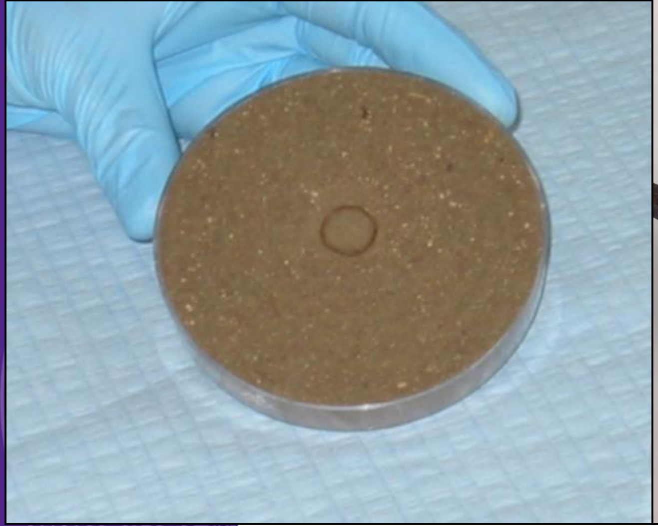
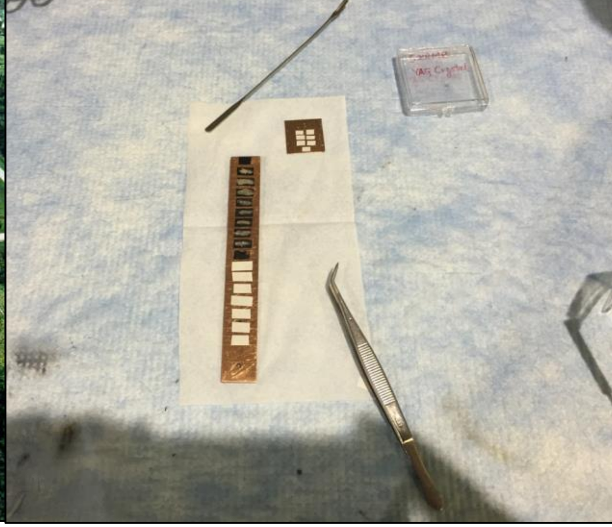


Can Humic substances be used as “enhancers” to alter fertilizer-phosphorus reaction pathways in soils?

Ganga Hettiarachchi and Joseph (Jay) Weeks Jr.

Department of Agronomy

KANSAS STATE UNIVERSITY

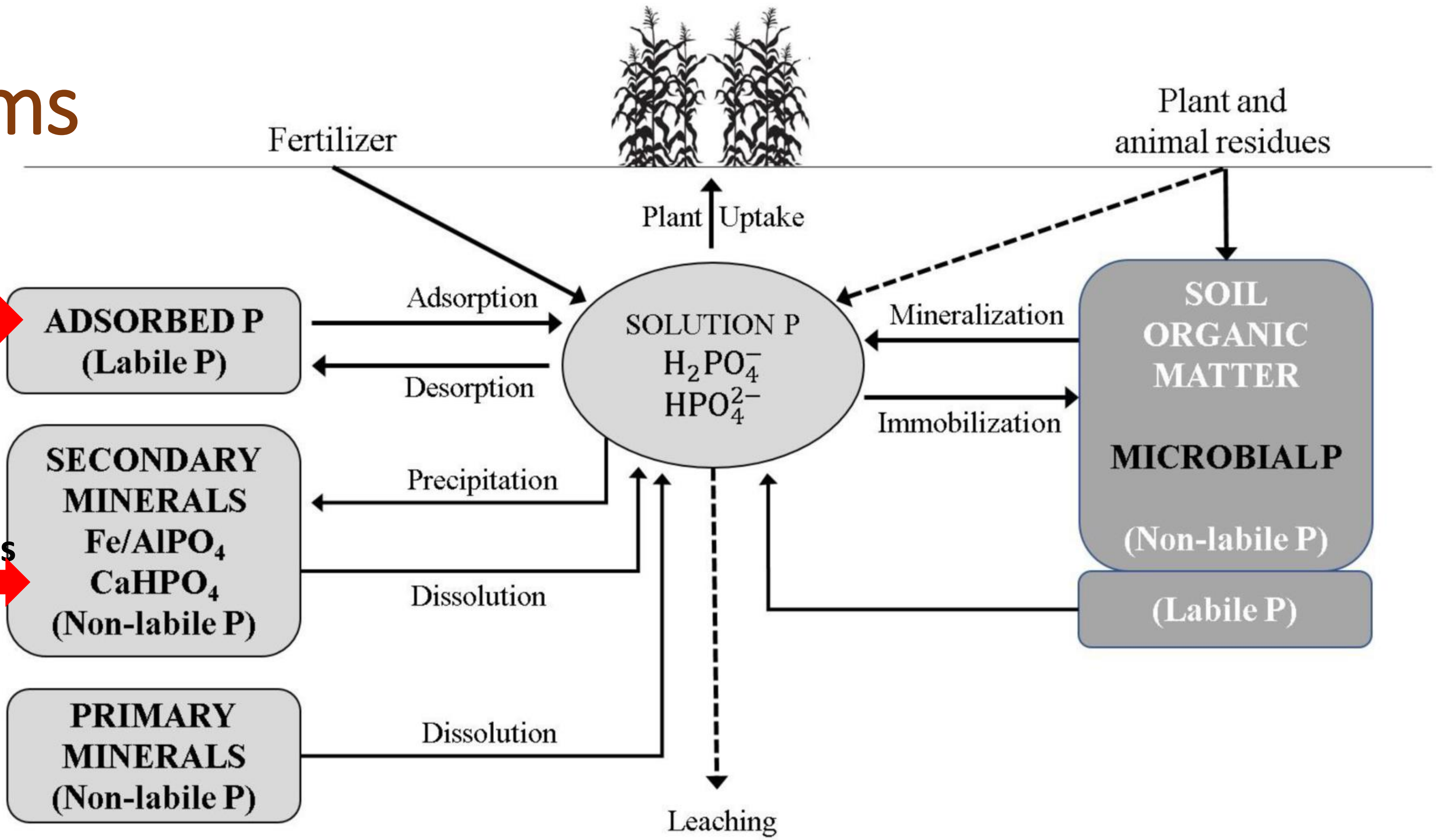
Fluid Fertilizer Forum 2020, Phoenix, AZ, 02/18/2020

Phosphorus Cycle

Problems

Acid Soils

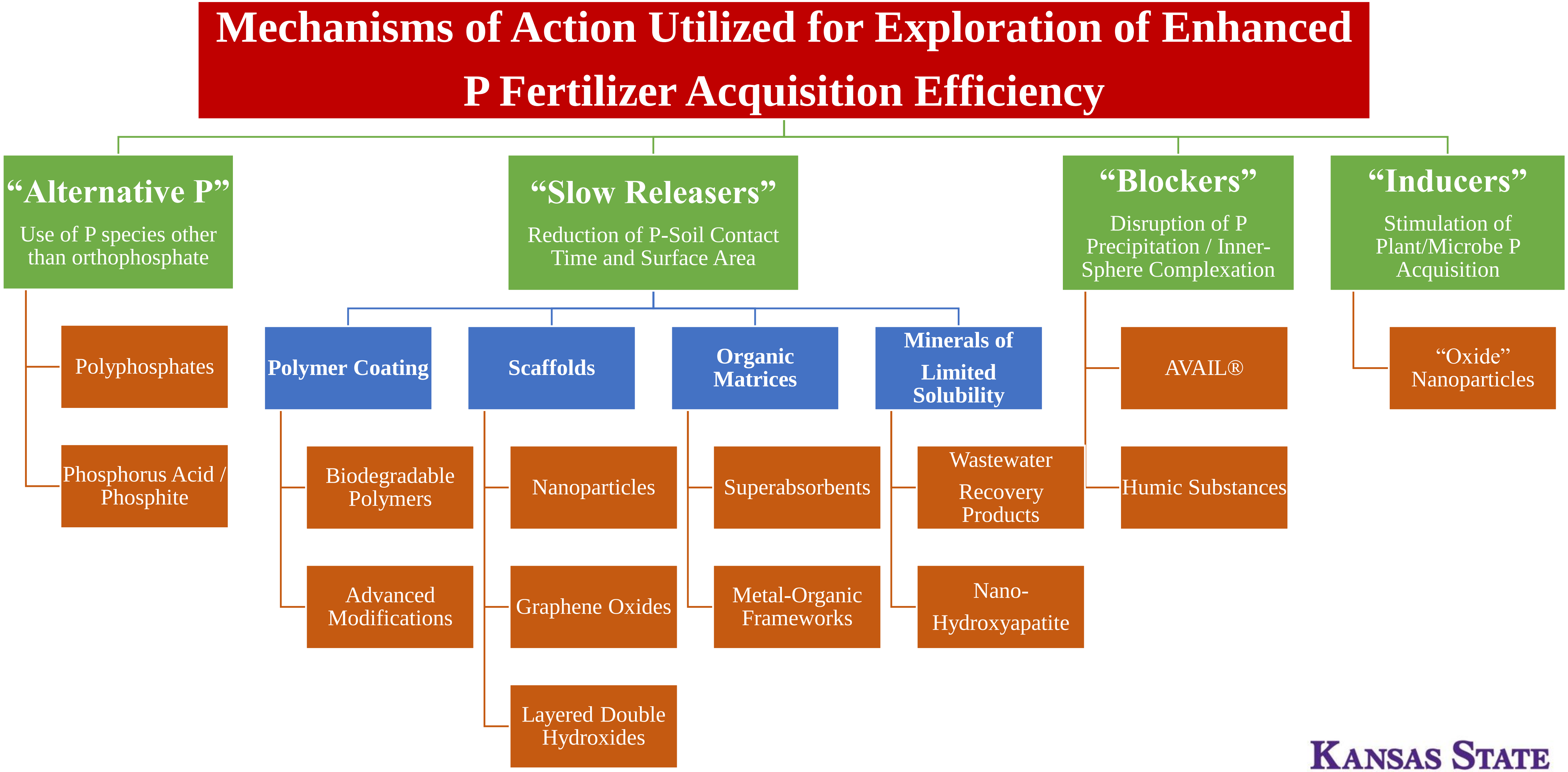
Calcareous Soils



(Sorour, 2017)

Figure 2. 1 Phosphorus cycle in an agricultural soil (adapted from Havlin et al., 2005).

