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Soil Sampling and Phosphorus in Calcareous Soils

Paul Stukenholtz

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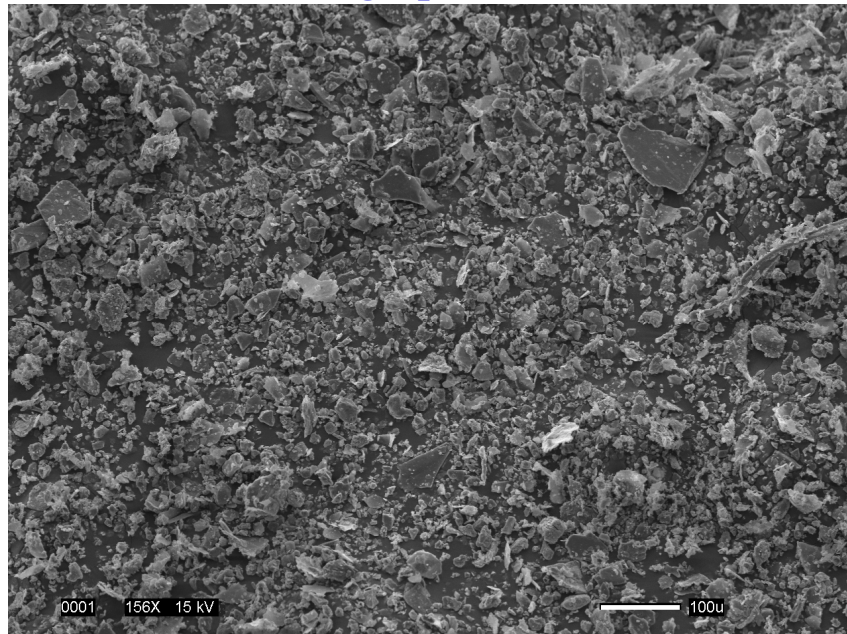
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Electron Micrograph of Sand Particles



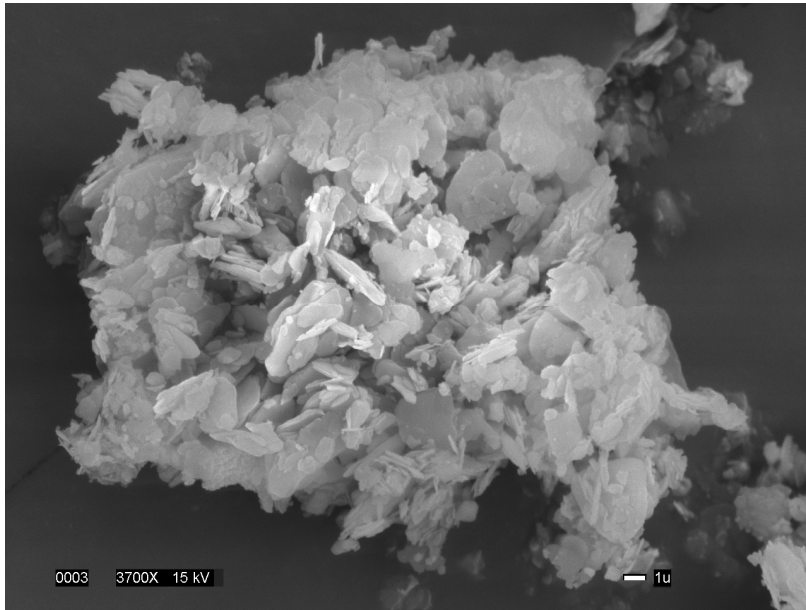
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Electron Micrograph of Silt Particles



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Electron Micrograph of Clay Particle



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Phosphorus - P

- Used for energy storage and transport
- Very important for root growth
- Very important for disease resistance
- Tied-up by excess lime in the soil
- Often never shows deficiency symptoms
 - even when severely stunting growth

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P Deficiency



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P Deficiency in Corn

Grand View, ID
6-21-2011



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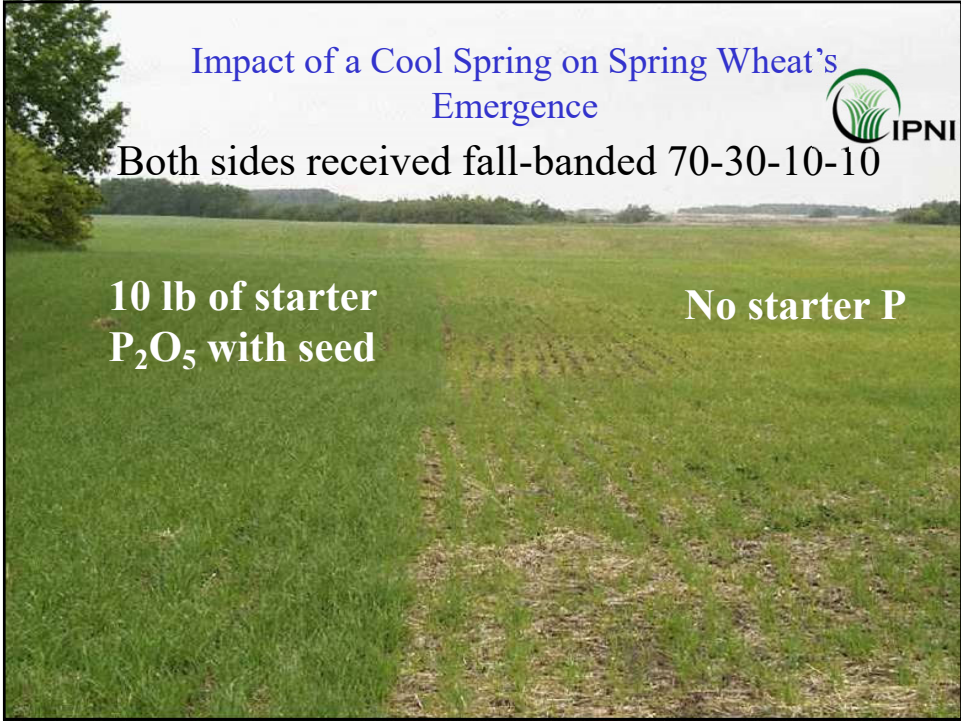
P Deficiency in Corn

