

Flue Gas Desulfurization Products as Sulfur Sources for Corn

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Nitrogen deficiency in the soil often limits corn (*Zea mays* L.) production. Recently, S deficiency in several crops, including corn, has been observed. Little information is available, however, related to the interactive effects of N and S fertilization on corn growth and yield using modern corn hybrids. Field experiments were conducted from 2002 to 2005 to test corn response to seven rates (0–233 kg ha⁻¹) of N and two rates (0 and 33 kg ha⁻¹) of S applied to a silt loam soil at Wooster, OH. The S was applied as flue gas desulfurization (FGD) products and was primarily in the form of gypsum. Corn grain yields were significantly ($P \leq 0.05$) increased by N fertilizer addition from 2003 to 2005. Sulfur addition also significantly increased the average yield of corn in 2002 and 2003. An N \times S interaction for corn yield was observed in 2005. Sulfur application at 33 kg ha⁻¹ significantly ($P \leq 0.05$) increased corn yield at the intermediate N rate of 133 kg ha⁻¹, and showed a general tendency to increase yield at lower N rates in 2004 and 2005. Nitrogen and S concentrations in corn grain were increased by application of 200 kg N ha⁻¹, and S concentration was increased by S application in 2005. These results suggest that application of S fertilizer, with N, can promote the uptake of N by corn in S-responsive soils. This will decrease the amount of N required for high-yield corn production and reduce production costs and degradation of water quality associated with oversupply of N.

Abbreviations: FGD, flue gas desulfurization; ICP–AES, inductively coupled plasma atomic emission spectrometry.

Nitrogen is one of the primary nutrients for higher plants. It has many functions in the growth and development of crops as a constituent of proteins, nucleic acids, chlorophyll, and alkaloids (Marschner, 1995). Soils and crops are more commonly deficient in N than any other element. In the United States, 97% of the area planted to corn requires the use of N fertilizers (Economic Research Service, 1996). The optimal N fertilizer rate is very different among fields and is influenced by a number of factors including soil conditions. Scharf et al. (2005) reported that economically optimal N fertilizer rates for individual fields in the United States ranged from 63 to 208 kg N ha⁻¹. Applying excess N not only increases costs but also is increasingly implicated in water quality degradation (Gehl et al., 2005). Jaynes et al. (2001) reported that when 114 to 135 kg N ha⁻¹ was supplied to clay loam and silty clay loam soils with corn plants, NO₃ loss in tile drainage water was 35 kg N ha⁻¹, but when 172 to 202 kg N ha⁻¹ was applied, NO₃ loss was significantly increased to 48 kg N ha⁻¹.

Sulfur is also an essential element for higher plants. It is one of the most important nutrients in terms of the concentra-

tion required in the plant, often ranking just below the primary nutrients N, P, and K (Salisbury and Ross, 1992). In recent years, deficiencies of S in crops have increased worldwide (McGrath and Zhao, 1995). This is attributed to the use of highly concentrated fertilizers containing little or no S, intensive cropping systems, increased crop yields that result in more S removal from the soil every year (Chen et al., 2005), and less S deposition from the atmosphere. In Wooster, OH, annual S deposition has gradually decreased from 34.8 kg ha⁻¹ in 1979 to 22.0 kg ha⁻¹ in 2005, which represents a 37% reduction (National Atmospheric Deposition Program, 2007).

Recently, Chen et al. (2005) reported that the yields of alfalfa (*Medicago sativa* L.) and soybean [*Glycine max* (L.) Merr.] were increased by application of S fertilizer in Ohio. For corn, yield responses to S application were reported during the past 30 yr mostly on sandy soils in the Atlantic Coastal Plain and Minnesota (Rabuffetti and Kamprath, 1977; Reneau, 1983; O'Leary and Rehm, 1990). There was little or no corn yield response to S fertilizer from non-sandy soils in Illinois, Missouri, or Iowa (Hoefl et al., 1985; Stecker et al., 1995; Sawyer and Barker, 2002). O'Leary and Rehm (1990) reported that S application increased corn yield at only two of eight sites with a silt loam texture. Recently, however, Rehm (2005) reported that corn yields at all of three sites with loam, silt loam, and sandy loam soils were increased when S was applied to the soil at a rate of 6.7 kg ha⁻¹ with conservation tillage in Minnesota. This suggests that deficiencies of S in corn are increasing in the United States.