We have a greater chance of innovating our way out of P problems than forcing/asking growers to modify their practices for the "good of society"



(Weeks and Hettiarachchi, 2019. J. Environ. Qual. 48: 1300-1313)

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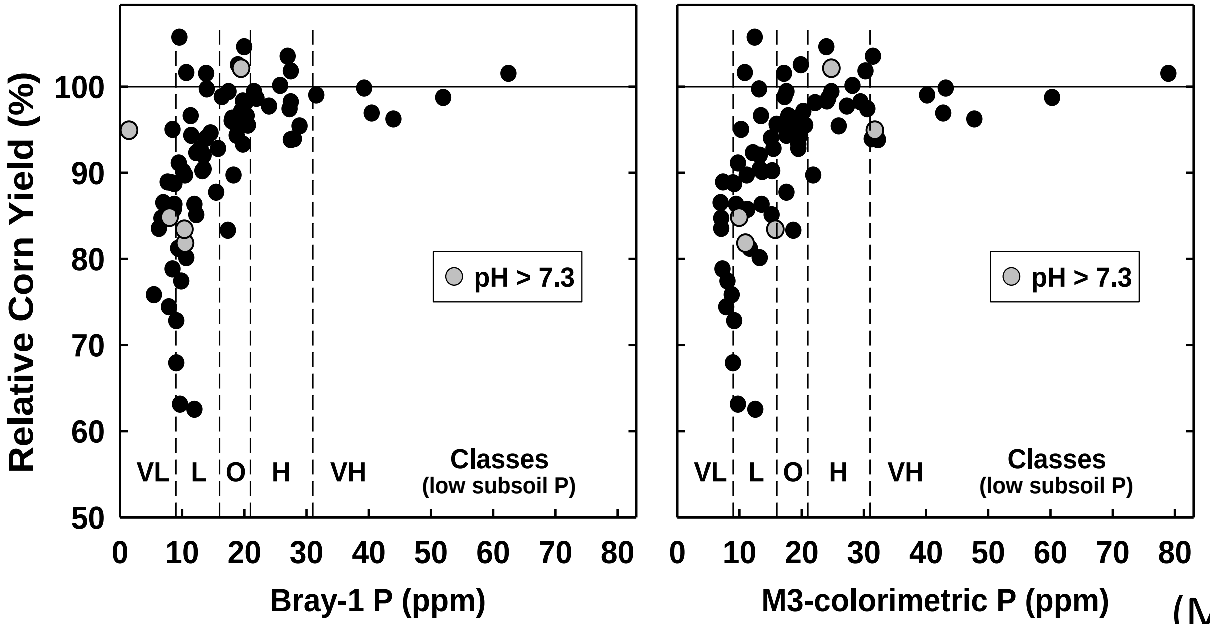
If this is going to happen, we need to better understand the underlying chemistry.

- Traditional soil tests have and continue to be important, but if further gains in P efficiency are going to be made, a more granular understanding based on specific soil and fertilizer properties is necessary.
  - The P “pools” being sourced in these tests do not necessarily replicate where the plants are obtaining P from; they just correlate to plot studies.



(Mallarino)

What were the objectives?

- Use liquid fertilizers formulations to better understand P fate and transport in calcareous and acid soils.
- **Hypothesis: Soil properties, such as the presence of free calcium carbonate, will influence which P speciation is optimal for plant uptake.**

- Investigate the co-application of fulvic acid products on P partitioning and diffusion in calcareous and acid soils.
- **Hypothesis: Co-applicants will improve P lability by blocking precipitation with polyvalent cations and/or outcompete P for high energy sorption sites on Fe/Al oxyhydroxides.**

Materials and Methods

Incubation studies are useful to investigate soil chemical mechanisms and validate concepts.

Soil	Classification	Texture (%)				pH	$CaCO_3$	CEC	Resin P	Total P
			Sand	Silt	Clay	(1:10)	%	cmol kg^{-1}	mg kg^{-1}	mg kg^{-1}
Finney 1	Aridic Haplustoll	Silt Loam	22	56	22	8.7	7.7	18.4	47	744
Finney 2	Aridic Haplustoll	Silt Loam	24	51	25	8.6	10.6	18.6	56	727
Brazil	Typic Haplustults	Sandy Clay Loam	67	8	25	5.4	-	4.3	6	206

Data courtesy of Joy Pierzynski, Buddhika Galkaduwa, and Fabio Cesar

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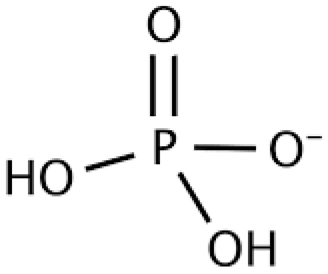
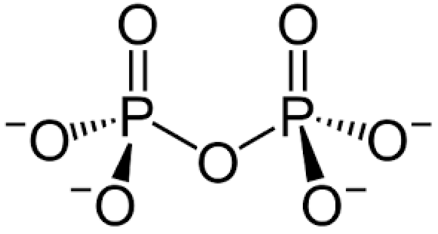
P Fertilizers

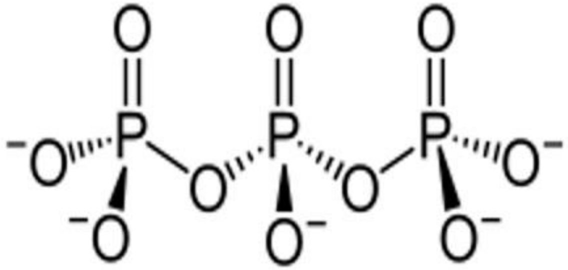
P Fertilizer		NPK	pH	P Species
PA	Phosphoric Acid	0-51-0	Very Acidic	H_3PO_4
MAP	Monoammonium Phosphate	11-52-0	4 – 4.5	$H_2PO_4^-$
DAP	Diammonium Phosphate	18-46-0	7.5 - 8	HPO_4^{2-}
APP	Ammonium Polyphosphate	11-37-0	~6	$H_2PO_4^-$ $H_2P_2O_7^{2-}$



Orthophosphate (OP)



Pyrophosphate (PP)



Triphosphate

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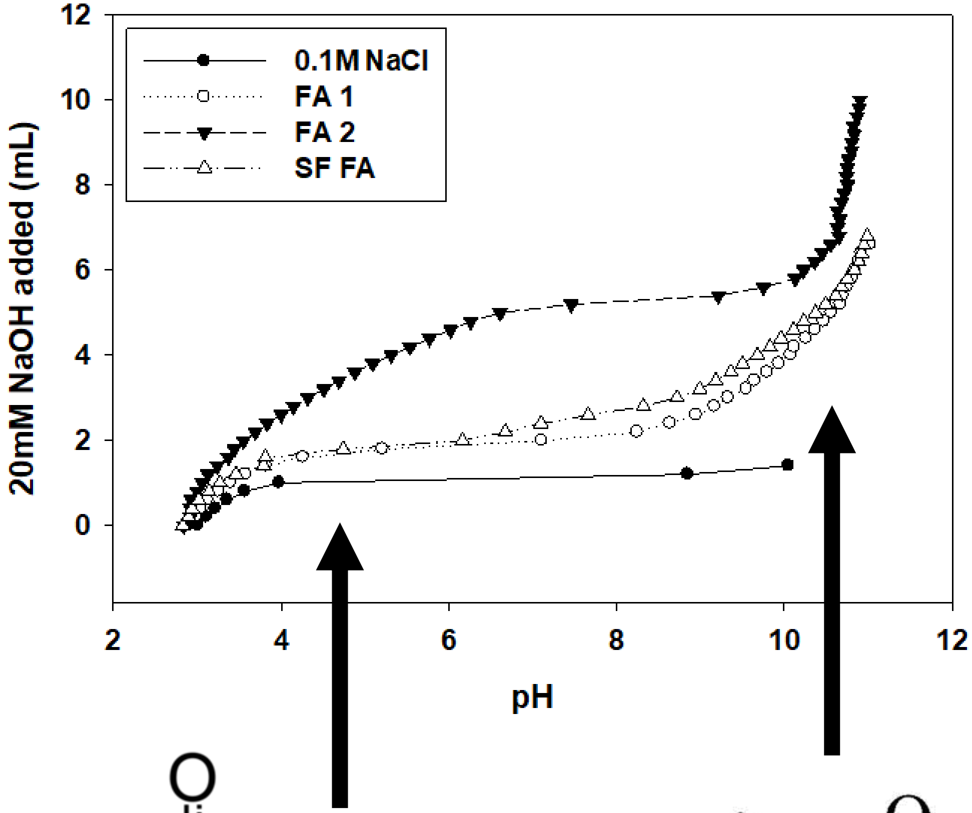
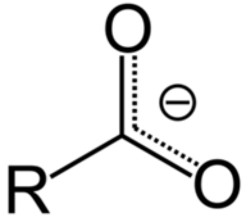
Fulvic Acid Products

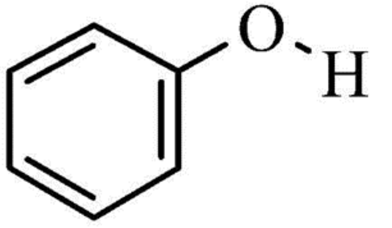
- Fulvic Acids:
  - FA 1 – Fulvic Acid 1
  - FA 2 – Fulvic Acid 2
  - SF FA – Sub-Fraction of Fulvic Acid

  - Soluble in acid and base
  - High molecular weight
  - Resistant to degradation
  - High cation exchange capacity
  - Can be diverse in actual structure



