Understanding mechanisms of sulfur cycling in Minnesota soils and availability from fertilizer

AFREC Project Report 03/31/2023 for

AFREC Project(s) R2022-R Year 4 Report

Crop Year - 2022

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Year 4 (2022) Summary Points

- Sulfur increased corn grain yield at two of four locations. Application of 10-20 lbs of S per acre was sufficient for medium to fine textured soils with soil organic matter concentrations of 4% or greater while 10-20 lbs of S was required for sandy soils (considering 2019 to 2022 data)
- Sulfate forms of sulfur generated the highest grain yield at one location while finely ground elemental S co-granulated with potash fertilizer (MST product) produced yield equal to sulfate.
- Year 4 continues to show a lack of oxidation of sulfate from Tiger 90 as indicated by PRS probe and yield and plant tissue data.
- All forms of sulfur produced equal yield potential at a sandy irrigated location.
- Ion probe data show that elemental S does take time to start oxidizing in Minnesota soils and may provide long-term S availability over the growing season. Finely ground elemental S was shown to be more effective in medium-fine textured soils than an elemental S- bentonite product such as Tiger 90.
- Recovery of sulfate S following oxidation of elemental S at 25ºC ranged from 27-79% across 26 Minnesota soils when incubated for 112 days.

Introduction

The response of corn grain yield to sulfur fertilization has been one of the major factors for increased productivity and profitability in some cropping rotations. Current projects on sulfur timing, rate, and placement have clearly demonstrated the need for sulfur. While a soil test is available for sulfur, differences in sulfate due to S application are difficult to detect with the soil test and soil test concentration of sulfate-S can be high even in soils where S responses occur. This highlights our limited understanding of how sulfur cycles among forms in the soil. Sulfate-S can be reduced in low oxygen situations but a complete reduction of sulfate to hydrogen sulfide which can be lost to the atmospheric via volatilization unlikely. Basic research on forms of sulfur in the soil is needed to better understand availability in soils across Minnesota.

Elemental sulfur is a low-cost option for supplying S to plants but must be oxidized to sulfate prior to plant uptake. Oxidation is mediated by bacteria, *Thiobacillus thiobacteria*. From previous work, we know that the activity of *Thiobacillus* tends to be low when soils remain cool. In fact, the optimum temperature for *Thiobacillus* activity is above 80ºF and even at these temperatures the oxidation of elemental sulfur can take 30 days. Developing an accurate model of oxidation is important to understand how to effectively utilize elemental sulfur in cropping systems. In addition, long-term studies where elemental sulfur sources are compared to sulfate are needed to assess whether oxidation later in the growing season can lead to a buildup of sulfate which, over time, will supply enough available sulfate sulfur to a crop.

Objectives

1. Evaluate the sulfur and nitrogen supply potential from soil organic matter in 26 Minnesota soil series at different incubation temperatures
2. Determine the oxidation potential of elemental sulfur in 26 Minnesota soils
3. Compare sulfur release and availability of a sulfate source of S versus two sources of elemental S in a continuous corn rotation
4. Evaluate changes in sulfur redox state and changes in soil sulfur pools sorbed to soil solids over time
5. Evaluate response among corn hybrids for single and split application of sulfur

Materials and Methods

Study 1: (Sulfur oxidation lab study) Soils from different growing regions, including from irrigated and rain-fed fields with sandy and medium or fine textures, were compared in a growth chamber. Twenty-six soils from differing crop growing regions were collected (southwest, south central, southeast, central sands, west central MN). Leaching columns are used to incubate soils in a growth chamber. The columns consist of ¾ inch PVC pipes cut to a length of 15 inches. A mixture of 40 grams of oven dry soil and 40 grams of a fine glass beads are added to each leaching column. Treatments consisting of a no sulfur control and two sources of sulfur are thoroughly mixed with the soil before adding to the columns. For the sulfur treatments, a rate of 200 ppm of sulfur (per unit soil) is applied as calcium sulfate (gypsum) or elemental sulfur (S was an analytical grade powder). A cap is placed at the bottom of each pipe with a 5/16 inch fitting will be connected to a collection vessel by plastic tubing to collect water. Glass wool is packed at the bottom of the column to prevent loss of soil and at the top of the column to prevent the dispersion of soil on the surface when water is added. At 0, 2, 4, 8, 12, 16 and 20 weeks approximately 150 mL of water was drawn through the leaching columns. The amount of water leached will be determined by weight then water will be analyzed for nitrate-N and sulfate-S by ion chromatography. To aid in leaching a vacuum was placed on the leaching columns.

Table 1. Soil series information, planted crop at each location, and initial potassium soil test data from phosphorus studies conducted in 2019. Soil test data was collected in the Fall at trial establishment from each main plot.

	Soil Test				SO_4-S			
Location	Bray-P1	K	pH	OM	0-6	6-12	12-24	Soil Series
	ppm			%	ppm			
Becker	127	164	6.8	1.6	8.8	8.8	8.3	Hubbard
Morris	37	198	7.9	5.8	12.4	14.2	13.2	McIntosh
Rosemount	29	171	5.4	4.2	11.5	10.5	8.3	Tallula
Waseca	17	170	5.7	4.7	10.1	9.4	7.1	Clarion-Webster

† K, Soil test potassium (K-ammonium acetate); CCE, calcium carbonate equivalency.

Study 2: (Long term S study) Long term S research trials were established at four locations in 2019 (Table 1) Since oxidation occurs later in the growing season a multi-year approach is needed to determine if the late oxidized S 1) can be carried over to the following year; and 2) if repeated application of elemental S can eventually provide adequate amounts of sulfate-S to corn. Studies will be established using a split plot design. Main plots will consist of S fertilizer rate and sub-plots will consist of S sources.

Sulfur source treatments will be a no sulfur control and three sources of S which consist of potassium sulfate, Tiger 90 (60-800 micron elemental S and bentonite mixture, and a co-granulated S source. Co-granulated S materials, similar to what is contained in the micro-essentials line of products, are becoming more available and allow for a more even distribution of elemental S as each fertilizer granule contains S along with N and P unlike Tiger 90 which is 90% S so the amount of product applied per acre is small. The co-granulated product used for this study is a potash-based material consisting of 49% K_2O and 13.6% S manufactured by Sulvaris (Calgary, AB) where the S is micronized to a smaller particle size ($\leq$40 microns) than Tiger 90. The use of a potash source eliminates the use of phosphate materials such as MAP, DAP, or TSP which can contain from 1-2% total S and can affect the ability to detect a response to S in a field study.

High P testing sites were selected, and additional P fertilizer was applied as a combination of in-furrow and 2x2 application of 6-24-6. Rates varied by site but typically were 5 gallons 6-24-6 in furrow at medium to fine textured sites plus 10 gallons 2x2. The in-furrow application rate was reduced to 3 GPA at Becker which is a sandy soil. The 6-24-6 product was tested by ICP and averaged 667 mg S L^{-1}.

All sulfur products will be applied to supply 5, 10, and 20 lbs of S per acre annually and treatments will be re-applied by hand to each plot every year. Additional K as 0-0-60 will be applied to balance K across plots and N will be applied at non-limiting rates. Plots are 20' in width (except for Waseca which was 15' in width) which allow for sub-dividing later during a second phase which will focus on draw-down of sulfur the soil. All treatments are replicated four times at each location and all fertilizer is applied in spring and incorporated prior to planting.

Corn grain yield response to S will be measured in all plots. Corn leaf tissue samples will be collected at V10 by sampling the uppermost fully developed leaf and at R1 sampling the ear leaf and the 2nd leaf from the top of the plant to be analyzed for total S concentration. A subsample of grain will be saved from each plot, ground, and analyzed for total S concentration. All samples will be analyzed for total S concentration using combustion analysis. Along with plant tissue tests canopy sensing was conducted at V5 using a crop circle 430 and at V10 and R1 using SPAD chlorophyll meters sampling the sample part of the canopy where leaf samples are collected.

Soil test S will be measured from each main block at the beginning of the trial at the 0-6, 6-12, and 12-24" depth and in the fall post-harvest at a 0-12 and 12-24" sampling depth. All soil samples were extracted using the mono-calcium phosphate procedure.

