



# **AVAILABLE-SULFUR STATUS OF SOME REPRESENTATIVE IOWA SOILS**

by John P. Widdowson and John J. Hanway  
Department of Agronomy

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## SUMMARY

Greenhouse experiments with ryegrass were conducted to evaluate and characterize plant availability of native and added sulfur in samples of Iowa soils. Fourteen surface soil (0-6 inches) and five subsoil (18-24 inches) samples from different sites in Iowa and two surface soil samples from S-deficient out-of-state sites were studied. Laboratory analyses were made to characterize the soil samples and to evaluate the results of different extractants as indexes of the S-supplying abilities of the soils.

Plant uptake of S from the soil samples with no added S during a 202-day cropping period (five harvests) varied from 1 to 39 mg S/1500 g of soil (39 mg S/1500 g of soil is approximately equivalent to 50 lb S/acre six inches of soil in the field). Sulfur uptake was greatest during the first 70 days of cropping (two harvests), but continued at a slower, essentially constant daily rate throughout the rest of the cropping period. Although relatively slow for all soil samples, the rate of S uptake during this later cropping varied markedly among the different soil samples, with the rates for the surface soil samples being directly related to the amounts of S taken up by the plants in the earlier cropping period. The rates of uptake were very slow from most of the subsoil samples, and many plants on these subsoils died. Air-drying the soil samples before cropping resulted in increased plant yields and increased S uptake by the plants.

Increased plant uptake of S in the harvested, above-ground portions of the ryegrass plants as a result of adding  $\text{CaSO}_4$  to the soil samples was generally equivalent to 84 percent of the added S. Total increased S uptake resulting from the S added as  $\text{CaSO}_4$  was similar for all soil samples except the two with high initial levels of available S.

The total S content of the Iowa soil samples varied from 78 to 452 ppm. Of the total S in the surface soil samples, 46 to 61 percent was HI-reducible, 5 to 14 percent was carbon-bonded, and 1 to 3 percent was present as water-soluble sulfate S. Of the total S, a higher proportion was present as HI-reducible S and as water-soluble sulfate S, and a lower proportion was present as carbon-bonded S in the subsoil samples than in the surface soil samples. The amounts of total S, HI-reducible

S, and carbon-bonded S were not related to plant availability of S in the soil samples.

The amounts of sulfate S extracted from the field-moist soil samples by a 0.1 M LiCl solution at a 1:5 soil:solution ratio were chosen as the basic estimates of water-soluble sulfate S in the soil samples. Increasing the soil:solution ratio to 1:10 resulted in an average increase of 1 ppm sulfate S extracted, and air-drying the soil samples resulted in an average increase of 2 ppm sulfate S extracted.

Water-soluble sulfate S contents of the soil samples varied from 1.6 to 10.4 ppm.  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  solution, containing 500 ppm P, extracted amounts of sulfate S similar to that extracted by the LiCl solution from all soils except the acidic (pH 5.2) Weller subsoil samples, from which  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  extracted 4 ppm more sulfate S than did the LiCl solution. Changing the pH of the  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  solution from 3.3 to 4.6 to 6.7 had no effect on the amounts of sulfate S extracted. These results indicate that Iowa soils contain little or no sorbed sulfate. A 1 M  $\text{NaHCO}_3$  solution extracted from 1.5 to 7.5 times as much sulfate S from the soil samples as did the LiCl or  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  solutions.

The amounts of sulfate S extracted by LiCl or  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  solution from the soil samples were highly, linearly correlated with the percentages of S in the ryegrass of the first harvest and with the total plant uptake of S in five harvests. Plant uptake of S, however, generally exceeded the amount of sulfate S extracted by these reagents, indicating that appreciable amounts of S were mineralized or dissolved during the cropping period. Cropping reduced the water-soluble sulfate S contents of the soil samples to less than 1 ppm in most soil samples and to less than 2 ppm in all samples.

Soil profile samples from six of the sites in May, July, and September showed relatively small, inconsistent differences with depth in sulfate concentrations to a depth of 48 inches. The mean sulfate S content of the soil profiles decreased from 5.0 to 3.6 ppm from May to September.

All the soils sampled, except possibly a loamy sand and a silt loam with very low organic matter contents, seemed to contain adequate amounts of available S to supply the needs of most crops.