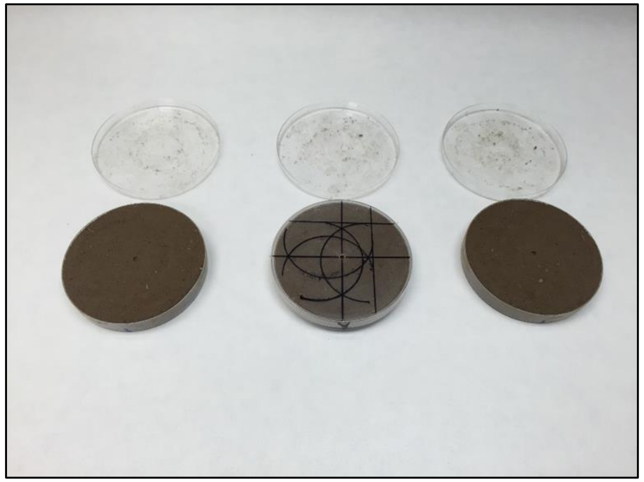


https://en.wikipedia.org/



www.coleparmer.com

Four Week Incubation Studies (Liquid Fertilizers):



- Finney 1 - 125µL solution – 9.2mg P (16.9% P_2O_5) – Five Reps

- MAP, APP, 80/20 blend of MAP and APP
- With / without – FA 1 (Fulvic Acid 1) – 0.73µL

- Finney 1 - 625µL solution – 9.2mg P (3.4% P_2O_5) – Three Reps

- MAP, DAP, APP
- With / without – FA 1 (Fulvic Acid 1) – 0.73µL

- Finney 2 - 125µL solution – 9.2mg P (16.9% P_2O_5) – Four Reps

- PA, MAP, APP, 80/20 blend of MAP and APP
- With / without – SF FA (Sub Fraction of Fulvic Acid) – 0.78µL (1X) and 2.34µL (3X)
- With / without – Sodium Alginate – 1.25mg

- Brazil – 125µL solution – 9.2mg P (16.9% P_2O_5) – Four Reps

- PA, MAP, DAP, APP, 80/20 blend of MAP and APP
- With / without FA 1, FA 2, SF FA – 0.73µL, 1.43µL, 0.78µL

Bulk Density:
1.1 g cm^{-3}

Moisture Content:
50% MWHC

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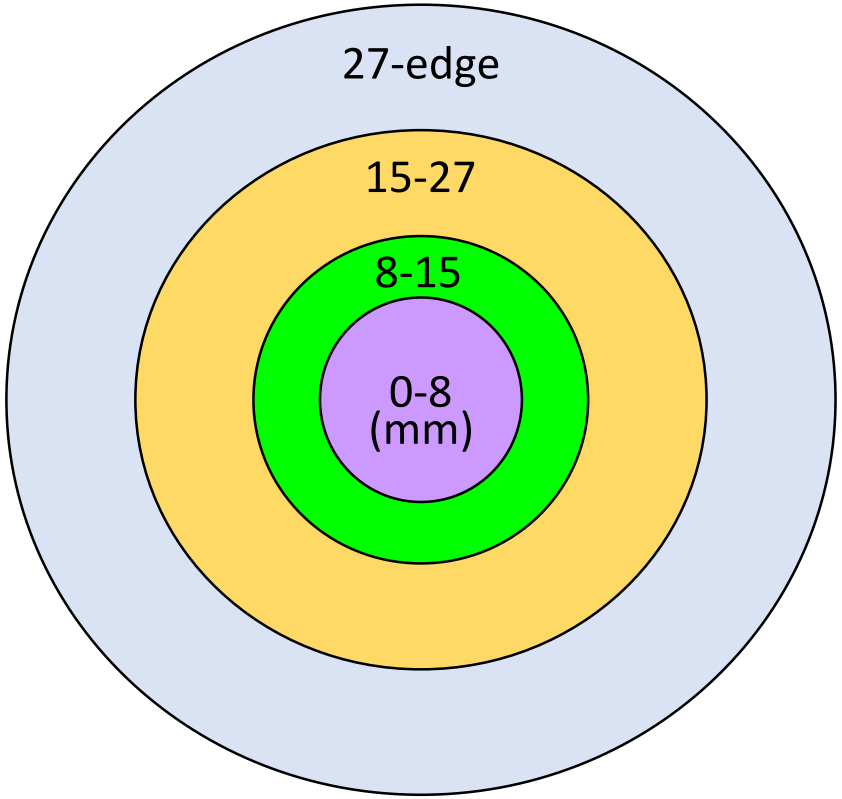
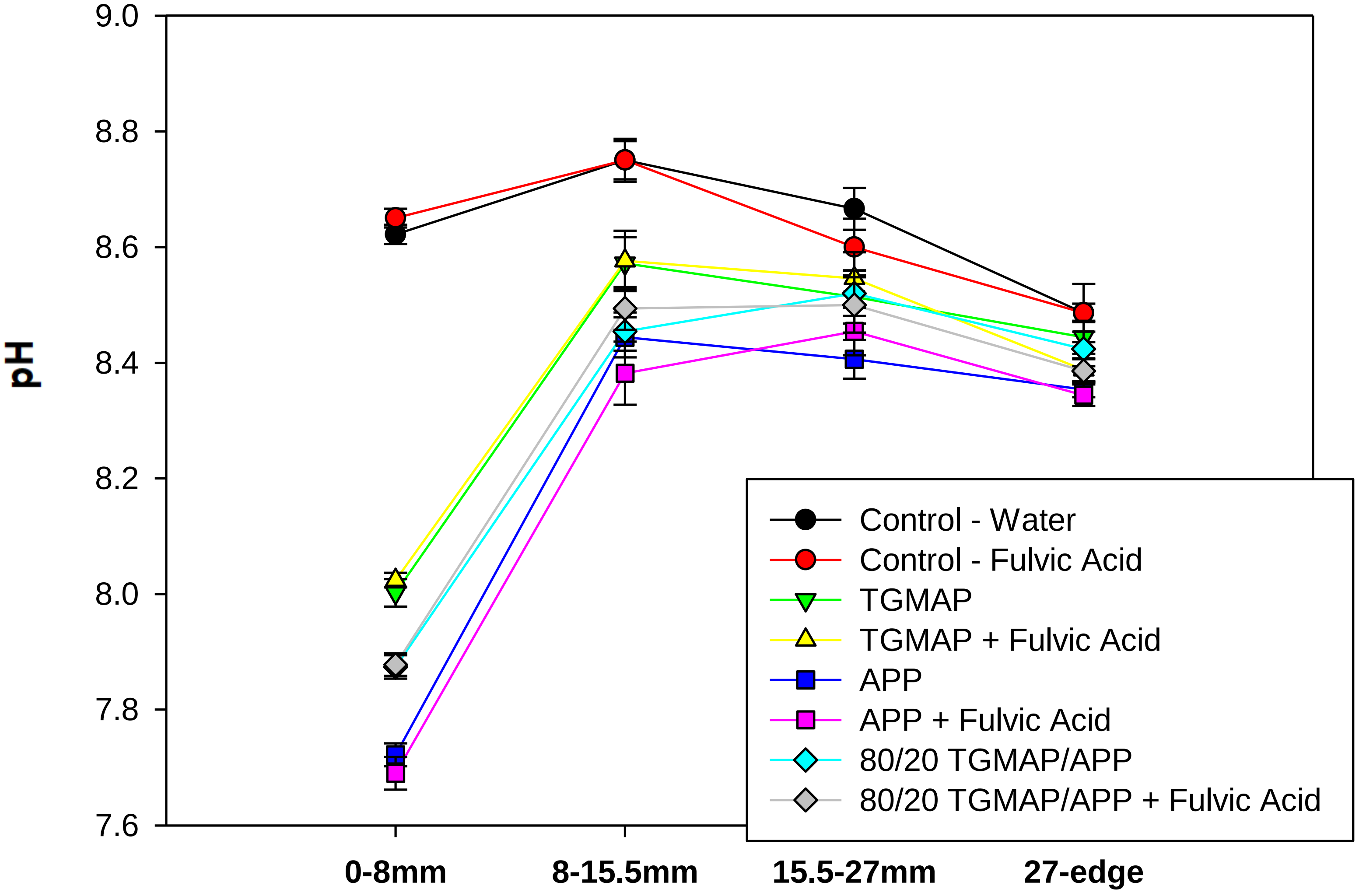
Sample Preparation and Analysis

- Incubation:
  - 25°C
  - 28 days
  - Complete darkness
- Sectioned radius (mm):
  - 0-8, 8-15.5, 15.5-27, 27-edge
  - Dried at 40°C
  - Homogenized
- Wet chemical extractions:
  - pH – 1:10 soil:water
  - Resin extractable P (Khatiwada et al., 2012) – Murphy and Riley (1962)
  - Total P – aqua regia digestion (Premarathna et al., 2010) – ICP-OES
  - Oxalate extractable Fe, Al, and P (Loeppert and Inskeep, 1996) – ICP-OES
- Statistics performed in SAS using Proc Mixed $\alpha = 0.05$