Sulfur is a structural constituent of the amino acids cysteine and methionine and hence of protein. When S is deficient, the cysteine and methionine concentrations in plants decrease and the synthesis of proteins is inhibited (Marschner, 1995). Therefore,

Soil Sci. Soc. Am. J. 72:1464–1470

doi:10.2136/sssaj2007.0221

Received 15 June 2007.

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the plant requirement for S is closely related to N nutrition. The interactions between N and S have been researched in many crops such as canola (*Brassica napus* L.) (Jackson, 2000; McGrath and Zhao, 1996), wheat (*Triticum aestivum* L.) (Wooding et al., 2000), and soybean (Sexton et al., 1998).

Flue gas desulfurization (FGD) products are created when coal is burned for energy and SO₂ is removed from the flue gas. The FGD products are usually composed of (i) CaSO₄, which is the SO₂ scrubbing reaction product, (ii) an excess of limestone, lime, and portlandite, and (iii) ash (Bigham et al., 2005; Kost et al., 2005; Chen et al., 2001). When the desulfurization process called limestone forced air oxidation is used, FGD gypsum (CaSO₄·2H₂O) is produced. The FGD gypsum has a higher CaSO₄·2H₂O content and fewer impurities than commercially available gypsum fertilizer and possesses a much smaller and more uniform particle size (Dontsova et al., 2005; Srivastava and Jozewicz, 2001). Gypsum is a quality source of S for plant nutrition and is slightly soluble in water, with solubility being 2.5 g L⁻¹. Thus gypsum can provide continued release of S to the soil for more than just the year it is applied (Shainberg et al., 1989).

The objectives of this study were to determine (i) the effects of S fertilizer applied as FGD product and (ii) the interaction effect of N and S fertilizer additions on the yield and element composition of corn grain and plant-available nutrient levels in the soil.

MATERIALS AND METHODS

For four consecutive years from 2002 to 2005, field experiments for corn production were conducted on an agricultural soil (Wooster silt loam, a fine-loamy, mixed, active, mesic Oxyaquic Fragiudalf) at the Ohio Agricultural Research and Development Center, Wooster, OH. The 2002 and 2004 corn crops were grown following soybean and the 2003 and 2005 corn crops were grown following corn. In 2002, a corn-soybean rotation field where soybean was grown in 2001 was selected for this study. There was no S fertilizer and no manure application in this field during the previous 10 yr. In 2003, the same field was used for the study but the plots, which now were on land that was previously cropped to corn, were located in a different part of the field to avoid the residual effects of the N and S fertilizers applied to the plots in 2002. Before treatments and fertilizers were applied, soil samples (0–20 cm) were collected, air dried, and analyzed as described in Sparks (1996) to determine pH, available P (Bray-1 P), exchangeable K, Ca, and Mg, cation exchange capacity, and organic matter content (Table 1). Available S was extracted by the Mehlich III extractant (Mehlich, 1984), and the S concentration was determined by inductively coupled plasma atomic emission spectrometry (ICP–AES). At the beginning of the experiment in 2002 and 2003, the experimental site was treated with 35 kg P ha⁻¹ as Ca(H₂PO₄)₂·H₂O and 50 kg K ha⁻¹ as KCl fertilizers based on soil test results and the Ohio Agronomy Guide (Ohio State University Extension, 1995) recommendations. In 2004 and 2005, a different soybean–corn rotation field on the same farm was used for this study, with the plots in this field moved in 2005 from their location in 2004. The 2005 plots were on land where a corn crop had been grown the previous year. This field was treated with 30 kg P ha⁻¹ as Ca(H₂PO₄)₂·H₂O and 50 kg K ha⁻¹ as KCl as recommended by soil analysis. Based on

Table 1. Selected characteristics of the Wooster silt loam soil (0–20-cm depth) from corn fields before application of N and S fertilizers.

Year†	pH	Bray-1 P	Exchangeable cations			CEC‡	Mehlich III S	Organic matter
			K	Ca	Mg			
2002	6.8	27.0	125	1050	208	7.4	33.9	25.2
2004	6.9	29.0	102	1170	245	8.1	46.7	30.1

† Soil characteristics for the field used in 2002 and 2003 noted as 2002 and for the field used in 2004 and 2005 noted as 2004.