Grand View, ID
6-21-2011

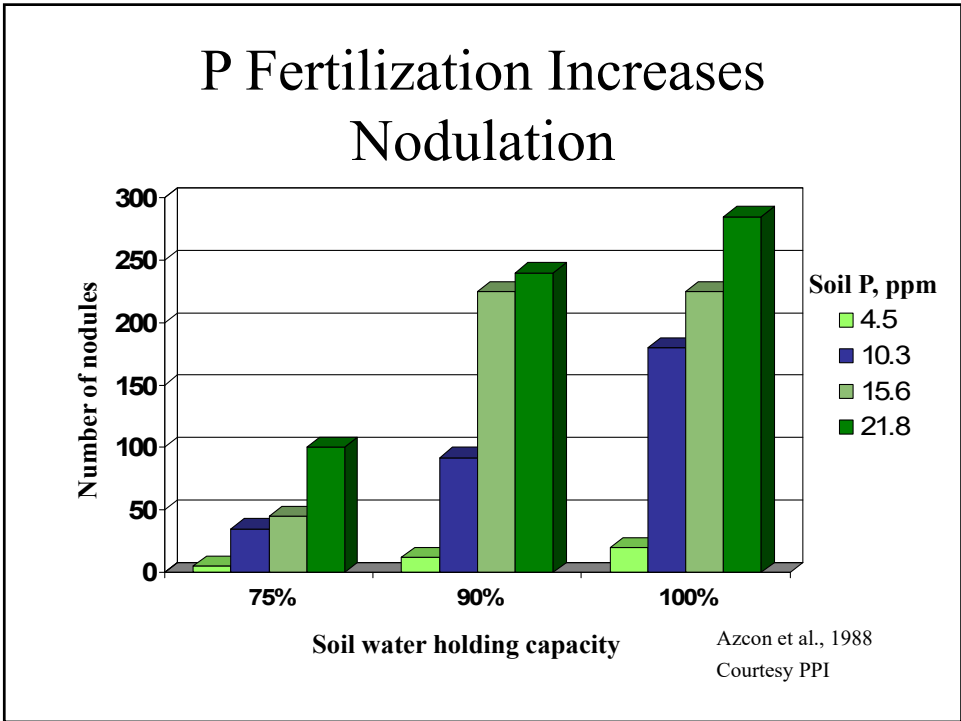


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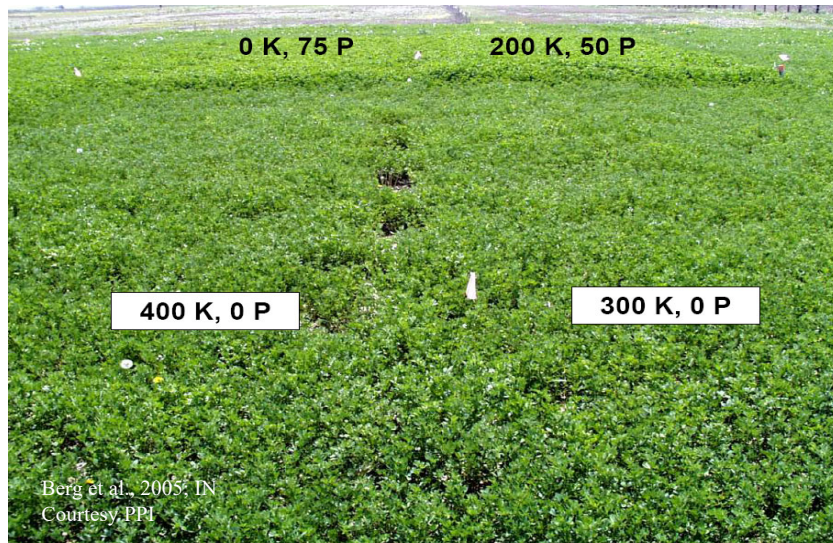


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P and K



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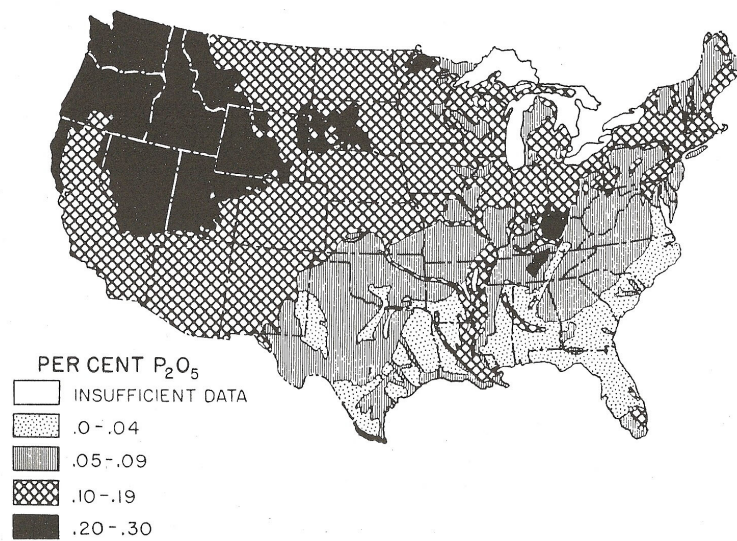


FIGURE 6.1 Phosphate content in the surface foot of soils in the United States.
Pierre and Norman, Eds., Agronomy, Vol. 4, p. 401, 1953

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pH and Phosphorus

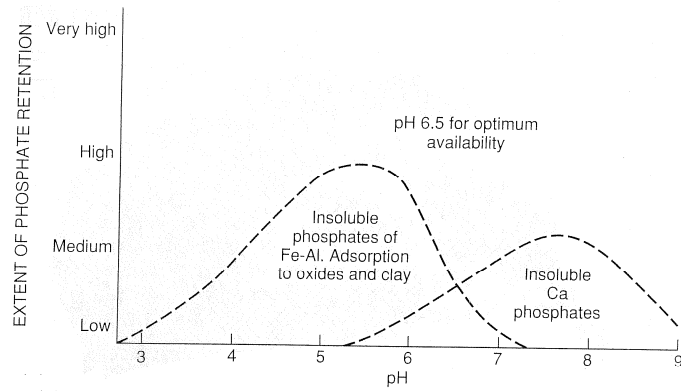
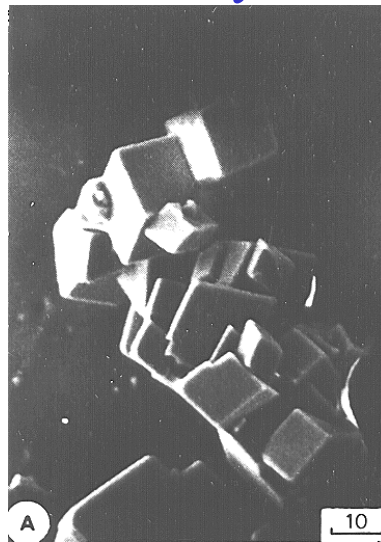


FIGURE 6.11 Soil pH effect on P adsorption and precipitation. Adapted from Stevenson, *Cycles of Soil*, p. 250, John Wiley & Sons, 1986.

