

P and S fertilizer reaction products in the seed-row as revealed by XANES spectroscopy

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Introduction

- Sulfur (S) and phosphorus (P) are an essential nutrients for crop production
- S and P fertilizers are commonly applied together in bands for crop production in Western Canada



Forms and Availability

Availability depends on

- Species formed after application
- Soluble (solution) sulfate and phosphate immediately available for root uptake
- Some fertilizers require transformation to these forms
- ***Understand the fate of applied S and P!***
- Will help to most beneficially use S and P containing fertilizers

Traditional Approaches to Study of S and P Fertilizer Fate

Examining plant availability of the S and P

- Through plant nutrient uptake and yield response
- Measuring content of total or available forms in soil before and after plant growth



Photo courtesy T. King

Research Justification

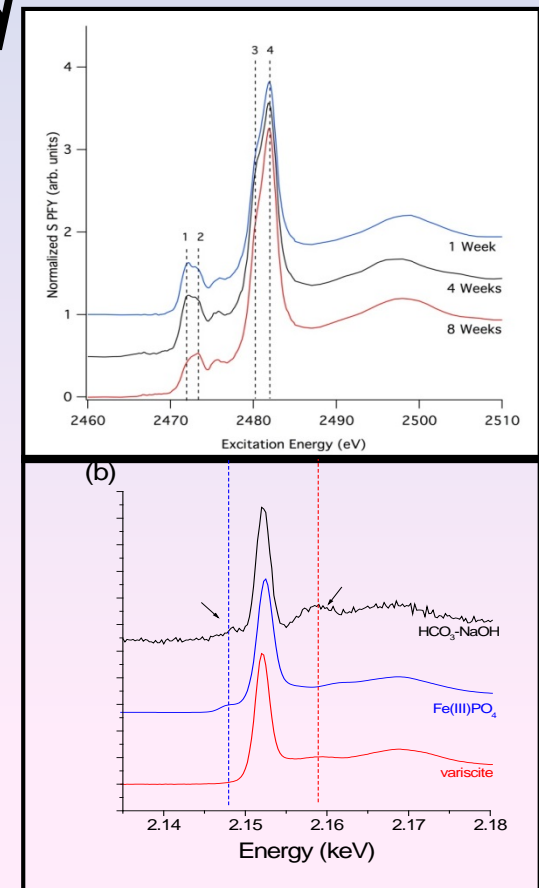
- **There has been little recent work to follow the fate and transformation (speciation) of applied S and P fertilizers in prairie soils in the weeks following application**
- **XANES spectroscopy is under-utilized as a tool to reveal chemical speciation in agricultural soils**

Why XANES

Traditional wet chemical analyses methods

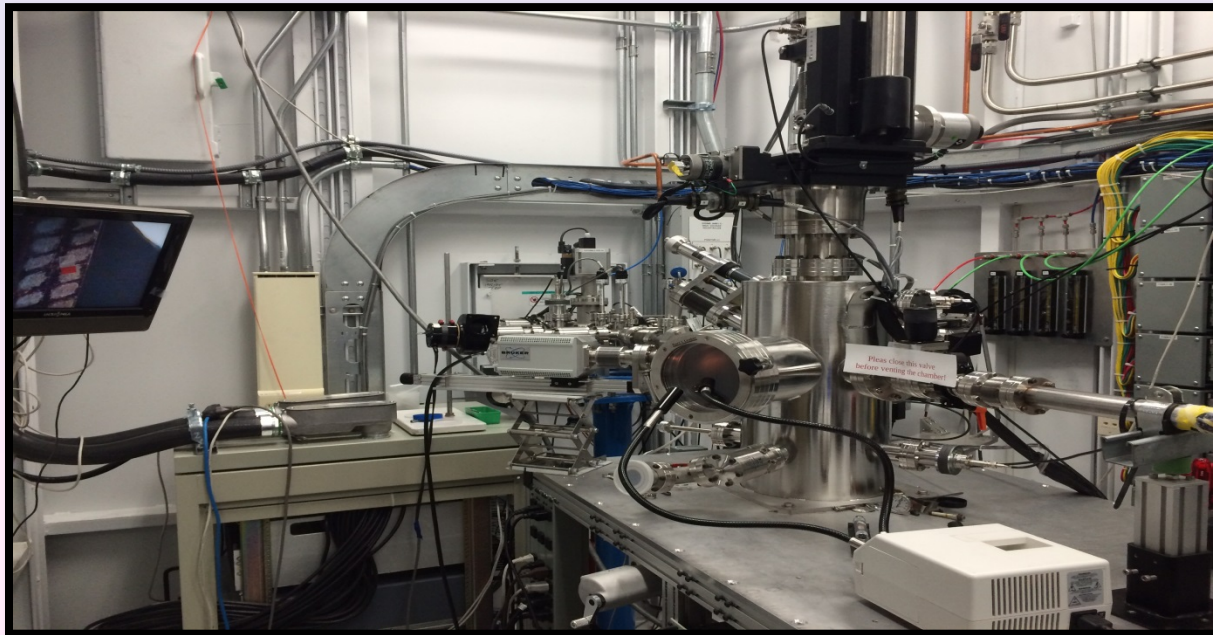
- *May not be able to identify particular S and P species in soil, artifacts created*