‡ Cation exchange capacity.

analyses we conducted, the total amount of S applied with these fertilizers totaled <1 kg ha⁻¹.

Two sources of S fertilizer were used in this study. One was FGD product from Sorbent Technologies Corporation (Twinsburg, OH) produced when a perlite-based sorbent removed S from the flue gases (Chen et al., 2005). The other was FGD gypsum as a limestone forced-air oxidation product obtained from Cinergy Corporation (Cincinnati, OH). Total elemental concentrations of these materials were determined by ICP–AES and are reported in Table 2. The FGD gypsum has higher purity than commercially available agricultural gypsum (Dontsova et al., 2005).

Nitrogen fertilizer as NH₄NO₃, a readily available source of N, was applied at rates of 0, 67, 100, 133, 167, 200, and 233 kg N ha⁻¹ and S fertilizer (FGD product in 2002 or FGD gypsum in 2003, 2004, and 2005) was applied at rates of 0 and 33 kg S ha⁻¹ in April. The 33 kg S ha⁻¹ rate was used as it supplies sufficient nutrient compared with that taken up by crops or leached from the soil (Kost et al., 2008). The experimental design was a split plot in a randomized complete block with four replicates. Different N rates were applied to plots of 6.1 by 7.6 m as the main plot treatments. Sulfur applications were the subplot (3.0 by 7.6 m) treatments. The S and N fertilizer treatments were broadcast and immediately incorporated into the soil to a depth of 20 cm using a rototiller. Corn (Pioneer 34G81 in 2002

Table 2. Concentrations of major and trace elements in the flue gas desulfurization (FGD) product and FGD gypsum†.

Element	FGD product	FGD gypsum
Major elements, g kg ⁻¹		
Al	19.6	0.228
Ca	260	213
Mg	27.1	0.112
S	67.1	164
Fe	16.5	0.222
Trace elements, mg kg ⁻¹		
As	118	<11
B	194	5.8
Ba	122	5.5
Cd	<0.12	<1.0
Cr	123	<1.0
Cu	1.57	<3.0
Mn	302	1.3
Mo	13.2	<3.0
Ni	72.4	<3.0
Pb	139	<5.0
Se	<6.0	<25.0
Zn	33.2	4.8

† FGD product was from Sorbent Technologies Corporation (Chen et al., 2005) and FGD gypsum was from Cinergy Corporation.

Table 3. Monthly precipitation and average temperature at Wooster, OH, from 2002 to 2005.

Month	Precipitation					Avg. temperature				
	2002	2003	2004	2005	Normal†	2002	2003	2004	2005	Normal†
	mm					°C				
Jan.	72	47	87	149	77	1	-6	-6	-2	-3
Feb.	50	58	34	42	59	1	-4	-1	0	-2
Mar.	119	77	112	32	88	4	5	5	2	3
Apr.	104	70	102	105	85	11	11	10	10	9
May	101	136	201	58	100	13	15	18	13	15
June	83	278	228	138	100	21	20	20	23	20
July	22	182	92	102	104	24	22	21	23	22
Aug.	50	95	124	122	92	23	22	20	22	21
Sept.	90	138	86	69	80	20	17	18	19	17
Oct.	49	46	48	74	60	10	10	12	11	11
Nov.	71	80	65	52	71	4	8	7	7	5
Dec.	90	67	79	22	73	-1	0	0	-3	-1
Total	901	1275	1255	965	989					
Total (May–Sept.)	346	830	731	490	476					

† Average from 1982 to 2005.

and 2003, Pioneer 35P80 in 2004, and Pioneer 36B10 in 2005) was planted at a population of 79,000 plants ha⁻¹ at a row width of 76 cm on 22 May 2002, 19 May 2003, 14 May 2004, and 5 May 2005. Herbicides were used to control weeds. Corn was harvested from the middle two rows of the four-row plots on 23 Oct. 2002, 24 Oct. 2003, 1 Nov. 2004, and 8 Dec. 2005. Corn yields were calculated based on 15.5% moisture content.

