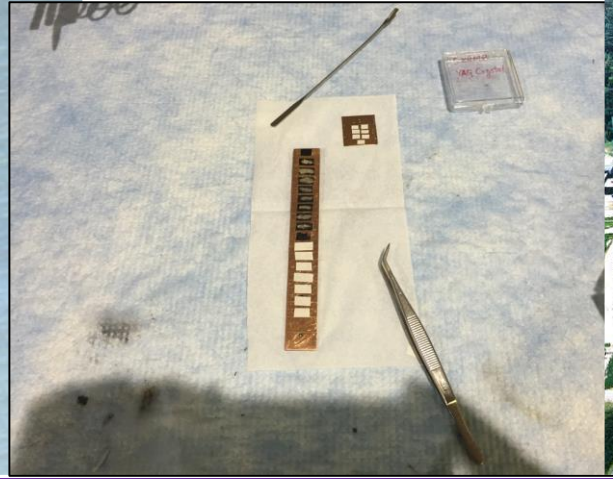

Can Humic Substances be Used as 'Enhancers' to Alter Fertilizer Reaction Pathways in Soils?

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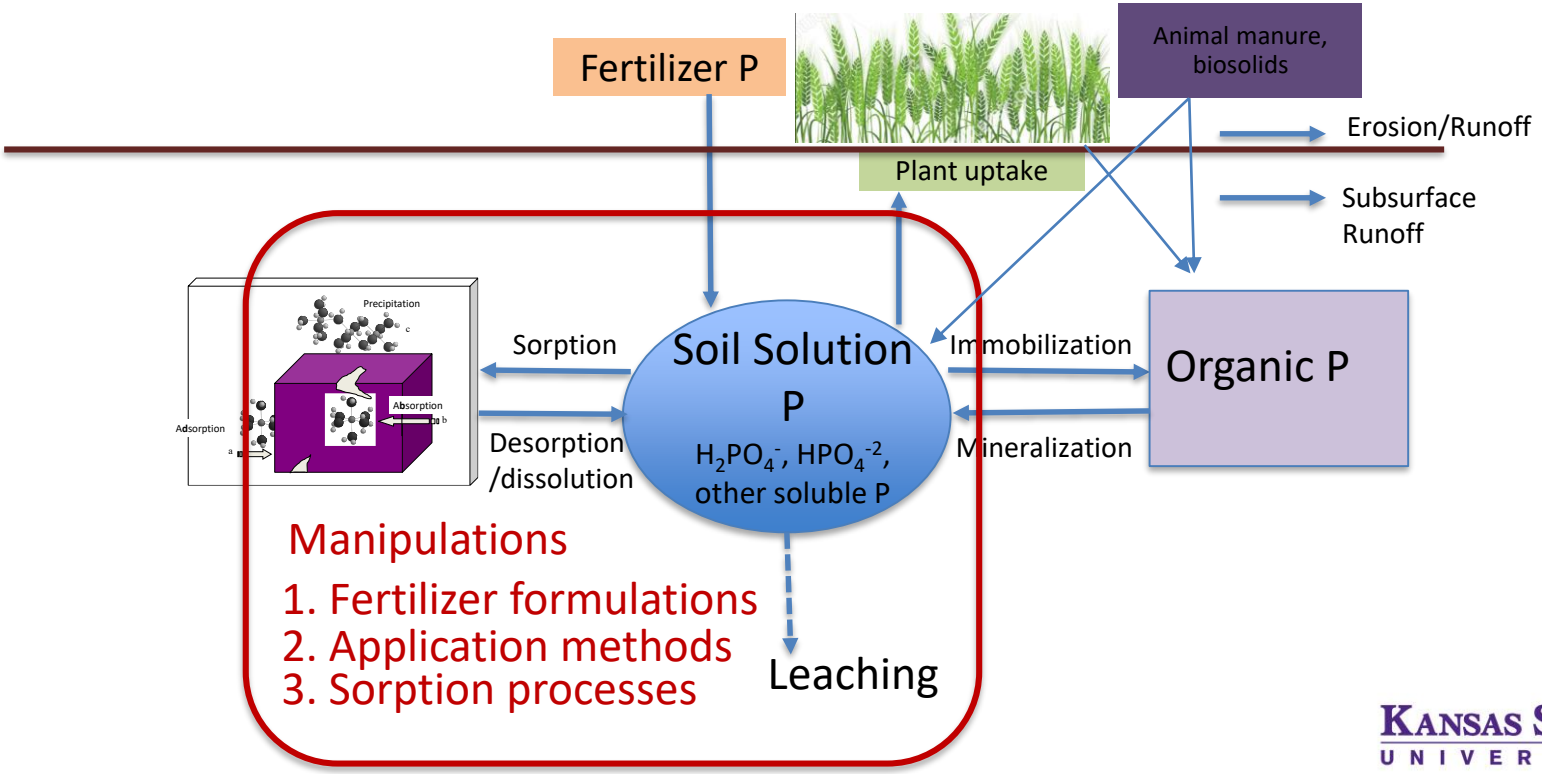
Introduction

Problem:

- Phosphorus (P) fixation reactions in acid and calcareous soils: Fe-, Al-, and Ca-minerals tie-up the P in sparingly soluble forms
- Poor use efficiency costs grower's money as translation into plant growth is not maximized
- "Fixed P" not available to crops but can erode causing eutrophication

Possible solution:

Manipulating fertilizer P reaction pathways



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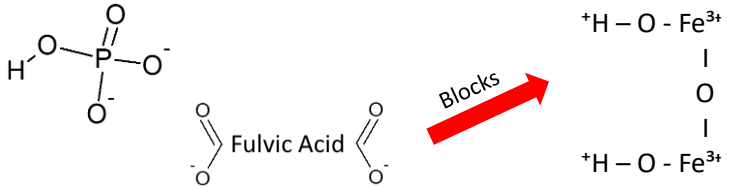
Possible Solution (cont.)