- ❑ ***XANES spectroscopy can distinguish different oxidation states of an element***
- ❑ ***Offers unique ability to follow transformation of fertilizers to different forms of varying plant availability over time.***



Objective

- ❑ To develop and employ a synchrotron technique to assess the fate of different fertilizer S forms and P added in the seed-row



Field Study Sites

Saskatchewan, Canada



★ **Black Chernozem**
Melfort

★ **Brown Chernozem**
Central Butte

Experiment Details

- Research design: RCBD
- Treatment: *Urea, ammonium sulfate, calcium sulfate, elemental S, and monoammonium phosphate*
- Application rate: 20 kg S and P₂O₅ ha⁻¹ in seed-row
- Soil sample collection: from the seed-row 1, 4 and 8 weeks after seeding canola.



Photo courtesy T.King
U of S

Analytical Techniques

Wet chemical analysis:

- CaCl_2 extractable available sulfate
- Available P by modified Kelowna method

XAS spectroscopic techniques:

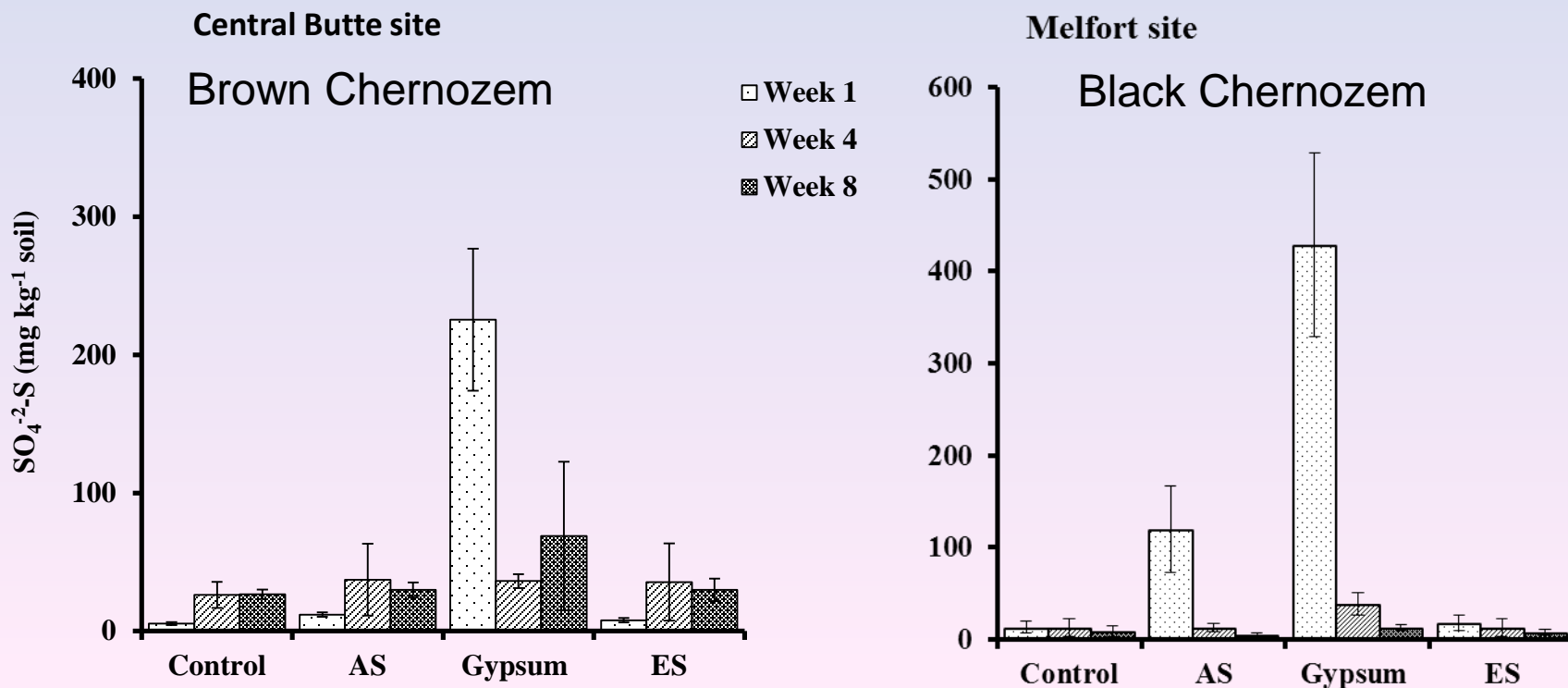
- S and P K-edge XANES

Data analysis:

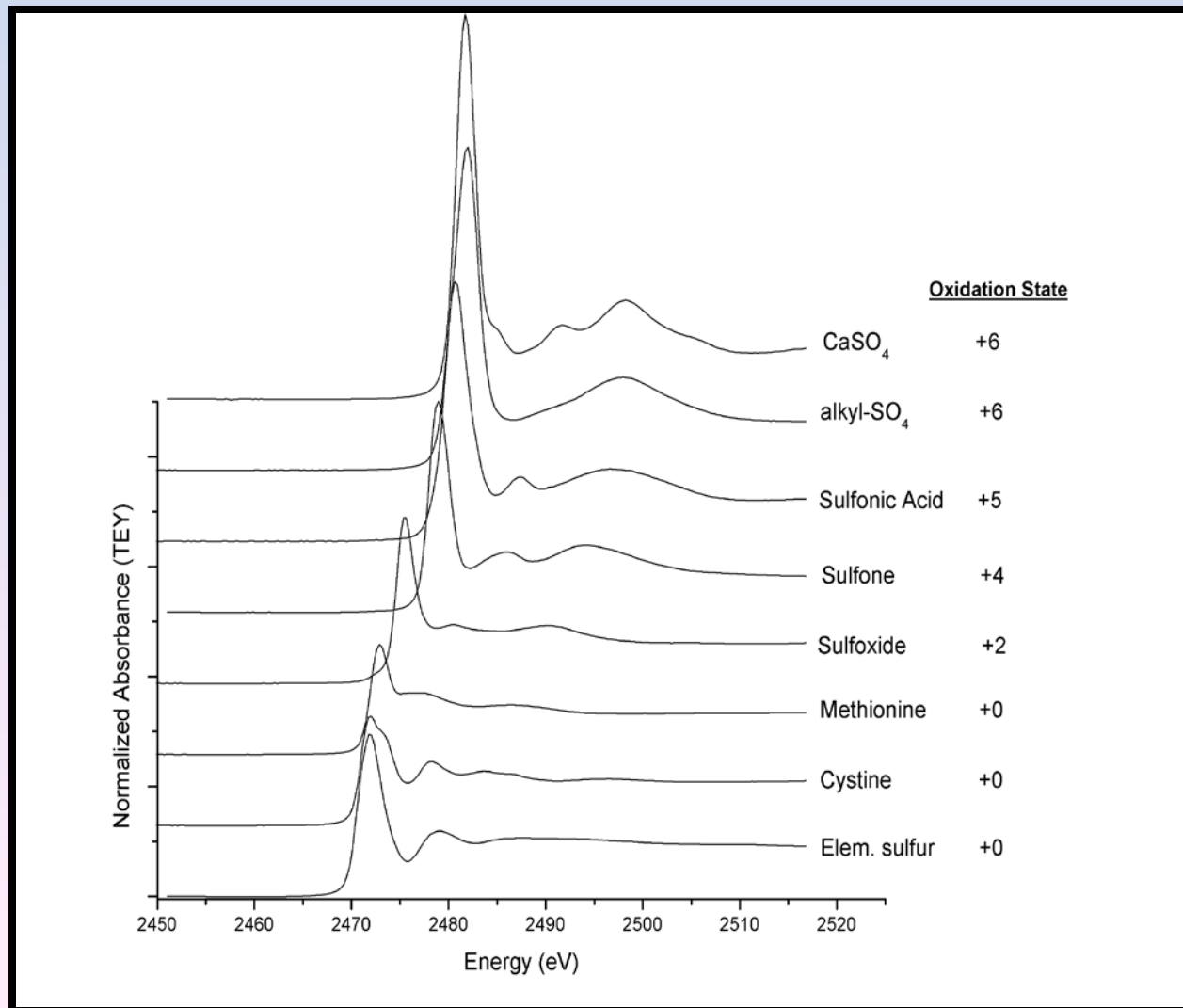
- Gaussian curve fitting
- Linear combination fitting

