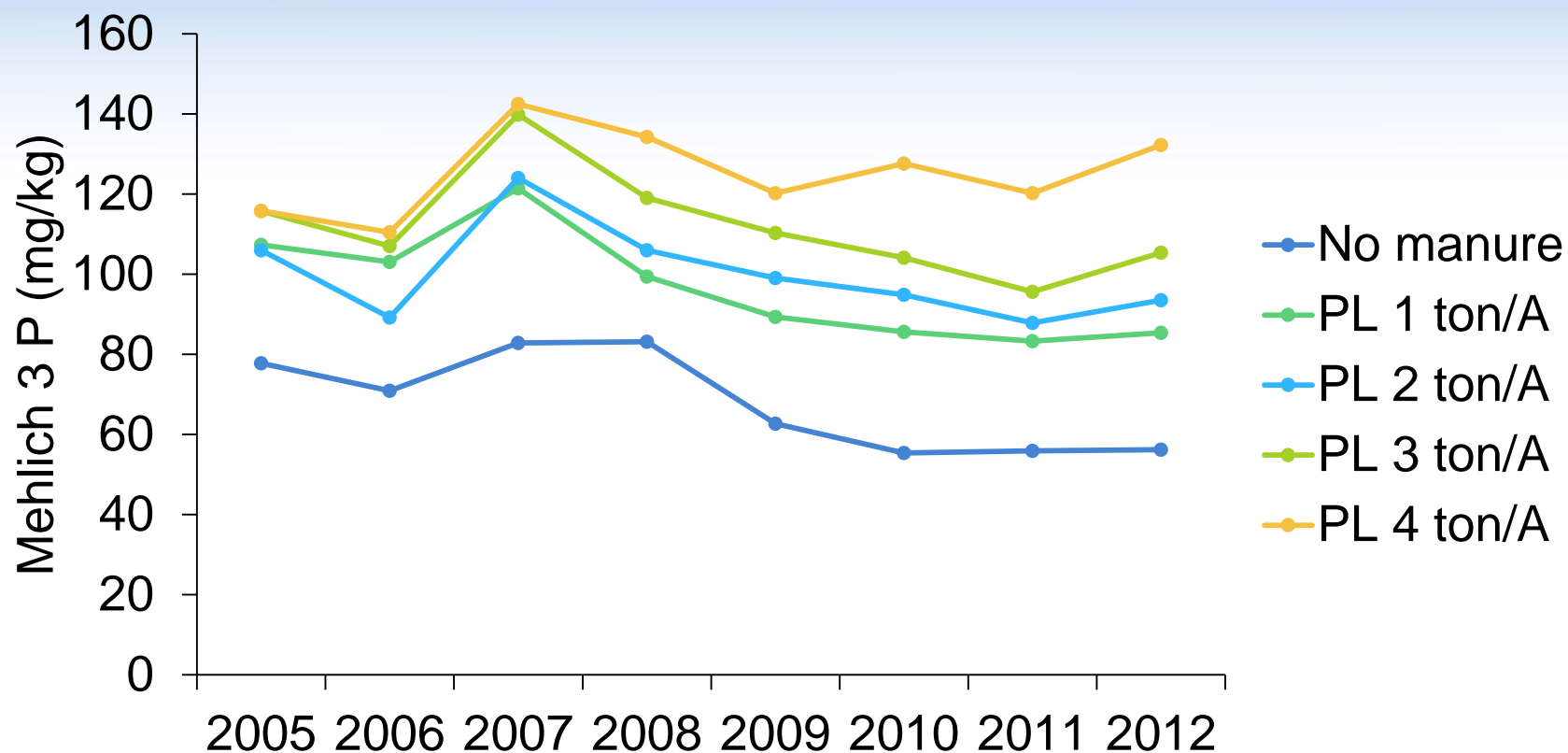
# **LONG-TERM FATE OF P IN RESIDUAL-AMENDED SOILS**