- Humic substances (e.g. fulvic acid) possess a high affinity for polyvalent cations in soil
- Co-application of these compounds with fertilizer may inhibit immediate fixation allowing P to diffuse further from the POA thus:
  - Preventing precipitation
  - Favoring weak adsorption to soil colloids
  - Increasing the volume of enriched soil
  - Translating into greater P plant acquisition efficiency



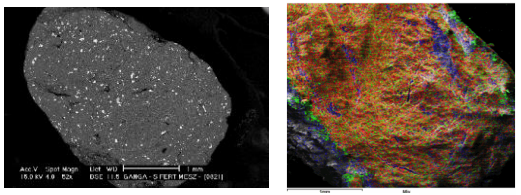
Materials and Methods

- **Duration:** 28 day incubation study (total darkness)
- **Soil:** mildly calcareous soil from Finney county, Kansas
- **Bulk Density:** ~1.1 g cm^{-3} (packed in Petri dish - diameter: 86mm, depth: 11.5mm)
- **Moisture Content:** 50% Maximum Water Holding Capacity
- **Replications:** Four
- **Liquid Fertilizers: 9.2mg P in 125µL water added to center of dish**
- **Additives: 0.78 µl/9.2 mg of P (X rate) and 2.34 µl/9.2 mg of P (4X rate)**

Approach

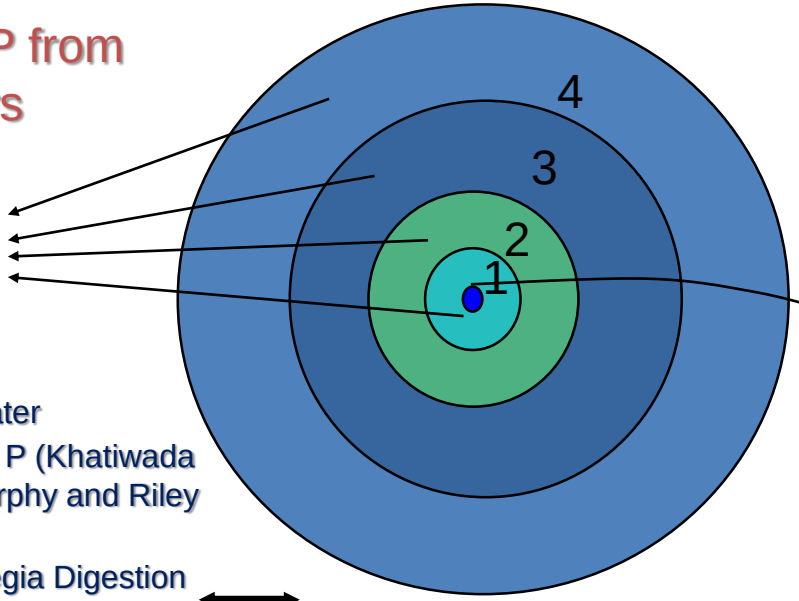
Reaction products in granules and soils

SEM-EDX and/or XRD



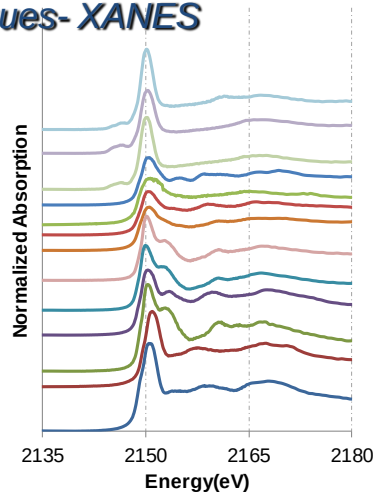
Diffusion of P from fertilizers

Samples



- 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 in the Dark Extractable Fe, Al, and P (Loeppert and Inskeep, 1996) – ICP-OES

Synchrotron based X-ray techniques- XANES



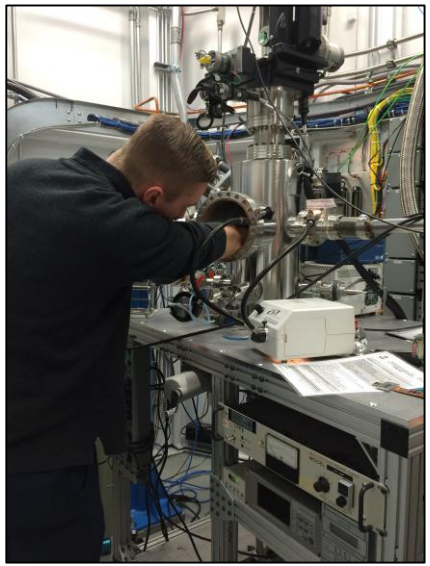
Reaction products of fertilizers in soils using synchrotron based X-ray techniques

Advanced Photon Source

(Argonne National Laboratory, Argonne, IL, U.S.A.)

Canadian Light Source

Saskatchewan, Canada



Jay Weeks at the Canadian Light Source

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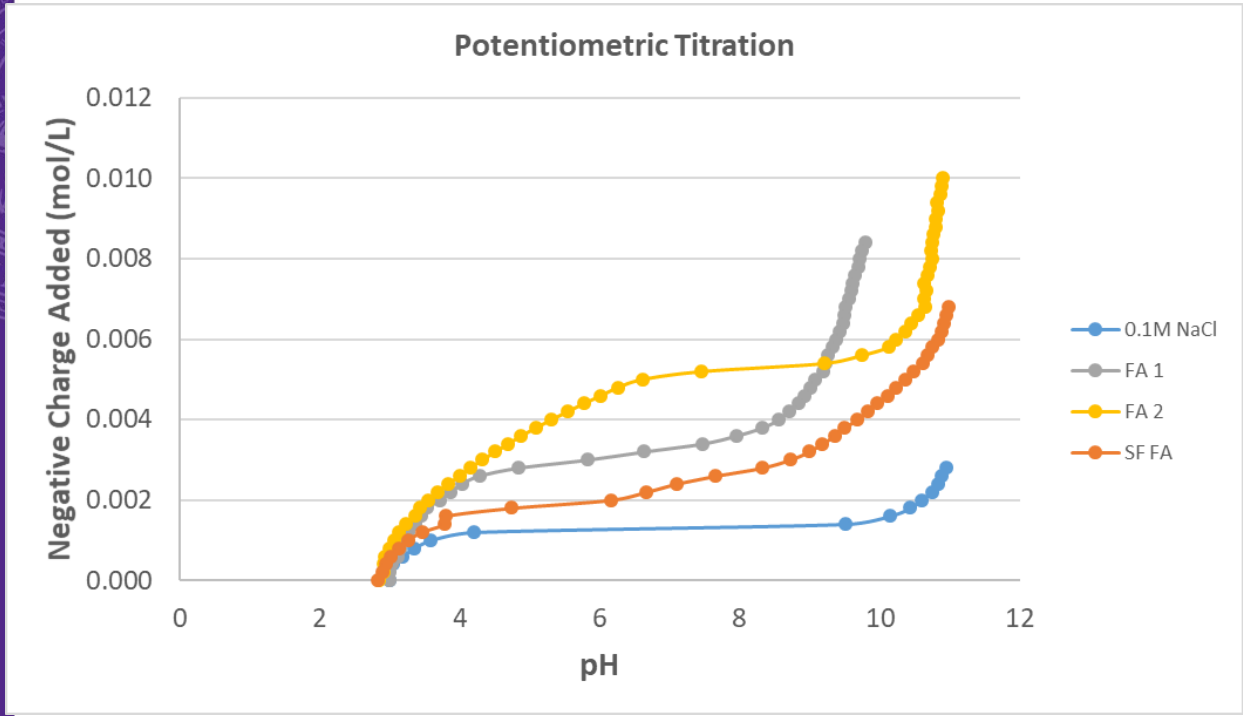
Product characterization