Results

Available soil sulfate concentration in the seed-row after 1, 4 and 8 weeks of crop growth

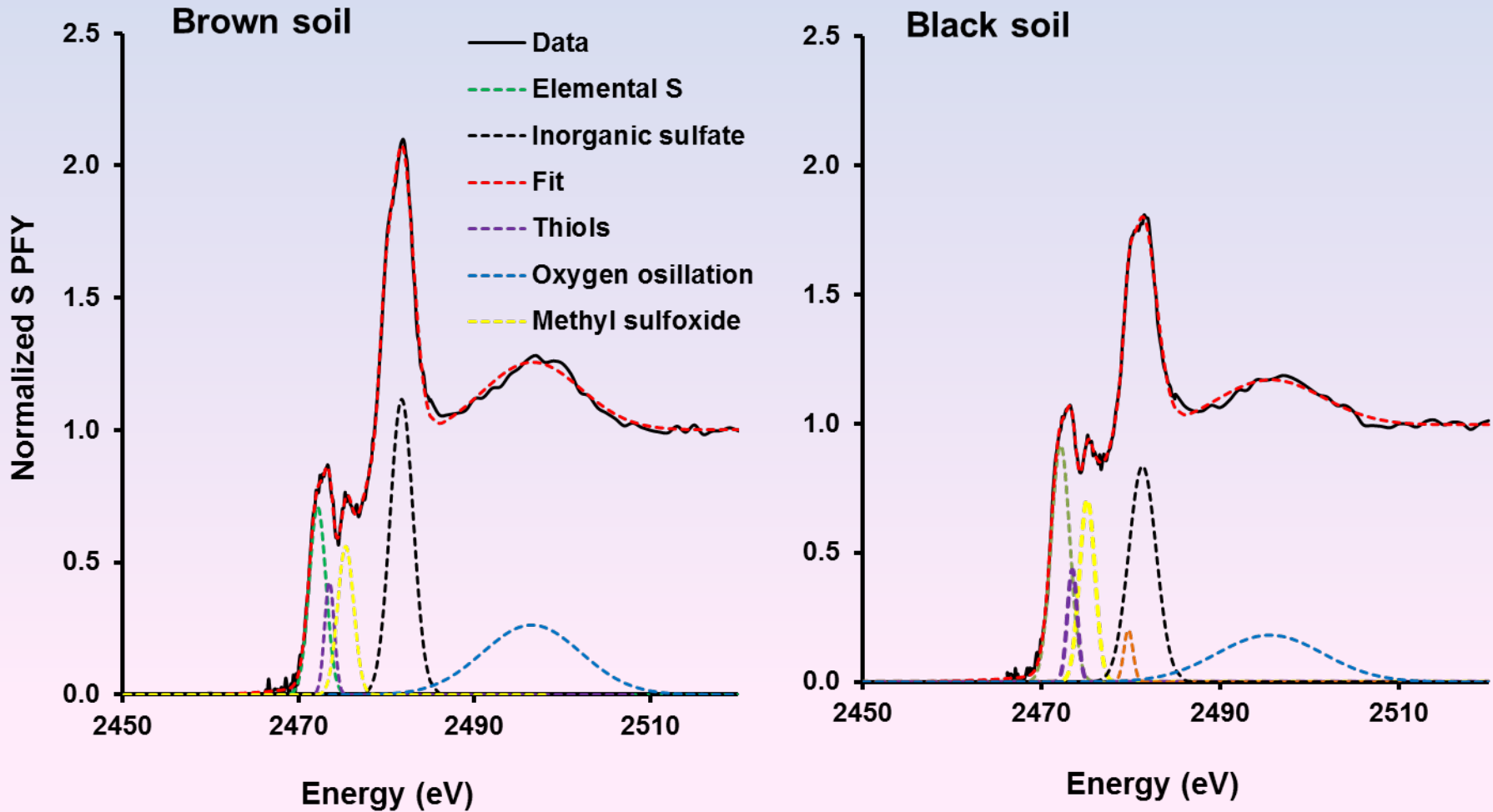


XANES Fits for S Reference Compounds



Gaussian Curve XANES Fits:

Elemental S fertilized



XANES Fit Results

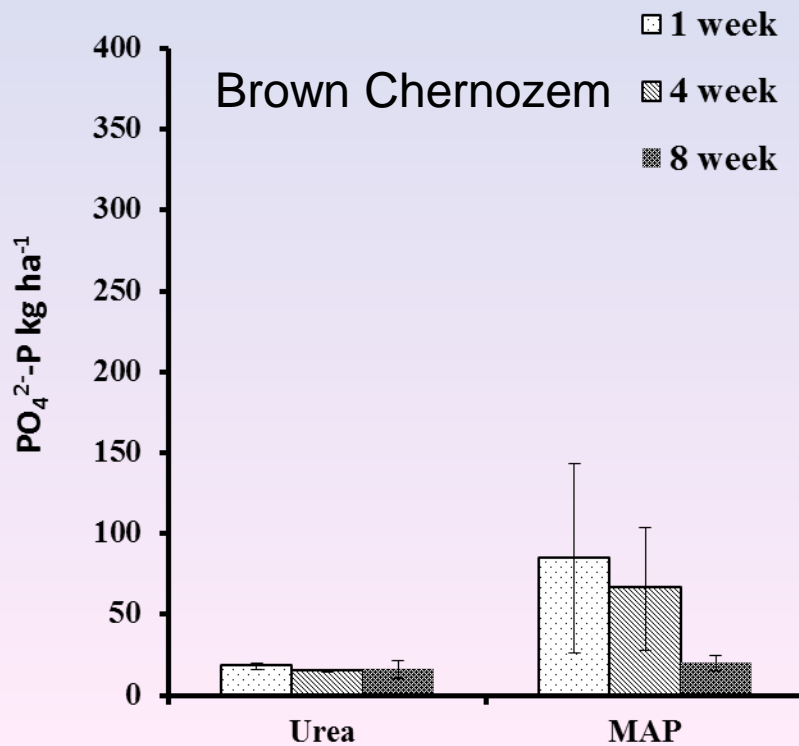
Time	Elemental S	Thiols	Sulfoxide	Ester S	Inorganic sulfate
Calculated % of S Forms Present in Seed-Row					
<i>Brown</i>					
<u><i>Chernozem</i></u>					
<i>Control</i>					
Week 1	15	5	9	9	63
Week 4	7	6	4	21	62
Week 8	6	2	11	5	76
<i>Elemental S</i>					
Week 1	13	8	6	17	56
Week 4	13	7	5	21	54
Week 8	11	2	11	12	63
<i>Ammonium sulfate</i>					
Week 1	7	2	9	7	74
Week 4	8	2	15	10	65
Week 8	7	2	17	11	63
<i>Gypsum</i>					
Week 1	7	1	8	3	81
Week 4	8	2	8	8	75
Week 8	8	2	16	10	63