Results - pH

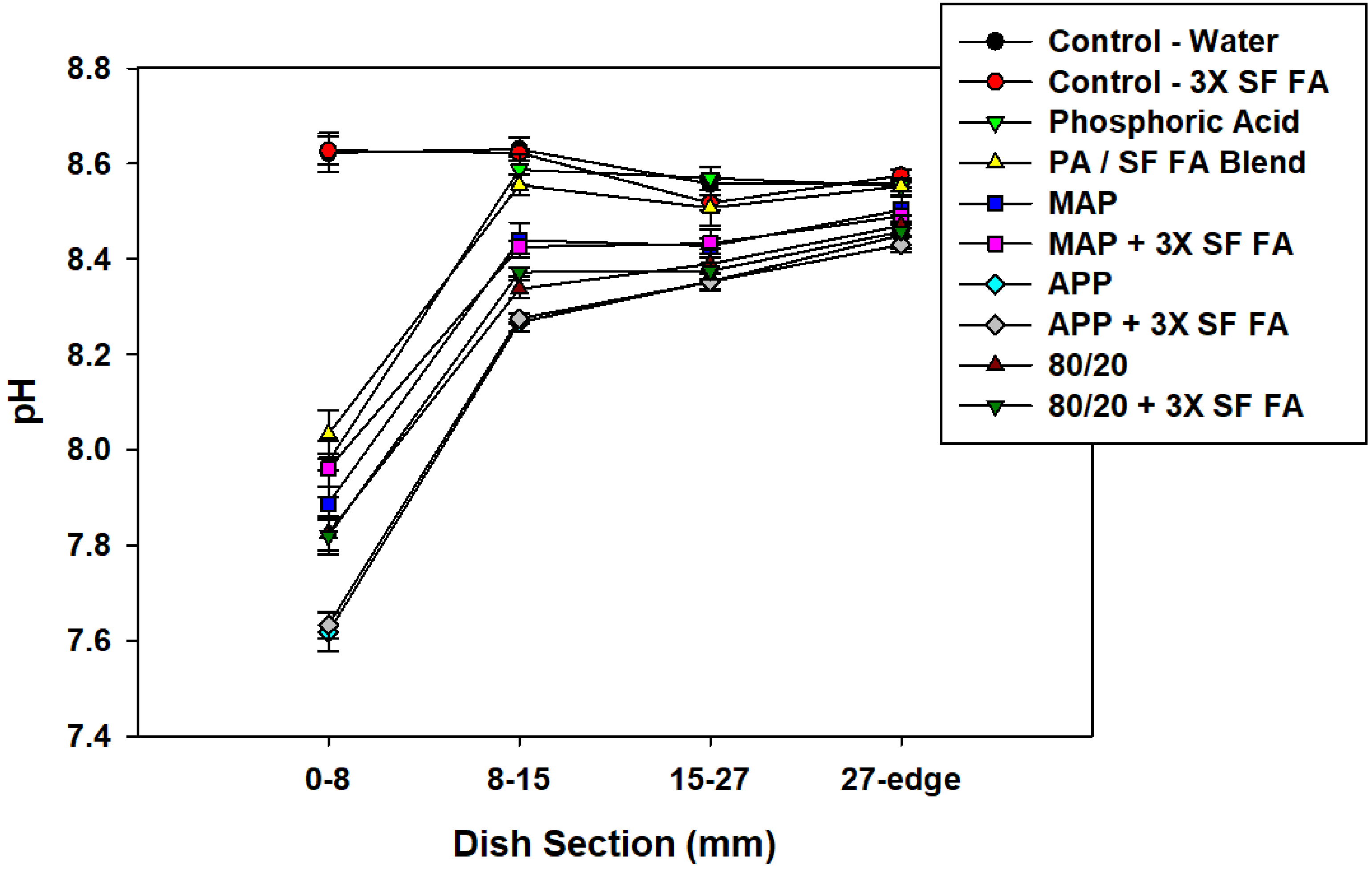
Finney 1 - 125µL – pH



APP caused the greatest pH drop, MAP the least.

No FA effect.

Finney 2 - 125µL – pH



Despite being the most acidic product, PA had the least acidifying effect.

No FA influence.

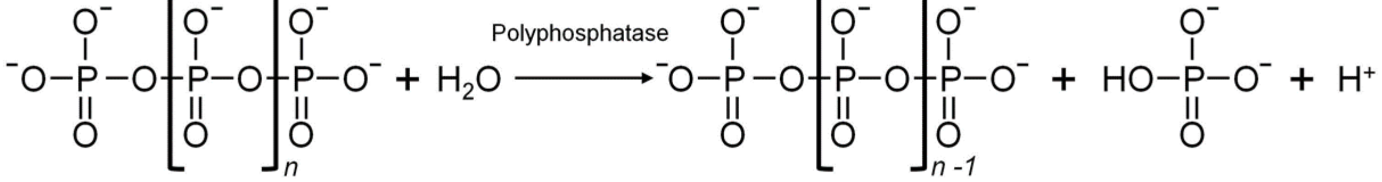
Discussion - pH

- **Acidulation was driven by:**
  - **Addition of acidic fertilizer solutions (MAP = pH ~4, APP = pH ~ 6)**
  - **Nitrification**

$$2NH_4^+ + 3O_2 \xrightarrow[\text{bacteria}]{\text{Nitrosomonas}} 2NO_2^- + 4H^+ + 2H_2O + \text{Energy}$$

$$2NO_2^- + O_2 \xrightarrow[\text{bacteria}]{\text{Nitrobacter}} 2NO_3^- + \text{Energy}$$

  - **Polyphosphate hydrolysis**

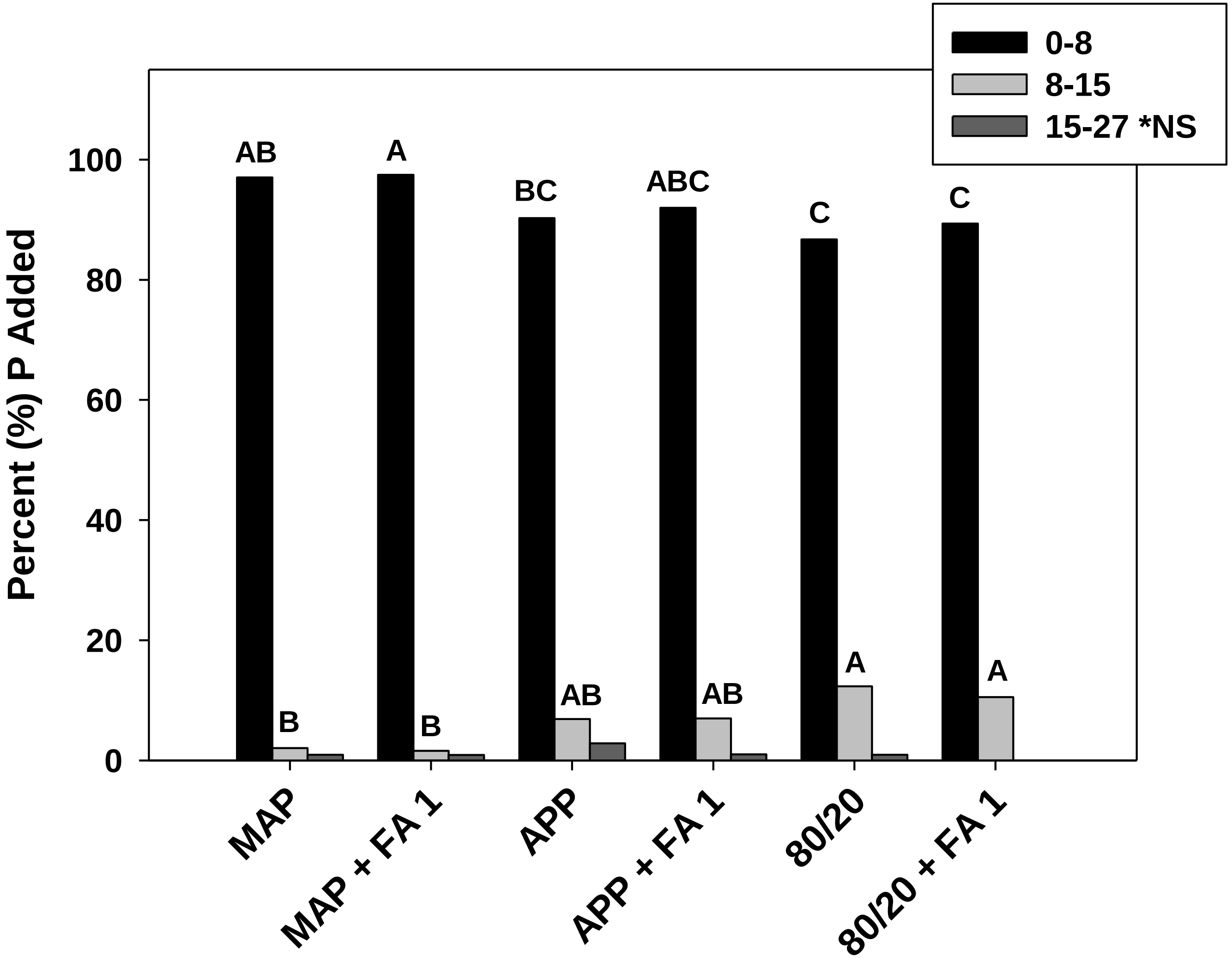


http://www.bio-protocol.org/e1874

Diffusion

Increased P movement away from the point of application should increase root interception and exploitation.

Finney 1 - 125µL – Total P Diffusion



Most phosphorus remained close to the POA and the fulvic acid addition appeared to have no effect.

