

Fate of Seed-Placed Sulfur Fertilizers in a Brown Chernozem Soil as Assessed by S K-Edge XANES Spectroscopy

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Introduction

Sulfur is an essential plant nutrient and sulfur fertilizers are important to increase the supply of plant available sulfur in soil. The availability of sulfur depends on the chemical form present in soil system after application, as sulfate is required for plant root assimilation. Synchrotron-based S K-edge X-ray absorption near-edge structure (XANES) spectroscopy can successfully be used to identify the different sulfur species present in soil after amendment with S fertilizer.

Objective

To develop and employ novel methodology using the new SXRMB beamline at the Canadian Light Source to determine the forms of S present in the soil following S fertilization.

Materials and Methods

Field Study

A field experiment was conducted in 2013 near Central Butte, SK on a loamy Brown Chernozem. The experimental design was a randomized complete block experimental design with four blocks of replicate treatments. A single row seeder was used to seed and seed-place the sulfur fertilizers at the time of seeding.

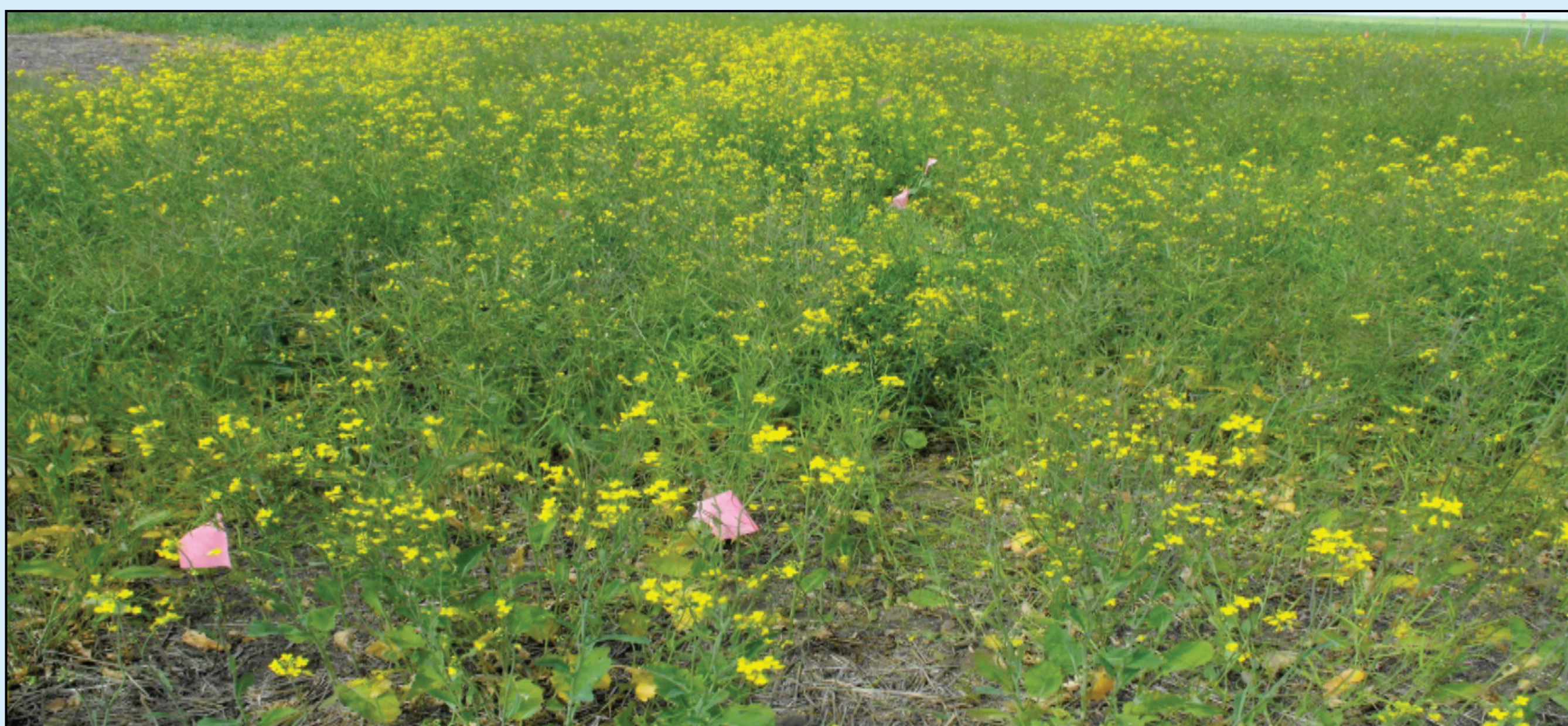


Photo : Canola at Brown Chernozem site in 2013.