# Available-Sulfur Status of Some Representative Iowa Soils<sup>1</sup>

by John P. Widdowson<sup>2</sup> and John J. Hanway<sup>3</sup>

In recent years, deficiencies of S in crop plants have been reported in soils from many parts of the world. It has been predicted (12) that a much greater area will become increasingly S deficient in the future because of the expanding use of sulfur-free fertilizers, increasing crop yields that make greater demands on soil nutrients, decreasing returns of S from the atmosphere as a result of less combustion of coal and other sulfur-containing fuels, the implementation of air-pollution-control schemes, and the decreasing use of S-containing fungicides and insecticides.

In the United States, crop responses to applied S have been reported in most western and southeastern states (30). More recently, responses to S have been reported for corn, sorghum, alfalfa, and small grains in Kansas, Minnesota, Nebraska, North Dakota, and Wisconsin (7, 18). These responses generally have occurred on soils that are coarse-textured, low in organic matter, and well-drained.

In Iowa in the 1920s, Erdman (15) and Erdman and Bollen (16) carried out unreplicated field trials with gypsum on soils in north-central and north-eastern Iowa. Although their results were variable, they obtained responses with alfalfa, oats, and red clover, but not with corn. Apart from this early work, little had been done to assess the S needs of Iowa soils until very recently. In 1972, Tabatabai and Bremner (48, 49) reported results of laboratory analyses of some Iowa soil samples, including samples from this study.

This study was undertaken to obtain basic information on the available-S status of some representative soils as a preliminary step in evaluating the S requirements of crops on Iowa soils (56). The main objectives of the study were to evaluate plant availability of S in some representative soil samples, to measure by laboratory techniques the amounts of various forms of S present in these soil samples, and to determine which of these measurements provides the best index of S availability to plants. Other objectives were to examine the distribution of available S with depth and time in some soil profiles, to assess the availability to ryegrass of applied sulfate, and to assess the effect of drying soil samples on S availability.

## LITERATURE REVIEW

Sulfur in organic combination accounts for at least 90 percent of the total S in the surface soils of humid regions (1, 4, 49, 53), and mineralization of these organic forms is believed to be an important source of S to plants. Broadly, soil organic S has been divided into two fractions: carbon-bonded S (C-S), as in S-containing amino acids such as cystine and methionine, and non-carbon-bonded S, as in the ester sulfates (R-O-SO<sub>3</sub>), which, because of the method of determination, usually is referred to as HI-reducible S. Carbon-bonded S accounts for 12 to 35 percent of the total S in mineral soils as compared with 47 to 50 percent in organic soils of Quebec (34). The non-carbon-bonded fraction of organic S, which includes phenolic sulfates, choline sulfates, and sulfate esters of carbohydrates, has been found to comprise about 50 percent of the total S in soils (49).

Inorganic S in well-drained, arable soils occurs primarily as the sulfate ion. This sulfate may be associated with cations such as calcium, magnesium, potassium, or ammonium in the soil solution, precipitated as salts of these elements, especially in arid soils, or adsorbed by 1:1 clays and hydrous oxides of iron and aluminum in acid soils. Reduced forms of inorganic sulfur, such as sulfides and polysulfides, occur mainly under reducing conditions caused by poor drainage or submergence and normally are not found in well-drained, upland soils.

Inorganic sulfate in soils can be divided into two components: a water-soluble fraction usually extracted with neutral solutions such as 0.15% CaCl<sub>2</sub> (59) or 0.1 M LiCl (3), and an adsorbed fraction extractable with KH<sub>2</sub>PO<sub>4</sub> (13) or Ca(OH)<sub>2</sub> (59). Both water-soluble and adsorbed sulfate are considered readily available to plants (44), although a recent study of Barrow (6) suggests that adsorbed sulfate is taken up more slowly from soils that have the capacity to adsorb large amounts of sulfate. Typical values for water-soluble sulfate S in surface soils of humid regions are normally less than 10 ppm, which, in many soils, amounts to less than 5 percent of the total S present.

Most soils have the capacity to adsorb some sulfate (39), although the amount retained at pH 6 or above is not significant. The nature of sulfate adsorption sites, discussed recently by Harward and Reisenauer (26) is not well understood.

Studies concerning available S in soils generally are restricted to samples of surface horizons. The few studies that have been made on a soil-profile basis (9, 13, 41) indicate, however, that levels of extractable S in subsoils often exceed those found in surface soils. In humid regions, accumulations of

<sup>1</sup>Project 1899 of the Iowa Agriculture and Home Economics Experiment Station, Ames, Iowa.