Dissociated groups provided evidence for negative charge excess in FA products

Selected soil properties

Parameter	Value
pH (1:10 soil:water)	8.8±0.02
EC mS/cm	1.3
CEC, $cmol_c/kg$	18.3
TOC %	1.1
$CaCO_3$%	5.6
Total Zn mg/kg	52.1±0.02
DTPA Extractable Zn mg/kg	1.3
Total P mg/kg	634±1
Available P mg/kg	61.5
Available Ca mg/kg	4461.9
Available Mg mg/kg	418.1
Available K mg/kg	767.9
DTPA Extractable Fe mg/kg	5.1
Available NH_4^+-N mg/kg	5.7
Available NO_3^--N mg/kg	34.9
Total N %	0.17
Sand, Silt, and Clay %	24.9, 52.4, 22.7 (Silt Loam)

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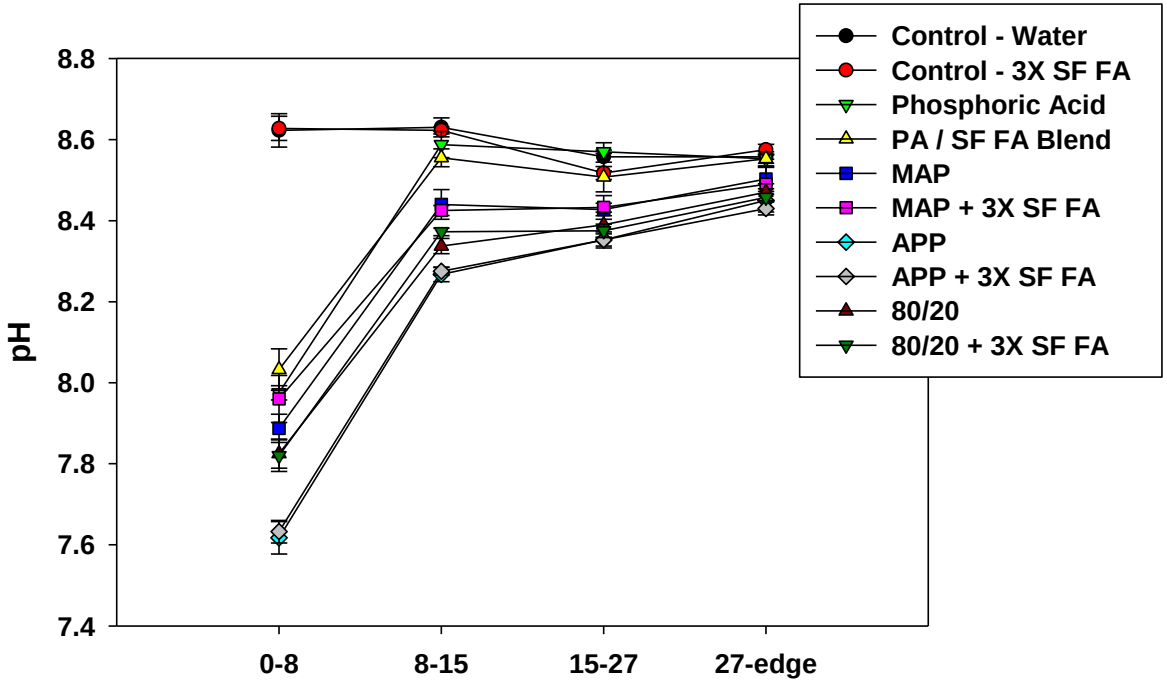
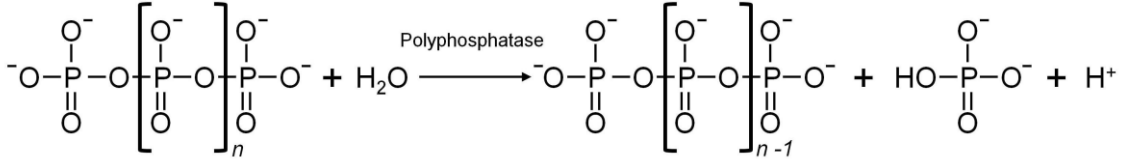
Treatments and Abbreviations

- MAP – Technical Grade Monoammonium Phosphate
- DAP – Technical Grade Diammonium Phosphate
- APP – Ammonium Polyphosphate (11-37-0)
- 80/20 – 80% MAP / 20% APP
- FA – Fulvic Acid
- SF FA – Sub-fraction of Fulvic Acid
- MAP with FAs or SF FA
- DAP with FAs or SF FA
- APP with FAs or SF FA
- 80/20 with FAs or SF FA
- PA/SF FA – Phosphoric Acid/SF FA

Soil pH by section



Treatment impact on soil pH was attributed more to the P form in the fertilizer than co-application of fulvic substances



