Phosphorus Chemistry and Sequestration in Soil

Ohio Lake Erie Phosphorus Task Force Meeting
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Ohio State University

Soil and Environ. Chem. Research program at Ohio State

- **Environmental chemistry - chemical (metals, pesticide, nutrient) impact**
  - soil to water / food chain transmission
  - soil ecotoxicology
  - soil remediation of contaminated soil
- **Beneficial Use of Residuals or By-products**
  Soil Substitute Blends (topsoil)
  Sorbent Technology to Reduce Nutrient / Pesticide Runoff

Prior to Ohio State
Soil / Environmental Chemistry Program at Oklahoma State Univ.

- **Professor of Soil Environmental Chemistry (1991-2003)**
  Oklahoma State University

Soil and Environmental Chemistry
Phosphorus and Water Quality

Combined 27 yrs experience with Soil P issues

Use of Sorbent Technologies to Reduce P Impact

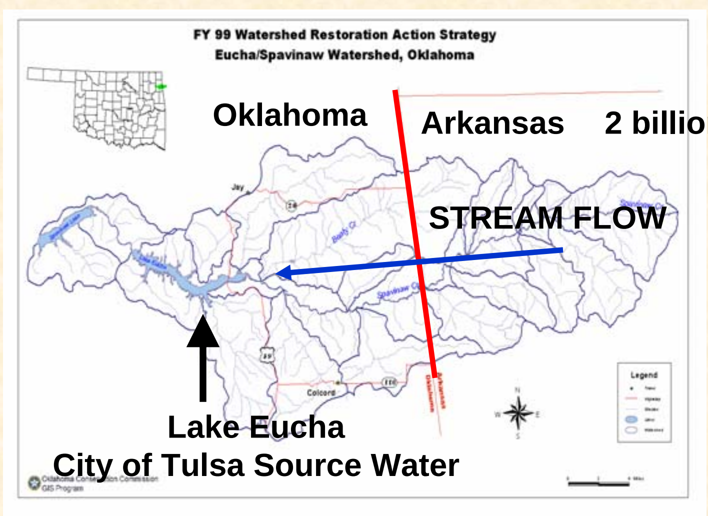
Research on Use of Soil Test Methods to Measure P Impact

Many publications in refereed scientific journals

many regional/ national / international presentations in conferences focused on P impact

Journal of Environmental Quality editorial board
N. Basta (Technical editor, 11 yrs)
E. Dayton (Associate editor, 2 yrs)

OK – AR Phosphorus Border Wars



2 billion chickens / yr

Federal court: producers pay City of Tulsa > $50 million
Currently issues between States of OK and Arkansas

Today's Presentation

- Soil Chemical Processes Important to
  P sequestration and solubility / mobility / leaching

- Soil Testing of "labile P":
  Crop production and environmental soil testing

- Using soil chemical processes to reduce excessive P
  Sorbent Technology

Soil Phosphorus Cycle

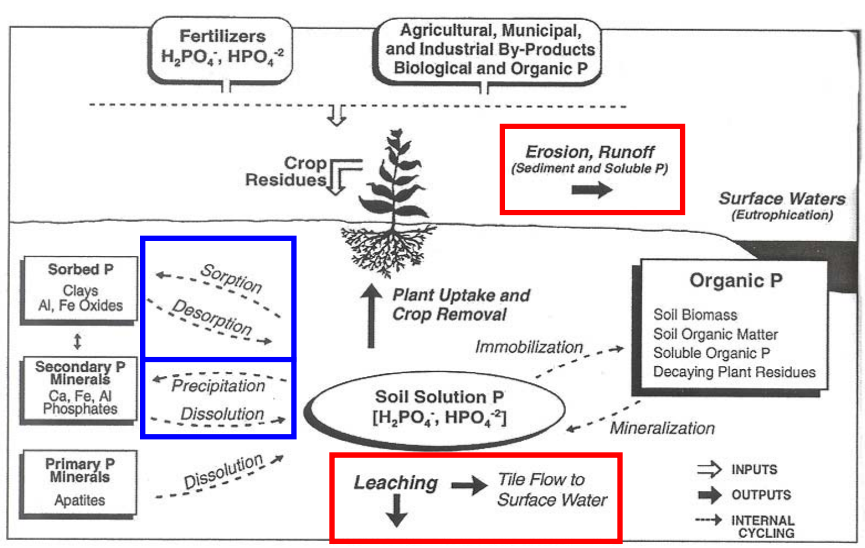


Figure 6.9 The soil P cycle. An overview of the physical, chemical, and microbiological processes controlling the availability of P to plants and P transport in runoff or leaching waters. (Adapted from Gachon, 1969.)