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Lime Crystals



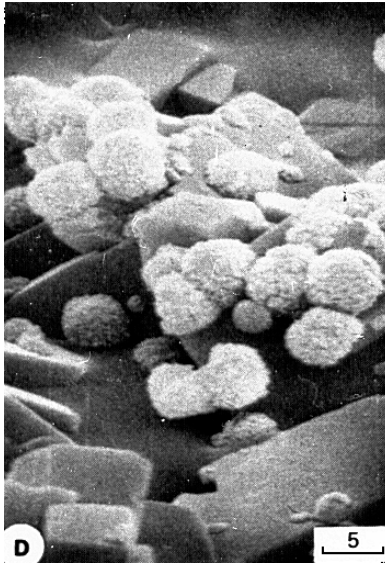
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P Solution on Lime



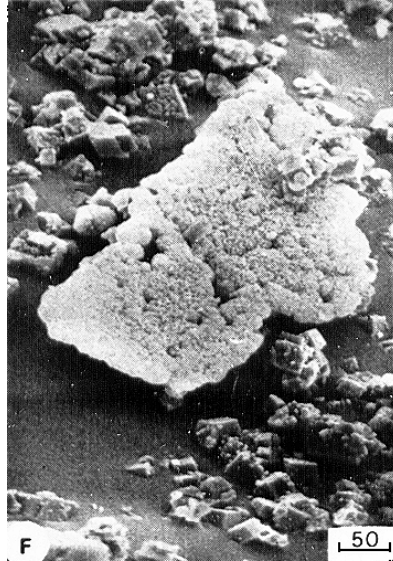
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P Solution on Lime



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P Solution on Lime



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Total vs. Available P_2O_5 at pH of 8.1 5% Excess Lime

<u>Total in Soil</u>	<u>Soil Solution</u>	<u>Labile</u>
0.05-0.25%	0.02-0.05 ppm	10-30 ppm
2000-8000 lbs/Ac·ft	0.1-0.2 lbs/Ac·ft	40-80 lbs/Ac·ft

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SOIL TEST DATA	Sample 1	Sample
pH	8.0	H
Salts, mmhos/cm	1.7	M
Chlorides, ppm	15	L
Sodium, meq/100g	0.20	VL
CEC, meq/100g	17.5	M
Excess Lime, %	3.3	M
Organic Matter, %	2.80	H
Organic N, lb/Acre	11.0	H
Ammonium - N, ppm	2.8	VL
Nitrate - N, ppm	5	VL
Phosphorus, ppm	6	L
Potassium, ppm	129	L
Calcium, meq/100g	13.9	VH
Magnesium, meq/100g	3.0	M
Sulfate - S, ppm	20	M
Zinc, ppm	0.5	VL
Iron, ppm	12.3	H
Manganese, ppm	2.4	L
Copper, ppm	0.5	L
Boron, ppm	0.79	M

Moderately High Lime

Very Low Phosphorus

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What is P_2O_5 ?

RECOMMENDATIONS, lbs Nutrients or Units per Acre

Nitrogen	35	Pound of Phosphorus nutrient expressed as an oxide = "Units Phosphate"
P_2O_5 – Phosphate	135	
K_2O - Potash	200	
Calcium	0	
Magnesium	0	
Sulfate - Sulfur	35	
Zinc	7	
Iron	0	

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P vs. P_2O_5

P = Phosphorus

PO_4^{-3} = Phosphate Ion

P_2O_5 = Diphosphorus Pentoxide

Slang name “Phosphate”

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P vs. P_2O_5

$$P_2O_5 \times 0.44 = P$$

$$P \times 2.3 = P_2O_5$$

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- DCPD
 - Dicalcium phosphate dihydrate $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$
 - Ca:P ratio: 1:1
- DCP Dicalcium phosphate CaHPO_4
 - Ca:P ratio: 1:1
- OCP
 - Octacalcium phosphate $\text{Ca}_8\text{H}(\text{PO}_4)_3 \cdot 2.5\text{H}_2\text{O}$
 - Ca:P ratio 4:3
- BTCP
 - Beta-tricalcium phosphate $\text{Ca}_{18}(\text{Mg,Fe})\text{H}_2(\text{PO}_4)_{12}$
 - Ca:P ratio 3:2
- HA Hydroxyapatite $\text{Ca}_5(\text{PO}_4)_3\text{OH}$
 - Ca:P ratio 5:3

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Phosphorus Immobilization Can Occur Quickly

- In laboratory incubations, DCPD to HA in 20 hours
- In soil tests, generally DCPD to OCP in 4 months
- OCP to B-TCP in 8-10 months

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It isn't this simple

- Technical phrase: “not completely understood”
- Clay, Organic Matter, & metals may bind and release Phosphorus ions.
- In some soils, DCPD, OCP, or B-TCP dominate, even when they “shouldn't”.
- Solution P “holds” at certain levels.
- New forms of soil P are continuously being discovered.