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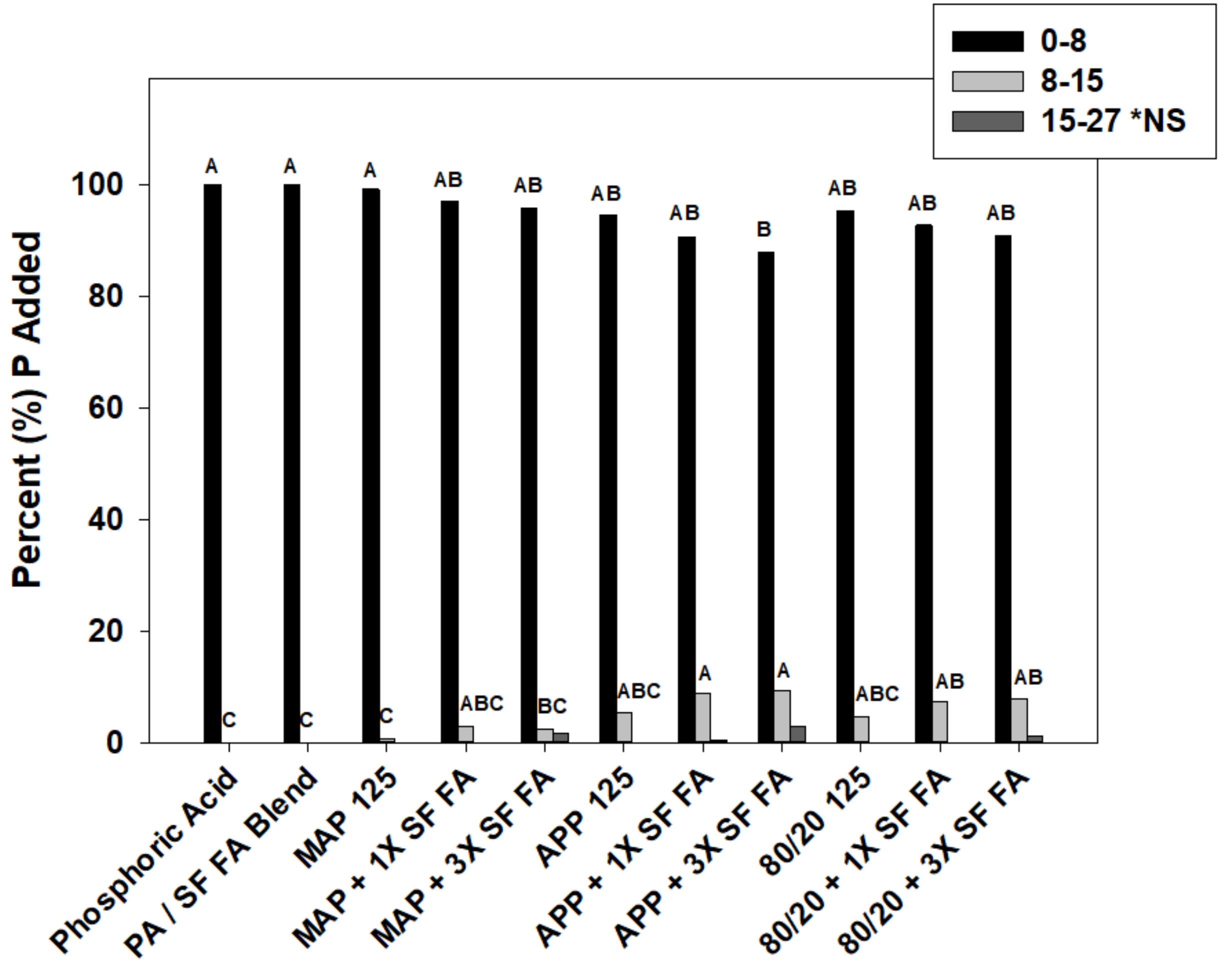
Finney 2 - 125µL – Total P Diffusion



More P remained close to the POA relative to Finney 1.

Although not statistically significant, SF FA addition reliably increased diffusion.

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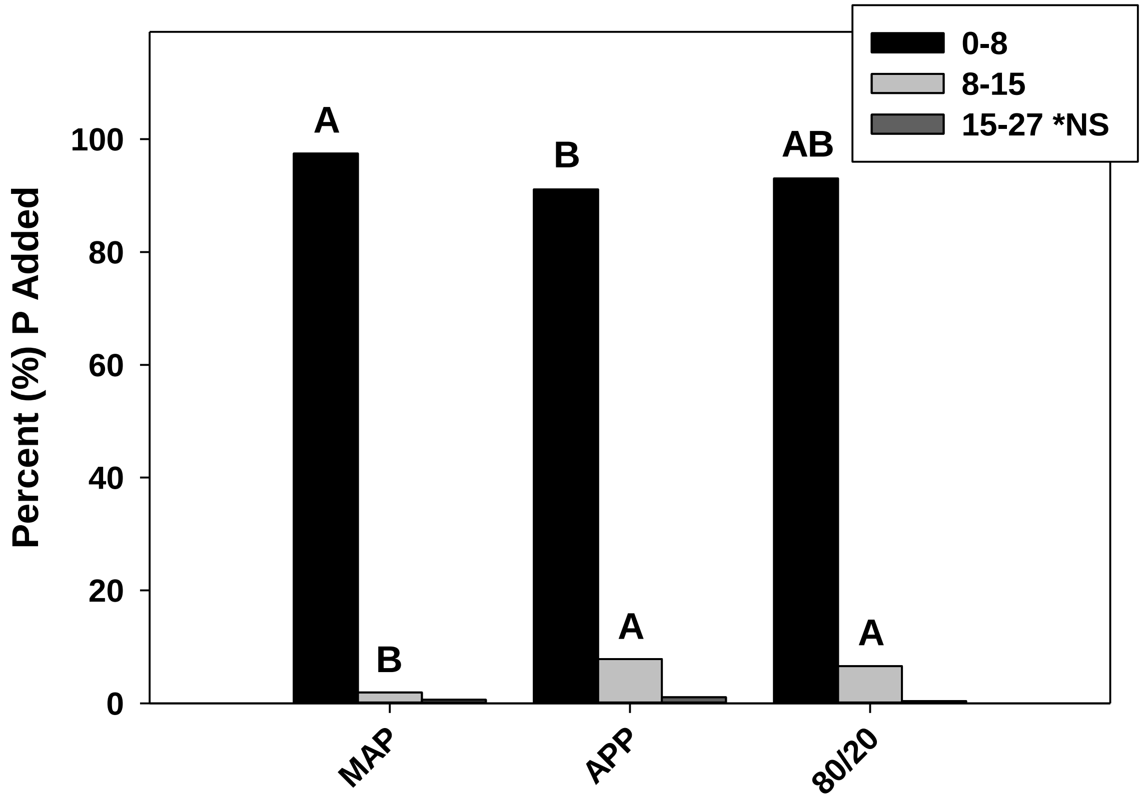
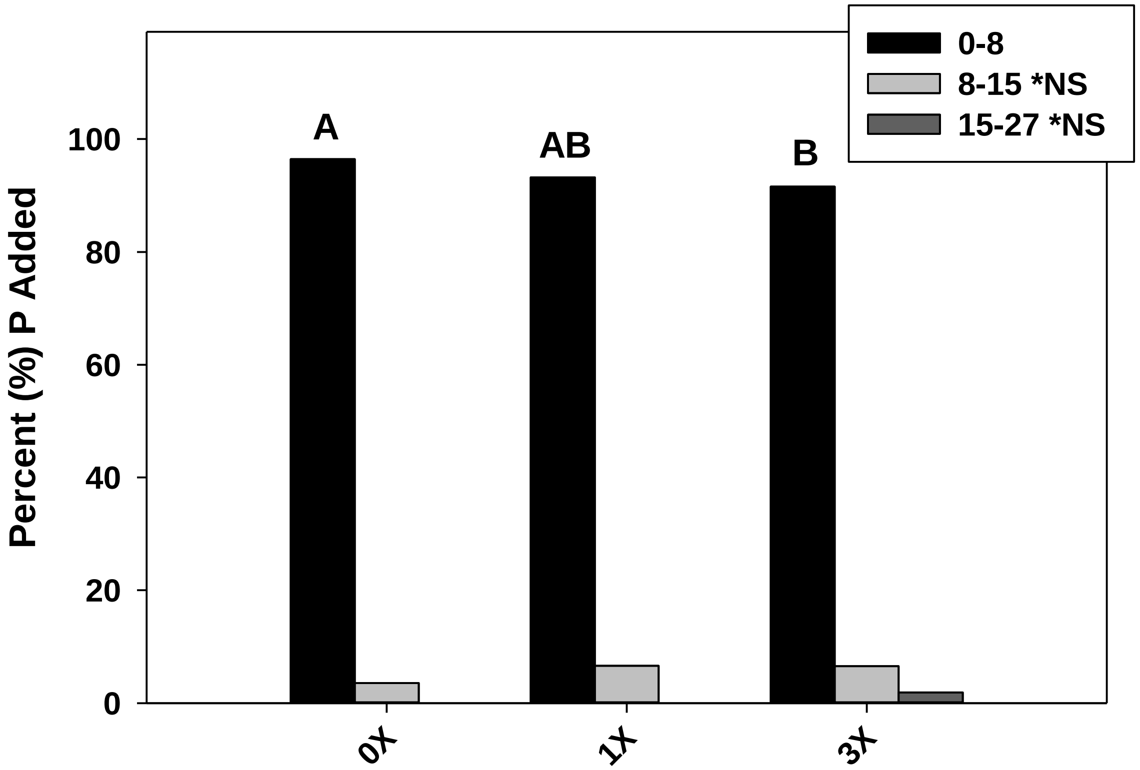
SF FA addition increased diffusion.





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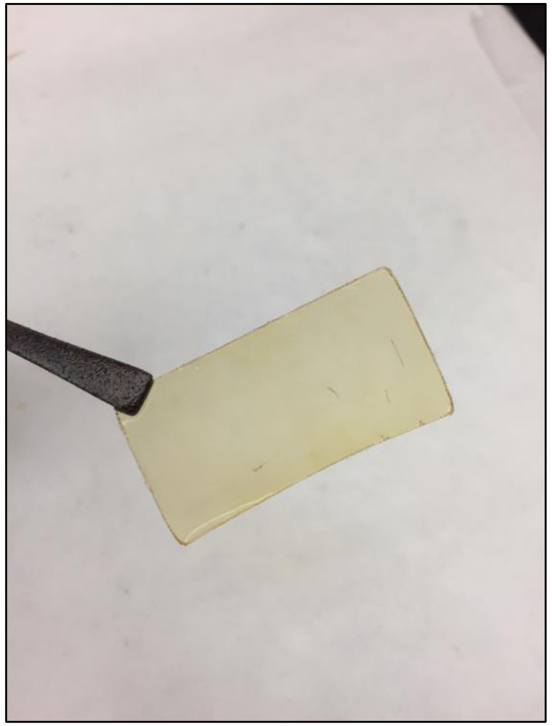
Discussion - Diffusion

- Soils are high clay and calcareous
- Finney 2 < Finney 1 – higher clay and $CaCO_3$ content
- PP > OP – polyphosphates may be preventing precipitation
- Phosphoric acid reacted strongly with $CaCO_3$
- SF FA increase P diffusion