# Nutrient Content in Residuals

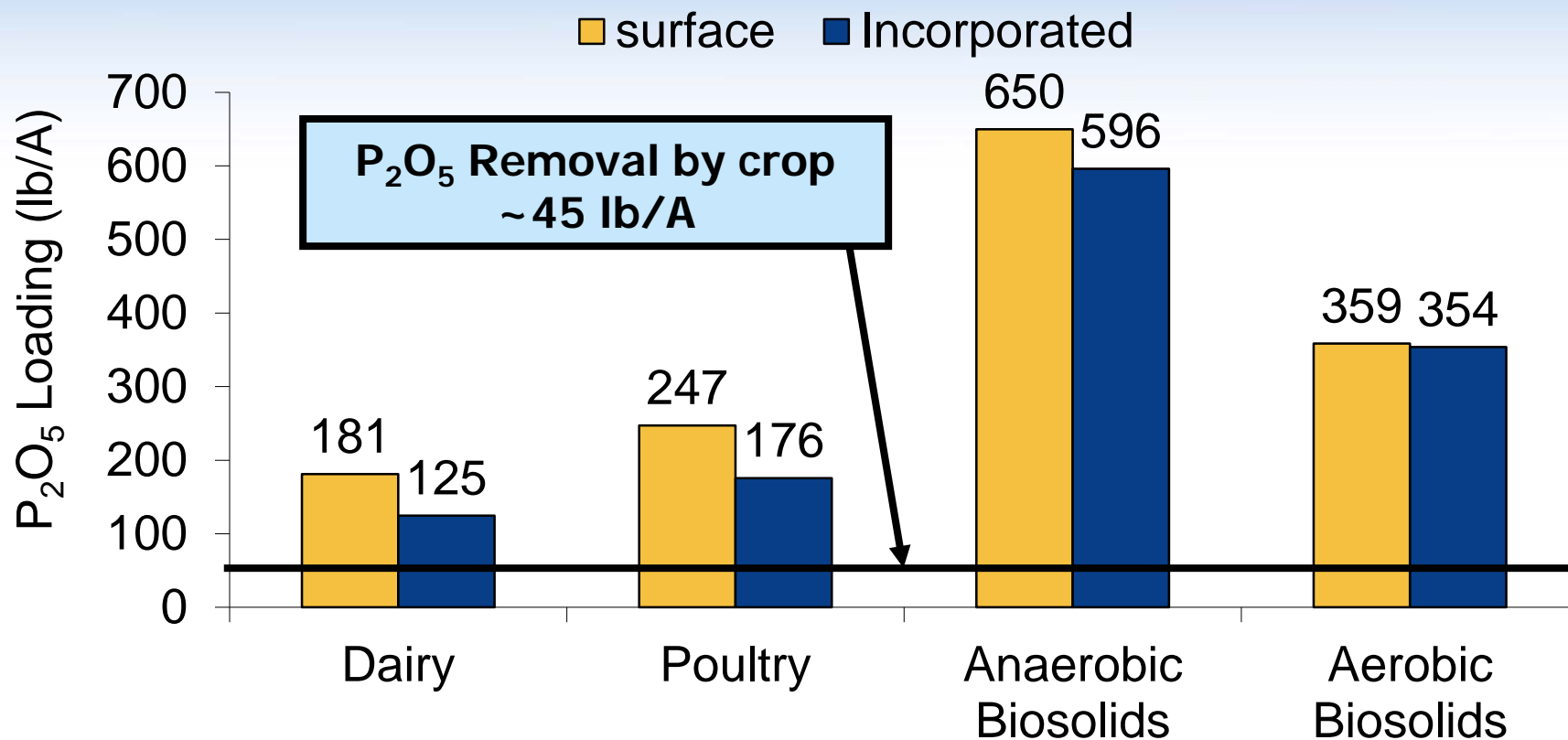
Residual Type	Total N	Total P <sub>2</sub> O <sub>5</sub>	N:P <sub>2</sub> O <sub>5</sub> ratio
<u>Solids</u>	———— lbs/ton ————		
Beef cattle	12	5	2.40
Biosolids	95	104	0.91
Broiler litter	57	45	1.27
Dairy	10	4	2.50
<u>Liquids</u>	———— lbs/1,000 gal ————		
Dairy	28	13	2.15
Swine	27	19	1.42