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Compound	Mineral name	Compound	Mineral name
$\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$	Variscite	$\text{FePO}_4 \cdot 2\text{H}_2\text{O}$	Metastrongite
$\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$	Metavariscite	$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$	Vivianite
$\text{Al}(\text{NH}_4)_2\text{H}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	—	$\text{FeNH}_4(\text{HPO}_4)_2$	—
$\text{Al}_2(\text{NH}_4)_2\text{H}_2(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$	—	$\text{Fe}_2\text{NH}_4\text{H}_2(\text{PO}_4)_4 \cdot 6\text{H}_2\text{O}$	—
$\text{Al}_2(\text{NH}_4)_2\text{H}_2(\text{PO}_4)_4 \cdot 18\text{H}_2\text{O}$	NH_4 -taranakite	$\text{Fe}_2\text{K}(\text{H}_2\text{PO}_4)_4 \cdot 6\text{H}_2\text{O}$	—
$\text{AlNH}_4\text{PO}_4\text{OH} \cdot 2\text{H}_2\text{O}$	—	$\text{Fe}_2\text{K}(\text{PO}_4)_2\text{OH} \cdot 2\text{H}_2\text{O}$	K-leucophosphate
$\text{AlNH}_4\text{PO}_4\text{OH} \cdot 3\text{H}_2\text{O}$	—	$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$	Newberryite
$\text{Al}_2\text{NH}_4(\text{PO}_4)_2\text{OH} \cdot 2\text{H}_2\text{O}$	—	$\text{Mg}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	—
$\text{Al}_2\text{NH}_4(\text{PO}_4)_2\text{OH} \cdot 8\text{H}_2\text{O}$	—	$\text{Mg}_2(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$	—
$\text{AlKH}_2(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	—	$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$	Struvite
$\text{Al}_2\text{K}_2\text{H}_2(\text{PO}_4)_4 \cdot 18\text{H}_2\text{O}$	K-taranakite	$\text{Mg}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$	Schertelite
$\text{Al}_2\text{K}(\text{PO}_4)_2\text{OH} \cdot 2\text{H}_2\text{O}$	Leucophosphate	$\text{Mg}_2(\text{NH}_4)_2(\text{HPO}_4)_4 \cdot 8\text{H}_2\text{O}$	Hannayite
$\text{AlKPO}_4\text{OH} \cdot 0.5\text{H}_2\text{O}$	—	$\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$	—
$\text{AlKPO}_4\text{OH} \cdot 1.5\text{H}_2\text{O}$	—	$\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$	—
$\text{Al}_2\text{K}(\text{PO}_4)_2(\text{F},\text{OH}) \cdot 3\text{H}_2\text{O}$	Minyulite	$\text{Al}(\text{NH}_4)_2\text{P}_2\text{O}_7\text{OH} \cdot 2\text{H}_2\text{O}$	—
CaHPO_4	Monetite	$\text{Ca}_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	—
$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	Brushite	$\text{Ca}_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$	—
$\text{Ca}_8\text{H}_4(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$	Octocalcium phosphate	$\text{Ca}_3\text{H}_2(\text{P}_2\text{O}_7)_2 \cdot 4\text{H}_2\text{O}$	—
$\text{Ca}_9(\text{PO}_4)_6(\text{OH})_2$	Hydroxyapatite	$\text{Ca}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$	—
$\text{Ca}_9(\text{PO}_4)_6\text{F}_2$	Fluorapatite	$\text{Ca}_2(\text{NH}_4)_2(\text{P}_2\text{O}_7)_2 \cdot 6\text{H}_2\text{O}$	—
$\text{CaAlH}(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$	—	$\text{Ca}_2(\text{NH}_4)_2(\text{P}_2\text{O}_7)_2 \cdot 6\text{H}_2\text{O}$	—
$\text{Ca}_2\text{Al}_2\text{H}_2(\text{PO}_4)_3 \cdot 20\text{H}_2\text{O}$	—	$\text{CaNH}_4\text{HP}_2\text{O}_7$	—
$\text{CaNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$	—	$\text{Ca}_2\text{NH}_4\text{H}_2(\text{P}_2\text{O}_7)_2 \cdot 3\text{H}_2\text{O}$	—
$\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	—	$\text{CaK}_2\text{P}_2\text{O}_7$	—
$\text{Ca}_2\text{NH}_4\text{H}_2(\text{PO}_4)_4 \cdot 2\text{H}_2\text{O}$	NH_4 -Flatt's salt	$\text{Ca}_2\text{K}_2(\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$	—
$\text{Ca}_2(\text{NH}_4)_2(\text{HPO}_4)_3 \cdot 2\text{H}_2\text{O}$	—	$\text{Ca}_2\text{K}_2(\text{P}_2\text{O}_7)_2 \cdot 6\text{H}_2\text{O}$	—
$\text{CaKPO}_4 \cdot \text{H}_2\text{O}$	—	$\text{Ca}_2\text{KH}_2(\text{P}_2\text{O}_7)_2 \cdot 3\text{H}_2\text{O}$	—
$\text{CaK}_2\text{H}(\text{PO}_4)_2$	—	$\text{CaNa}_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$	—
$\text{Ca}_2\text{KH}_2(\text{PO}_4)_4 \cdot 2\text{H}_2\text{O}$	K-Flatt's salt	$\text{Fe}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	—
$\text{CaFe}_2\text{H}_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$	—	$\text{Mg}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$	—
$\text{CaFe}_2\text{H}_2(\text{PO}_4)_4 \cdot 8\text{H}_2\text{O}$	—	$\text{Mg}(\text{NH}_4)_2(\text{P}_2\text{O}_7)_2 \cdot 6\text{H}_2\text{O}$	—
$\text{Ca}_2\text{Mg}_2(\text{PO}_4)_4$	—	$\text{Mg}(\text{NH}_4)_2\text{H}_2(\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$	—
$\text{FePO}_4 \cdot 2\text{H}_2\text{O}$	Strengite	$\text{Ca}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	—

From Sample et al., 1986. *The Role of Phosphorus in Agriculture*, Khasawneh, F.E., Sample, E.C., and Kamprath, E.J., Eds., p. 284. With permission of American Society of Agronomy.