Monthly precipitation and average temperature at the experimental sites are presented in Table 3. The annual total precipitation and the total rainfall from May to September of the corn growing season were below normal in 2002 and also below the typical water requirement of 510 to 560 mm during the corn growing season (Ohio State University Extension, 1995). In July, corn plants were in the stages of early tassel, silking, and blister kernel, which require approximately 6.6 to 7.6 mm of water each day and are the highest water-requiring stages for corn growth and development (Ohio State

University Extension, 1995). The total precipitation for the entire month of July in 2002 was only 22 mm, however. Thus the growing season of 2002 could be classified as a drought year.

In 2002, 2003, and 2005, harvested corn grain was dried at 60°C in a forced-air oven and ground to pass a 1-mm sieve. The grain was then analyzed for N by the combustion method (AOAC International, 2002) and for P, K, Ca, Mg, S, B, Cu, Fe, Mn, Mo, Zn, As, Ba, Cd, Cr, Pb, and Se by ICP–AES after digestion with a mixture of HClO₄–HNO₃ (Isaac and Johnson, 1985). Corn grain from 2004 was not analyzed. In October 2003 and 2005 (6 mo

after applying treatments), 16 soil samples were collected from the plots where 0 or 200 kg N ha⁻¹ (with and without S) were applied. Five soil cores from a depth of 0 to 30 cm were collected in each plot and combined to form one sample. Soil samples were air dried, crushed, passed through a 2-mm sieve, and extracted with Mehlich III extractant. Extracted elements (P, K, Ca, Mg, S, B, Cu, Fe, Mn, Mo, and Zn) were determined by ICP–AES. In July 2006, soil samples were collected from the control areas in the 2004 experimental field to a depth of 90 cm in increments of 10 cm using a hydraulic coring device. The soil was extracted with water, and S in the extract was analyzed by ICP–AES.

Data were subjected to ANOVA using the PROC GLM statement of the SAS statistics program (SAS Institute, 2004). When ANOVA generated a significant *F* value for a treatment (*P* ≤ 0.05), the means were compared by the LSD test. Comparison of S effects on corn yield at an individual N rate was analyzed by paired *t*-test using Sigmaplot (Systat Software, San Jose, CA).

RESULTS AND DISCUSSION

Soil Sulfur Concentrations

Concentrations of water-soluble S in surface (0–20 cm) soil samples from the 2004 untreated control area were only 3.8 mg kg⁻¹ (Fig. 1). In the subsoil, concentrations of water-soluble S were 4.9, 9.5, 7.9, and 6.4 mg kg⁻¹ in the 20- to 30-, 40- to 50-, 60- to 70-, and 80- to 90-cm soil layers, respectively. Water is commonly used as a S extractant (Tabatabai, 1996), and the critical water-extractable soil S concentration value for corn is 5.6 mg kg⁻¹ (Fox et al., 1964). These results indicate that corn would possibly respond to S application in this experimental field. The other common extractant used to assess available soil S content in the United States is Ca(H₂PO₄)₂ and the critical soil S concentration value for corn for this extractant is 8.0 mg kg⁻¹ (Fox et al., 1964). Because the Mehlich III extractant was used for soil analysis before treatments, higher concentrations of S were removed than if water or Ca(H₂PO₄)₂ was used as the extractant. Matula (1999) reported that only 5.3% of the total S in soils was extracted by Ca(H₂PO₄)₂ and 7.3% of the total S in soils was extracted by water, but 31.3% of the total S was extracted by the Mehlich III extractant. If we use

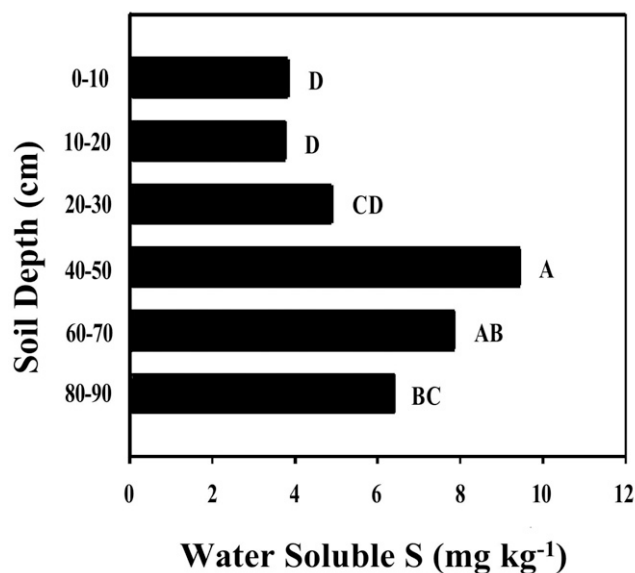


Fig. 1. Concentrations of S in water extracts at six depths of soil. Soil samples were collected in July 2006. Different letters to the right of each bar represent a significant difference at *P* ≤ 0.05.