<sup>2</sup>Former Research Associate, Department of Agronomy, Iowa State University. Present address: Soil Bureau, Department of Scientific and Industrial Research, Lower Hutt, New Zealand.

<sup>3</sup>Professor of Soils, Department of Agronomy, Iowa State University, Ames, Iowa.

extractable S in subsoils are associated with the presence of appreciable amounts of hydrous oxides of iron or aluminum and kaolinitic clay minerals under moderately to strongly acid conditions (26). Such subsoils have the capacity to retain appreciable amounts of adsorbed sulfate. The subsoils of these soils normally have a lower degree of saturation of adsorption sites with other anions, such as phosphate, and a higher clay content than do the surface soils. In arid regions, accumulations of extractable sulfate in subsoils may occur as gypsum or co-precipitated or co-crystallized sulfate associated with calcium carbonate in calcareous soils (55). This extractable S in subsoils can be an important source of S for plants, especially deep-rooting crops.

Laboratory methods for extracting and estimating plant availability of S in soil samples can best be evaluated by correlating the S extracted with the responses to added S and (or) the uptake of S by greenhouse plants grown on the soil samples. Considerable variation in greenhouse technique exists with regard to kinds and density of plants used, weight of soil taken, and duration of growth period. Any technique should be satisfactory that gives an uptake of S by plants either equal to or proportional to the total amounts of potentially available S in the soil sample. With nutrients such as S, however, where a portion of the S in the soil is in a form readily taken up by plants, but part is as organic S that is mineralized and thus made available during the growing period, the greenhouse technique used can determine which laboratory method will provide results most highly correlated with plant uptake of the nutrient.

Although total S contents of soils are unrelated to S responses of plants (52), Fox et al. (19), on Nebraska soils, obtained correlation coefficients of 0.95 and 0.94 in relating S uptake by alfalfa over 4 cuttings in a greenhouse experiment to S extracted by calcium phosphate and water, respectively. Results of methods that extracted S associated with organic matter (viz., heat-soluble S and autoclave-soluble S) were less well correlated with plant uptake of S (18). Roberts and Koehler (41) used 53 surface and subsurface soil samples and a greenhouse technique based on that of Stanford and DeMent (45) whereby wheat plants were pre-grown in sand culture and then "nested" in 200 g of the test soil for 3 weeks. Correlation coefficients of 0.89 and 0.86 were obtained between S uptake by the plants and S extracted by 0.1 M LiCl and 5 mM MgCl<sub>2</sub>, respectively. Jones et al. (29) found that plant availability of S in soils of England and Wales was closely correlated with sulfate extracted with a KH<sub>2</sub>PO<sub>4</sub> solution. Growth of millet on Brazilian soils in a greenhouse experiment was highly correlated with ammonium acetate extractable S (36). Rehm and Caldwell (38), however, found that S uptake by grain sorghum grown for 21 days on samples of 79 Minnesota soils was not significantly correlated with S extracted with calcium phosphate, sodium bicarbonate, or ammonium acetate ( $r = 0.12, 0.13,$  and  $0.03$ , respectively). Significant correlations were obtained when the coarse-textured, gray-brown

podzolic and gray wooded soils of north-central Minnesota were considered separately. It seems that these Minnesota results for plant uptake of S were influenced by one or more problems in technique, mentioned previously, which resulted in variability in plant uptake of S.

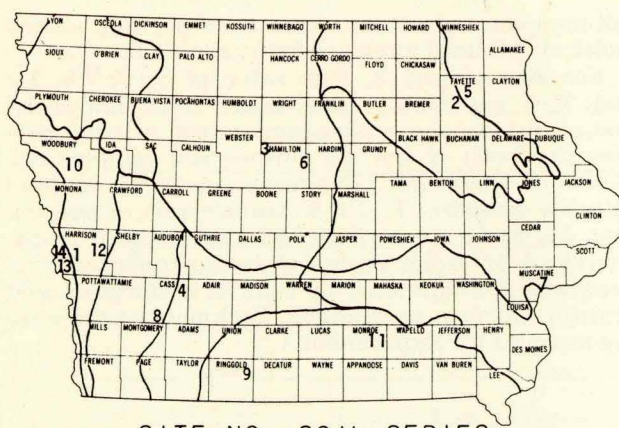
Some workers [e.g., Bardsley and Lancaster (4)] consider that estimates of available S in soils should include a part of the organic S that will be mineralized during the growing season. Extractants used by different workers to remove a labile fraction of soil organic S in addition to water-soluble and adsorbed S include hot water (44), neutral salt solutions after heating air-dry soil to 100 C (58), 0.5 M NaHCO<sub>3</sub> at pH 8.5 (33), and HAc-NaH<sub>2</sub>PO<sub>4</sub> solution after ignition at 500 C (4). From the correlations obtained by these workers, one may conclude that, with certain groups of soils, differences in plant uptake of S among soils are perhaps more dependent on the labile fraction of organic S than on water-soluble and adsorbed S.