Soil Phosphorus Pools

Sequestered P
very insoluble forms of P
insoluble P minerals
strongly adsorbed P

Intensity

Soil solution P
dissolved P
bioavailable P

"Labile P"
P in Equilibrium with soil solution P
strongly adsorbed P
soluble P minerals
weakly adsorbed P

Quantity

Q-I is a 2 way street
replaces losses of dissolved P
removes additions of dissolved P

Sequestered >> Quantity >> Intensity

Chemical Fate of Introduced Soluble P

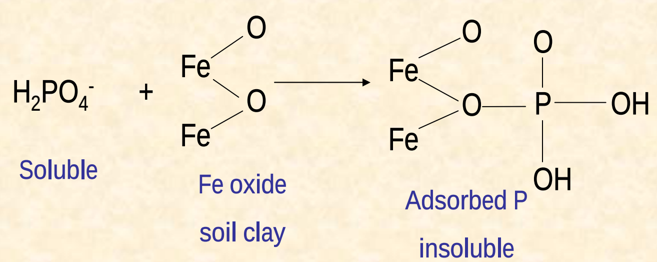
Fertilizer / Manure Additions

↓

Soluble $H_2PO_4^-$

→ **Adsorption in Soil (Fe, Al, Mn oxides)**

→ **Precipitation (Fe, Ca, Al phosphates)**

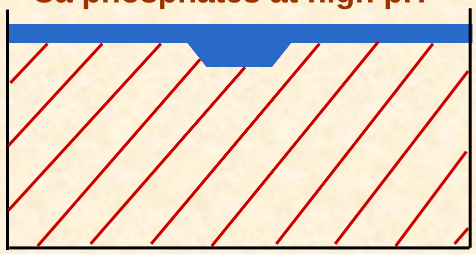


Precipitation / Dissolution of P Minerals

Which P minerals limit P solubility?

Fe, Al phosphates at low pH
Ca phosphates at high pH

% of Total Soil P



soluble P
available P

insoluble P
unavailable P

Soil pH

Very insoluble at most pH
maximum solubility at pH 5 to 7

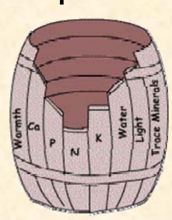
plant available P can be very low in unfertilized soil
plant growth and crop yield can be limited by P

Phosphate mineral solubility and availability

P fertilizer and Law of the Minimum

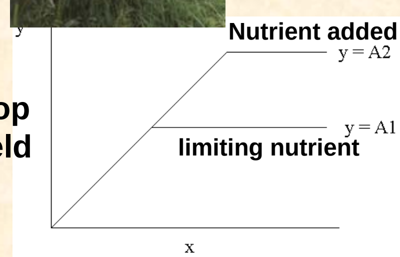
Justin von Liebig
1803-1856

Law of the Minimum: The capacity of a barrel made of many wooden staves is limited by the shortest piece.



Liebig's Barrel Analogy

Crop Yield



P limited soils
Fertilize with P
Grow more crop !

Phosphate mineral solubility and availability
P fertilizer and Law of the Minimum

P is very insoluble in soil --can be the limiting nutrient to plants -- the shortest shank in the barrel.

Why? Native soil P minerals are very insoluble

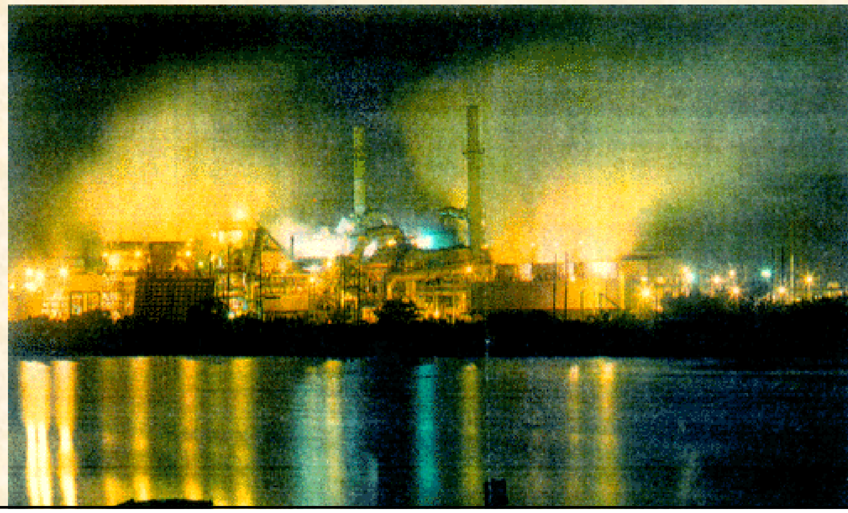
Solution: add soluble P to soil (fertilize) --make more soluble P minerals