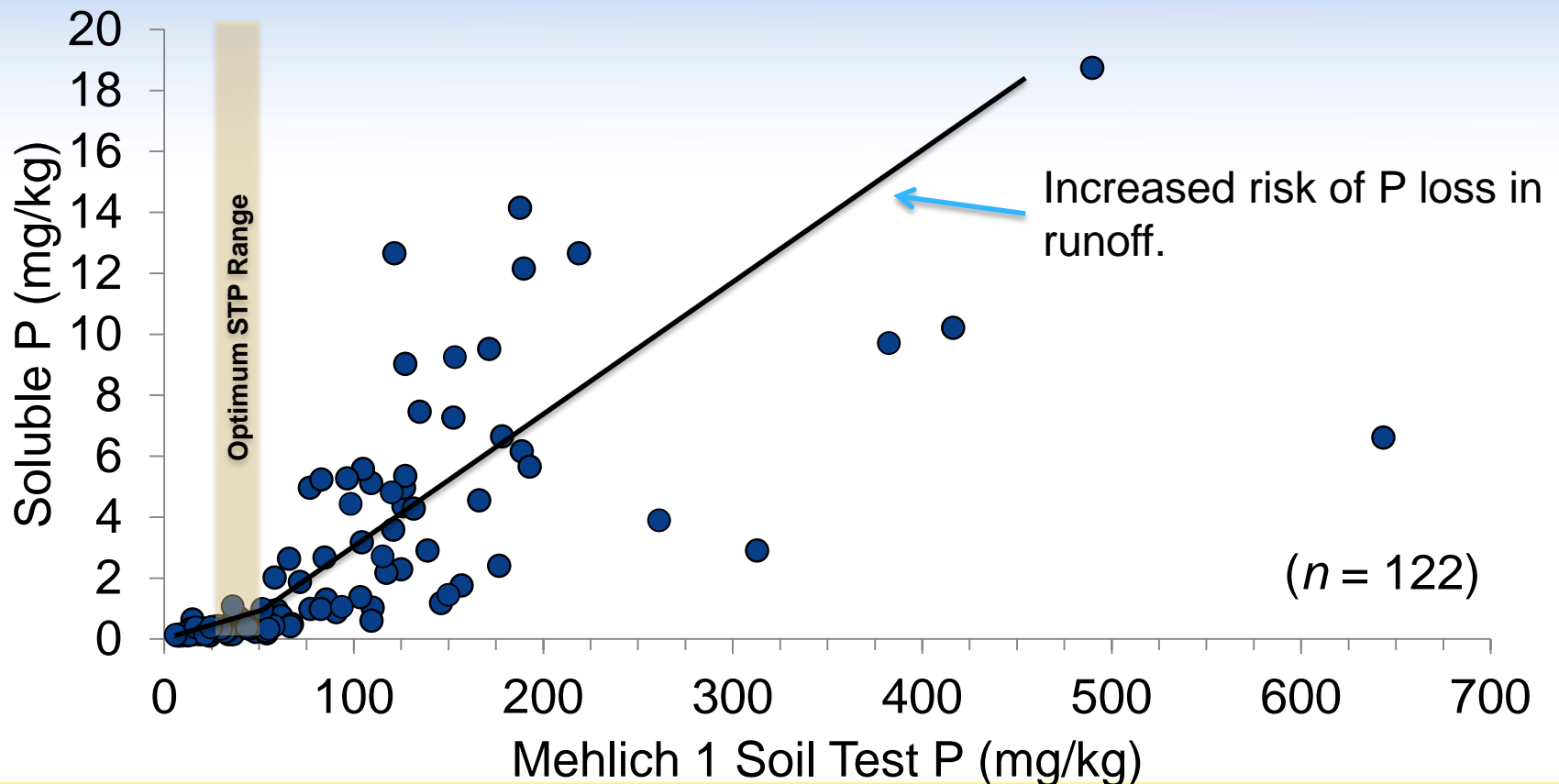
# Application of Manure at Crop P Removal