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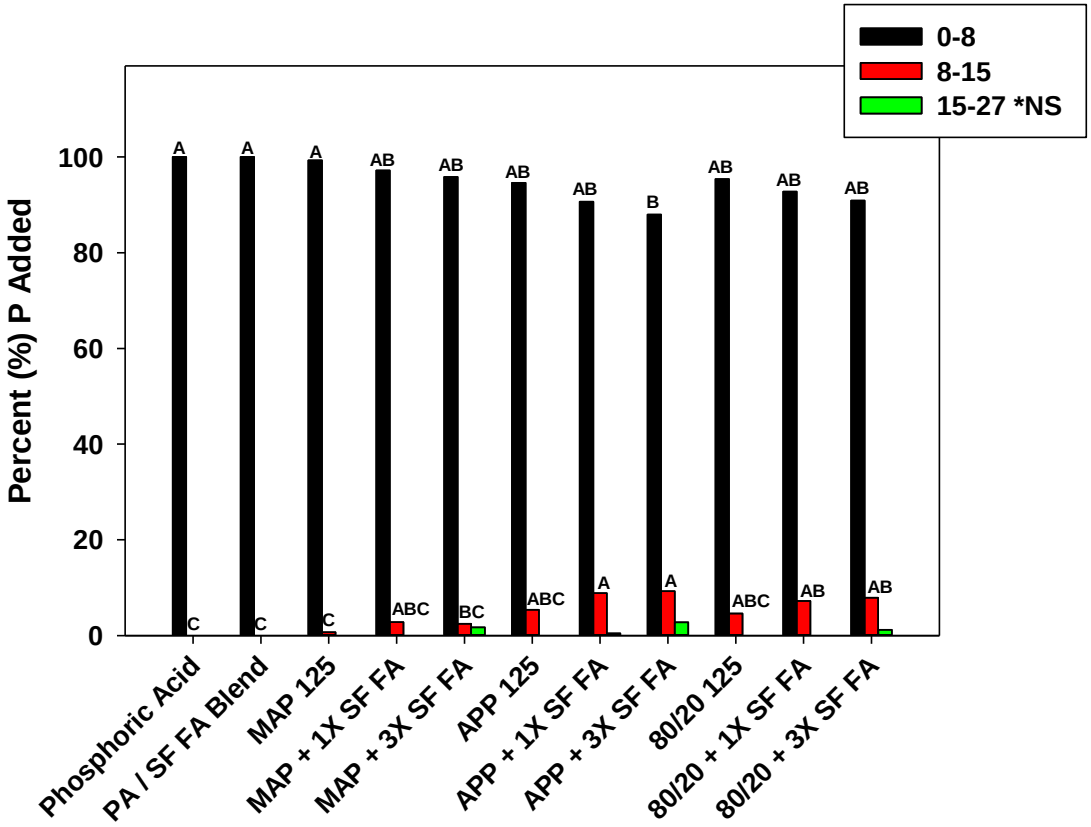
Percent P added by section



P diffusion was greater in polyphosphate treated samples

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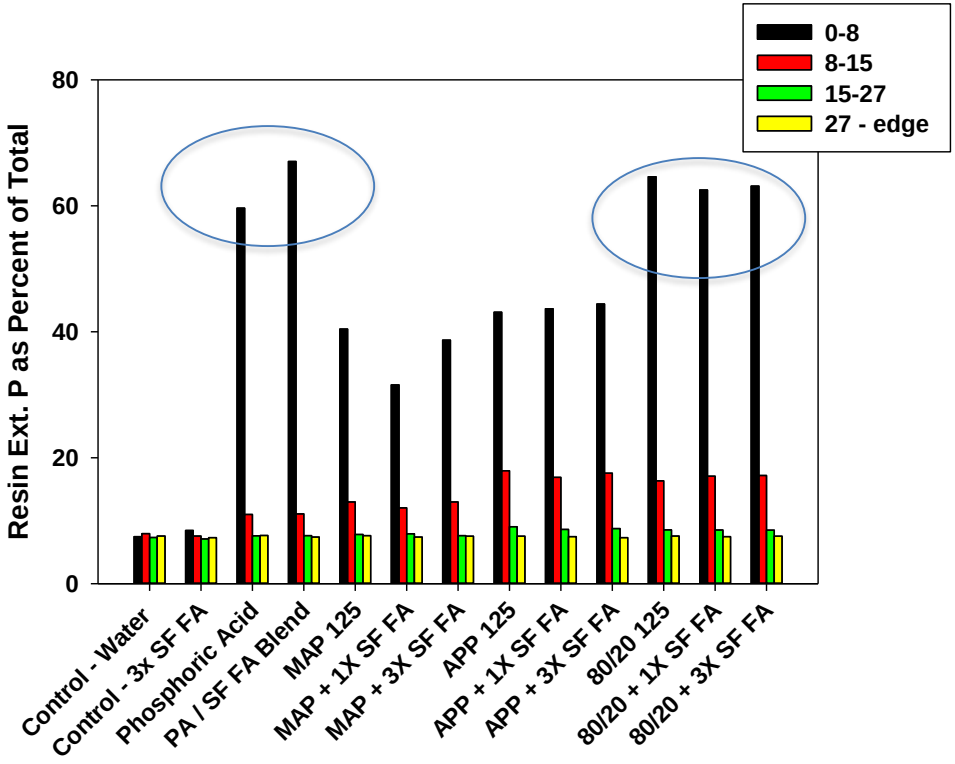
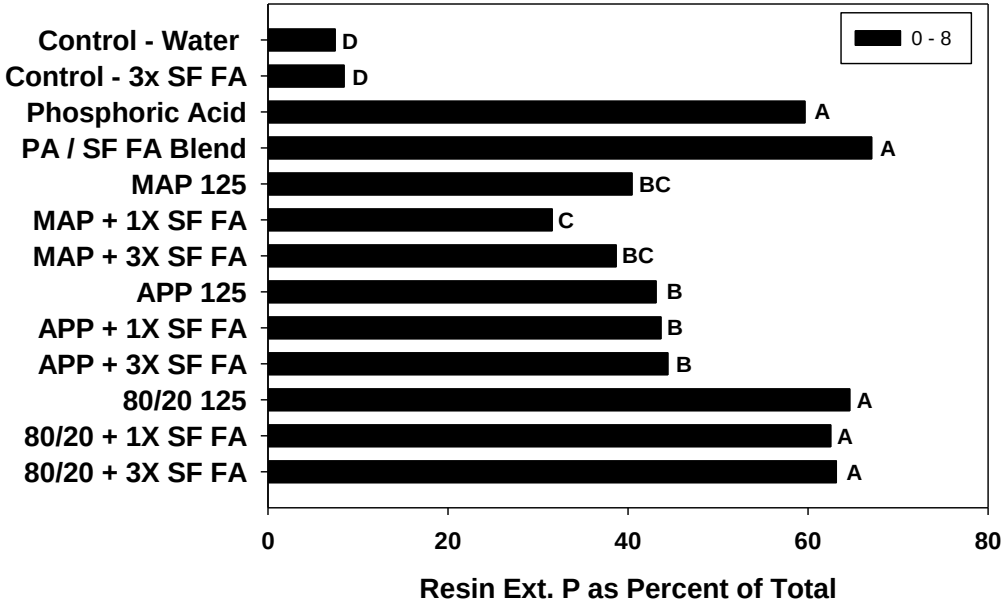
Percent resin extractable P by section



In general, it appeared PA and 80/20 MAP/APP blend performed superior to the MAP and APP treatments in the center section.