## EXPERIMENTAL PROCEDURES

### Soil Samples

During July 1968, bulk soil samples of about 45 kg (110 lb) each were collected from the 0-6 inch depth at 14 sites in Iowa and from the subsoil (18-24 inch depth) at five of the sites. The locations of the field sites sampled are shown in fig. 1. Because other studies have shown that the amount of available S in soils can be related to such properties as amount and kind of clay (11), soil-reaction (19), and organic-matter content (44), soils were selected to show a range in these properties. Care was taken in selection of the sites to ensure that neither farmyard manure nor S-containing fertilizer, such as superphosphate, had recently been applied. In this way, the S status of the soil samples should reflect that inherent to the soils, together with additions from the atmosphere, rather than the effects of recent management. The undried soil samples were passed through a 6.4-mm (¼-inch) mesh screen, thoroughly mixed, subsampled for laboratory analyses, and stored in polyethylene bags in a cool place until potting for greenhouse Experiment 1. Air-dried samples of two S-deficient soils from Nebraska (19) and Minnesota (42) were included to provide soils of known low available-S status.

In November 1968, additional bulk 0-6 inch soil samples of 45 kg each were collected from six of the original sites (Hamburg, Webster, Clarion, Tama, Sarpy, and Marshall) to examine the effect of air-drying the soil samples on the availability of S to plants (Experiment 2). The methods of collection and screening were the same as those for Experiment 1. After mixing, the soil was divided into two 18-kg (40-lb) portions. One part was stored un-



SITE NO. SOIL SERIES

1	HAMBURG	8	MARSHALL
2	HAGENER	9	GRUNDY
3	WEBSTER	10	IDA
4	SHARPSBURG	11	WELLER
5	FAYETTE	12	MONONA
6	CLARION	13	SARPY
7	TAMA	14	ALBATON

Fig. 1. Locations of field sites sampled in Iowa.

dried in polyethylene bags; the other was air-dried at 35 C. Subsamples for chemical analyses were taken from both undried and dried bulk samples.

On three occasions in 1969, soil samples were taken from six of the sites (Hamburg, Hagener, Webster, Sharpsburg, Fayette, and Clarion) to study changes in available S with time and depth under field conditions. Four of the sites were in corn, one was in unfertilized native pasture, and one was in fallow. Samples were taken in May at corn planting, in August after silking, and in November after harvest. At each site, a sampling area 30 feet square was marked out and divided into four plots, each 15 feet square. At each sampling date on each plot, a composite sample, composed of four cores, was taken from the 0-6, 6-12, 12-24, 24-36, and 36-48 inch depths. The composite samples were subsampled for the determination of moisture content, air dried, passed through a 2-mm sieve, and stored before analysis for LiCl-extractable sulfate, pH, available phosphate, and organic carbon.

## Laboratory Analyses

Analyses for the following forms of S were made on air-dried soil samples. Total S was determined by wet oxidation of soil S compounds to sulfate by using alkaline sodium hypobromite solution according to the method of Tabatabai and Bremner (46), and the oxidized sulfate was then determined according to the procedure of Johnson and Nishita (28). HI-reducible S was determined by the method of

Freney (20), which consisted of digestion of the soil with a mixture of hydriodic, formic, and hypophosphorus acids in a modified Johnson-Nishita apparatus. The reduced S was finally determined colorimetrically as methylene blue (28). Carbon-bonded S was determined according to Lowe and DeLong (34) by digestion of soil with 0.1 g of Raney nickel alloy, 5 ml of 5 percent NaOH and 25 ml of water in a 200 ml boiling flask by using a modified Johnson-Nishita (46) digestion-distillation apparatus. The digest was then acidified with 1:1 HCl, and the reduced S was determined colorimetrically as methylene blue.