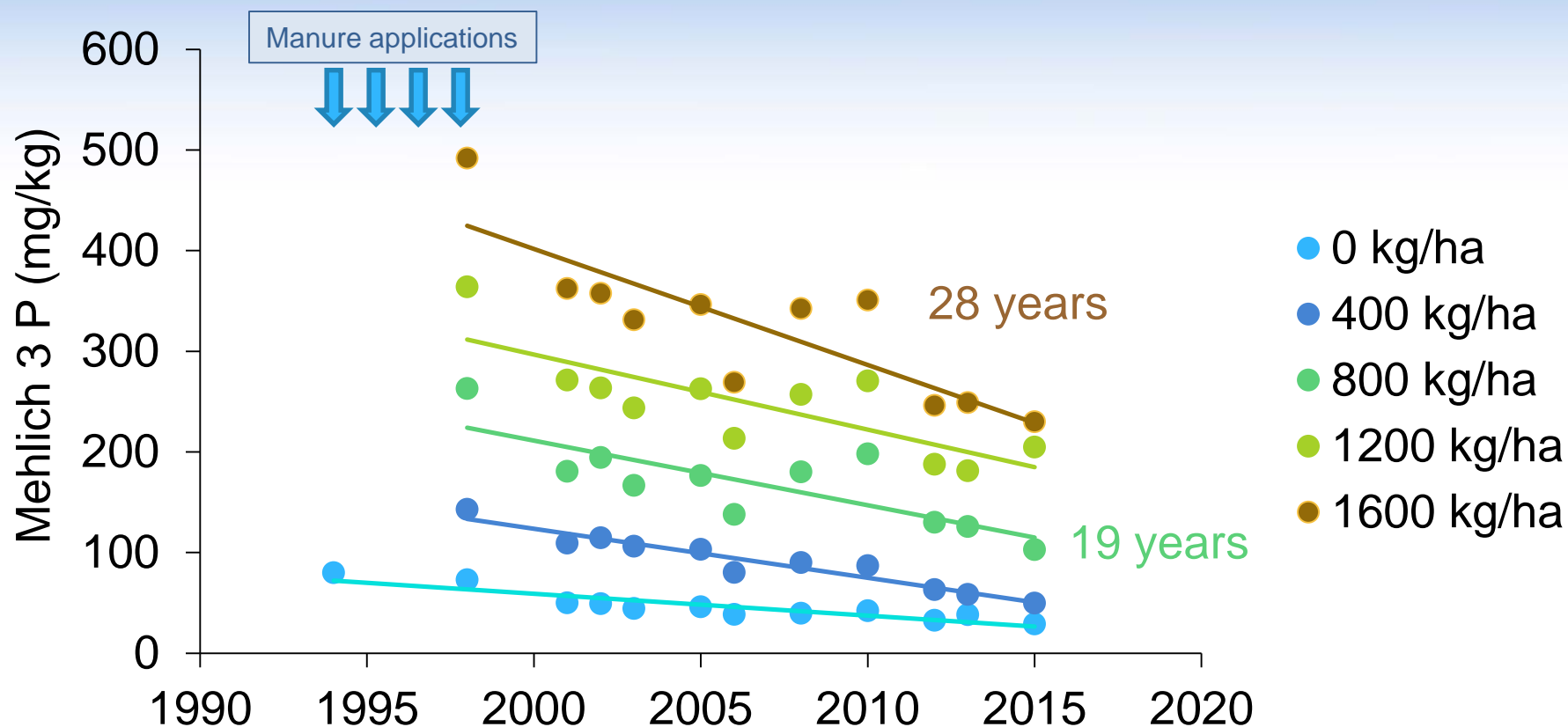
# $P_2O_5$ Loadings for Residual Application at N-based Rates



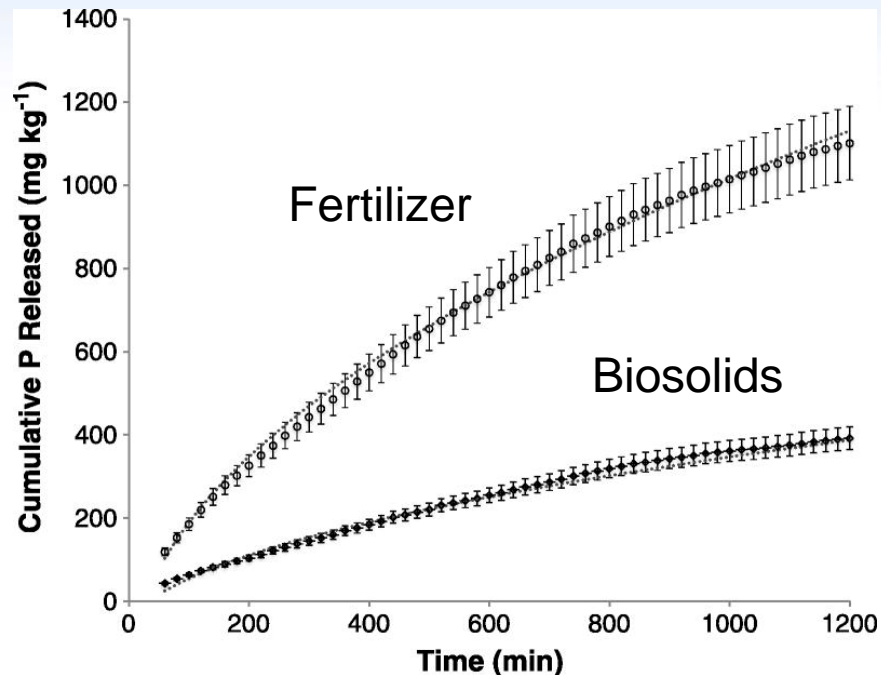
# Relationship Between Soil Test P and Soluble P in Soils