Treatments

Five different sulfur fertilizer forms: ammonium sulfate, potassium sulfate, gypsum, elemental S, and liquid ammonium thiosulfate were applied @ 20 kg S/ha along with N fertilizer @ 100kg N ha⁻¹ to provide the same rate of N for all treatments.

Sample Collection and Lab Analysis

Soil samples were collected from the S fertilizer band in the field using a micro-coring device 1 week, 4 weeks and 8 weeks after seeding. The collected soil samples were air-dried, ground, and analyzed for S forms by S K-edge XANES spectroscopy and total sulfur was determined using LECO sulfur determinator. The S XANES spectra of all the soil samples and S standards was conducted at the Soft X-ray Micro-characterization beamline (SXRMB) at the Canadian Light Source (CLS), Saskatoon, Canada.

Results and Discussion

Running S standard fertilizer S reaction products (Fig. 1a) along with seed-row soil samples shows that how the oxidation state affects the energy level, allowing identification of S compounds. The XANES spectroscopy showed that elemental sulfur fertilizer was transformed into reduced thiols, oxidized S including ester sulfate, and eventually into inorganic sulfate forms that were removed by plant uptake. The proportion of reduced and insoluble forms of S in the seed-row decreased with time (Fig. 1b). Assessment of total S concentrations in the seed-row using combustion analyses technique showed that the amounts of sulfur remaining after application were decreased over the eight week period for all the sulfur fertilizers applied, indicating that significant plant uptake of all the different sulfur fertilizer forms was occurring (Table 1).