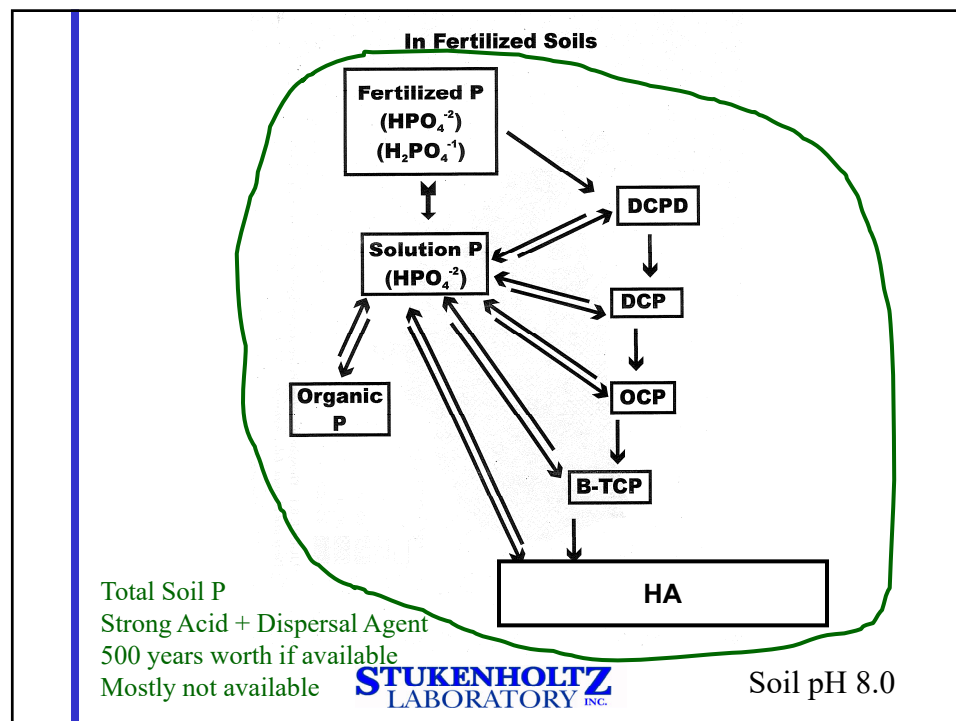
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Predicting P Fertilizer Response

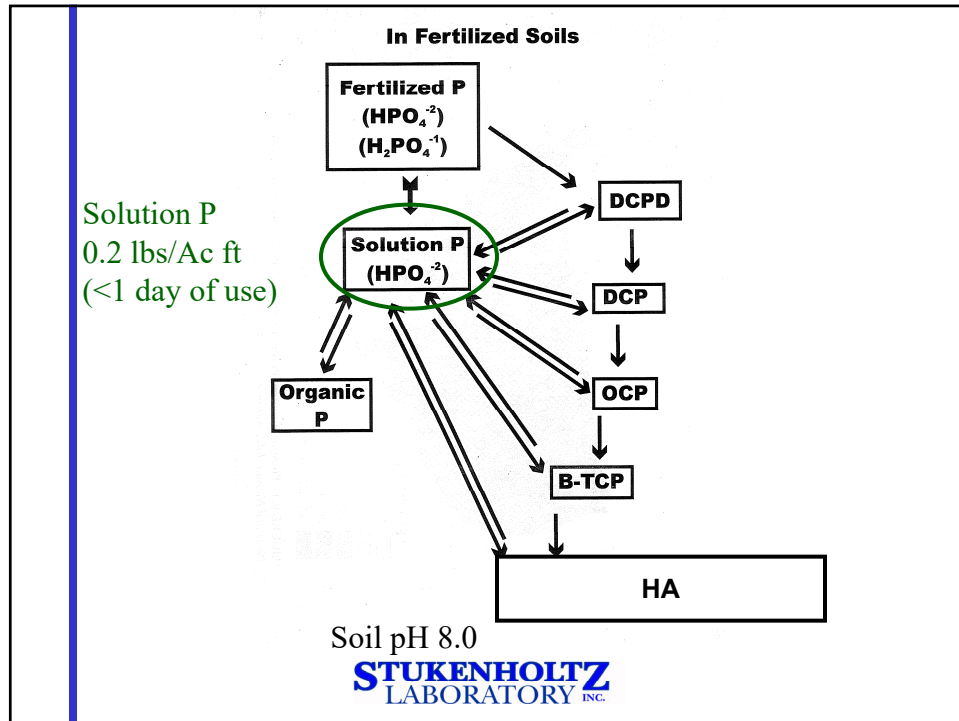
- An “Extract” is used to pull some of the P from the soil.
- The amount of P removed should correlate to the amount of increased growth from a fertilizer addition.