Past research has shown limited impacts of S application on increasing soil test S measurable. Plant root simulator (PRS) probes, sold by Western Ag. Innovations, were installed in the 10 lb S rate main blocks in all fertilizer sources and were sampled over a period of 8 sampling dates. A total of four anion probes were installed between the center two corn rows in an area 5' in each direction from the center of each plot. The PRS probes were installed in the soil to a depth of roughly 4-5 inches. At each sampling date the probes were removed from the soil, washed with deionized water, and new probes were re-installed into the slots created by the old probes. A garden knife was used to apply back pressure on the probes to ensure good contact between the soil and ion exchange membranes. Probes were sent to Western Ag. Innovations to be extracted and analyzed for sulfate-S sorbed.

Soil samples (0-6 and 6-12") were collected prior to the initial PRS instillation and each time PRS probes are installed and removed. A total of three cores were sampled from between the rows where PRS probes were installed and were analyzed for sulfate-S using the mono-calcium phosphate procedure.

A second set of cores were collected from the no-sulfur sub-plot using a zero-contamination soil core and sleeve for XANES analysis. A total of four cores were taken, one from each sub-plot, were vacuum sealed and were frozen to be stored for later analysis.

Table 2. Summary of cultural practices for studies conducted from 2019 to 2021. Soil test data was collected in the Fall at trial establishment from each main plot.

			Date of		
Year	Location	Cultivar†	Spring Fert.	Planting	Harvest
2019	Becker	DK 50-08	3-May	4-May	24-Oct
	Morris	DK 50-08	14-May	15-May	14-Nov
	Rosemount	DK 50-08	7-May	16-May	28-Oct
	Waseca	DK 50-08	15-May	16-May	24-Oct
2020	Becker	DK 51-38	6-May	6-May	15-Oct
	Morris	DK 51-38	11-May	11-May	26-Oct
	Rosemount	DK 51-38	1-May	12-May	13-Oct
	Waseca	DK 51-38	4-May	7-May	15-Oct
2021	Becker	DK 49-44	7-May	7-May	25-Oct
	Morris	DK 49-44	12-May	12-May	3-Nov
	Rosemount	DK 49-44	10-May	10-May	14-Oct
	Waseca	DK 49-44	10-May	10-May	2-Nov
2022	Becker	DK 49-44	15-May	16-May	28-Oct
	Morris	DK 49-44	25-May	26-May	20-Oct
	Rosemount	DK 49-44	6-May	10-May	27-Oct
	Waseca	DK 49-44	16-May	16-May	13-Oct

† Dk, Dekalb.

‡ Fall fertilizer (fert.) was applied the fall the previous year in which the study was harvested.

Table 3. Summary of PRS probe installation and removal dates at four Minnesota locations during 2019, 2020, and 2021 growing seasons.

			Date of removal for individual sampling times							
Year	Location	Install	1	2	3	4	5	6	7	8
2019	Becker	6-May	23-May	10-Jun	25-Jun	11-Jul	2-Aug	23-Aug	13-Sept	3-Oct
	Morris	15-May	30-May	13-Jun	2-Jul	16-Jul	6-Aug	28-Aug	16-Sept	16-Oct
	Rosemount	17-May	4-Jun	18-Jun	3-Jul	17-Jul	8-Aug	29-Aug	20-Sept	15-Oct
	Waseca	16-May	3-Jun	18-Jun	3-Jul	23-Jul	12-Aug	29-Aug	20-Sept	15-Oct
2020	Becker	6-May	21-May	3-Jun	17-Jun	30-Jun	23-Jul	12-Aug	2-Sept	28-Sept
	Morris	11-May	26-May	8-Jun	22-Jun	7-Jul	27-Jul	20-Aug	8-Sept	9-Oct
	Rosemount	12-May	28-May	9-Jun	24-Jun	7-Jul	29-Jul	11-Aug	9-Sept	7-Oct
	Waseca	7-May	20-May	5-Jun	16-Jun	2-Jul	21-Jul	11-Aug	2-Sept	30-Sept
2021	Becker	7-May	21-May	4-Jun	18-Jun	2-Jul	23-Jul	13-Aug	2-Sept	4-Oct
	Morris	12-May	26-May	9-Jun	23-Jun	7-Jul	27-Jul	18-Aug	8-Sept	7-Oct
	Rosemount	11-May	25-May	8-Jun	22-Jun	6-Jul	26-Jul	17-Aug	7-Sept	30-Sept
	Waseca	10-May	25-May	7-Jun	22-Jun	6-Jul	26-Jul	17-Aug	7-Sept	30-Sept
2022	Becker	16-May	1-Jun	15-Jun	30-Jun	14-Jul	2-Aug	22-Aug	13-Sept	6-Oct
	Morris	26-May	9-Jun	22-Jun	7-Jul	20-Jul	9-Aug	30-Aug	20-Sept	10-Oct
	Rosemount	10-May	24-May	7-Jun	21-Jun	5-Jul	25-Jul	15-Aug	8-Sept	6-Oct
	Waseca	16-May	31-May	16-Jun	29-Jun	12-Jul	4-Aug	23-Aug	15-Sept	7-Oct

Table 4. Summary of ANOVA analysis for measured agronomic variables for four sulfur trial locations studied during 2022.

Main Effect	V5 NDRE	V10 Leaf S	V10 SPAD	R1 Ear Leaf S	R1 Up. Leaf S	R1 EL SPAD	R1 UL SPAD	Yield	Grain S	Fall SO_4-S
					--*P*>F--					
					Becker					
S rate	0.76		0.21			0.91	0.77	0.24		0.12
S Source	0.62		0.35			0.18	0.07	0.20		0.18
Srt.xSource	0.39		0.82			0.21	0.23	0.38		0.19
					Morris					
S rate	0.90		0.60			0.46	0.99	0.86		0.24
S Source	0.96		0.57			0.78	0.33	0.93		0.19
Srt.xSource	0.55		0.82			0.44	0.33	0.12		0.29
					Rosemount					
S rate	0.07		*			*	0.07	***		0.62
S Source	***		***			***	***	***		0.87
Srt.xSource	0.41		0.16			0.47	0.38	0.17		0.83
					Waseca					
S rate	0.56		0.51			***	*	0.07		0.41
S Source	0.55		***			***	***	***		0.12
Srt.xSource	0.34		0.22			0.31	0.20	0.36		0.50

Asterisks denote significance at $P \leq 0.001$ (***), $P \leq 0.01$ (**), and $P \leq 0.05$ (*) probability levels.

Results and Discussion

Location Characteristics

Table 1 summarizes soil series information and soil chemical properties for the four locations. The four locations were selected as they have differing soil types. The target crop rotation was corn following corn. Corn was the previous crop in 2018 at Rosemount and Waseca, Becker was previously planted to Rye, and Morris was planted to soybean in 2018 before all sites were planted to continuous corn. All sites were rain-fed except for Becker which was irrigated. The total irrigation applied at Becker in 2019 was 8.05 inches of water, 10.6 inches were applied in 2020, 14.3 inches in 2021, and 13.05 inches in 2022. Well water samples indicated an average of 29.8 mg SO_4-S L^{-1} water at Becker in 2019, 31.0 in 2020, 27.1 in 2021, and 26.2 in 2022 which equates to 6.7, 7.0, 6.1, and 5.9 lb SO_4-S per inch of water applied, respectively. A total of 53.9, 74.3, 87.2, and 76.9 lbs SO_4-S was applied over 2019, 2020, 2021, and 2022 growing season through the irrigation water, respectively. The amount of S in rainfall was not determined at any of the locations. Planting information and PRS probe sampling dates are given in Tables 2 and 3, respectively.

Early and mid-season sensing and tissue S concentration

A summary table for the ANOVA for all measured variables is given in Table 4.

Table 5. Summary of early plant vigor measured at the normalized difference red-edge (NDRE) data collected with a Crop Circle 430 active sensor collected at the V5 growth stage.