Water soluble P

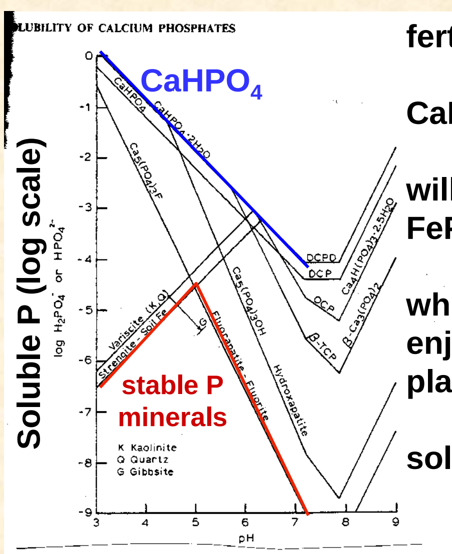
Rock Phosphate Mines (Florida, North Carolina)

Commercial Phosphate Fertilizers Manufactured from Rock Phosphate

Insoluble Rock Phosphate ➔ Water soluble fertilizer



Does P fertilizer increase P solubility? How does it work?



fertilizer P becomes $CaHPO_4$ in soil

$CaHPO_4$ is metastable

will eventually become $FePO_4$, $AlPO_4$ or a Ca apatite

while $CaHPO_4$ is still around-- enjoy a higher soluble P and plants grow well

soluble P fertilizer works

P solubility and Time

Soluble Fertilizer / Manure P

↓ short time (days to yr, < 10, 20)

Less soluble soil minerals
P adsorbed
to soil minerals (i.e., oxide clays)

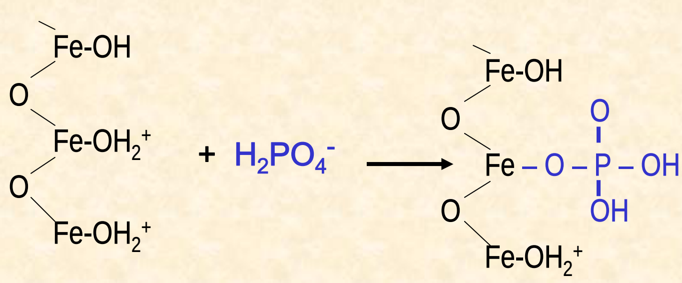
Water quality problem paradigm

↓ long time (years to decades)

Sequestered P
Very insoluble soil minerals
Strong adsorbed to soil minerals

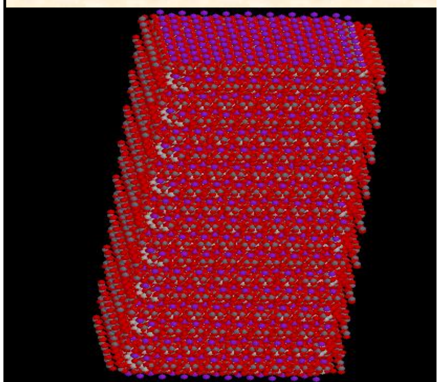
P adsorption is an important player in soil P and water quality in fertilized soils