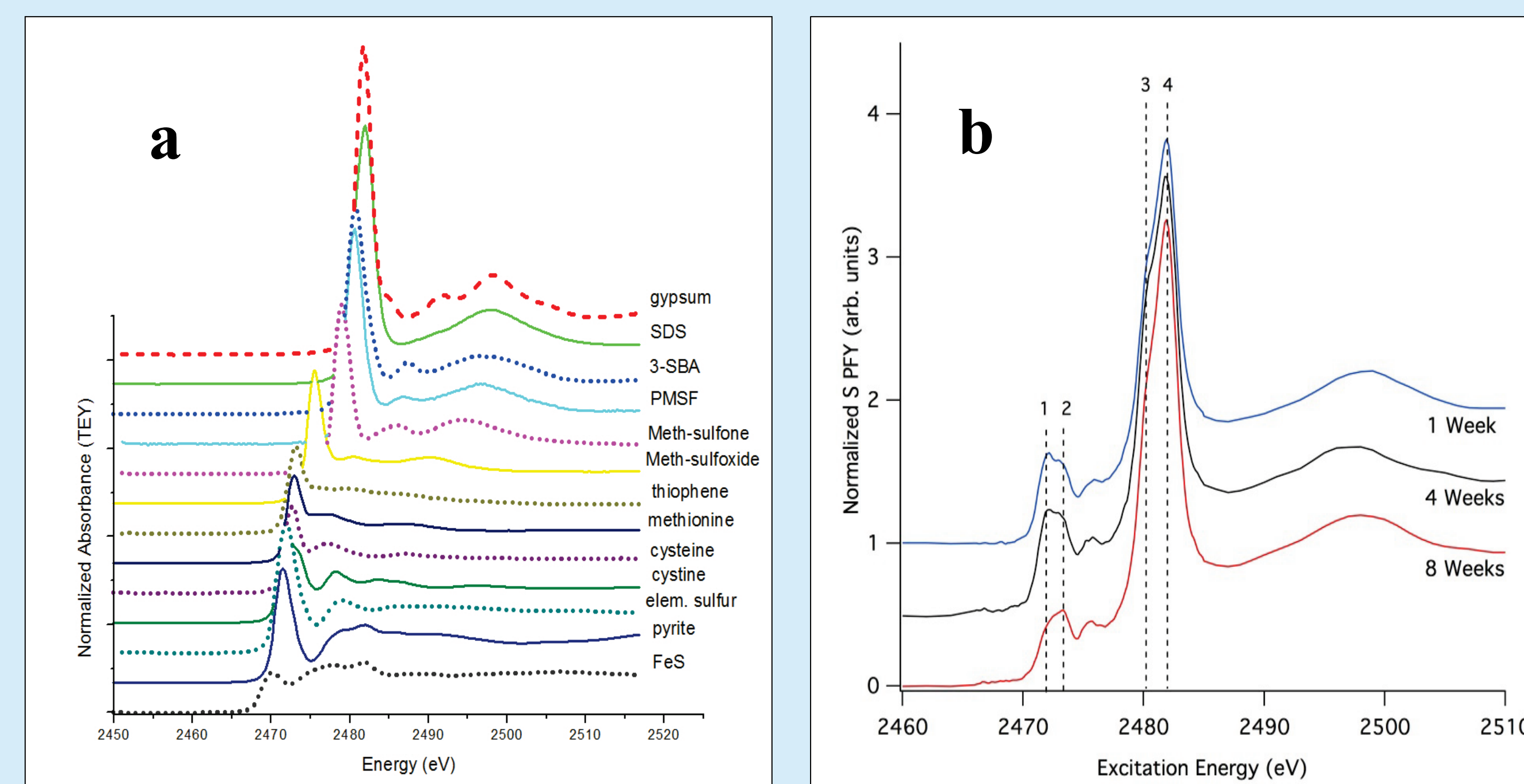


Figure 1: (a) S standards and (b) S K-edge XANES of Central Butte soil receiving elemental S fertilizer prior. The dashed lines denote different S species as follows: (1) elemental S (2) thiols (3) ester sulfates (4) inorganic sulfate.

Treatment	Week 1	Week 4	Week 8
Control	21±2¶	22±4	22±4
Ammonium sulfate	31±10	26±5	25±2
Ammonium thiosulfate	39±3	26±3	22±3
Gypsum	41±9	44±21	27±4
Potassium sulfate	32±8	24±1	26±1
Elemental sulfur	37±20	30±12	23±3

Table 1. Effect of application of different sulfur fertilizer forms on soil total sulfur concentration in the seed-row after 1 week, 4 weeks, and 8 weeks of canola plant growth. ¶SD, standard deviation of mean

The synchrotron spectra (Figure 1b) indicates that the elemental sulfur fertilizer in the Brown Chernozem (Central Butte) soil underwent significant oxidation in the four to eight weeks after application. Ester sulfates likely arose as a result of microbial uptake and appear to be a transient S form as they disappeared later on. The removal by plants of the sulfate forms is reflected in the decrease of intensity of peak height after 8 weeks but reduced difference in peak height for inorganic sulfate between four and eight weeks suggests some replenishment of sulfate by oxidation of reduced forms or mineralization is occurring over this period.

The effects of canola uptake of S on the S concentrations in the seed-row in the field over time are evident, with declines in the concentrations of total S in all the fertilizer treatments from week 1 to week 8 to levels similar to the control. Declines in total S from week 4 to week 8 were evident especially for slightly soluble (gypsum) and reduced (thiosulfate, elemental S) forms, a consequence of the more slowly available nature of these S forms compared to soluble sulfates.

Conclusions

The SXRMB beamline at the Canadian Light Source was used successfully to identify S species formed in the soil from addition of sulfur fertilizers, and to follow their transformations in the soil in the growing season following application.

The ability to track the oxidation of reduced S fertilizers like elemental S into more oxidized forms and eventually into plant available sulfate over time is of particular interest.

The results indicate oxidation of the elemental S fertilizer form proceeded over the eight weeks following application in this study.

The wet chemical analysis result shows that the amounts of sulfur after application of different sulfur fertilizers were decreased with time by plant uptake which agrees with XANES results.

Acknowledgements

Financial support from Agriculture Development Fund, SaskCanola, Western Grains Research, Sask Pulse Growers and NSERC. Thanks to Dr. Yongfeng Hu for his assistance at the SXRMB beamline during data collection. Assistance in the field from Ron Urton, Ryan Hags and Tom King is greatly appreciated.

Reference

G'Erardine S., J. Connan, M. Kasrai, G. M. Bancroft, A. C. DUHAUT, S. Lemoine, P. ADAM, P. Albrecht, and L. Eybert-B'Erard. 1999. Chemical forms of sulfur in geological and archeological asphaltenes from Middle East, France, and Spain determined by sulfur K- and L-edge X-ray absorption near-edge structure spectroscopy. *Geochimica et Cosmochimica Acta.* 63 (22): 3767–3779.