Sulfate S was extracted from both field-moist and air-dried samples at soil-to-extractant ratios of 1:5 and 1:10. Three different solutions were used to extract inorganic S from the soils. The solutions used were 0.1 M LiCl, according to Arkley (3);  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  solution containing 500 ppm P, according to Fox et al. (19); and 0.5 M  $\text{NaHCO}_3$  adjusted to pH 8.5, according to Kilmer and Nearing (33). Ten grams of air-dried soil or its field-moist equivalent were shaken for 30 min with 50 ml of extracting solution (1:5) in 80-ml centrifuge tubes. Five grams of soil and 50 ml of extracting solution were used to obtain a ratio of 1:10. The tubes were then centrifuged and a suitable aliquot of the supernatant solution, containing 5-50  $\mu\text{g}$  S, was transferred to a 50-ml digestion-distillation flask and taken to dryness in a drying oven at 100 C. To each flask, was added 1 ml of deionized water and 4 ml of a reducing mixture, containing hydriodic, formic, and hypophosphorus acids in the ratio of 4:2:1 by volume. The flasks were connected to the modified digestion-distillation apparatus, and the sulfate was determined according to the method of Johnson and Nishita (28). When the  $\text{NaHCO}_3$  extractant was used, 1.5 ml of 6 N HCl (to neutralize the carbonate) instead of water was added to the digestion-distillation flask after oven-drying before the addition of the reducing-acid mixture. The presence of free carbonate reduced the effectiveness of the reducing acids by giving lower values for extractable sulfate.

Samples of field-moist soils (10 g oven-dry basis) were moistened to 60 percent of water-holding capacity and incubated at 30 C for 10 weeks before extracting with 0.1 M LiCl at a 1:5 soil:solution ratio to determine the S mineralized.

Air-dried soil samples were analyzed for particle size using the pipette method of Kilmer and Alexander (32),  $\text{CaCO}_3$  equivalent according to the method of the United States Salinity Laboratory Staff (51), and soil moisture content at 1/3 atmosphere tension according to Richards (40). Organic carbon was determined after grinding to pass a 100-mesh sieve according to the method of Mebius (35).

Field-moist soil samples stored at 3 C were analyzed in the Iowa State University Soil Testing Laboratory. Soil pH values were determined with a glass electrode pH meter using a 1:2 soil:water ratio. Inorganic-N was determined by steam distillation of 5 g of soil in 10 ml of water with 18 ml of 2.7 N KCl, 0.17 g of ignited heavy  $\text{MgO}$ , and 0.4 g of Devarda alloy. The distillate was trapped in boric acid and titrated (10).

The S content of plant material was determined turbidimetrically by the method of Tabatabai and Bremner (47). After digestion of a sample of plant material with concentrated nitric and perchloric acids, a mixture of barium chloride and gelatin was added to an aliquot of the diluted digest, and the resultant turbidity was measured with a Klett-Summerson photoelectric colorimeter fitted with a blue no. 42 filter.

## Greenhouse Methods

Annual ryegrass, *Lolium multiflorum*, was pre-grown for each greenhouse experiment. For Experiment 1, seeds (0.6 g/culture) were sown on Aug. 5, 1968, on 500 g of moist, acid-washed silica sand enclosed in a cardboard ring 15 cm in diameter, covered with 200 g of sand, and watered daily with deionized water and twice weekly with minus-S nutrient solution (27). During the 40-day pregrowing period, each culture received 168 mg N, 20.7 mg P, 180 mg K, and 0.5 mg S. The S addition was necessary to overcome an acute S deficiency, which developed in the ryegrass 20 days after seeding. Plants harvested at the time of transfer to the potted soils contained 0.16 percent S, which is below the 0.20 percent accepted as a critical level (37).

Five rates of S—0, 11.25, 22.5, 33.75, and 45 mg S/pot (equivalent to 0, 7.5, 15, 22.5, and 30 ppm S on a dry-soil basis)—were mixed with subsamples of each of the soil samples before potting. Field-moist soil (equivalent to 1500 g of oven-dry soil) was spread in a thin layer on brown paper. An aliquot of a  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  solution was added and thoroughly mixed with the soil. A basal layer of acid-washed silica sand was placed in polyethylene-lined, no. 10 metal cans (15.5 cm in diameter and 17.5 cm high) so that the can, plus sand, weighed 1600 g (or 2150 g for pots of sandy soil). A 1.2-cm diameter plastic hose placed in the center of each can extending from the top to within 1 cm of the base provided means of adding nutrient solutions directly to the basal sand layer. The soil sample was then placed on top of the basal sand layer and uniformly consolidated to give a bulk density of 0.95 for silt loam and silty clay loam and 1.20 for sandy-textured soils. The ryegrass in sand culture was transferred on top of the soil in the pots on Sept. 16. The experimental design was a split plot, with soils as a whole plots and S treatments as subplots, with three replicates. Deionized water was added to maintain the moisture content of the soils. A minus-S nutrient solution was added to the basal sand layer in amounts to supply 120 mg N, 15.5 mg P, 136 mg K between each harvest. Ryegrass was harvested 31, 70, 114, 164, and 202 days after transfer by clipping 2.5 cm above the sand surface. Plant samples were dried at 65 C for 48 hr, weighed, and ground in a Wiley mill through a 20-mesh screen. After the final harvest, representative