Percent resin extractable P in 0-8 mm section



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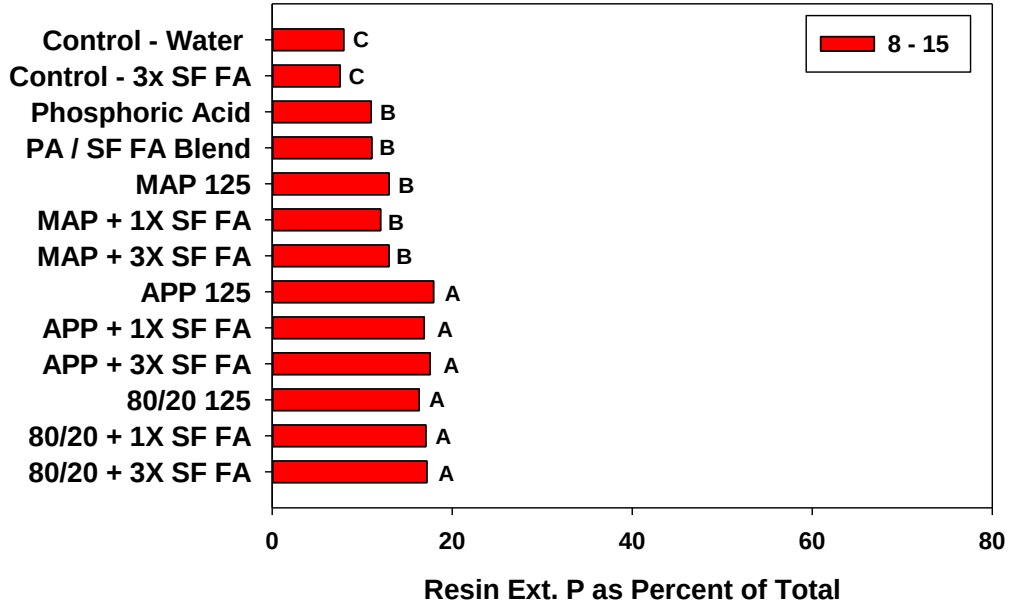
Percent resin extractable P in 8-15 mm section



All P treatments performed superior to the control treatments in the second section. APP treatments performed better than the PA and MAP treatments.

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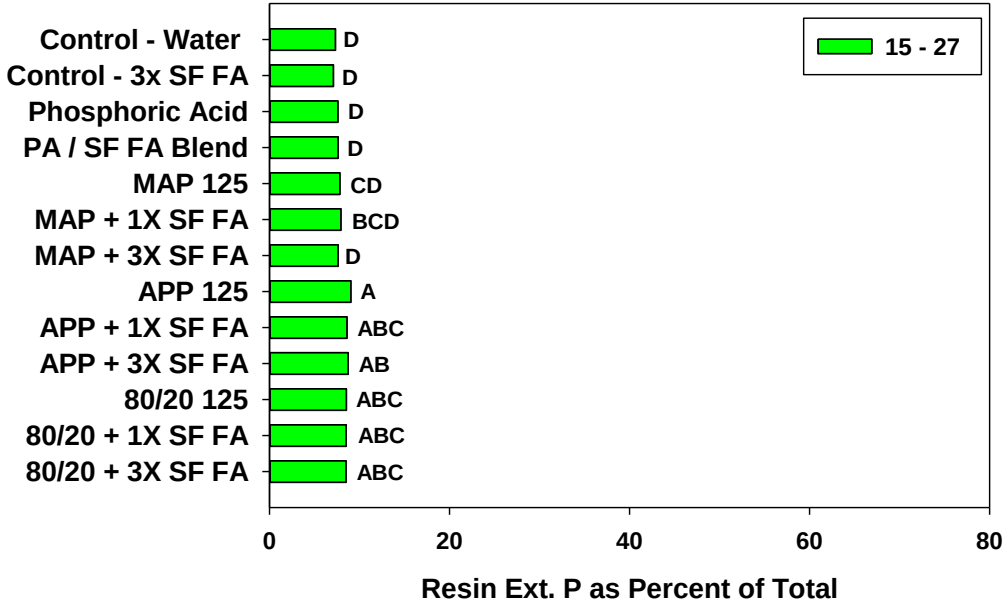
Percent resin extractable P in 15-27 mm section



APP treatments performed superior to the control, PA and MAP treatments in the third section.

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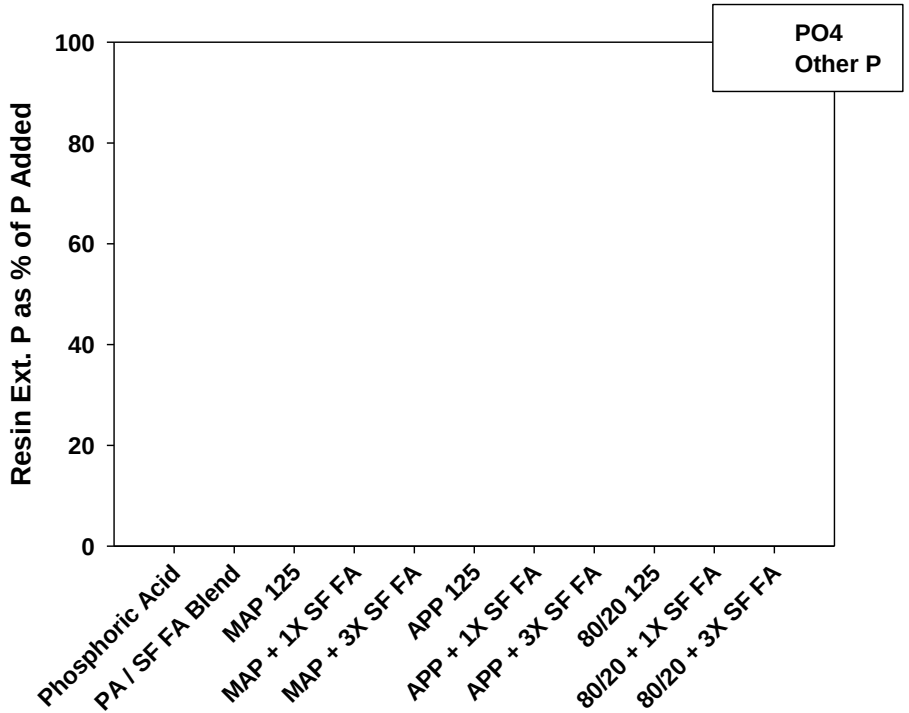
Percent resin extractable P in 0-8 mm section after acid digestion