the comparative values for water, $\text{Ca}(\text{H}_2\text{PO}_4)_2$, and Mehlich III, as reported by Matula (1999), then we can conclude that S concentrations in our soils before treatment should also be much lower with $\text{Ca}(\text{H}_2\text{PO}_4)_2$ as the extractant. In fact, according to the Mehlich III results reported in Table 1, the site used for our experiment in 2002 was actually lower in S concentration than the site used in 2004. This would suggest that the site used for our experiments in 2002 and 2003 may be more deficient in supplying S to promote good corn growth than the site used in 2004 and 2005.

Grain Yield

It must be initially noted that corn was grown following soybean in 2002 and 2004 and following corn in 2003 and 2005. This probably impacted the N response curves but should have had much less impact on the response of the S treatment. In 2002, the corn grain average yield was 2.62 Mg ha⁻¹ for the no-S treatment and 2.97 Mg ha⁻¹ for the S application (Table 4), which represented an increase of 13.4% ($P \leq 0.05$). Because 2002 was a severe drought year at Wooster (Table 3), however, the corn yield was significantly lower than normal years and did not even respond to N fertilizer (Tables 5 and 6), and the data were considered not representative of years with normal rainfall.

In 2003, corn grain yield increased with an increase in N application rates and reached a plateau at the rate of 133 kg N ha⁻¹ (Table 5). Sulfur application significantly ($P \leq 0.05$) increased the average corn yield compared with the no-S treatment (Table 4). Average yield was 10.7 Mg ha⁻¹ for the no-S treatment and 11.6 Mg ha⁻¹ for the S application treatment. This represented an 8.1% increase due to S application. There was no interaction between the N application rate and the S application rate (Table 6) on corn grain yield in 2003, similar to the results reported by O'Leary and Rehm (1990) in Minnesota.

The literature generally reports that increased corn yields are associated with S fertilizer additions to sandy soils (O'Leary and Rehm 1990). Few studies have been reported for other soils (Rehm, 2005; O'Leary and Rehm 1990). Our study indicates that S fertilizer was required to achieve improved yields of corn in Ohio, even in a silt loam soil, and agreed with the research of Rehm (2005) in Minnesota.

In 2004, compared with the control, corn yields increased with an increase in N application rates (0–233 kg ha⁻¹) when

Table 4. Effects of S fertilizer on mean yields of corn grown in Wooster silt loam from 2002 to 2005.

Treatment	Corn yield			
	2002	2003	2004	2005
kg S ha ⁻¹	Mg ha ⁻¹			
0	2.62 b†	10.74 b	9.56	5.36
33	2.97 a	11.61 a	9.96	5.86
LSD(0.05)	0.34	0.47	0.56	0.52

† Means in a column followed by different letters are significantly different at $P \leq 0.05$.

no S was applied (Table 5) and increased with N treatment up to the rate of 133 kg ha⁻¹ and then reached a yield plateau with S application. We observed an interaction of S in the FGD gypsum with N fertilizer by ANOVA ($P \leq 0.07$) (Table 6). At the rate of 133 kg N ha⁻¹, S application increased corn yield compared with no S application. At the lower rates of 0 to 100 kg N ha⁻¹ and higher rates of 200 and 233 kg N ha⁻¹, corn yields did not significantly respond to the S addition (Table 5). There was a strong tendency, however, for yield increases to occur with S application at the N rates of 0 to 100 kg N ha⁻¹. Weil and Mughogho (2000) also noted an interaction effect of N and S fertilizer additions on corn yield. They observed no response to S without N application, but with 80 kg N ha⁻¹, an application of 20 kg S ha⁻¹ significantly increased corn yield. Slightly different results were reported by Rabuffetti and Kamprath (1977). They found that corn yields were unaffected when S was applied with N at 112 kg N ha⁻¹; however, yields were increased significantly by the addition of S when N was applied at rates of 168 and 224 kg ha⁻¹.