# Phosphorus Drawdown Following Manure Application

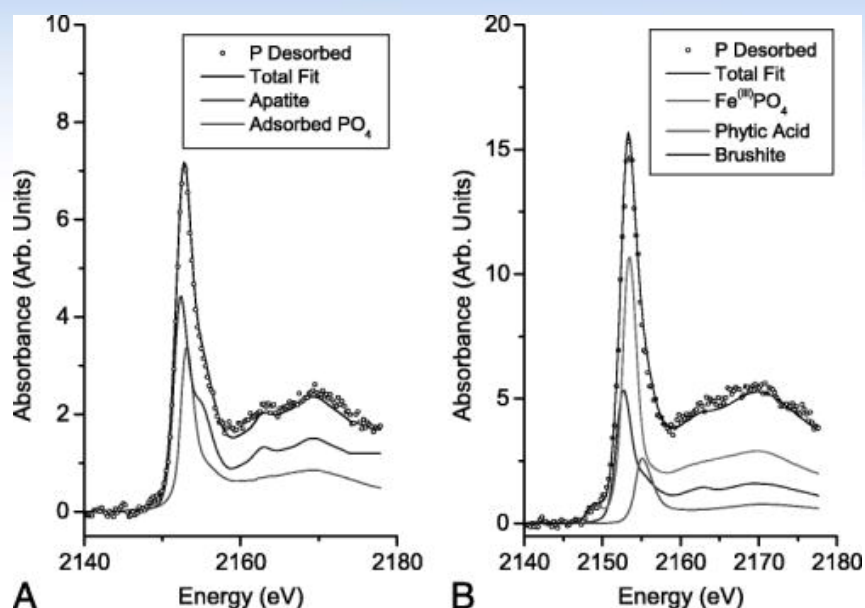


# Dissolution of P from Soils Receiving Biosolids or Fertilizer



- Anaerobically digested biosolids (Chicago) application for 32 yr (67.2 Mg ha<sup>-1</sup> yr<sup>-1</sup>)
- Continuous flow desorption with 0.1 M NaNO<sub>3</sub>
- 4 × slower dissolution of P from biosolids-amended soils

# Dissolution of P from Soils Receiving Biosolids or Fertilizer



XANES analysis on soils after  
dissolution experiment  
(Peak et al. 2012)

- Fertilizer: apatite (Ca-P) and adsorbed PO<sub>4</sub>
- Biosolids: brushite (Ca-P), strengite (Fe-P), organic P
- Slow dissolution of Ca-P and Fe-P minerals

# What is the Fate of Biosolids P in Acid Soils?

- Lime Biosolids: Slow solubilization of crystalline Ca-P
- Fe Biosolids: Ferrihydrite-P should remain stable; Excess ferrihydrite may sorb native soil P
- Fe & Lime: pH change = Ca-P solubilization; Ferrihydrite may act as P sorbent
- BPR and Digested biosolids: Ca-P solubilization; Al-P fairly stable

# Summary

- Advanced techniques have improved our understanding of P speciation in residuals
- Treatment processes have large impact on P solubility and speciation
- Lower P solubility related to Fe- and lime-stabilization
- P losses controlled by residuals properties (surface applied); residuals and soil properties (incorporated)



# Acknowledgements

- Research was conducted (in part) at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Division of Materials Science and Division of Chemical Services
- Funding provided by Metropolitan Washington Council of Governments, Washington, DC, USA