		Sulfur Source				
Location	S Rate (lb/ac)	Control	K_2SO_4	K-MST	Tiger 90	Rate Avg
Becker	5	0.345	0.350	0.349	0.357	0.350
	10	0.356	0.344	0.351	0.346	0.349
	20	0.352	0.350	0.357	0.353	0.353
	Source Avg.	0.351	0.348	0.352	0.352	
Morris	5	0.322	0.321	0.295	0.308	0.311
	10	0.308	0.305	0.316	0.302	0.308
	20	0.312	0.297	0.321	0.322	0.313
	Source Avg.	0.314	0.308	0.310	0.311	
Rosemount	5	0.237	0.293	0.304	0.272	0.277b
	10	0.250	0.317	0.308	0.288	0.291a
	20	0.255	0.318	0.308	0.306	0.297a
	Source Avg.	0.247c	0.309a	0.307a	0.289b	
Waseca	5	0.244	0.223	0.246	0.216	0.232
	10	0.241	0.235	0.241	0.234	0.238
	20	0.243	0.253	0.226	0.239	0.240
	Source Avg.	0.243	0.237	0.237	0.230	

Plant vigor was assessed at the V5 growth stage using a Crop Circle 430. A summary of the normalized difference red-edge index is given in Table 5. Early season NDRE differed based on sulfur rate and source at Rosemount. Unlike in years past, there was no rate by source interaction at any location. The

Rosemount data found similar NDRE values for the sulfate and MST treatments and no increase in NDRE when more than 10 lbs of S were applied per acre.

Table 6. Summary of leaf S concentration measured from the uppermost fully developed corn leaf at the V10 growth stage at four Minnesota locations during the 2022 growing season.

Location	S Rate (lb/ac)	Sulfur Source				Rate Avg
		Control	K_2SO_4	K-MST	Tiger 90	
		--------------V10 Upper Leaf %S--------------				
Becker	5					
	10					
	20					
	Source Avg.					
Morris	5					
	10					
	20					
	Source Avg.					
Rosemount	5					
	10					
	20					
	Source Avg.					
Waseca	5					
	10					
	20					
	Source Avg.					

Corn V10 leaf S concentration data is being analyzed but the data has not been returned from the U of MN soil testing laboratory that was collected in 2022.

Corn V10 leaf SPAD meter readings were impacted only by sulfur source at Rosemount and Waseca. Rate and source main effects were only significant at Rosemount, and the rate by source interaction was not significant at any location. Sources did vary at Rosemount and Waseca with V10 SPAD readings being similar between sulfate-S and MST, followed by Tiger 90, and finally the control which averaged the lowest SPAD values (Table 7). At Rosemount the 5 and 10 lb S rates did not differ in average SPAD values but both had lower values than the 20 lb S rate.

Table 7. Summary of SPAD meter reading collected from the middle of the uppermost fully developed corn leaf at the V10 growth stage at four Minnesota locations during the 2022 growing season.

Location	S Rate (lb/ac)	Sulfur Source				Rate Avg
		Control	K_2SO_4	K-MST	Tiger 90	
Becker	5	43.5	42.8	42.9	44.3	43.4
	10	43.7	45.0	44.4	44.6	44.4
	20	44.8	43.8	43.6	46.3	44.6
	Source Avg.	44.0	43.9	43.6	45.0	
Morris	5	40.9	40.5	39.4	42.0	40.7
	10	41.5	42.3	42.1	41.9	41.9
	20	39.7	41.9	40.2	40.9	40.7
	Source Avg.	40.7	41.5	40.5	41.6	
Rosemount	5	40.7	46.4	46.9	42.7	44.2b
	10	39.8	46.4	46.6	44.9	44.4b
	20	42.6	49.9	47.6	48.6	47.2a
	Source Avg.	41.0c	47.6a	47.0a	45.4b	
Waseca	5	47.0	51.5	52.0	50.1	50.1
	10	46.2	51.5	52.1	51.0	50.2
	20	48.4	52.7	51.0	51.5	50.9
	Source Avg.	47.2c	51.9a	51.7ab	50.8b	

Table 8. Summary of leaf S concentration measured from the corn leaf opposite and below the ear at the R1 growth stage at four Minnesota locations during the 2022 growing season.

Location	S Rate (lb/ac)	Sulfur Source				Rate Avg
		Control	K_2SO_4	K-MST	Tiger 90	
		--------------R1 Ear Leaf %S---------------				
Becker	5					
	10					
	20					
	Source Avg.					
Morris	5					
	10					
	20					
	Source Avg.					
Rosemount	5					
	10					
	20					
	Source Avg.					
Waseca	5					
	10					
	20					
	Source Avg.					

Corn R1 leaf S concentration was collected and processed and submitted to the U of MN soil testing laboratory. However, the laboratory is still analyzing the samples so the data are not available at this time for this report. Table 8 and 9 are left blank and the data will be added when available.

Table 9. Summary of leaf S concentration measured from the uppermost fully developed corn leaf at the R1 growth stage at four Minnesota locations during the 2022 growing season.

		Sulfur Source				
Location	S Rate (lb/ac)	Control	K_2SO_4	K-MST	Tiger 90	Rate Avg
		--------------R1 Upper Leaf %S---------------				
Becker	5					
	10					
	20					
	Source Avg.					
Morris	5					
	10					
	20					
	Source Avg.					
Rosemount	5					
	10					
	20					
	Source Avg.					
Waseca	5					
	10					
	20					
	Source Avg.					

Table 10. Summary of SPAD meter reading collected from the middle of the leaf opposite and below the ear at the R1 growth stage at four Minnesota locations during the 2022 growing season.

		Sulfur Source				
Location	S Rate (lb/ac)	Control	K_2SO_4	K-MST	Tiger 90	Rate Avg
Becker	5	49.7	49.6	48.1	48.6	49.0
	10	48.5	49.3	49.1	50.3	49.3
	20	48.5	49.4	48.6	49.4	49.0
	Source Avg.	48.9	49.4	48.6	49.4	
Morris	5	48.6	49.6	46.8	48.7	48.4
	10	49.1	49.9	48.2	48.1	48.8
	20	49.4	48.5	50.5	49.1	49.4
	Source Avg.	49.0	49.3	48.5	48.6	
Rosemount	5	48.7	53.4	53.5	50.7	51.6bb
	10	47.6	54.9	52.1	52.3	51.7
	20	50.6	56.2	55.7	56.0	54.6a
	Source Avg.	49.0c	54.8a	53.8ab	53.0b	
Waseca	5	36.9	43.8	44.9	42.7	42.1c
	10	38.8	47.8	45.3	43.9	43.9b
	20	38.2	48.2	48.4	48.0	45.7a
	Source Avg.	38.0c	46.6a	46.2ab	44.9b	

Table 11. Summary of SPAD meter reading collected from the uppermost fully developed corn leaf at the R1 growth stage at four Minnesota locations during the 2022 growing season.

		Sulfur Source				
Location	S Rate (lb/ac)	Control	K_2SO_4	K-MST	Tiger 90	Rate Avg
Becker	5	42.6	38.9	41.2	41.2	41.0
	10	41.4	40.5	41.0	43.4	41.5
	20	39.5	40.0	43.4	42.1	41.2
	Source Avg.	41.1ab	39.8b	41.8a	42.2a	
Morris	5	50.7	52.1	48.9	50.4	50.5
	10	50.0	52.6	49.5	50.1	50.6
	20	51.1	49.7	51.3	49.9	50.5
	Source Avg.	50.6	51.5	49.9	50.1	
Rosemount	5	41.3	46.5	46.1	43.9	44.4b
	10	41.3	47.4	44.0	44.1	44.2b
	20	45.3	48.2	47.4	48.4	47.3a
	Source Avg.	42.6c	47.3a	45.8b	45.5b	
Waseca	5	38.8	44.3	45.6	42.7	42.8b
	10	39.2	46.7	47.4	45.0	44.6a
	20	39.7	47.5	48.2	47.3	45.7a
	Source Avg.	39.2d	46.1b	47.1a	45.0c	

Leaf SPAD readings from the leaf opposite and below and the uppermost fully developed leaf at the R1 growth stage are summarized in Tables 10 and 11, respectively. Leaf SPAD meter readings were only impacted by sulfur rate and source at Rosemount and Waseca, but the rate by source interaction was not significant. Results did vary for both the ear- and upper leaves. Sulfate application resulted in the greatest SPAD readings except for the upper leaf readings at Waseca where SPAD readings were greater with MST. Tiger 90 generally resulted in lower SPAD values compared to sulfate but sometimes did not differ with MST. The results over the four years (not shown) have generally indicated greater leaves when sulfate was applied followed by MST then Tiger 90 which sometimes did not differ from the no sulfur control.

Table 12. Summary of corn grain yield response to S source and rate at four Minnesota locations during the 2022 growing season.