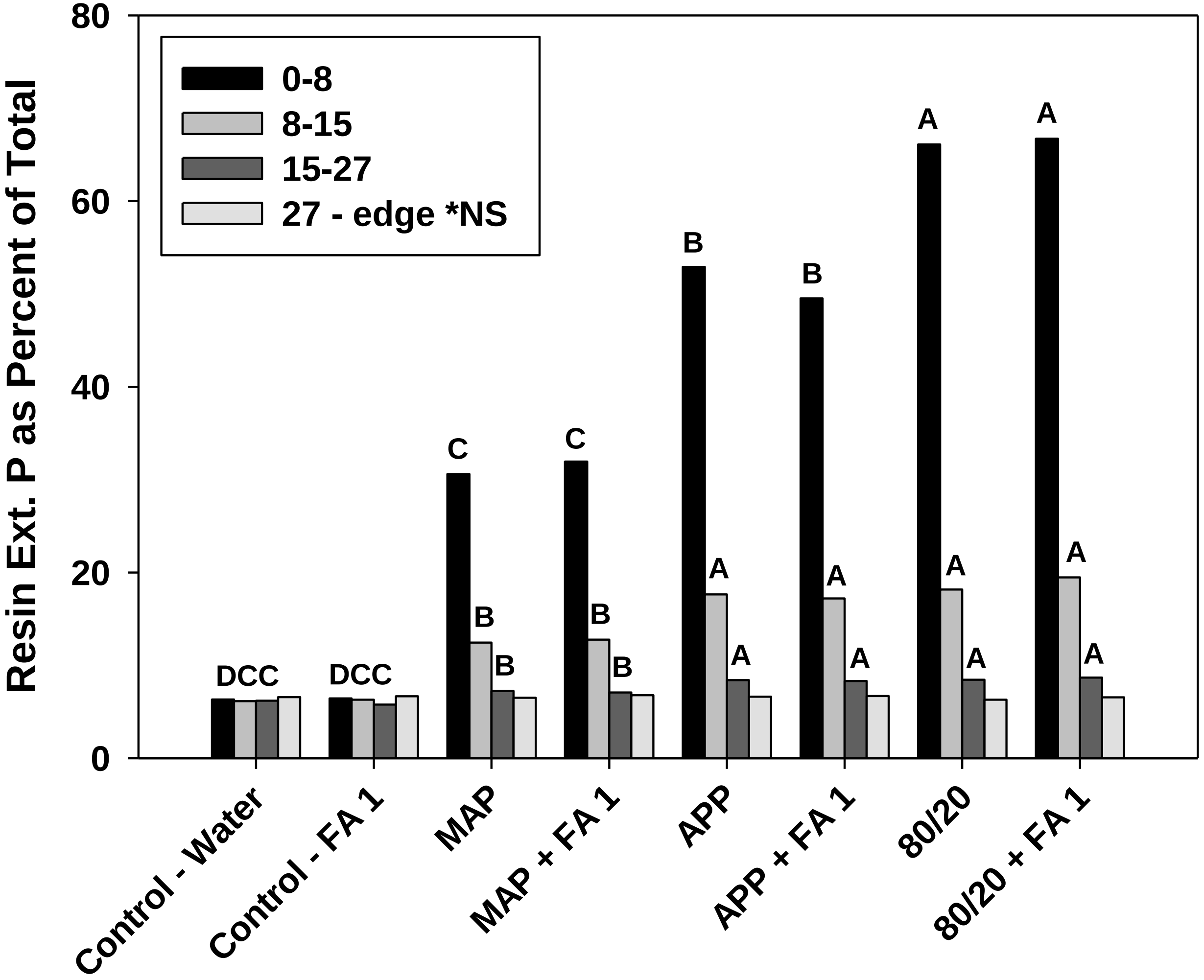
Resin Extractability

Resin extractability correlates relatively well with plant availability.

Finney 1 - 125µL – Resin Extractable OP

The 80/20 TGMAP/APP blend exhibited the most resin extractable OP

Diffusion is greater in polyphosphate treated samples.



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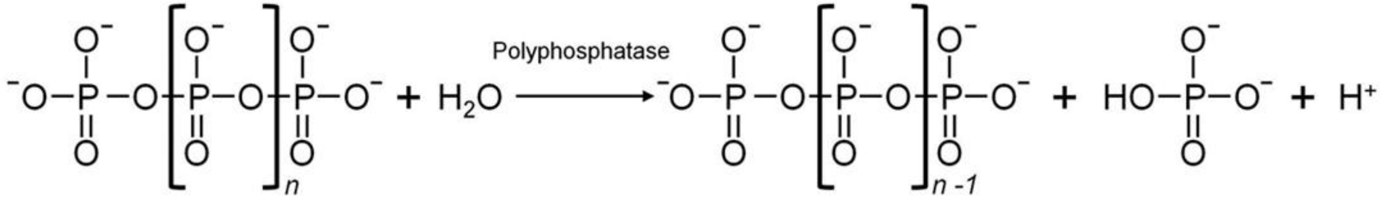
Digestion of Resin P Extracts

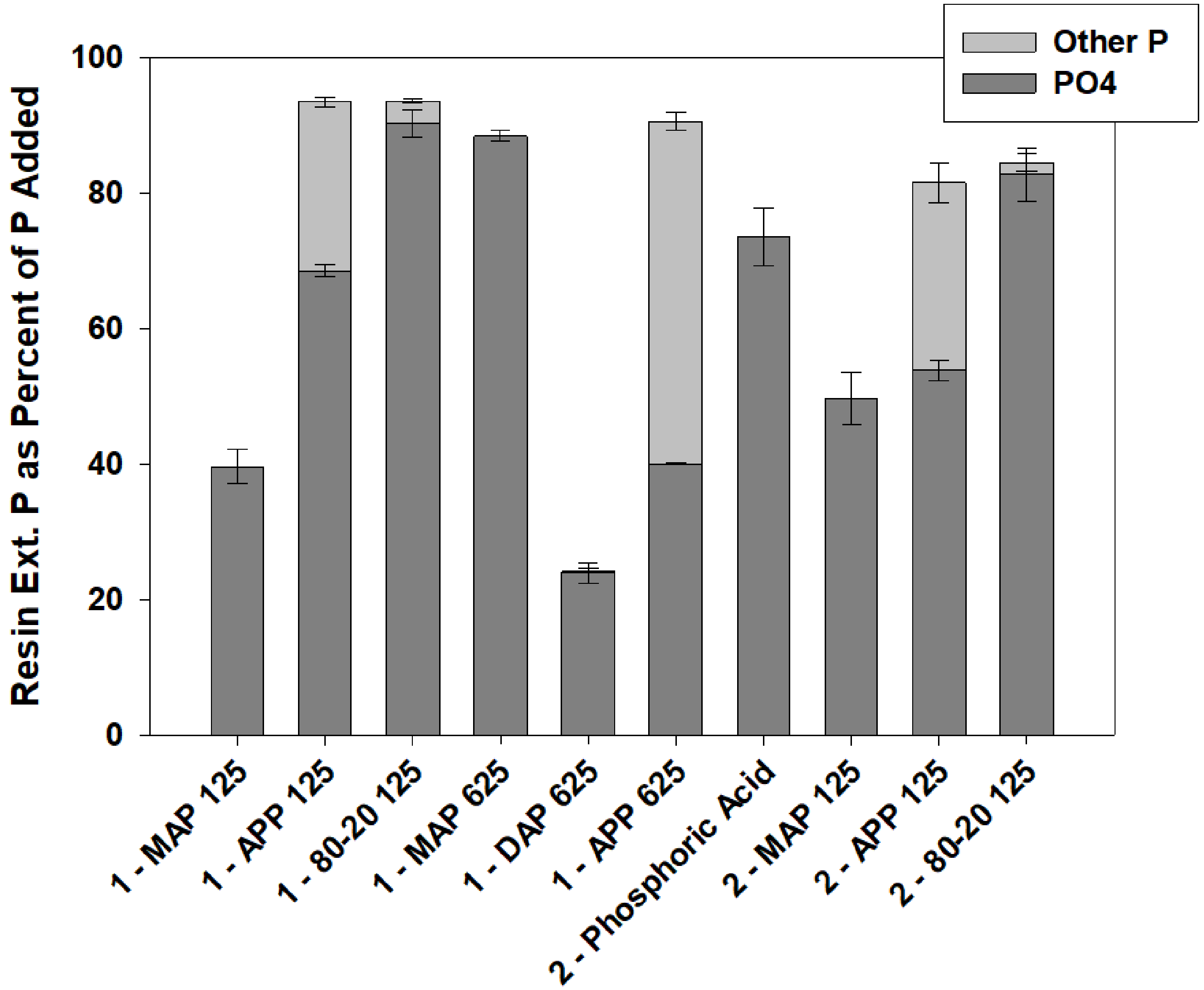
- 2.5mL of extract (0.5M HCl) from 0-8mm section
- Added 400µL concentrated sulfuric acid (H_2SO_4)
- Heated at 100°C for one hour
- Diluted with E-Pure water to 25mL
- Analyzed via Murphy Riley (1962)

Modified McBeath (2006)



http://www.bio-protocol.org/e1874

Resin Extractable P – 0-8mm Section 125µL vs. 625µL



A sizable portion of the P extracted by the anion exchange resin for APP treatments was in forms other than orthophosphate.

APP hydrolysis rate appeared to be slower when applied in a more dilute solution.