In 2005, the addition of N increased yields compared with no N addition (Tables 5 and 6). There was a tendency for the overall mean yield of corn to also increase by application of 33 kg S ha⁻¹ ($P \leq 0.06$; Table 6). There was also a significant N × S interaction ($P \leq 0.05$; Table 6). Again this year, at the rate of 133 kg N ha⁻¹, S application significantly ($P \leq 0.05$) increased corn yield compared with no S application. At the lower rates of 0 to 100 kg N ha⁻¹ and higher rates of 200 and 233 kg N ha⁻¹, corn yields did not significantly respond to the S additions (Table 5); however, there was a general tendency for yield increase with S application at the lower rates of 0 to 100 kg N ha⁻¹.

Table 5. Effects of N and S fertilizers on corn yields grown in Wooster silt loam from 2002 to 2005.

N rate	Corn yield							
	2002		2003		2004		2005	
	0 kg S ha ⁻¹	33 kg S ha ⁻¹	0 kg S ha ⁻¹	33 kg S ha ⁻¹	0 kg S ha ⁻¹	33 kg S ha ⁻¹	0 kg S ha ⁻¹	33 kg S ha ⁻¹
kg ha ⁻¹	Mg ha ⁻¹							
0	2.69	2.76	7.93 d†	9.33 c	6.56 e	7.64 c	4.11 b	3.80 d
67	2.55	2.79	10.05 c	11.28 b	8.06 d	9.30 bc	4.16 b	5.60 c
100	2.42	2.96	10.14 bc B	11.33 b A	9.25 c	9.88 b	4.77 b	5.34 c
133	2.66	2.99	11.54 abc	12.00 ab	10.05 bc B	11.85 a A	5.59 ab B	8.24 a A
167	2.45	3.30	11.48 abc	12.04 ab	10.65 b	10.44 ab	7.35 a	6.93 b
200	2.91	3.20	11.90 ab	12.87 a	10.73 ab	10.11 ab	6.16 ab	5.26 c
233	2.64	2.83	12.12 a	12.41 ab	11.65 a	10.48 ab	5.36 ab	5.83 bc
LSD(0.05)	1.02	0.89	1.77	1.29	1.00	1.88	2.05	1.21

† Means in a column for each year followed by different lowercase letters are significantly different at $P \leq 0.05$ by ANOVA. Means in a row for each year followed by different uppercase letters are significantly different at $P \leq 0.05$ by a *t*-test.

Table 6. Statistical summary for the effect of N and S fertilizers on corn yields in Wooster silt loam from 2002 to 2005.

Treatment	P value			
	2002	2003	2004	2005
N	0.97	<0.0001	<0.0001	0.0014
S	0.04	0.0009	0.16	0.06
N × S	0.90	0.78	0.07	0.02

Table 7. Mean concentrations of plant essential major elements in corn grain harvested from plots treated with N and S fertilizer (i.e., flue gas desulfurization [FGD] product or FGD gypsum) in 2002, 2003, and 2005.