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

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XANES analysis confirmed less Ca-PO_4 formed and more Fe- or clay- adsorbed P in soils receiving APP

0-8 mm dish section

Component values expressed as %

	PO_4-CaCO3	Apatite	OCP	MONT Al PO_4	PO_4 - Fh	PO_4 - Goethite	red. X^2
Control - Water	38.7	19.4	26.5	-	15.4	-	0.0055
Control - Fulvic Acid	31.1	50.8	11.5	6.6	-	-	0.0027
MAP	59.4	8.4	32.2	-	-	-	0.0024
MAP + Fulvic Acid	70.6	11.6	17.8	-	-	-	0.0034
APP	44.5	25	-	-	21.7	8.8	0.0109
APP + Fulvic Acid							
80/20	31.7	35.9	-	19.1	13.3	-	0.0070
80/20 + Fulvic Acid	34.9	-	40.6	11.7	12.8	-	0.0035

XANES work with other FA products will be conducted in April 2019

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Conclusions

- Although there were some changes with FA addition to liquid P, FA addition did not seem to significantly improve P mobility or lability
- Growers on calcareous soils will benefit from applying liquid polyphosphate-based fertilizers, rather than orthophosphates
- Further research will be required to determine why some growers observe substantial yield increases when humic substances are applied to fields
  - Stimulation of soil biota and native P cycling?
  - Plant hormonal response?
  - Increased micronutrient lability?

Highlights from acid soil work

- **Duration:** 28 day incubation study (total darkness)
- **Soil:** Brazilian Oxisol
- **Bulk Density:** 1.1 g cm^{-3} (packed in Petri dish - diameter: 86mm, depth: 11.5mm)
- **Moisture Content:** 50% Maximum Water Holding Capacity
- **Replications:** Four (three displayed in presented data)
- **Liquid Fertilizers (9.2mg P in 125µL water added to center of dish):**

Origin	Classification	Texture	pH	$CaCO_3$	CEC	Total P	Oxalate Extractable Fe	Oxalate Extractable Al
			(1:10)	%	cmol kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Brazil	Typic Haplustults	SCL	5.4	-	4.25	206	1565	666

SCL: Sandy clay loam

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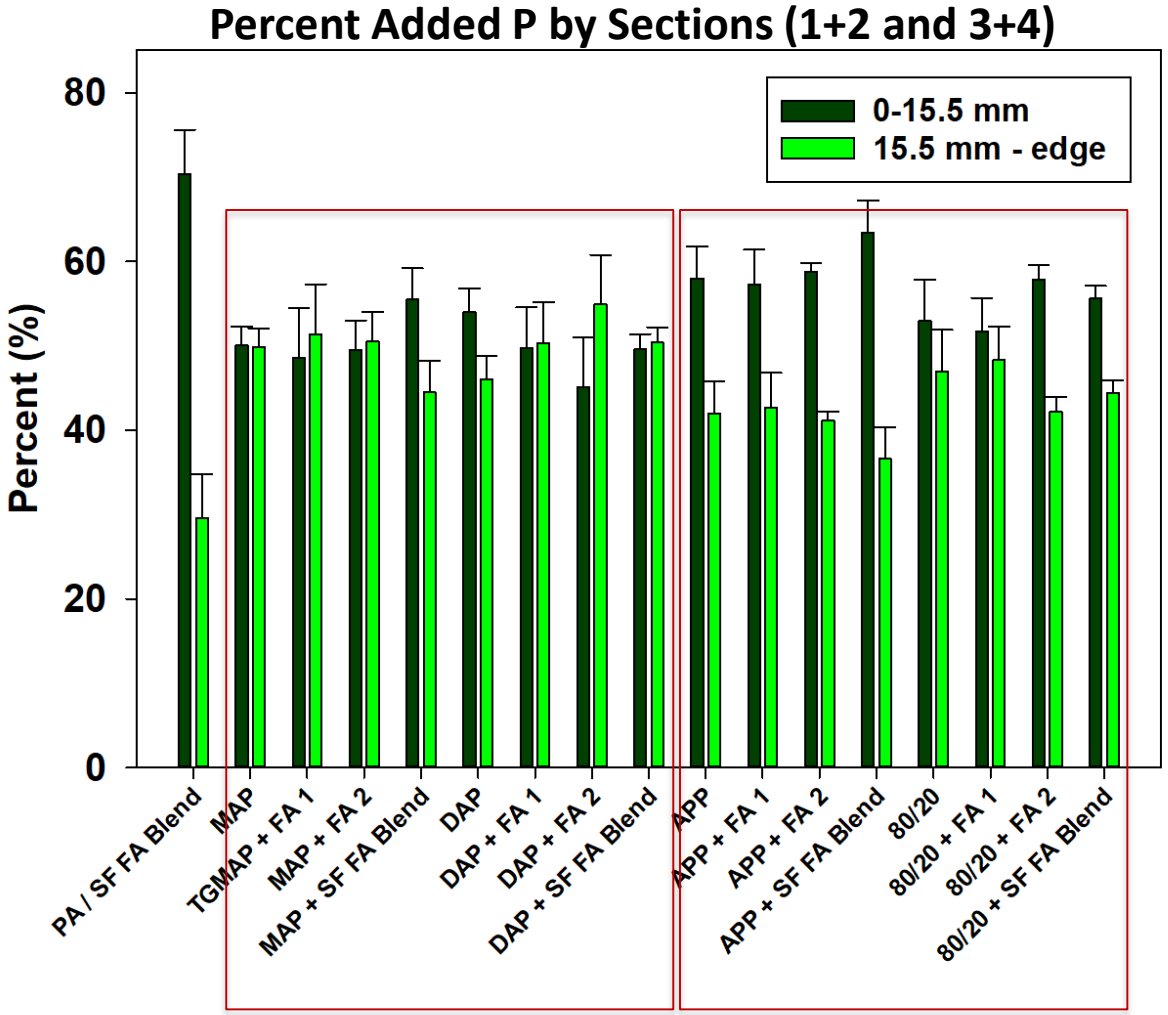

Orthophosphate treatments diffused further than polyphosphate treatments.