P adsorbs to Al, Fe, Mn oxide soil surfaces

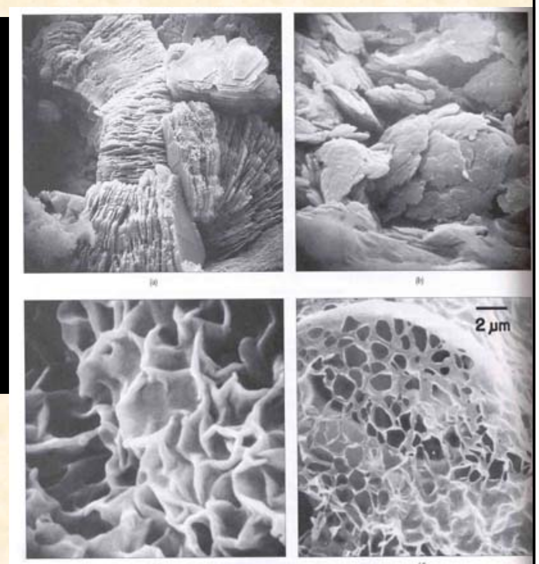


Soil oxide clays have large surface area

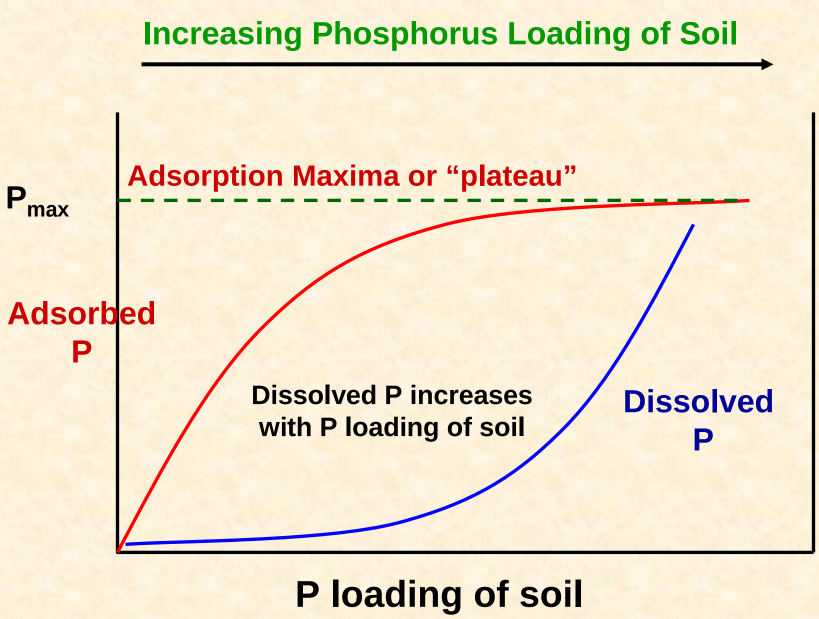
hydrous oxide clays (goethite, gibbsite) have large sorption capacity and affinity for phosphate



Large surface area of soil clay

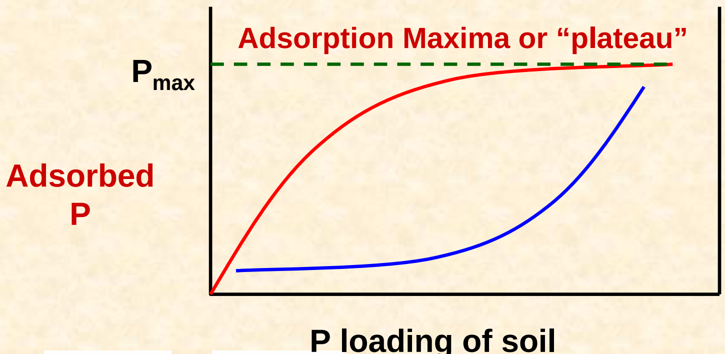


Dissolved / Adsorbed P



Dissolved / Adsorbed P

Increasing Phosphorus Loading of Soil



Cup leaks more as you fill it up

more dissolved P leaks as you fill up the soil with P

Low sorption capacity soil
sandy, low clay soil

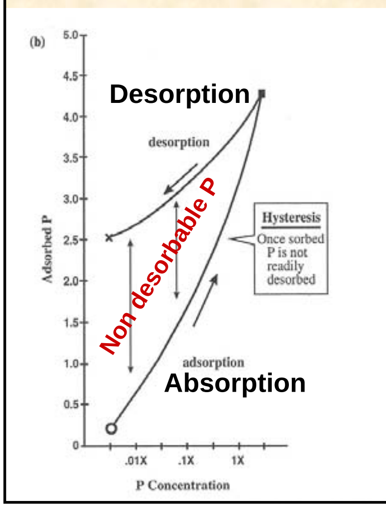
High sorption capacity soil
high clay (Al / Mn oxide)

Soil chemistry controlled P loss

Desorption of Adsorbed P

$$\text{Clay-}H_2PO_4 \xrightarrow{\text{Desorption}} H_2PO_4^-$$

water soluble P in runoff

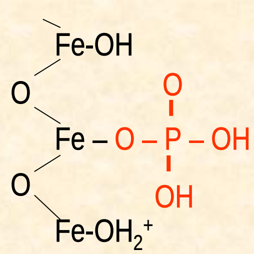


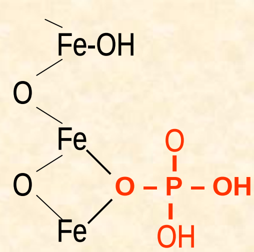
Hysteresis: difference between adsorption and desorption

Only some P is desorbable.