Fertilizer rate kg ha ⁻¹	N	P	g kg ⁻¹			
			K	Ca	Mg	S
<u>2002</u>						
N rate						
0	16.1	2.39	2.82 a†	0.051	1.09	1.04
100	16.8	2.41	2.83 a	0.040	1.10	1.05
200	16.5	2.28	2.69 b	0.048	1.07	1.07
LSD(0.05)	0.9	0.16	0.12	0.016	0.08	0.08
S rate						
0	16.6	2.37	2.78	0.045	1.10	1.05
33	16.3	2.34	2.79	0.048	1.07	1.05
LSD(0.05)	0.6	0.12	0.09	0.016	0.05	0.03
P value						
N	0.18	0.18	0.045	0.33	0.43	0.69
S	0.34	0.56	0.87	0.63	0.29	0.90
N × S	0.45	0.88	0.74	0.59	0.66	0.68
<u>2003</u>						
N rate						
0	12.3	2.56	3.24 a	0.050 b	1.02	0.90
100	12.7	2.44	2.98 b	0.051 b	0.96	0.92
200	13.3	2.45	3.00 b	0.076 a	0.97	0.96
LSD(0.05)	1.7	0.22	0.21	0.022	0.10	0.07
S rate						
0	13.1 a	2.39 b	2.99 b	0.058	0.95 b	0.92
33	12.4 b	2.58 a	3.16 a	0.060	1.02 a	0.93
LSD(0.05)	0.5	0.13	0.16	0.015	0.05	0.03
P value						
N	0.40	0.38	0.03	0.05	0.38	0.17
S	0.01	0.007	0.04	0.71	0.01	0.35
N × S	0.06	0.36	0.23	0.03	0.41	0.19
<u>2005</u>						
N rate						
0	12.6 b	3.19	2.42	0.038	0.87	1.00 b
100	13.5 b	3.14	2.06	0.033	0.86	1.01 b
200	15.4 a	3.40	2.21	0.038	0.90	1.12 a
LSD(0.05)	1.5	0.47	0.50	0.016	0.15	0.06
S rate						
0	13.9	3.20	2.31	0.038	0.89	1.03 b
33	13.8	3.29	2.15	0.035	0.87	1.06 a
LSD(0.05)	0.7	0.14	0.19	0.015	0.07	0.03
P value						
N	0.01	0.42	0.30	0.68	0.78	0.005
S	0.64	0.21	0.10	0.72	0.50	0.02
N × S	0.90	0.004	0.04	0.54	0.32	0.02

† Different letters in the same column within an area represent a significant difference at $P \leq 0.05$.

In both 2004 and 2005, there was a tendency for corn grain yields to decline at the highest N rates, especially when they were combined with S fertilizer additions. The reasons for this are not clear and could be simply due to statistical anomalies. It is also possible that at the higher N rates, the Ca applied with the S as gypsum (i.e., CaSO₄) may have reduced the availability of the essential cations K⁺ and Mg²⁺. This is not a totally satisfactory answer, however, as the amount of Ca added is small compared with that already in the soil.

According to *t*-tests, the only individual N application rates for which there was a significant ($P \leq 0.05$) difference between the S and no-S treatments were the intermediate N application rates of 100 kg N ha⁻¹ (2003) and 133 kg N ha⁻¹ (2004 and 2005) (Table 5). There was a tendency for yield increase with S application at the lower rates of 0 to 100 kg N ha⁻¹ (2004 and 2005). This suggests that one way to improve the efficiency of fertilizer N for growing corn is to add S with these rates of N fertilizer in S-deficient soils. This has the potential to both improve profitability and reduce NO₃ contamination of water due to excess N fertilizer use.

Concentration of Nutrients in Grain

Concentrations of N, S, and other major plant essential elements in the corn grain grown at the rates of 0, 100, and 200 kg N ha⁻¹ in 2002, 2003, and 2005 are presented in Table 7. For the N and S concentrations in corn grain, the tendencies were to increased concentrations in 2002 and 2003, and these increases were statistically significantly ($P \leq 0.05$) in 2005 by application of 200 kg N ha⁻¹ fertilizer. These results agree with the results of Rabuffetti and Kamprath (1977). Duarte et al. (2005) and Feil et al. (2005) also recently reported that the N concentration in corn grain was increased by N application. O'Leary and Rehm (1990) observed that the S concentration in whole corn plant tissue was increased by N application. Application of N significantly decreased K concentrations in 2002 and 2003 and there was a tendency to decrease K in 2005. Application of N at the rate of 200 kg ha⁻¹ increased the Ca concentration in corn grain in 2003. Application of N did not affect P and Mg concentrations in corn grain.

In 2005, the S concentration in corn grain was increased by application of S fertilizer (Table 7). In 2003, concentrations of P, K, and Mg were increased and concentrations of N were decreased by S fertilizer. The concentrations of all the other elements were not affected by the treatments of S fertilizer. Daigger and Fox (1971) and Rabuffetti and Kamprath (1977) also reported that S fertilizer (gypsum) increased the S concentration in corn grain. These increases in concentrations of N and S in the corn grain by N and S fertilizer suggest that application of N with S fertilizers may also improve the nutritional quality of corn.