The PA acid / SF FA blend was the least mobile.

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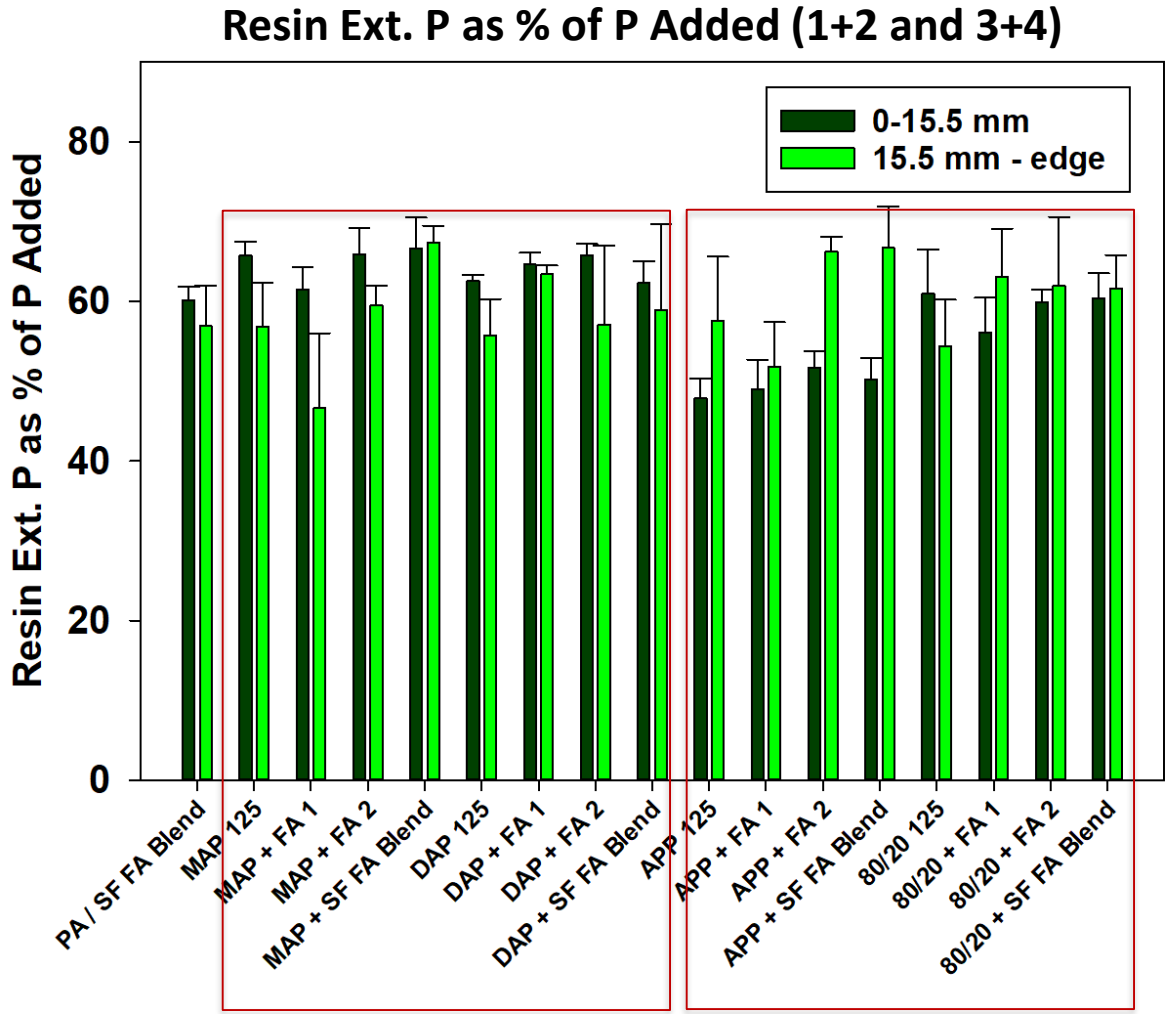

Orthophosphate treatments performed superior to the APP and 80/20 treatments in the center sections