Type of P Sorption Sites and Sequestration

There are more than one type of adsorption site in soil

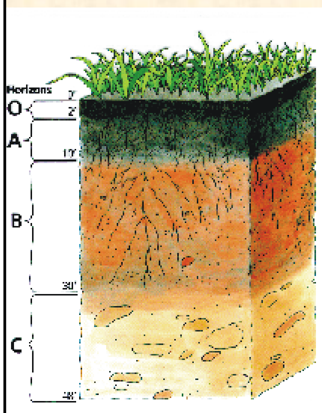




Monodentate P sorption
Desorbable

Binuclear inner sphere surface complex
Not Desorbable

Soil Depth and P Sorption



Typical Soil Profile

A Horizon

zone of organic matter accumulation
less clay than B horizon
lower P sorption than B horizon

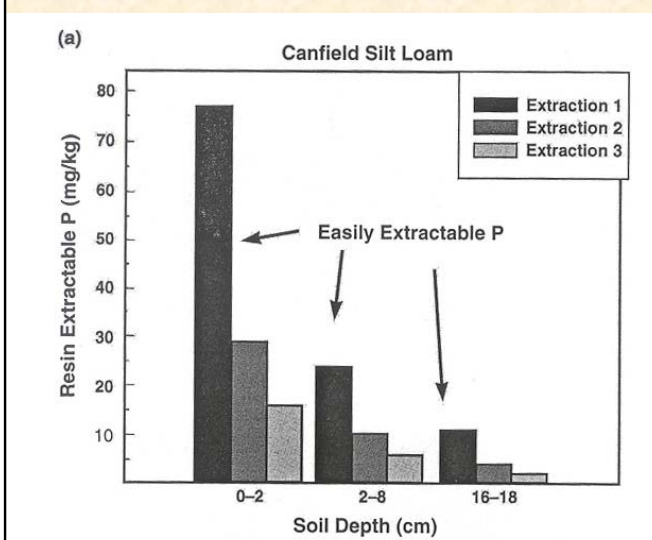
B Horizon

zone of clay accumulation
increase in P sorption
decrease in soluble P

Non conservation tillage:
incorporation of P 6 to 8 inch depth

Conservation tillage: shallower incorporation of P (< 2 inch)
more P in A horizon which has lower sorption capacity.
More dissolved P

Extractable P and Soil Depth



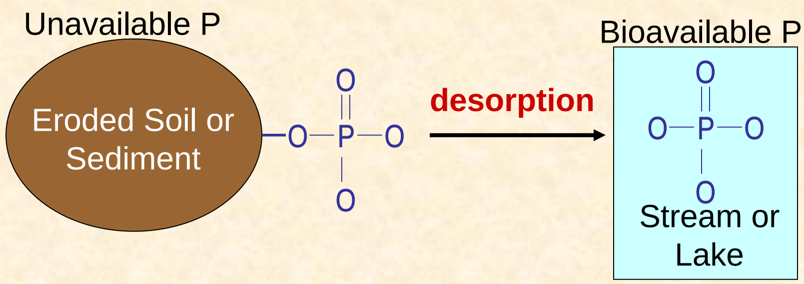
Extractable P decreases with soil depth

Clay increases

extractable P decreases with depth

Effect of P Sorption from eroded soil/sediment?

Will P become bioavailable to algae?



Eroded surface soils with lower sorption capacity more likely to desorb P than subsoil with high P sorption capacity

Soil Testing of P to Set Environmental Limits

Crop production soil tests: **Measure the "labile" nutrient pool that will be available to the crop during some / all of the growing season**

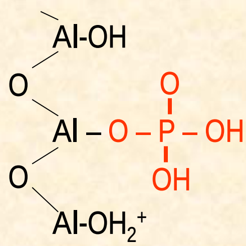
Professor Bray's Requirement for a "good soil test" (1948)

1. **Extract a proportionate part of plant available forms of nutrient from different soils**

2. **Extracted nutrients should correlate with uptake of nutrient and crop yield**

Soil Test P
Acid - Fluoride Extractant

Soil tests: Bray 1 (Ohio), Bray 2, Mehlich 3, Morgan



$+ H^+ + F^- \rightarrow Al F_6^{3-} + H_2PO_4^-$

Available

Mineral or Adsorbed P

Acid + F$^-$ dissolve Al mineral surfaces releasing P
also dissolved other P minerals (Ca-P from manure)