Location	S Rate (lb/ac)	Sulfur Source				Rate Avg
		Control	K_2SO_4	K-MST	Tiger 90	
		--------Corn Grain Yield at 15.5% Moisture (bu/ac)--------				
Becker	5	182	177	167	182	177
	10	180	196	192	200	192
	20	195	187	184	196	190
	Source Avg.	186	187	181	192	
Morris	5	212	217	193	200	205
	10	196	200	199	200	199
	20	204	180	216	205	201
	Source Avg.	204	199	203	202	
Rosemount	5	151	192	197	185	181b
	10	154	213	173	178	179b
	20	175	212	220	211	205a
	Source Avg.	160c	206a	196ab	191b	
Waseca	5	106	147	146	135	133b
	10	108	162	148	150	142ab
	20	115	168	153	162	150a
	Source Avg.	110c	159a	149b	149b	

Corn grain yield data are summarized in Table 12. There was no effect of sulfur source and rate on corn grain yield at Becker or Morris in 2022. Sulfur source and rate affected corn grain yield at both Rosemount and Waseca in 2022. At Rosemount, corn grain yield was increased by roughly 45 bushels per acre when sulfate was applied. Tiger 90 did increase corn grain yield at Rosemount but not to the level of sulfate and MST produced yields somewhere between sulfate and Tiger 90. Waseca on the other hand had much greater yield when sulfate was applied and no difference between MST and Tiger 90, both which yielded more than the control but less than sulfate. At both sites the 20 lb S rate yielded greater than 5 or 10 lbs S, which did not differ from each other. Overall yield levels were lower at Waseca due to high Western corn rootworm pressure which resulted in lodging throughout the study. The corn hybrid planted was rootworm resistant but it appears that the genetic resistance in the plant is breaking down at Waseca. We will be implementing different strategies in 2023 to hopefully reduce rootworm pressure at this site.

Table 13. Source and rate main effect means across four years 2019, 2020, 2021, and 2022 at four Minnesota locations. Within each main effect, within rows, numbers followed by the same letter are not significantly different at *P*≤0.10.

	Source Rate Effect				Rate Main Effect		
Location	Control	K-Sulfate	K-MST	Tiger 90	5	10	20
	Bushels per acre at 15.5% moisture						
Becker	197	200	196	197	189b	200a	202a
Morris	200	199	199	203	201	200	200
Rosemount	186b	207a	207a	201a	197b	195b	209a
Waseca	119c	177a	174a	153b	147b	158a	162a

Three-year yield means are summarized in Table 13. Only main effects were studied for the combined analysis as the data analysis never found a significant source by rate interaction. Source effects only occurred at Rosemount and Waseca. At Rosemount the three-year yield average indicated no difference in corn grain yield among the sulfur source and all increased yield compared to the control. At Waseca, sulfate and MST produced similar yield that were greater than yield produced with Tiger 90. Tiger 90 did increase corn grain yield at Waseca compared to the control. Rate effects were significant at Becker and Waseca. Source effects were not significant at Becker indicating little difference in yield based on the source applied. However, it is puzzling that the three sulfur sources did not increase corn grain yield over the control at Becker yet there was a response to rate. In addition, the sulfate sulfur concentration in well water has been high at Becker and should provide more available sulfur to a crop that is required. At Becker and Waseca, the 10 lb rate resulted in the greatest yield and there was no advantage of applying 20 lbs of S compared to 10. At Rosemount 20 lbs of S on average was required to maximize corn grain yield.

Corn grain S concentration was measured but the data has not been returned from the U of MN soil testing lab. Table 14 is left blank and the data will be added when available.

Table 14. Summary of corn grain S concentration response to S source and rate at four Minnesota locations during the 2022 growing season.

Location	S Rate (lb/ac)	Sulfur Source Control	K_2SO_4	K-MST	Tiger 90	Rate Avg
		--------------Corn Grain %S Concentration--------------				
Becker	5					
	10					
	20					
	Source Avg.					
Morris	5					
	10					
	20					
	Source Avg.					
Rosemount	5					
	10					
	20					
	Source Avg.					
Waseca	5					
	10					
	20					
	Source Avg.					

Soil sulfate-S content was measured post-harvest and was not affected by sulfur source or rate at any locations (Table 15).

Table 15. Summary of post-harvest two-foot soil extractable sulfate-S response to S source and rate at four Minnesota locations during the 2022 growing season.

Location	S Rate (lb/ac)	Sulfur Source Control	K_2SO_4	K-MST	Tiger 90	Rate Avg
		--------------Fall 2' Soil Sulfate-S (lb/ac)--------------				
Becker	5	93	86	89	79	87
	10	84	96	88	85	88
	20	95	87	102	89	93
	Source Avg.	90	90	93	85	
Morris	5	85	82	68	82	79
	10	91	157	94	90	108
	20	91	98	96	96	95
	Source Avg.	89	112	86	89	
Rosemount	5	112	109	102	110	108
	10	113	104	109	101	107
	20	112	108	117	115	113
	Source Avg.	112	107	109	109	
Waseca	5	102	101	105	95	101
	10	135	99	108	98	110
	20	115	109	97	101	105
	Source Avg.	117	103	103	98	

PRS Soil Ion Probe Results

Table 16. Summary of ANOVA for plant root simulator (PRS) probe data collected from only the 10 lb S application rate plots at four Minnesota locations during 2022.

Main Effect	Becker	Morris	Rosemount	Waseca
	-----------------------------------	---------*P*>F	-----------------------------------	
		Change in 0-12” Soil Test S		
Time	***	***	***	***
Source	0.79	0.10	**	*
Time x Source	0.90	0.62	0.48	0.91
		Daily S Supply Rate		
Time	***	***	***	***
Source	*	*	***	***
Time x Source	0.37	0.42	**	***
		Cumulative S Recovery		
Time	***	***	***	***
Source	**	**	**	**
Time x Source	*	*	**	***

Table 16 summarizes the ANOVA results for 0-12” soil sample and PRS data collected over the summer of 2022. Plant root simulator (PRS) probes were installed in plots receiving 10 lbs of S at all locations. The use of the PRS probes is to better determine availability of S from the fertilizer sources over time as the probes simulate potential sulfate-S uptake form the soil by a plant’s root. Soil samples were additionally collected at the time the PRS samples were taken and before the initial PRS application at 0-6 and 6-12” depths. For simplicity, data from both sampling depths were combined for the analysis presented in this paper. Figure 1 summarizes the change in soil sulfate-S assessed using the mono-calcium phosphate procedure from the initial PRS plot sampling at a depth of 0-12”. Change in soil sulfate-S predictably varied based on sampling time but was seldom impacted by S source or rate in 2022. There are a few exceptions as noted by asterisks in the figures where the sources varied at specific dates. The soil test data in Figure 1 shows that the soil test itself has an inability to detect differences among treatments and that there is significant variation in soil test sulfate-S over time. In fact, values for total sulfate-S varied by as much as 20 lbs per acre from one time to the next. While we will continue to measure soil sulfate-S it has little value in helping determine when sulfate is made available from various sources.

Figure 2 summarizes the average daily flux in sulfate-S measured with the PRS probes (calculated based on the total amount of sulfate sorption divided by burial time). Like the change in soil sulfate-S, sulfate-S flux always varied with time at all locations. Unlike previous years, source main effects were significant at all locations, but the source by time interaction was only significant at Rosemount and Waseca. Asterisks again denote dates at the two locations where sources did vary. The fluxes in general were greater for the sulfate sources but also differences could be seen for the MST sources while Tiger 90 was seldom different from the control. This would match with the yield data where sulfate and MST typically yielded more than Tiger 90 indicating less available S from Tiger 90. What is interesting is that the differences in sulfate flux were magnified earlier or later in the growing season similar to 2021. I have not matched any of this data with the soil moisture data collected to see if the lack of moisture would slow the amount of sulfate sorption to the PRS probes. It is likely that as soils dry the amount of sulfate sorbed would change, especially in the upper part of the soil profile where the PRS probes were installed. The lack of a crop, or less crop growth with roots competing for uptake of sulfate also may explain some of the effect. What we can clearly say is that the PRS probes are better at determining when sulfate is available from the fertilizer sources compared to using soil test sulfate-S.