XANES Fit Results

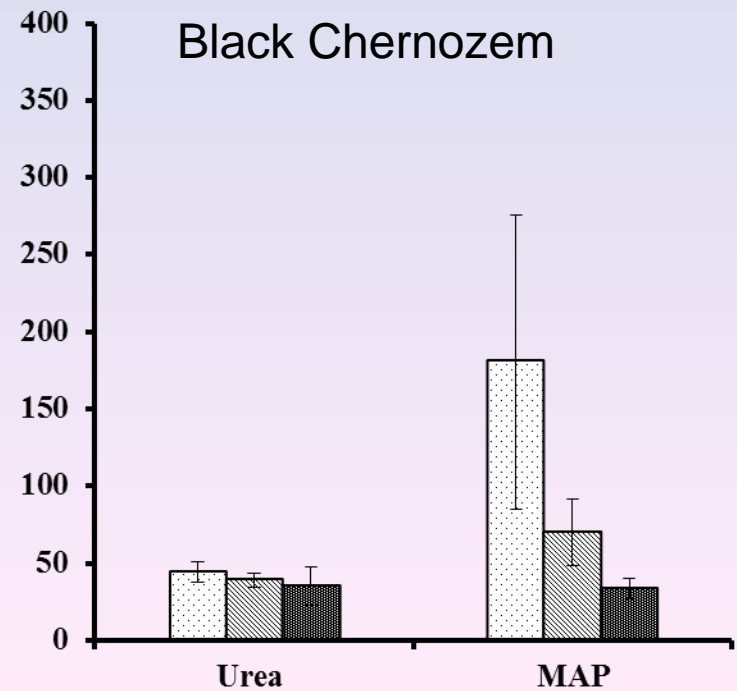
Time	Elemental S	Thiols	Sulfoxide	Ester S	Inorganic sulfate
%Calculated % of S Forms Present in Seed-Row					
<i>Black Chernozem</i>					
<i>Control</i>					
Week 1	12	7	11	13	57
Week 4	10	6	13	19	52
Week 8	12	7	12	15	54
<i>Elemental S</i>					
Week 1	24	13	8	16	39
Week 4	8	2	13	1	76
Week 8	13	8	10	16	54
<i>Ammonium sulfate</i>					
Week 1	5	3	11	3	79
Week 4	13	8	13	16	51
Week 8	11	9	11	13	56
<i>Gypsum</i>					
Week 1	6	4	11	3	76
Week 4	8	7	12	8	65
Week 8	12	6	13	12	56

Available soil phosphate concentration in the seed-row after 1, 4 and 8 weeks of crop growth