Concentrations of the plant essential trace elements B, Cu, Fe, Mo, and Zn, except for Mn, were not affected by N and S fertilizers, and the data are not shown. In 2003, concentrations of Mn were decreased by N application. Concentrations in corn grain of Resource Conservation and Recovery Act (RCRA) regulated elements such as As, Ba, Cd, Cr, and Se were below detection levels (As < 2.25, Ba < 0.10, Cd < 0.10, Cr < 0.25, and Se < 5.0 mg kg⁻¹) in 2002, 2003, and 2005. The concentration of Pb was not affected in 2005 but was increased from

1.17 to 2.14 mg kg⁻¹ in 2002 and from 1.73 to 3.00 mg kg⁻¹ in 2003 by the application of 200 kg N ha⁻¹. This suggests that one way to avoid an increase in Pb concentration in corn grain is to reduce N fertilizer use by adding S with lower rates of N in S-deficient soils.

Available Nutrients in Soil

Mean concentrations of selected plant essential elements in Mehlich III extracts obtained from the 0- to 30-cm soil layer of plots treated with N at rates of 0 and 200 kg N ha⁻¹ in 2003 and 2005 are presented in Table 8. Other elements measured (i.e., Ca, Fe, Mg, Mn, Mo, and P) did not respond to N or S fertilizer application and data are not presented here. Mehlich III is a weak acid extractant commonly used to estimate the availability of nutrients in soil available for plant uptake. In 2003, application of 200 kg N ha⁻¹ increased ($P \leq 0.05$) soluble S and Zn in the soil, and application of 33 kg S ha⁻¹ increased soluble Cu. In 2005, application of 200 kg N ha⁻¹ increased available B, and application of 33 kg S ha⁻¹ increased available S and K. These results indicate that application of N or S fertilizer might increase other nutrients available for plants. Warman and Havard (1998) reported sweet corn grain S was positively correlated with concentrations of Mehlich III-extractable S in the soil from experiment plots. We also observed a concomitant increase in corn grain S concentrations from 1.03 to 1.06 g kg⁻¹ with an increase in the concentration of available soil S from 50 to 58 mg kg⁻¹ in 2005 (Tables 7 and 8).

SUMMARY AND CONCLUSIONS

Average corn yields were increased by S application in 2002 and 2003. An interaction of N × S for corn yields was observed in 2005, and there was a strong tendency for an interaction in 2004. Sulfur application at 33 kg ha⁻¹ significantly ($P \leq 0.05$) increased corn yield at the intermediate N rate of 133 kg ha⁻¹, and showed a general tendency to increase yield at lower N rates in 2004 and 2005. This suggests that less N fertilizer can be used by addition of S, and the S addition has the potential to both improve profitability and reduce NO₃ contamination of water due to excess N fertilizer use. Application to soil of N with S may also increase concentrations of N and S in corn grain.

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Table 8. Mean concentrations of essential elements in Mehlich III extracts obtained from the 0- to 30 cm soil layer of the corn field in 2003 and 2005 6 mo after treating the soil with N and S (i.e., flue gas desulfurization gypsum) fertilizers.

Fertilizer rate kg ha ⁻¹	mg kg ⁻¹				
	B	Cu	K	S	Zn
<u>2003</u>					
N rate					
0	3.00	4.30	228	61.0 b†	2.49 b
200	2.99	4.45	235	88.1 a	4.21 a
LSD(0.05)	0.21	0.22	16	8.1	1.55
S rate					
0	2.95	4.20 b	237	73.9	3.16
33	3.04	4.55 a	227	75.2	3.54
LSD(0.05)	0.10	0.20	20	14.0	1.95
P value					
N	0.86	0.11	0.30	0.0018	0.04
S	0.07	0.0052	0.28	0.84	0.66
N × S	0.39	0.12	0.79	0.57	0.34
<u>2005</u>					
N rate					
0	1.26 b	1.13	94.3	51.9	2.70
200	1.30 a	1.44	159	56.3	3.09
LSD(0.05)	0.03	0.73	110	17.4	1.04
S rate					
0	1.27	1.26	113 b	50.4 b	2.70
33	1.29	1.31	141 a	57.8 a	3.10
LSD(0.05)	0.06	0.08	28	3.2	0.55
P value					
N	0.03	0.27	0.16	0.47	0.31
S	0.59	0.16	0.05	0.001	0.13
N × S	0.59	0.05	0.67	0.88	0.17

† Different letters in the same column within an area represent a significant difference at $P \leq 0.05$.

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