Cumulative sulfate-S sorption is summarized in Figure 3. The cumulative data makes it easier to visualize the amount of sulfate coming from the fertilizer sources. Main effects and interactions were significant at all locations. Asterisks again denote specific dates were sources varied except for at Waseca were sources varied at all dates and the interaction was a result of situations where sulfate and MST did vary at early sampling dates but did not vary at the last three dates. By examining the data it can be clearly seen that sulfate and MST provided more available sulfate over the growing season at 3 of the 4 locations. The exception was Becker where Tiger 90 supply was greater over the growing season compared to sulfate and MST which were greater than the control. At two of four locations Tiger 90 did not result in significant sulfate sorption on the PRS probes compared to the control. At Waseca, Tiger 90 was only marginally better than the control. There was a lag in availability of the MST where oxidation appeared to be slow within the first month after application. This effect has been consistent across years of the study. However, yield data would confirm that this lack of initial availability did not impact corn grain yield.

Since elemental S is not mobile it is not surprising to start to see greater S sorption at mid to late stages of the growing season as soils warm and the elemental S begins to oxidize. Elemental S is hydrophobic by nature and do not dissolve in water. Some have reported that elemental S co-granulated will tend to clump together as the fertilizer granule dissolves in the soil thereby increasing the surface area of the elemental S in the soil and decreasing the oxidation rate. The previous statement can explain the poor performance of the Tiger 90 product in most soils. The smaller pore size in the medium and fine textured soils would limit the ability of the ground elemental S particles to move in the soil. The MST on the other hand has a much smaller particle size and might move slightly farther away from other particles in the same fertilizer granule which could explain a greater effectiveness of the product. It did appear that elemental S in Tiger 90 was supplying some S to the plant based on S uptake and grain yield data. However, the supply of S from Tiger 90 is consistently less compared to elemental S in MST. The exception is Becker where sources did not differ, but grain yield was impacted by rate. However, the total amount of sulfate S applied in irrigation water at Becker should have negated any need for sulfur at the site. The data indicates that sulfate S or elemental S ground finer are better options for corn production.

Table 17. Summary of ANOVA for soil sulfatase activity for the 2019 soil samples collected as PRS probes were sampled during 2019.

Main Effect	Becker	Morris	Rosemount	Waseca
	------------------------------------	-----*P*>F-----	------------------------------------	
Time	**	***	***	***
Source	0.24	0.69	0.58	0.99
Time x Source	0.87	**	0.65	**

Sulfatase activity was measured on all 0-6" soil samples collected with the PRS samples. A summary of the analysis of variance for the 2019 soil test results is given in Table 17 and treatment means are summarized in Figure 4. Sulfatase activity varied over time at all locations, but sources generally did not vary. Overall activity was greatest at Morris, least at Becker, and in the middle and similar between Rosemount and Morris. Sulfatase activity itself cannot be used to determine where a sulfur response will occur. The source main effect was not significant. However, significant source by time interactions might indicate some difference among sources at specific sample times. A further analysis of the data will be needed to sort through these interactions. We will be analyzing data again following the 2022 growing season before the start of Phase II. The samples are currently being run but the data are not available. The plan is to run the full set of samples taken during the PRS collection from 2022. If treatments do not differ then I will not run any further samples collected in 2020 or 2021.

Lab incubation work and XANES analysis

The lab study focused on elemental S oxidation at 25ºC was completed in 2022. Table 18 and 19 summarize the amount of sulfate-S and nitrite- and nitrate-N for the initial leaching event and at 112 days incubation are given in Tables 18 and 19, respectively. The calcium sulfate treatment was included to determine whether all sulfate can be leached form the soils with the amount of water applied. The total amount of sulfate-S leached ranged from 15-24% with the first leaching event (Table 18) and roughly 22 to 78% was leached by the last sampling (Table 19). I need to double check the calculations for the % leached as the amount of sulfate leached from gypsum is low compared to previous runs. One thing that I need to determine is how the data was reported from the ion chromatagraph to make sure that the data does not need to be adjusted. We should be getting almost full recovery of the sulfate from the gypsum as it is water soluble and should be readily leached.

Of main interest was the oxidation potential for elemental S. In this case, total oxidation of elemental S ranged from 27 to 79% across the soil following 112 days incubation at 25ºC. Values were greater than what was found for the 15ºC run which is not surprising as temperature should have a major impact on oxidation of elemental S. I have not fit curves to the oxidation rates for all the soils for the 5, 15, and 25ºC runs. My plan is to model each run then use the slope of the linear regression to regress with the run temperature. This should give an estimate of oxidation rate based on temperature. The same will also be conducted looking at mineralization rate of sulfate and nitrate based on temperature. No additional runs are planned for this work.

Results of the XANES analysis are summarized in Figures 5 and 6. Figure 5 summarizes the specific types of sulfur identified over time in each soil. For discussion purposes I am going to focus on Figure 6 which summarizes the data comparing inorganic and organic sulfur sources and reduced and oxidized sulfur sources. The bulk of the sulfur identified over time could be classified as organic sulfur which is not surprising as it is estimated that as much as 95% of total available S comes from mineralized organic sulfur on a yearly basis. There were some slight variations between organic and inorganic sulfur over time but they were relative small except for a few occasions where the amount of measured inorganic sulfur reached roughly 50% of the total S. One item I need to address is how this data matches with soil moisture content over time. I have gravimetric soil moisture content for all soils collected. The bulk of the sulfur was in the oxidized form. There were fluctuations over time between oxidized and reduced forms of sulfur. The most extreme case was Becker 2020 where most of the sulfur was identified in the reduced form. Higher variability would be expected at Becker due to a lower total S concentration in the soil (not shown). Lower S concentrations might be more impacted by subtle changes in sulfur forms over time. Again, I have not matched this data with soil moisture. Greater soil moisture should limit soil aeration which should increase the amount of reduced S forms. Becker should be more porous where there should be more oxidized sulfur forms. What I wanted to see is whether more reduced forms of S might be present at Morris as the soils at Morris tended to be more saturated with higher water contents (not shown). Total reduced S forms did not appear to be more over time at Morris compared to the other locations. I will be looking at this data more as there is a lot of data between the XANES analysis and the laboratory studies. Both will be discontinued after 2022 as we have enough information at this time and need to work through the data that is available before collecting anything new.

Table 18. Summary of the initial sulfate-S and nitrate- and nitrite-N leaching at time 0 and percent recovery of sulfate from the gypsum treatment for soils incubated at 25ºC.

Soil	Control	Elemental S	Calcium Sulfate	% Recovery	Nitrite-N	Nitrate-N
	------------------------ ug g^{-1}	------------------		--%--	-------- ug g^{-1}	--------
Barnes	1	1	22	21	1	0
Canisteo	3	2	10	7	23	0
Clarion	2	2	17	15	1	0
Colvin	12	17	14	2	5	0
Cordova	3	3	14	11	7	0
Estherville	3	3	16	13	4	0
Fargo	4	4	16	12	9	0
Formdale	1	1	17	16	2	0
Gunclub	4	5	17	13	16	0
Hegne	3	3	15	12	14	0
Hubbard	1	1	27	26	1	0
Lester	1	1	20	19	2	0
Nicollet	2	2	21	19	2	0
Normania	2	2	18	16	2	0
Okaboji	3	2	17	14	4	0
Pierz	1	2	18	17	2	0
Port Byron	2	1	12	10	4	0
Seaton	3	2	14	11	6	0
Storden	2	1	23	21	1	0
Tara	2	1	13	11	2	0
Verndale	1	1	23	22	1	0
Ves	2	2	15	13	1	0
Waukegan	1	2	14	13	4	0
Webster	2	2	15	13	3	0
Wheatville	5	5	13	8	13	0
Zimmerman	1	1	26	25	3	0

Table 19. Summary of sulfate-S and nitrate- and nitrite-N cumulative leaching at 112 days and percent recovery of sulfate from the elemental-S and gypsum treatment for soils incubated at 25°C.