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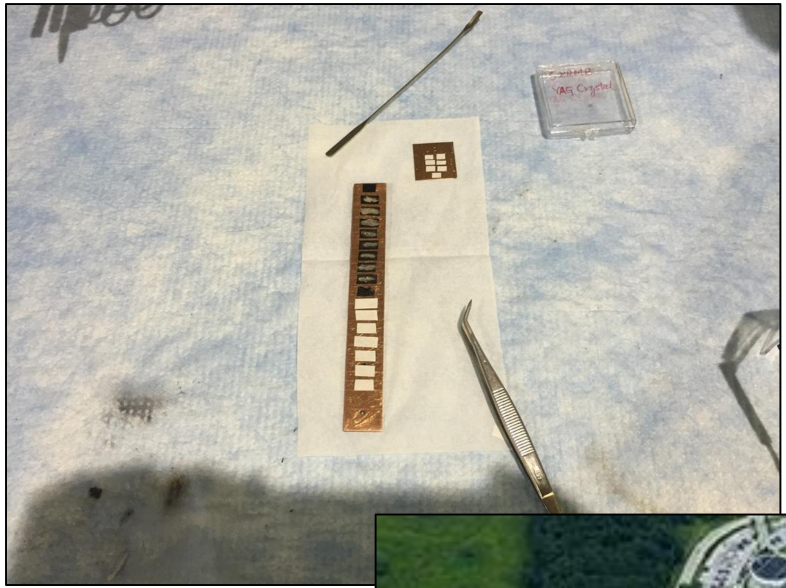
Synchrotron Analysis – K-edge



Canadian Light Source (Saskatoon, SK)

- **SXRMB**

Advanced Photon Source (Lemont, IL)

- **Sector 9-BM-B**

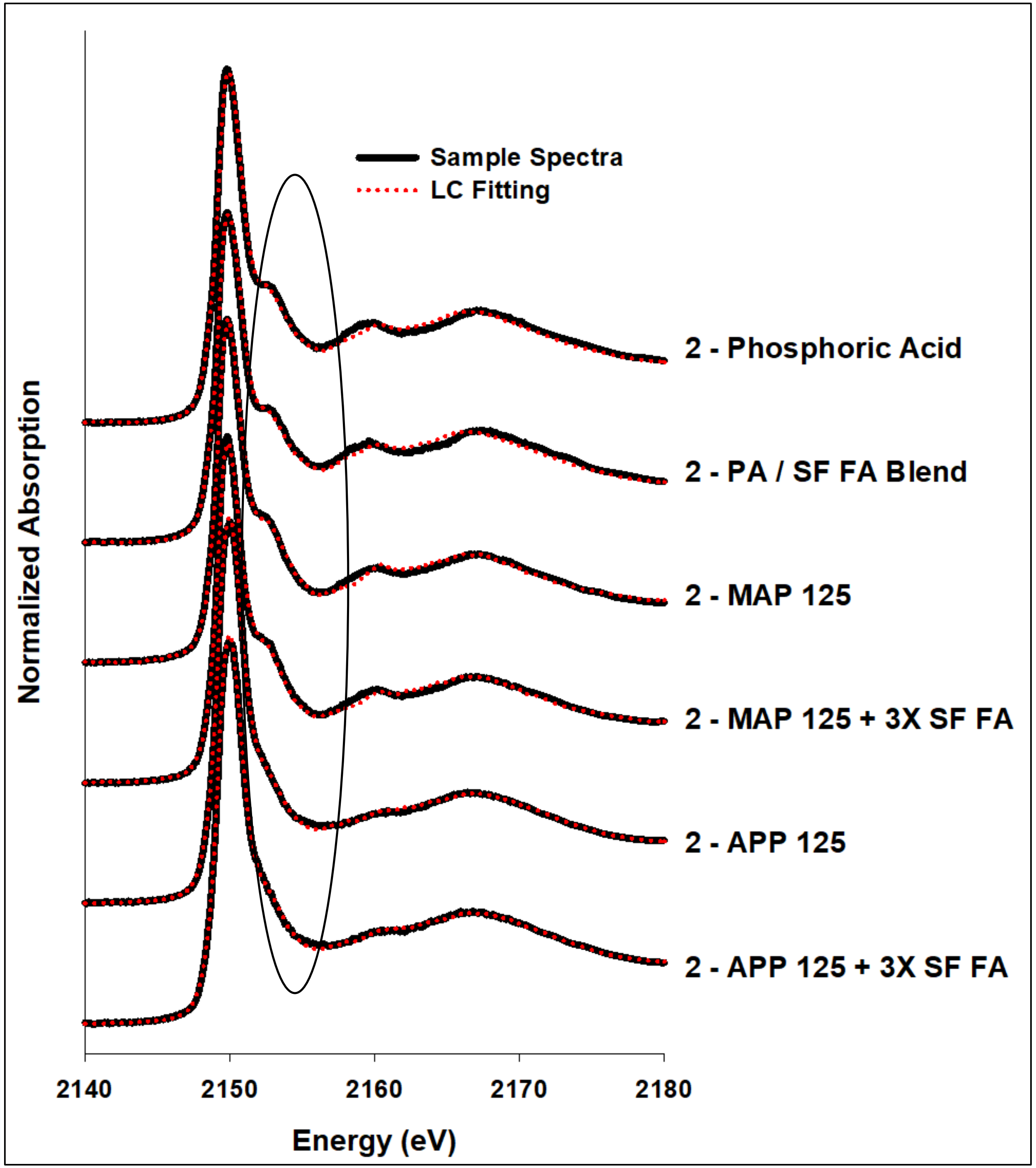
Fluorescence Mode:

- **P – 2149eV**
- **Fe- 7112eV**

Synchrotron Analysis

Direct speciation technique provides insight that wet chemical techniques may not.

Differences are Visible Amongst P Treatments



Ca-P shoulder was more visible in MAP added soils

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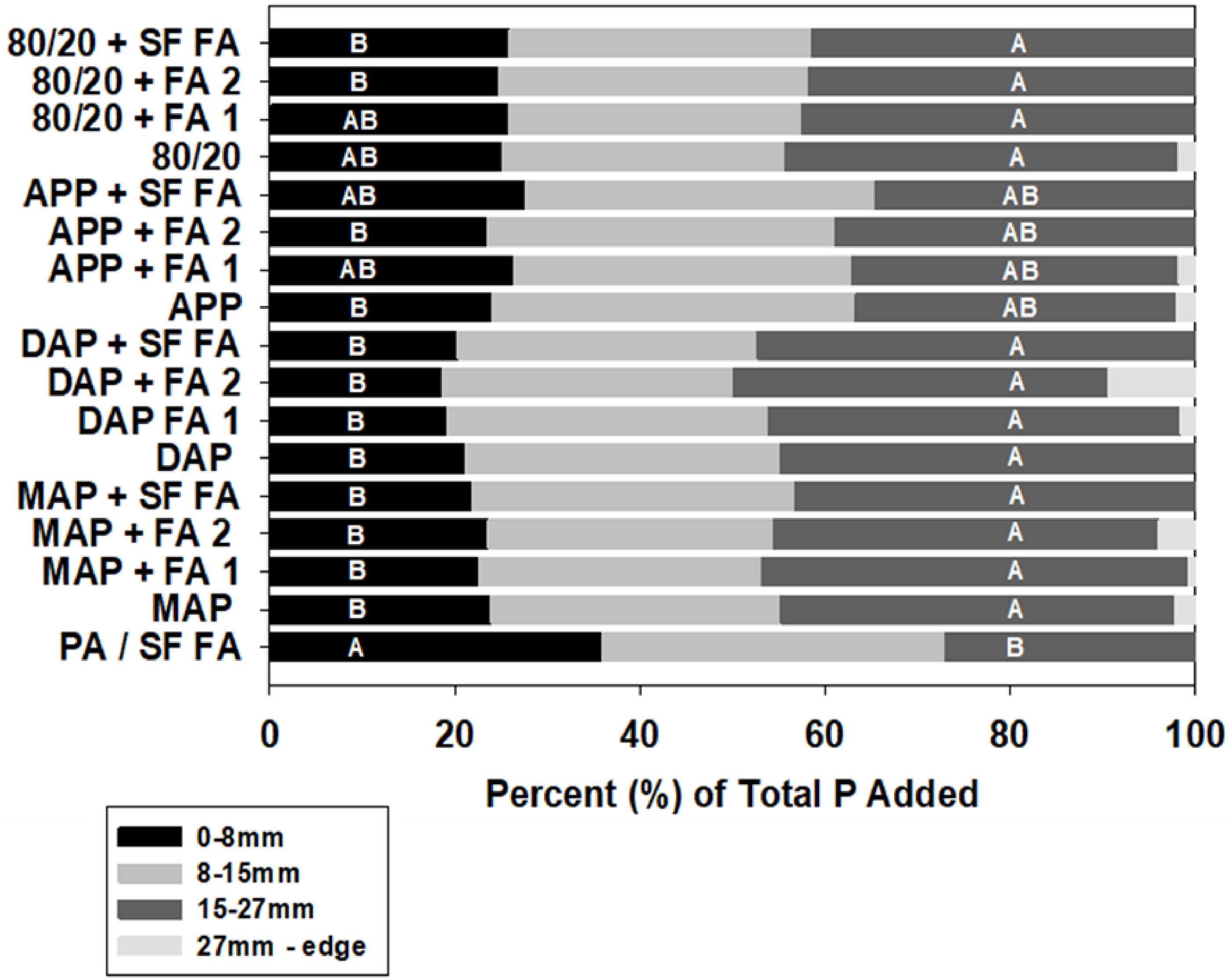
Calcareous Wrap-up

- Polyphosphate addition significantly alters P partitioning, even at small amounts
- FA addition to liquid P in this study did not significantly improve P lability but has had a influence on diffusion.
- Synchrotron-based analysis does hint that FA addition may be impacting P partitioning.
- It is possible that different pools are contributing to the same P resin extractability outcome.

Brazil Soil

Soil	Classification	Texture (%)				pH	$CaCO_3$	CEC	Resin P	Total P
			Sand	Silt	Clay	(1:10)	%	cmol kg^{-1}	mg kg^{-1}	mg kg^{-1}
Finney 1	Aridic Haplustoll	Silt Loam	22	56	22	8.7	7.7	18.4	47	744
Finney 2	Aridic Haplustoll	Silt Loam	24	51	25	8.6	10.6	18.6	56	727
Brazil	**Typic Haplustults**	**Sandy Clay Loam**	**67**	**8**	**25**	**5.4**	**-**	**4.3**	**6**	**206**

Brazil - 125µL – Total P Diffusion



Diffusion was much greater in the sandy clay loam soil.