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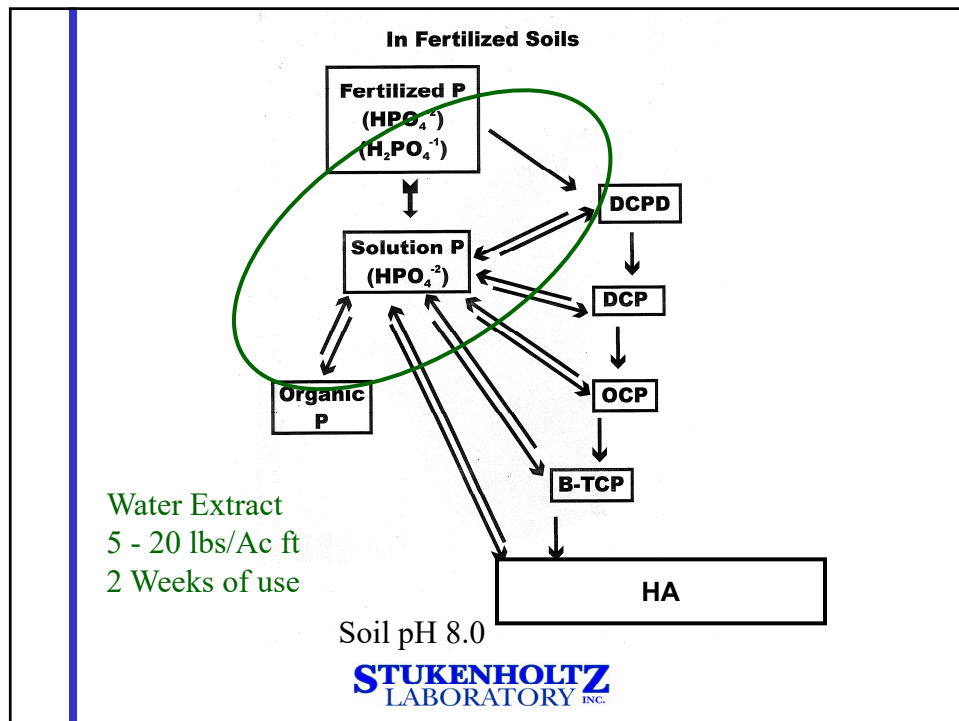
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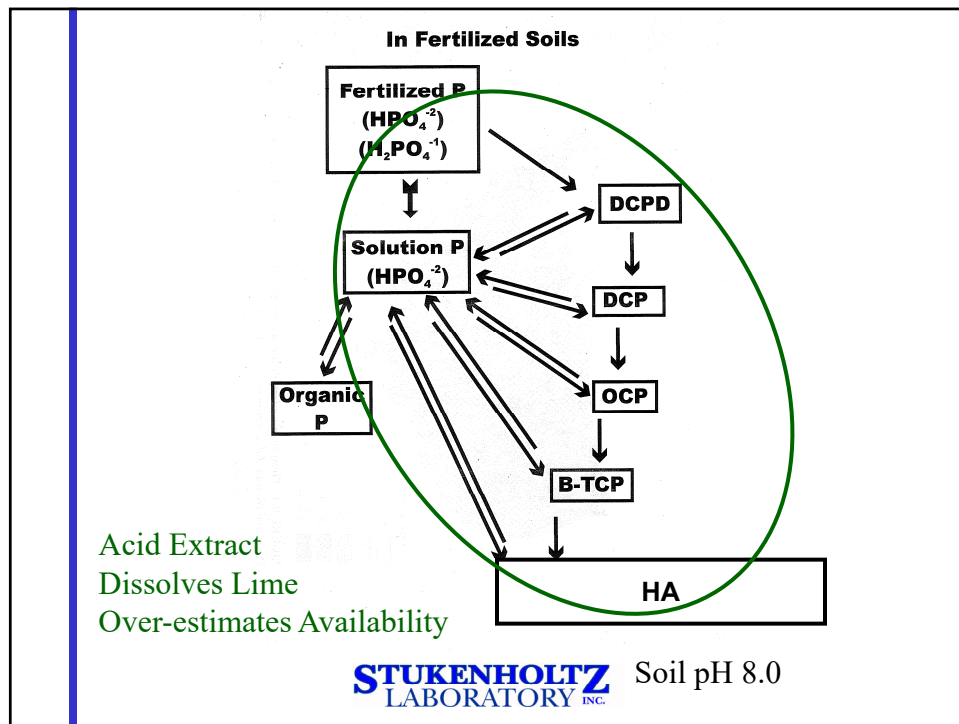
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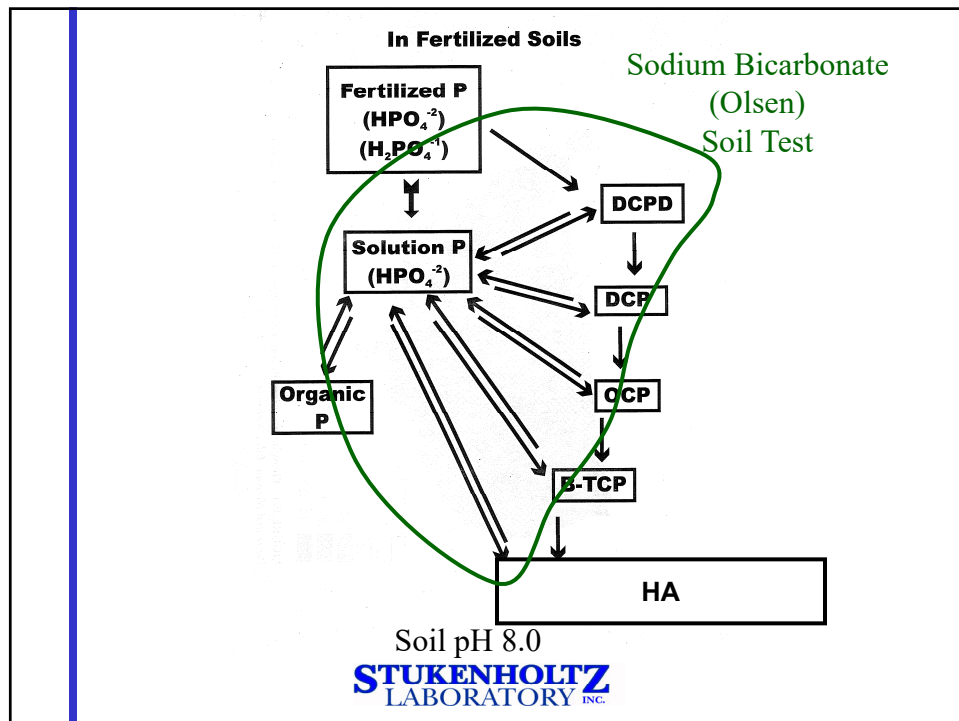
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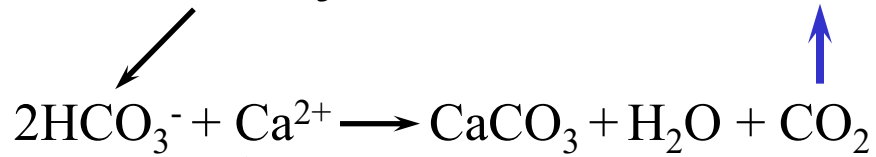
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Sodium Bicarbonate (Olsen) Extract

Sodium Bicarbonate (pH 8.5)



Calcium Phosphate(s)



Measured by Extract

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Major P Extraction Methods

<u>Method</u>	<u>Contains</u>	<u>Ext. pH</u>	<u>Soil pH</u>
Olsen (Na-Bicarb)	NaHCO_3	8.50	6.0-10.0
Bray 1	HCl NH_4F	2.60	4.0-7.5 (no Lime)
Mehlich 3	Acetic acid HNO_3 NH_4F EDTA	2.50	4.0-7.5 (no Lime)

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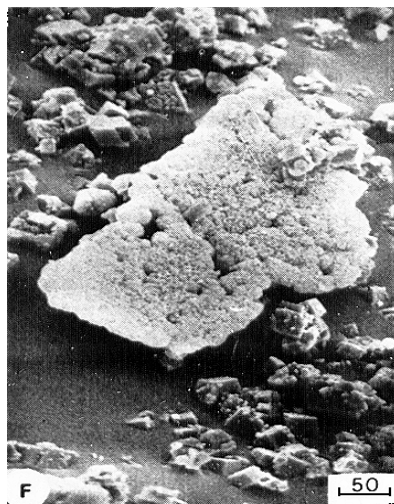
NAPTP Sample Exchange