Very aggressive (pH 2.3): short 5 to 15 min extraction time

Soil Test P
Dilute Base Extractant

Soil tests: Olson, AB-DTPA

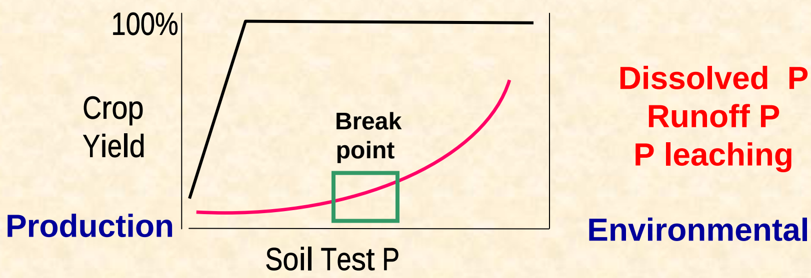
Olson's reagent, 0.5 M $NaHCO_3$

Better than Bray for calcareous soils

HCO_3^- desorbs $H_2PO_4^-$ and dissolves some Ca minerals

Commonly used in the western US

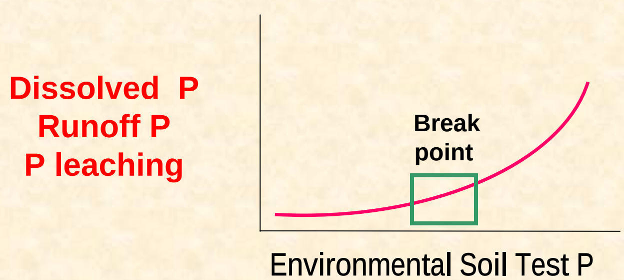
Using Crop Production Soil Tests as Environmental Soil Tests



Identify soil test level “break point” where P solubility increases

Set soil limit at break point to minimize soluble P

Environmental P Soil Tests



Similar approach -- but use water extractant

water extract test better correlated with dissolve P / runoff P/ P leaching than production-based soil tests (Bray, Mehlich, Olson)

Game called on account of Mehlich 3 rain

Criticism that acid soil tests Bray, Mehlich) are too aggressive to simulate rain

Acid-F supporters claim soil test is correlated with runoff P

Bray / Mehlich soil tests do not work for treated high P soils (to be discussed soon)

Environmental Tests Based on Soil P Quantity / Intensity

"Labile P"
P in Equilibrium with soil solution P
strongly adsorbed P
soluble P minerals
weakly adsorbed P

Soil solution P
dissolved P
bioavailable P

Quantity **Intensity**

Water only measures Intensity not the Quantity pool
Have to measure Quantity to determine the soil's ability to continue to replace solution dissolved P

Larger solution:soil ratio is a better measure of Q and I
water:soil ratio of 200:1 better than 100:1 better than 25:1

Environmental Soil Tests Using Quantity-Intensity Phosphorus Saturation Model

Soluble P + Amorphous Fe, Al Oxides $\longrightarrow$ Adsorbed P

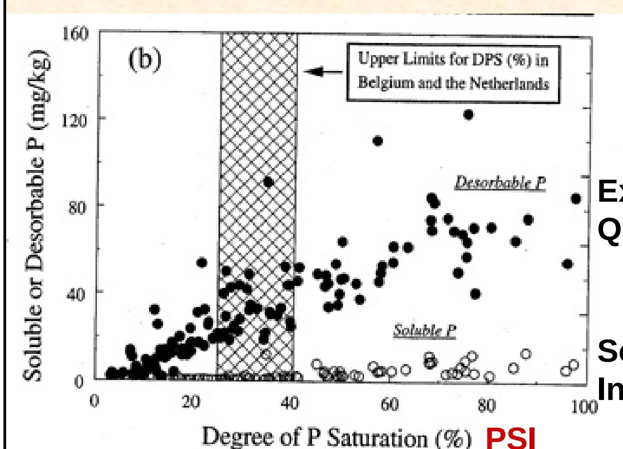
Soil PSC (P Sorption Capacity) = Fe, Al oxide sorption capacity

$$\text{P Saturation Index (PSI) of Soil (in \%)} = \left(\frac{\text{P sorbed to soil}}{\text{PSC}}\right) 100\%$$

Environmental soil test determines soil PSI

Phosphorus Saturation Model

Dissolved / Extractable P increases with PSI



PSI

Extractable P: Quantity + Intensity

Soluble P: only Intensity

Suggested Limit: PSI of 25 to 40%

Reducing P solubility and risk
NRCS P Index

Soluble P Source x Transport = P Index

Soil Test P — Rainfall

Soluble P In Manure — Distance To Stream

Erosion Class, etc.

What limits P solubility in soil or waste/by products?