OP diffused the farthest

PA / SF FA blend was least mobile

No FA effect

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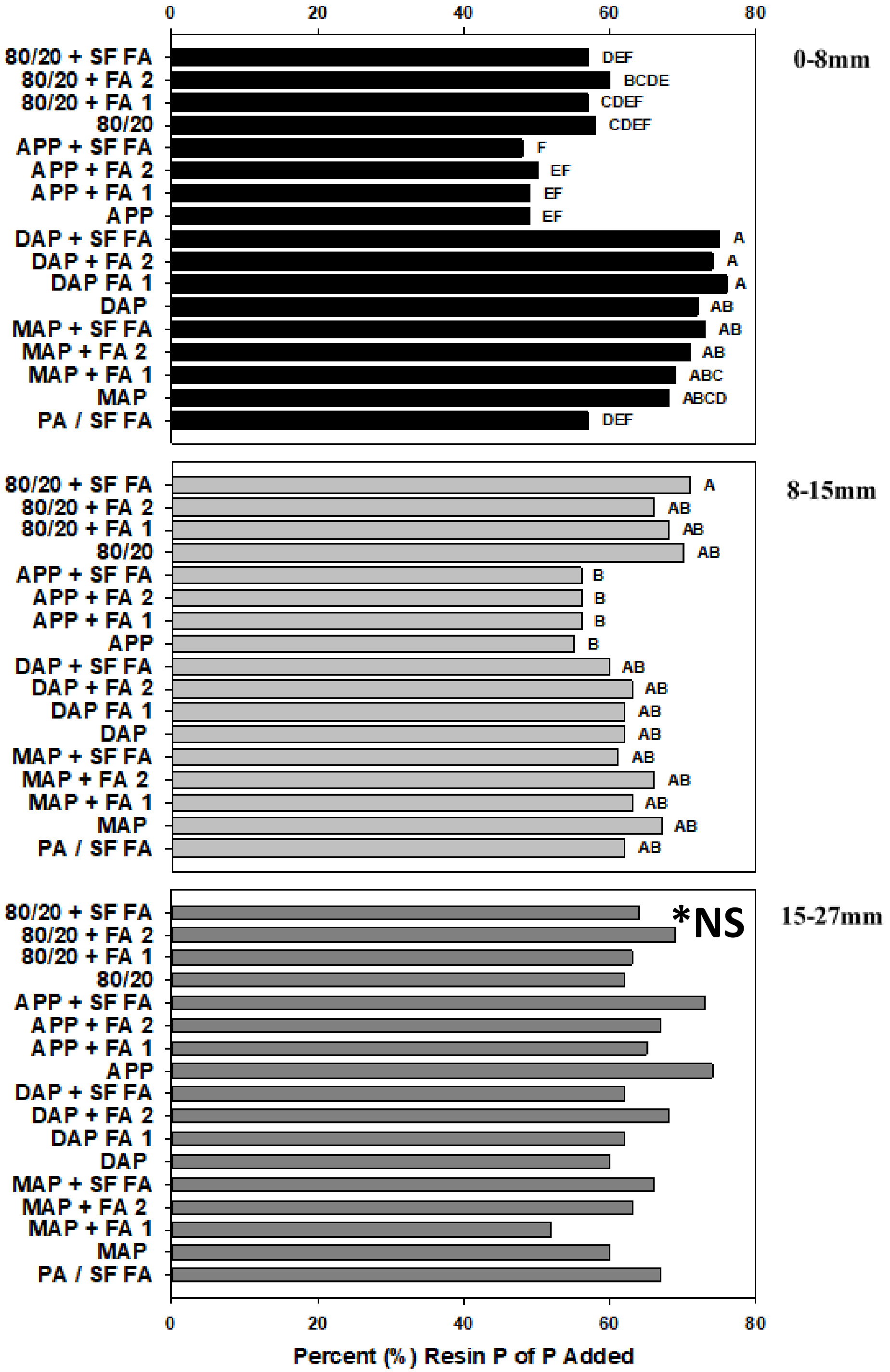
Brazil - 125µL – Resin Extractable OP



Resin extractability was relatively high.

OP outperformed PP

This may be demonstrating the PP preference for Fe/Al oxyhydroxides

OP FA effect?

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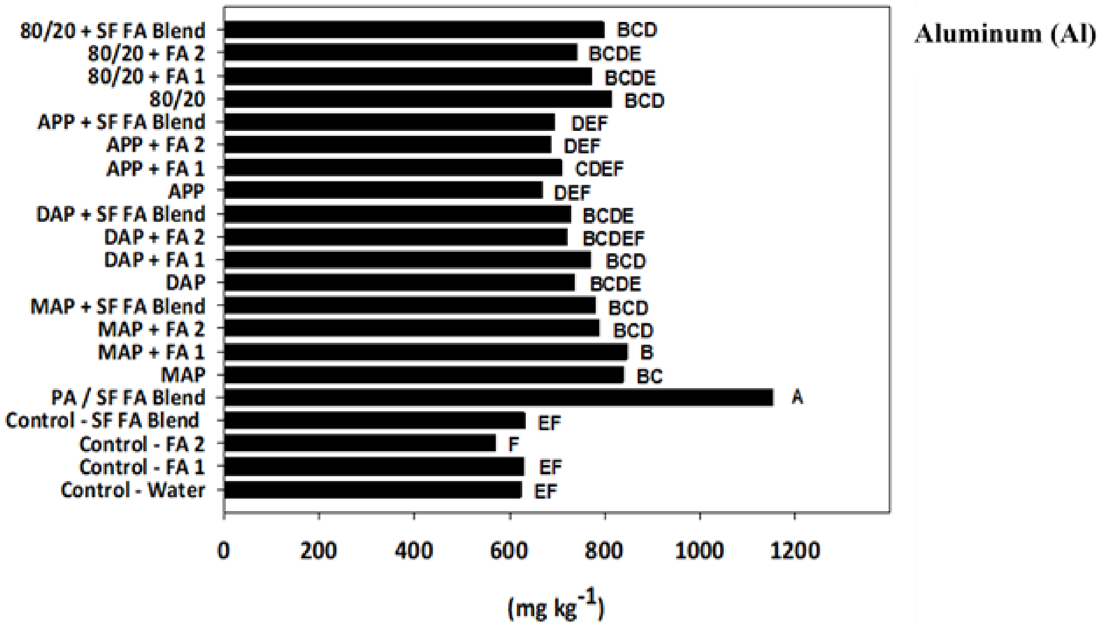
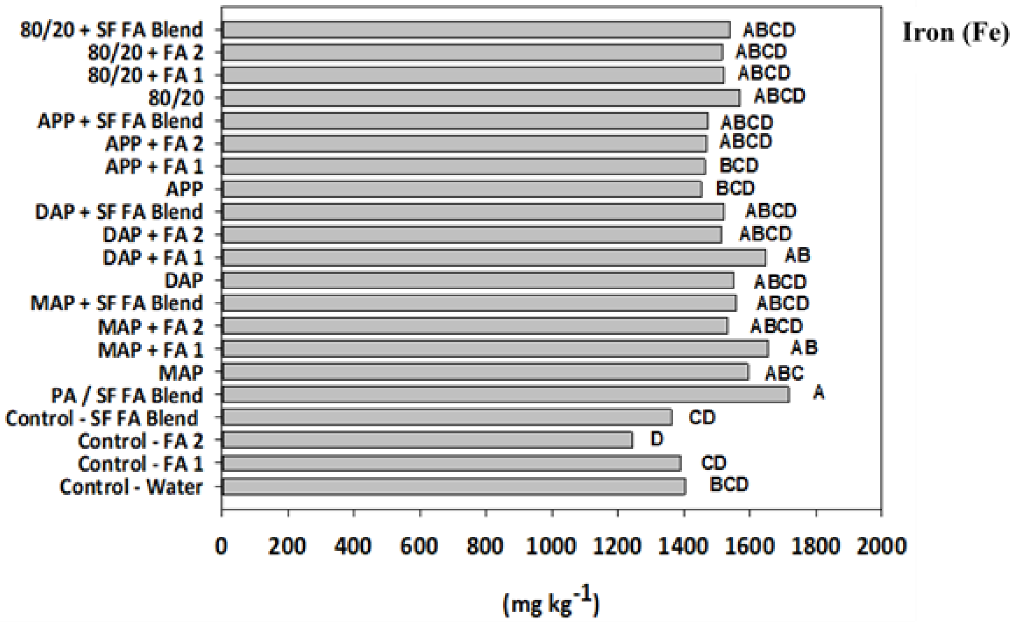
Brazil - 125µL – Ammonium Oxalate





Resin P may be higher because amorphous Fe/Al were relatively low

The acidic nature of PA / SF FA Blend dissolved more stable Al minerals.

All Treatments showed slight increase

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Brazil - 125µL – Synchrotron Analysis - P

	Mineral P		Sorbed P			
Treatment	**Fe-P**	**Ca-P**	**Al-P**	**Fe-P**	**Clay-Al-P**	**red χ^2**
MAP	-	-	31	20	49	0.0087
MAP + FA 1	-	-	31	-	69	0.0089
MAP + SF FA	27	-	41	26	6	0.0055
APP	18	6	-	13	63	0.0020
APP + FA 1	14	-	14	12	60	0.0023
APP + SF FA	32	-	20	13	35	0.0033

The co-application of SF FA specially to MAP and DAP seems to have drastically altered P speciation.

A substantial reduction in the Clay-Al-P fraction was simultaneously observed in these samples and was found in the APP + SF FA treatment.

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Brazil - 125µL – Synchrotron Analysis - Fe

Treatment†	Hematite	Goe	Sid	Fh	Viv	Mag	Non	Fe/Al Cop	Lep	Red χ^2
Control - Water	-	22	5		-	-	35	39	-	0.0000372
MAP	40	11	2	47	-	-	-	-	-	0.0000141
MAP + FA 1	41	-	2	47	-	-	-	-	10	0.0000165
MAP + SF FA	-	20	6	-	-	-	38	36	-	0.0000424
APP	24	7	-	55	-	-	-	14	-	0.0000229
APP + FA 1	34	14	1	52	-	-	-	-	-	0.0000215
APP + SF FA	27	45	4	-	-	25	-	-	-	0.0000339

Acid Soil Wrap-up

- DAP or MAP may perform better on acid soils.

- The impact of FA on P and Fe speciation is interesting.

- Practical significance requires further investigation.

Questions remain:

- How plants impact these results?
- What happens over time?
- How do environmental variables govern the observed effects?

Acknowledgements

- Advanced Photon Source Sector 9-BM-B and Canadian Light Source – SXRMB

- Fluid Fertilizer Foundation, Bio Huma Netics, Kansas State Research and Extension, USDA-NIFA NC1187 multistate project for funding support

Thank You!

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