Soils		Units	# Labs	2015-103		# Labs	2015-106	
				Median	MAD		Median	MAD
pH	Water (1:1)		85	7.59	0.09	90	8.16	0.08
XS Lime			15	9.70	0.84	13	2.00	0.30
Phosphorus								
PO4-P	Bray P (1:10)	mg/kg	47	14.1	2.53	47	27.7	2.37
PO4-P	Bray P1 (1:7)	mg/kg	9	14.3	2.72	12	22.1	3.65
PO4-P	Olsen/Bicarb	mg/kg	53	31	3.95	58	10.6	1.31
PO4-P	AB-DTPA	mg/kg	1	24.5	0	2	4.36	0.359
PO4-P	Modified Morgan	mg/kg	6	27.8	6.76	7	27.1	2.1
PO4-P	TRUE Morgan	mg/kg	7	21	2.5	7	25.8	1.4
PO4-P	Mod. Kewlona	mg/kg	1	34.5	0	3	20	1.5
PO4-P	Strong Bray (1:10)	mg/kg	9	399	70.9	9	130	7
PO4-P	Water Soluble	mg/kg	0	6.1		0	5.2	0
Mehlich-1 Multi Element		mg/kg	5	76.4	19.2	6	26.8	9.46
Mehlich-3 Mult-Element		mg/kg	50	94	7.7	50	41.1	2.94

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The Sodium Bicarbonate Test Alone is not Good Enough



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Early Research on Lime & Phosphorus

Dr. Dale Stukenholtz, Stukenholtz Laboratory

Dr. Jeff Stark, University of Idaho

Dr. Dale Westermann, USDA ARS



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Lime Effects on Phosphorus Availability in a Calcareous Soil

D.T Westermann, USDA-ARS, 3793 N 3600 E, Kimberly, ID 83341, 19 Apr 1991

Soil Science Society of America Journal 56:489-494 (1992) 677
Sough Segoe Rd., Madison WI 53711 USA

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Materials & Methods

- Bulk Portneuf Silt Loam soil collected
 - A Horizon (topsoil)
 - pH 7.5, 0.6% excess lime
- CaO mixed with soil at 3 rates
 - Mixed, wetted, dried repeatedly over 13 weeks
 - CaO converted to CaCO₃,
 - pH 8.0
- 1 RB Minituber added to each pot
- Roots and tops harvested after 35 days

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Table 2. Treatments, selected soil P characteristics, plant dry-matter yield, and P uptake for potato and sudangrass in Exp. 2a and 2b, respectively.

Experiment	Treatments		Soil characteristics				Plant	
	Lime	P application	NH ₄ CO ₃ -P	Root-P	Solution P	EDC ₂	Yield	P uptake
	g kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg L ⁻¹	L kg ⁻¹	g pot ⁻¹	mg pot ⁻¹
2a Potato	0	0	19.6	35.6	0.277	48	12.45	42
	6	25	32.8	61.0	0.855	38	14.29	62
	6	75	58.7	113.6	1.594	31	14.86	74
	30	0	12.5	43.3	0.172	104	8.85	25
	20	25	23.3	62.2	0.260	78	11.95	41
	20	75	61.8	104.1	0.763	53	12.95	50
	75	0	9.5	29.9	0.139	182	7.43	17
	75	25	19.5	48.3	0.172	129	10.88	33
	75	75	42.0	81.7	0.251	94	11.47	43
	126	0	1.2	20.1	0.020	624	6.52	10
	126	25	14.9	29.4	0.022	540	6.94	14
	126	75	32.7	51.2	0.070	338	7.53	20

D.T. Westermann, USDA-ARS, 3793 N 3600 E, Kimberly, ID 83341. Contribution from USDA-ARS. Received 19 Apr. 1991.
*Corresponding author.

Published in Soil Sci. Soc. Am. J. 56:489-494 (1992).

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Lime %	P Application ppm	Olsen-P ppm	Solution-P ppm	Yield g/pot	P Uptake mg/pot
0.6	0	19.6	0.277	12.45	42
0.6	25	32.8	0.455	14.29	62
0.6	75	58.7	1.094	14.06	74
3.0	0	12.5	0.172	8.65	25
2.9	25	23.3	0.260	11.95	41
2.8	75	45.8	0.763	12.95	59
7.5	0	9.5	0.139	7.43	17
7.5	25	19.5	0.172	10.88	33
7.5	75	42.0	0.251	11.47	43
12.6	0	7.2	0.020	6.52	10
12.5	25	14.9	0.022	6.94	14
12.6	75	32.7	0.030	7.43	20

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Lime %	P Application ppm	Olsen-P ppm	Solution-P ppm	Yield g/pot	P Uptake mg/pot
0.6	0	19.6	0.277	12.45	42
0.6	25	32.8	0.455	14.29	62
0.6	75	58.7	1.094	14.06	74
3.0	0	12.5	0.172	8.65	25
2.9	25	23.3	0.260	11.95	41
2.8	75	45.8	0.763	12.95	59
7.5	0	9.5	0.139	7.43	17
7.5	25	19.5	0.172	10.88	33
7.5	75	42.0	0.251	11.47	43
12.6	0	7.2	0.020	6.52	10
12.5	25	14.9	0.022	6.94	14
12.6	75	32.7	0.030	7.43	20

3x fertilizer for same Olsen value, 1/15 solⁿ P, 1/2 yield

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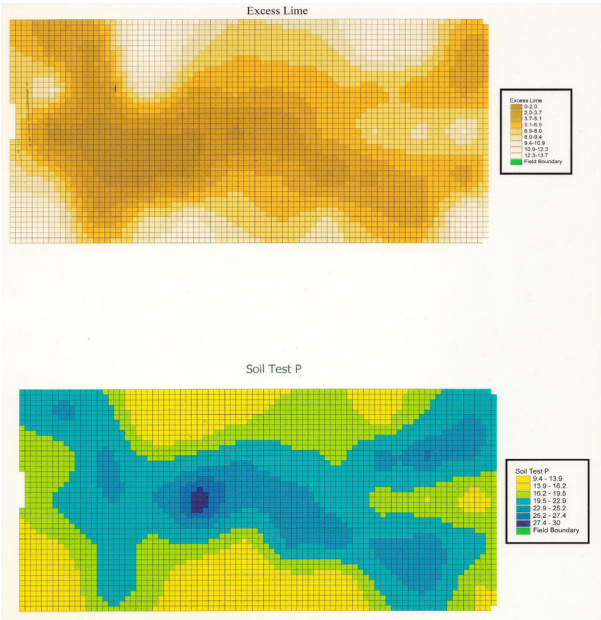
Alfalfa P Recommendation Comparison