Solubility of P Minerals in soil or in manure

P adsorption by Fe, Al oxides in soil or manure

Aluminum Treated Poultry Litter

Dr. Philip Moore USDA ARS, Fayetteville, Arkansas

$$Al_2(SO_4)_3 \longrightarrow 2\,Al^{3+} + 3\,SO_4^{2-}$$

Alum — Dissolves in water (wet manure)

$$Al^{3+} + H_2PO_4^- \longrightarrow AlPO_4 + 2H^+$$

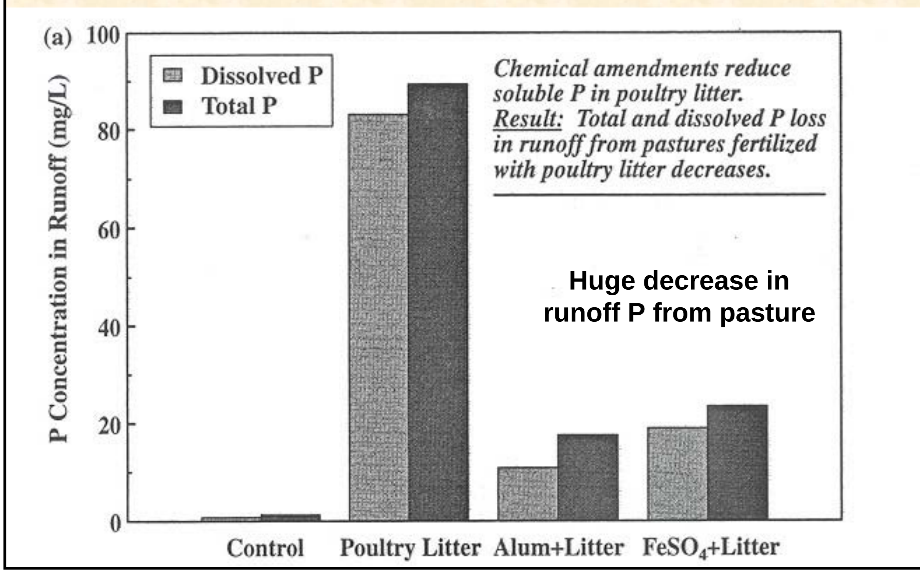
$H_2PO_4^-$: Soluble in Manure

$AlPO_4$: Insoluble P

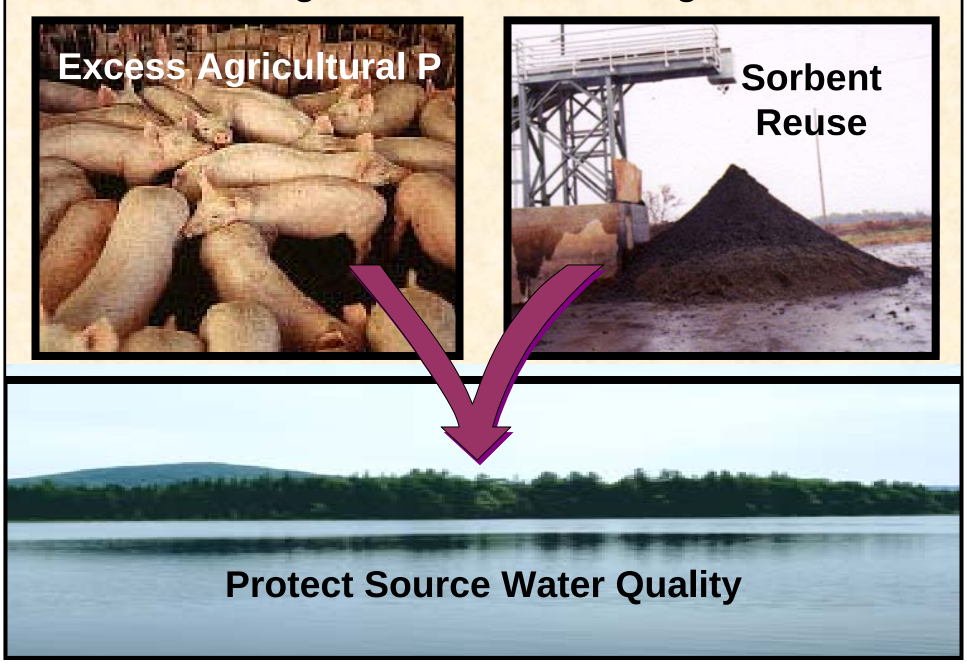
Lowers Runoff P of Litter

Lowers the P Index Score

Decreasing P mineral solubility
Poultry litter treated with Al, Fe salts



Using P Sorbents to Manage P



Using P Sorbents to Reduce dissolved P in Soil / Manures

Dissolved P + P Sorbent → Adsorbed P

$H_2PO_4^-$ + oxide sorbent → $Al\text{-}H_2PO_4$

soluble P

strongly adsorbed P

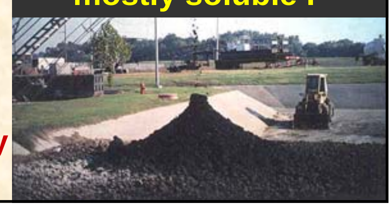
Sorbents **INCREASE** the soil sorption capacity