				% Recovery			
Soil	Control	Elemental S	Calcium Sulfate	Elemental S	Calcium Sulfate	Nitrite-N	Nitrate-N
	---------------------ug g^{-1}---------------			--------%--------		-------- ug g^{-1}--------	
Barnes	27	67	95	39	68	114	13
Canisteo	34	61	55	27	22	246	13
Clarion	28	86	75	57	46	125	1
Colvin	134	170	181	36	47	169	12
Cordova	33	78	76	45	43	216	13
Estherville	29	110	70	81	41	105	2
Fargo	51	84	90	33	39	226	26
Formdale	28	58	78	30	50	147	27
Gunclub	47	74	82	27	35	186	19
Hegne	39	71	79	32	40	195	34
Hubbard	15	79	89	64	75	36	0
Lester	25	89	79	64	54	143	1
Nicollet	29	100	90	71	61	118	5
Normania	24	64	76	40	52	115	3
Okaboji	39	82	86	43	48	128	23
Pierz	29	109	79	80	50	166	2
Port Byron	36	106	64	70	28	134	14
Seaton	26	81	68	55	42	106	2
Storden	31	72	95	41	64	125	0
Tara	30	67	68	38	38	155	3
Verndale	29	101	89	72	60	84	12
Ves	26	75	67	49	41	90	0
Waukegan	24	94	71	70	47	126	6
Webster	30	80	74	50	44	166	3
Wheatville	45	82	71	37	26	172	13
Zimmerman	20	98	97	79	78	71	11

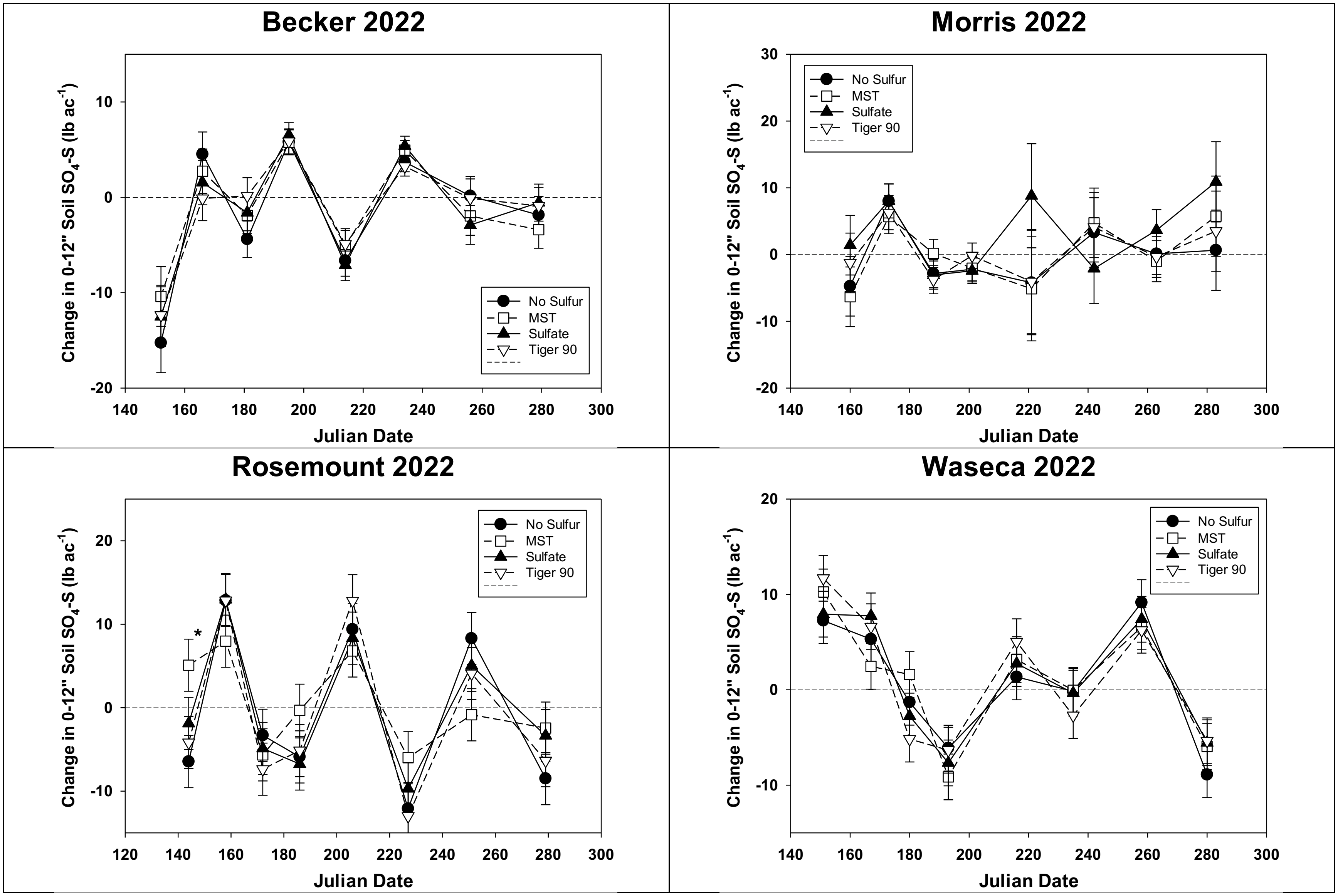

Figure 1. Summary of change in soil sulfate-S content at eight sampling dates from the initial soil sampling collected when the PRS probes were installed following the application of three sulfur sources at 10 lbs S/ac and a no-S control.

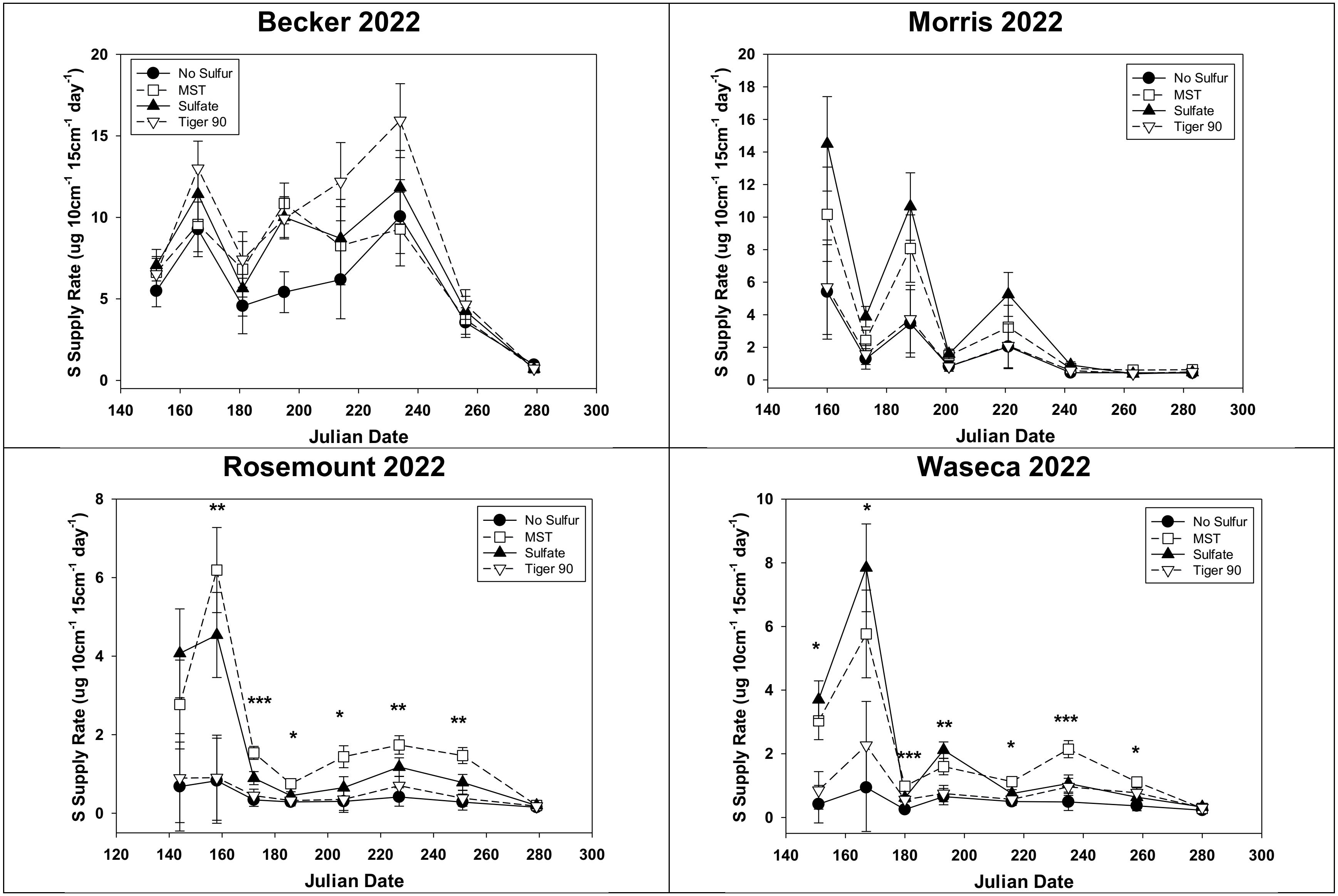

Figure 2. Summary of soil sulfate-S supply rate measured as daily sulfate-S flux by the PRS probes following application of three sulfur sources at 10 lbs S/ac and a no-S control.