Test 0-12"	Free Lime 0%		Free Lime 12%	
ppm P	--- pounds P ₂ O ₅ per acre ---			
0	210	300	325	420
4	190	225	300	345
8	150	150	235	270
12	110	100	170	220
16	90	50	140	170
20	80	0	125	120
24	70	0	115	70
	SL	U of I	SL	U of I

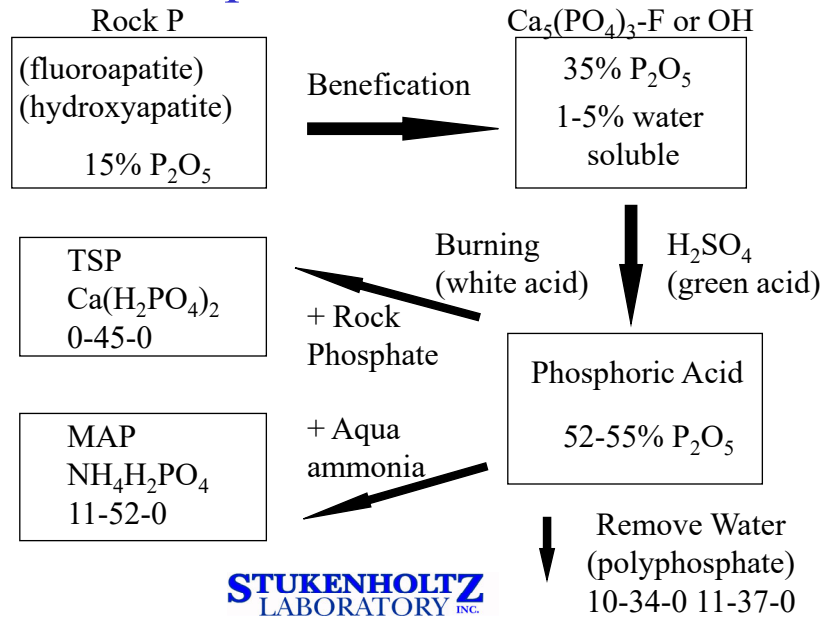
Assuming 6 T/Ac Yield Potential

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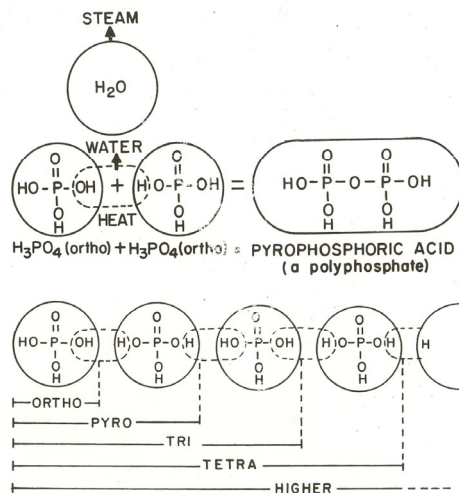


Phosphorus Fertilizer



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Polyphosphate



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Dry P Fertilizers

- Monoammonium Phosphate
MAP
11-52-0
 $\text{NH}_4\text{H}_2\text{PO}_4$
- 11% N, 52% P_2O_5 ,
- Good source of N & P
– especially in high pH soils
- Acid forming
- Has oily outer coating

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Liquid P Fertilizers

- Phos Acid
0-52-0
 H_3PO_4
- 50 - 52% P_2O_5
- $\text{pH} < 0$
- Not acid forming (it's already acid)
- 100% Orthophosphate
- Often blended with other nutrients

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Phos Acid

- Phos Acid
 - Will work in high Ca & bicarbonate water.
 - Improves water penetration
 - Dissolves lime, immediately reduces pH.
 - Is vulnerable to tie-up by excess lime.
 - Soil, water, and foliar applied phos acid is immediately available to the plant.
 - Best initial P movement

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Liquid P Fertilizers

- Ammonium Polyphosphate
 - 10-34-0
 - 11-37-0
- 34-37% P_2O_5
- pH 5.8-6.4
- Acid forming
- 50-65% Polyphosphate

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Ammonium Poly-P

- 10-34-0 & 11-37-0
 - Will not work through the water if the water has high Ca and bicarbonates.
 - Is safer through the water, especially if the water is pure (low buffering capacity).
 - Contains $\text{NH}_4\text{-N}$, which reduces soil pH near the fertilizer over time.
 - Can be used foliarly, but is ~60% polyphosphate which is not absorbed through the leaves.
 - More expensive per unit of P than 11-52-0.

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Liquid P Fertilizers

Neutral Liquid Phosphates

- 3-18-18
3%N, 18% P_2O_5 , 18% K_2O
100% Ortho-P
pH 7.4-7.8
- 6-24-6
6%N, 24% P_2O_5 , 6% K_2O
80% Ortho-P
pH 6.3-7.0

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Improving P Efficiency

- Prevent P from making $\text{Ca}_x(\text{PO}_4)_x$
 - Remove Ca from system
 - Use Manure or Compost
 - Blend with Humic or Fulvic Acids
 - Apply in Organic P form
 - Combine with Carbon & Sugars

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Improving P Efficiency

- Apply P when needed
 - Liquid starter fertilizer
 - Water application during growing season
 - Foliar application

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How to Improve P Efficiency

- In the soil
 - Use manure or compost
 - If topdressed, apply 11-52-0 in the fall
 - Blend 11-52-0 with dry humic acid
 - Incorporate
 - Liquid P during the growing season
 - Humic acids, Fulvic acids, with liquid applications
 - Acid forming sulfur with liquid P
 - Broadcast & band apply

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Improving P Efficiency

- Reduce Soil pH near P
 - Elemental Sulfur with dry P
 - Uniprill works best
 - Acid Forming Sulfur with liquid P
 - Thio-Sul
 - Flowable elemental sulfur
 - Acid-Forming fertilizers with P
 - Acid P

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How to Improve P Efficiency

- Applied through the water
 - Phos acid vs. 10-34-0
 - Add when needed, usually early in spring
 - Add Humic or Fulvic acid
 - About 1 gallon of each per 10 gallons 10-34-0
 - Apply with Thio-Sul or reduced Sulfur

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How to Improve P Efficiency

- Foliar application
 - 5 to 8 times more efficient than water or soil application
 - Often costs less than equivalent soil or water application
 - Avoids excess lime / high pH problems

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