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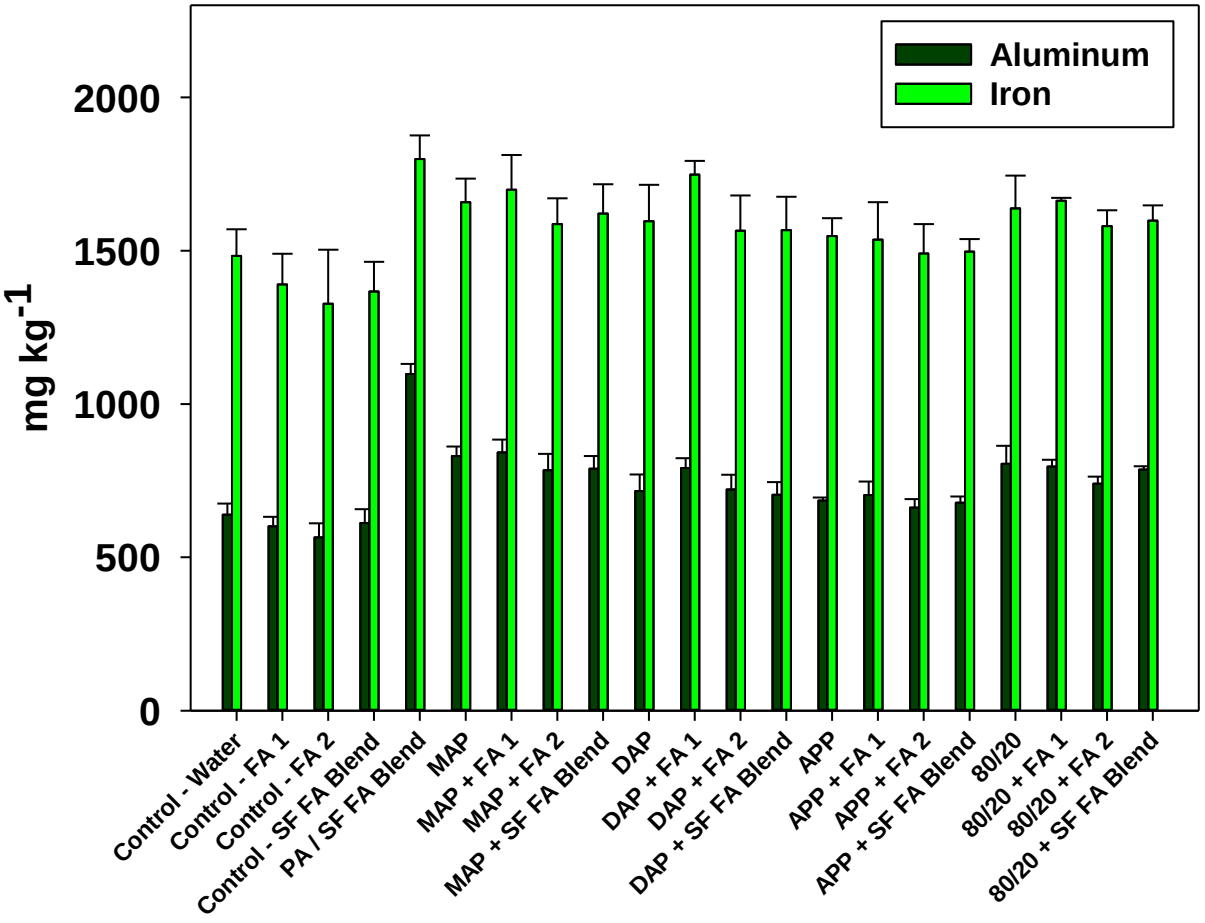
Ammonium Oxalate in the Dark - (0-8mm) Section



Addition of fertilizer to the soil appears to have slightly elevated the concentrations of amorphous Fe and Al as compared to controls.

The only treatment differs from the rest was the PA/ SF SA blend.

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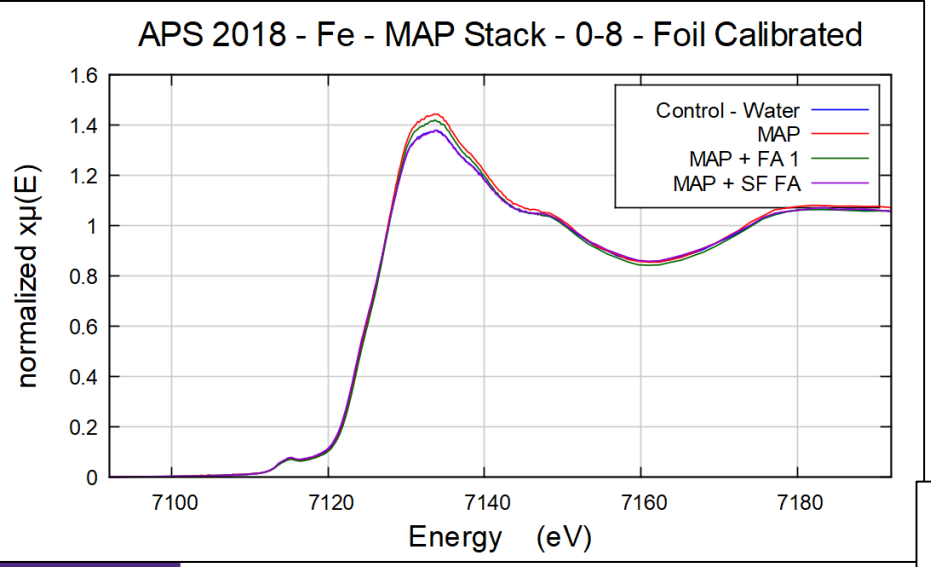
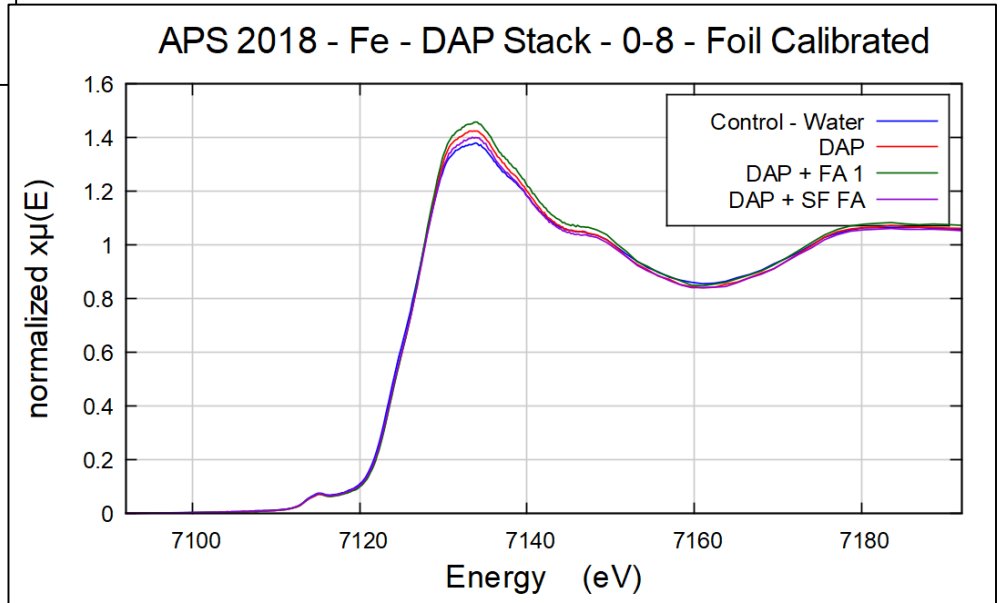
Fe Speciation-Brazil soil

Subtle differences in Fe speciation was evident by the X-ray absorption near-edge structure (XANES) spectroscopy



Work conducted at the Advanced Photon Source, April 2018



Acknowledgements

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