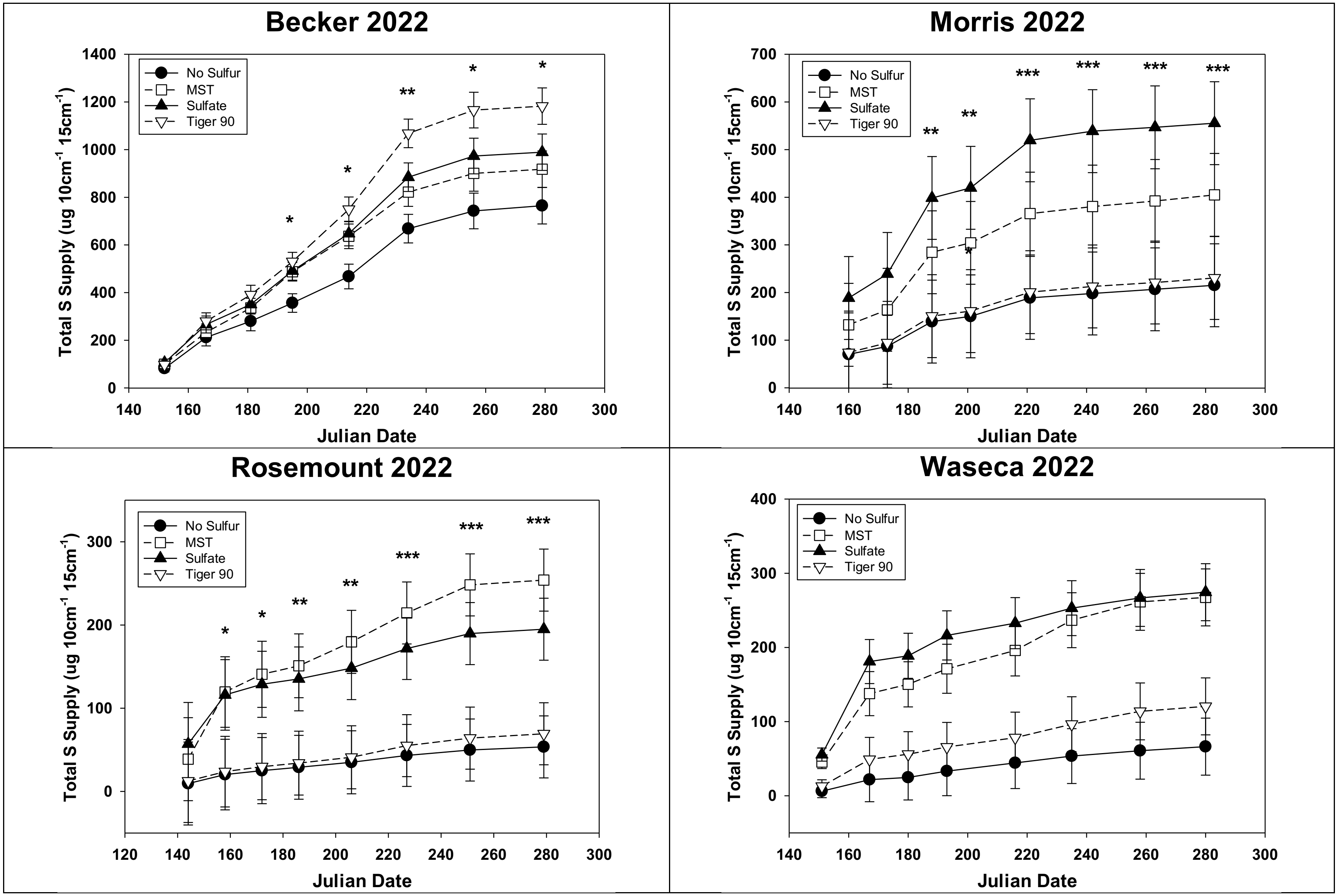

Figure 3. Summary of cumulative sulfate-S adsorption by the PRS probes following application of three sulfur sources at 10 lbs S/ac and a no-S control.

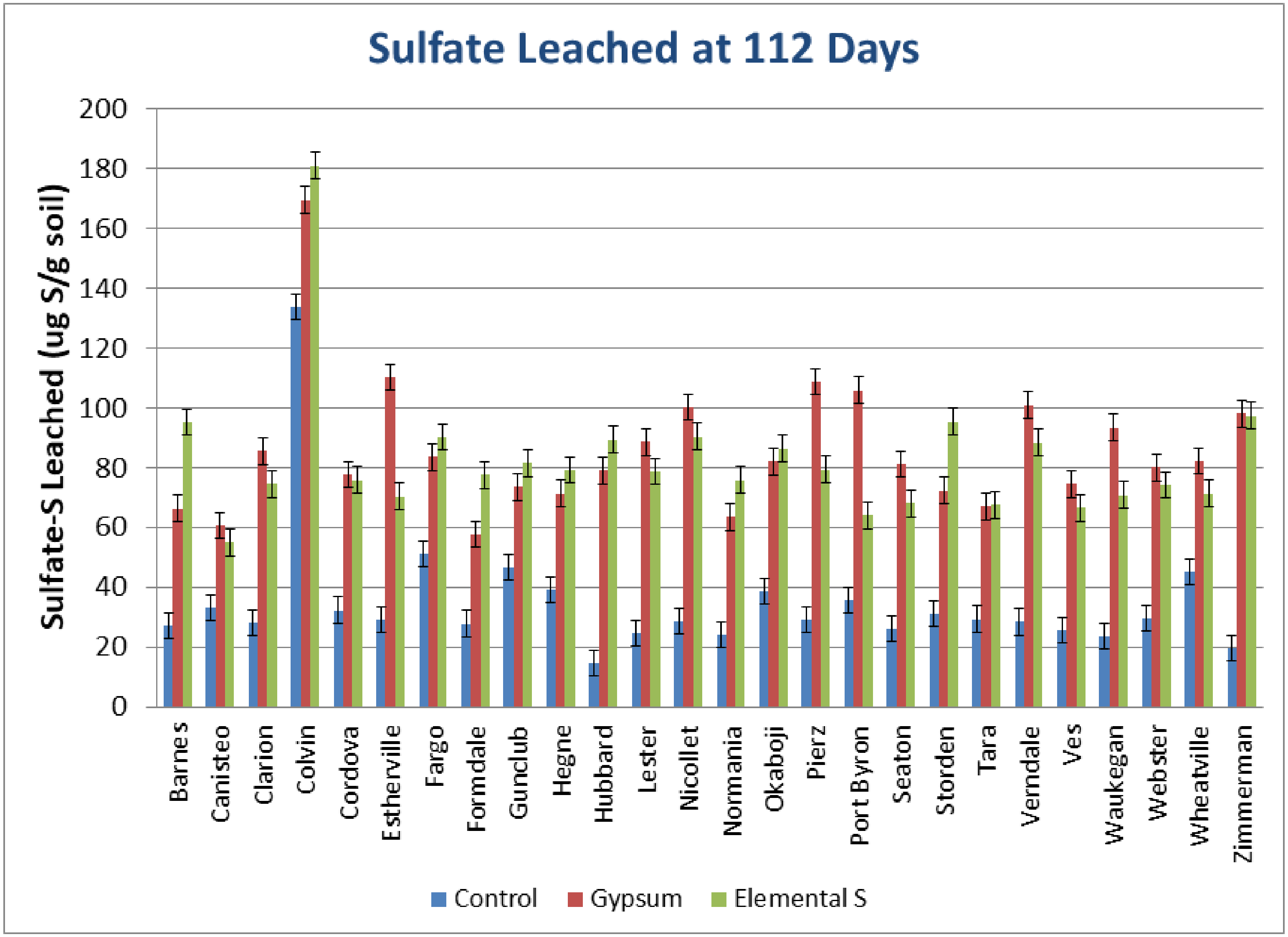

Figure 4. Summary of total sulfate-sulfur leached from soil column containing 26 separate soils from Minnesota treated with gypsum or elemental sulfur powder incubated at 25°C.