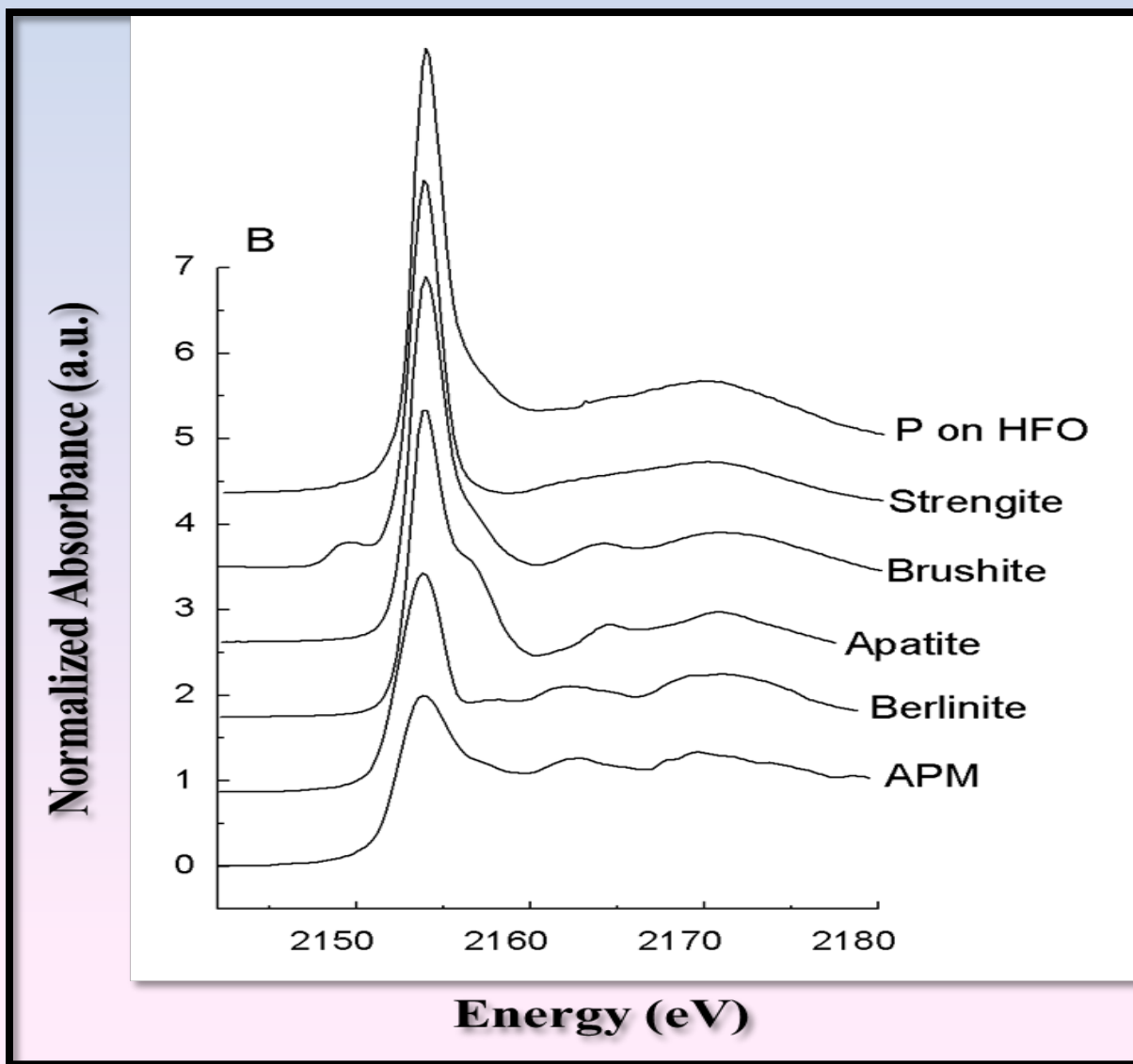
Central Butte site



Melfort site

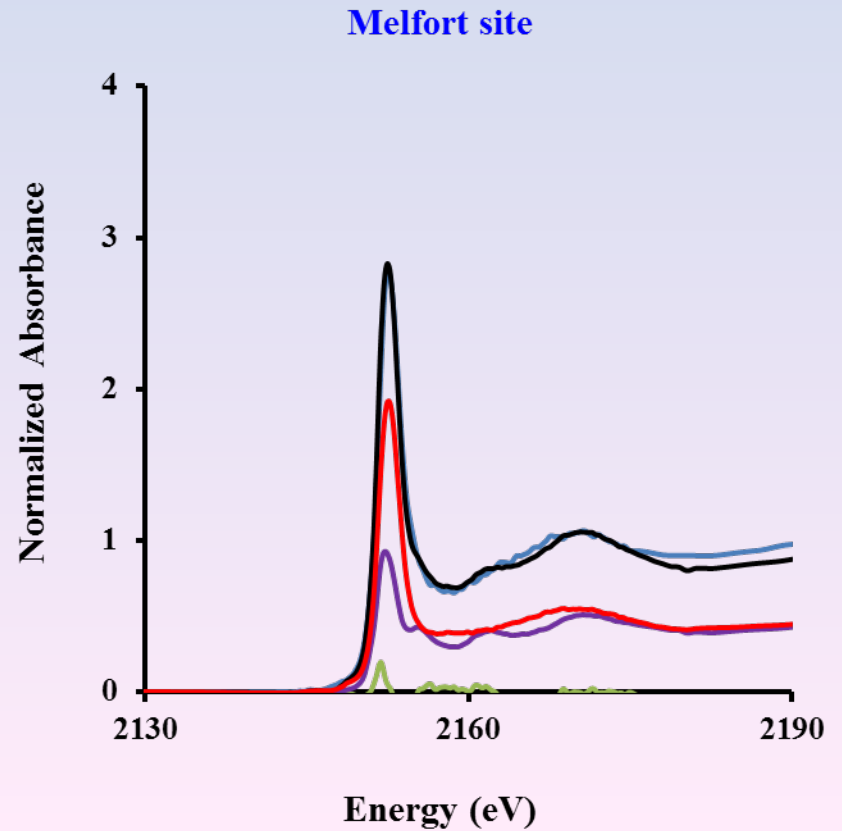
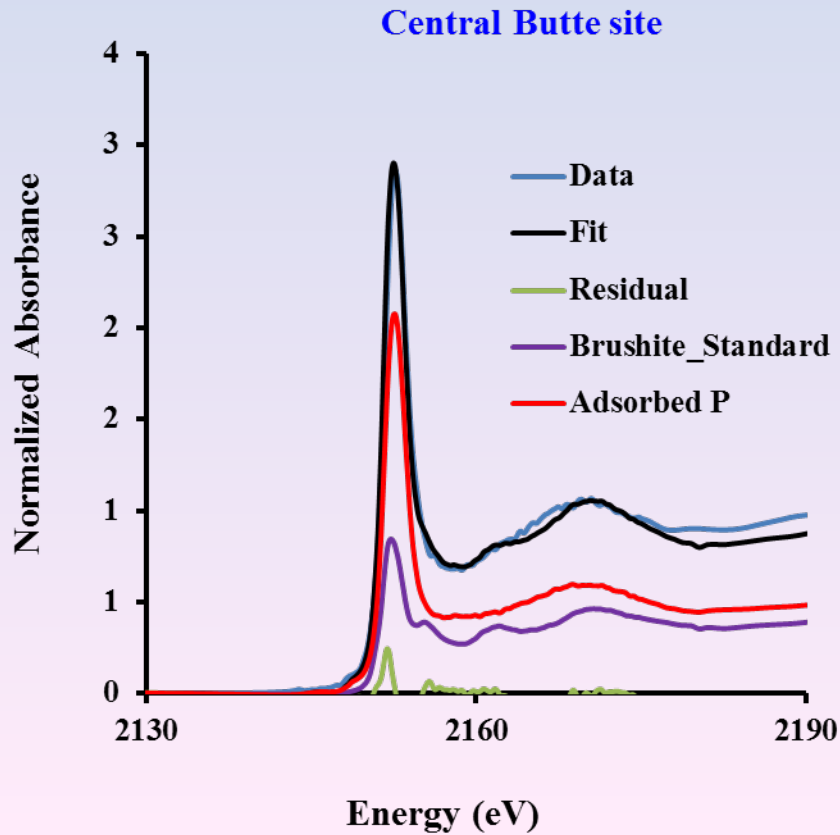


XANES Fits for P Reference Compounds



Gaussian Curve XANES Fits:

MAP fertilized after 1 week



XANES Fit Results

Time	Brushite	Adsorbed
	<i>% in form</i>	<i>% in form</i>
Brown Chernozem		
Week 1	51	47
Week 4	41	57
Week 8	43	57
Black Chernozem		
Week 1	45	52
Week 4	42	56
Week 8	43	55

Major speciation findings....

- **Species identified in the seed-row included:**
 - the initial forms as well as reduced thiols
 - organic S in the form of methyl sulfoxide, ester sulfates
- P was found as mainly brushite and adsorbed forms

Conclusions

- ✓ More residual fertilizer S was identified in the Brown Chernozem. Reflects drier environment.
- ✓ XANES was able to identify different S species and conversions in soil
 - *Transitory organic S likely from microbial immobilization of fertilizer S*
 - *Some oxidation of elemental S over the eight weeks after application*
- ✓ Both adsorbed and mineral P forms were identified as dominant reaction products
 - Adsorbed P lower initially but it increased over time, conversion stimulated by sulfate

***XANES is an effective tool to study
speciation of S and P applied to
soil***

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THANK YOU

Questions?