Sorbent Land Application Options to Reduce P loss

Incorporate sorbent into high STP soil
Reduce STP and P solubility/leaching

Surface Apply sorbent
Remove dissolved P from runoff

Manure/biosolids
mostly soluble P



Co-Blending sorbent with manure/biosolids
Reduce manure/biosolids P solubility

Managing Excessive Dissolved P Levels in Soil

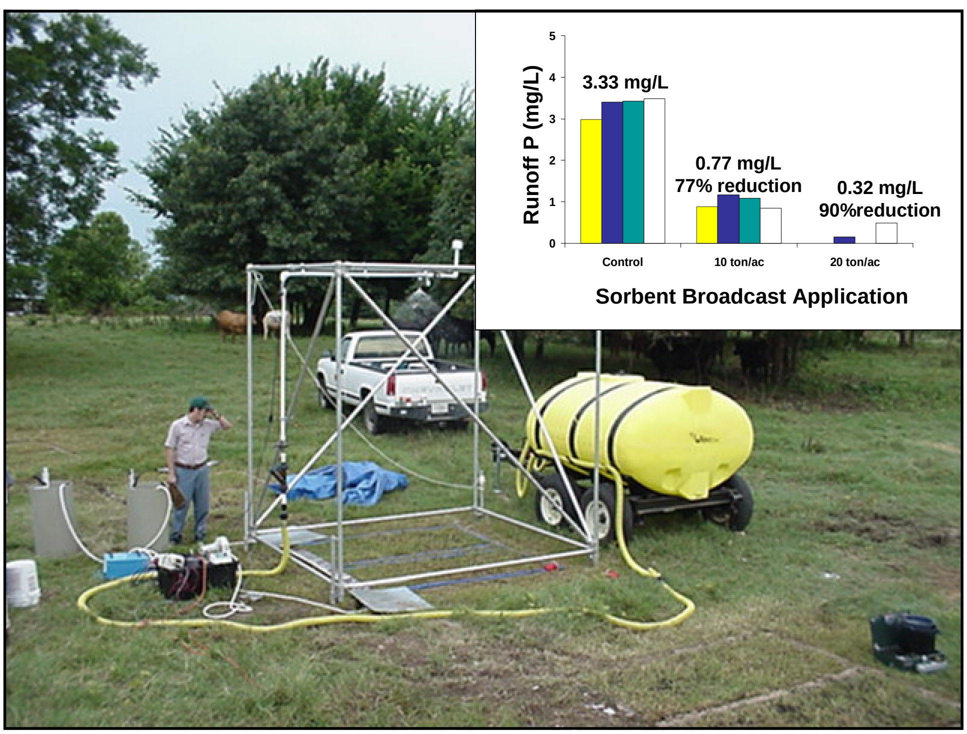
Reducing excessive levels of dissolved P in soil

- **Cropping down (long time to remove P)**

Sorbent technology to reduce dissolved P
blend sorbent into soil to decrease dissolved P / runoff /leaching

Reduce P losses from field

- **Enhanced buffer strips: P sorbent in grass waterways or buffer strips to sorb dissolved P from runoff**
- **Co-blending of sorbent with manures to decrease dissolved P / runoff /leaching**



Select OSU Previous WTR Research

Characterization	Results
E.A. Dayton & N.T. Basta. 2004. J Environ Qual. 34:1112-1118	Evaluated and modified soil tests for use with WTR
E.A. Dayton et al. 2001. Water Env. Res. 73:52-57	Characterized WTR use as soil substitute or as P sorbents
Land Application	
E. A. Dayton & N.T. Basta. 2005. J. Environ. Qual. 34:2112-2117	P reductions due to WTR can reduce P risk scores
E.A. Dayton et al. 2003. J. AWWA 95:151-158	Runoff P reduction related to WTR Pmax & Alox
Gallimore et al. 1999 J. Environ. Qual. 28:1474-1478.	Decreased runoff P from poultry litter-treated land
Basta & Storm, 1997	Decreased runoff P from poultry litter-treated land
Peters & Basta, 1996. J. Environ. Qual. 25:1236-1241.	Decreased soil test P and soluble P

Future Directions

- Interested in collaborative projects
- Field experiments with sorbent technology underway this summer at OSU and planned this year (USDA NRCS CIG)
- Environmental Soil Testing (Soil Chem. Group, Columbus)
  Soil PSI (P saturation index)
  Water extractable P
  P adsorption maxima (Langmuir adsorption isotherms)
  Screening / characterization of potential sorbents
  other soil / plant tests

Thank you for your attention

More information?

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