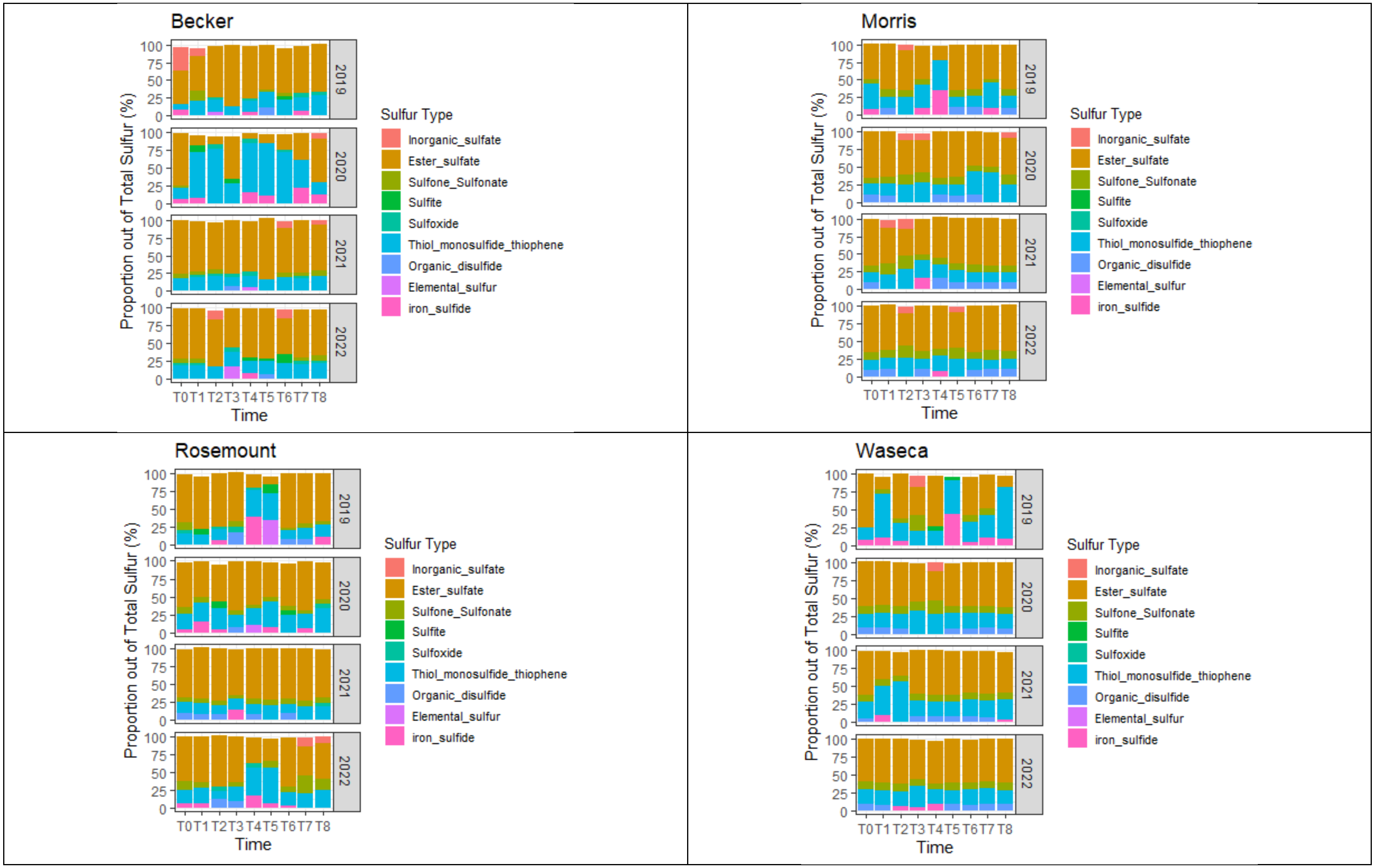

Figure 5. Summary of XANES analysis results broken down by sulfur type identified in the samples over time for the four research locations. Data was collected from plots where no sulfur was applied in 2-3 week intervals from planting to harvest.

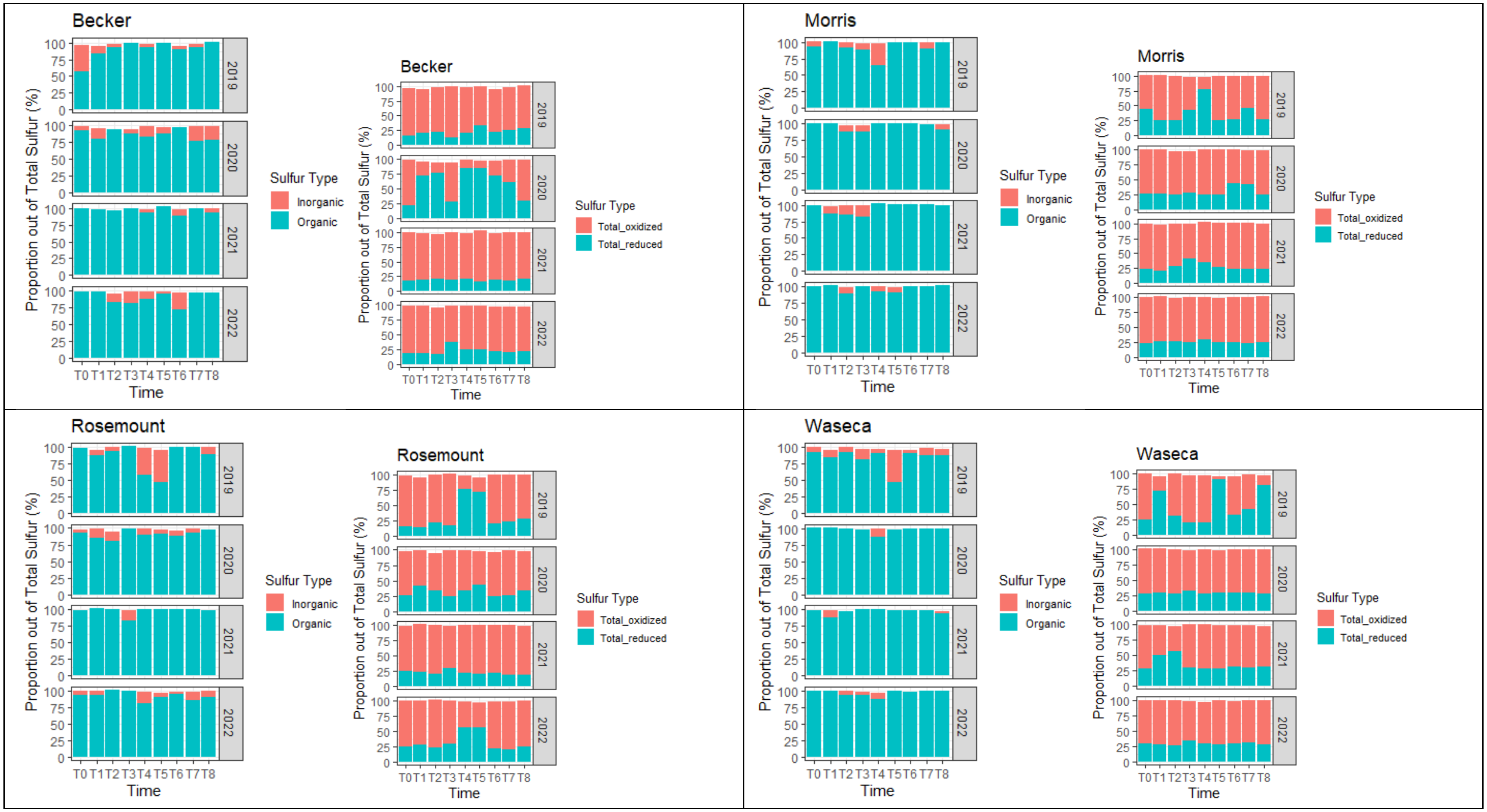

Figure 6. Summary of XANES analysis results summarized for inorganic or organic sulfur form or oxidized or reduced sulfur forms in the samples over time for the four research locations. Data was collected from plots where no sulfur was applied in 2-3 week intervals from planting to harvest.