soil samples were taken from each pot and stored moist at 3 C until analyses for available S.

For Experiment 2, four rates of S (0, 7.5, 15, and 22.5 mg S/pot) were mixed with field-moist and air-dried subsamples (equivalent to 1500 g of oven-dry soil) of the six surface soil samples collected in November. Ryegrass was sown in sand cultures on Nov. 7, 1968, transferred to pots on Dec. 16, and harvested 39 and 73 days after transferring. A split-plot design with two replicates was used with S treatments by soils as whole plots and drying treatment as subplots. Techniques used were the same as for Experiment 1.

## EXPERIMENTAL RESULTS

In tables and figures reporting the results of the greenhouse and laboratory studies, the soils are grouped into Iowa surface soils, Iowa subsoils, and out-of-state soils. Within each group, the soils are listed in order of increasing total plant uptake of S from the soil samples (see table 3). Each group is divided into subgroups, each consisting of 1 to 5 soils with similar plant yields and S contents.

### Soil Characteristics

Some physical and chemical properties of the soil samples used in this study are reported in table 1. The analyses show wide variations in the properties of soils sampled. Soil textures varied from sand to clay loam, with a range of 2 to 86 percent sand and 6 to 40 percent clay. Organic carbon varied from 0.1 to 2.8 percent carbon. Water held by the soil at 1/3 bar varied from 5 to 32 percent  $\text{H}_2\text{O}$ . pH values ranged from 5.2 to 8.3, with soils of pH greater than 7.0 generally containing free calcium carbonate. Inorganic N ( $\text{NO}_3\text{-N}$  plus  $\text{NH}_4\text{-N}$ ) ranged from 23 pp2m in unfertilized Hamburg surface soil to 235 pp2m in the Weller surface soil.

## Greenhouse Studies

### Experiment 1

*Plant dry-matter yields.* Ryegrass, which had been pre-grown in sand culture and transferred to the test soils in a S-deficient condition, assumed normal growth within 7 days. Where no S was added to the soils, differences in ryegrass growth among soils became evident at an early stage, were marked at the time of first harvest (31 days after transferring), and continued throughout the five harvests, as shown in table 2 for the individual soils and illustrated in fig. 2 for the different subgroups of soils.

Table 1. Some physical and chemical characteristics of the soil samples used in greenhouse and laboratory studies<sup>a/</sup>

Sub-group	Soil		Mechanical analyses				pH	H <sub>2</sub> O held at 1/3 bar %	Inorganic N pp2m	Cropping history of field site <sup>b/</sup>
	No.	Soil type	Sand 50 $\mu$ %	Clay 2 $\mu$ %	Organic carbon %	CaCO <sub>3</sub> Equiv. %				
<u>Iowa Surface Soil (0-6") Samples</u>										
Upland										
A	1	Hamburg sil	8	16	0.9	9.6	8.3	25	23	<u>G</u>
A	2	Hagener ls	79	7	0.5	0.2	6.9	6	36	<u>SbCCF</u>
B	3	Webster cl	26	33	2.8	--	6.3	30	45	<u>SbCSbC</u>
B	4	Sharpsburg sil	2	36	1.6	0.0	7.1	30	79	<u>SbCOMC</u>
B	5	Fayette sil	11	24	1.2	--	6.4	22	59	<u>CCCC</u>
B	6	Clarion l	42	21	2.1	--	6.1	22	56	<u>SbMSbC</u>
B	7	Tama sil	2	25	1.9	--	6.5	29	68	<u>CSbC</u>
B	8	Marshall sil	2	34	1.5	0.0	7.5	28	107	<u>MCCC</u>
C	9	Grundy sil	3	34	2.3	--	6.5	29	62	<u>CCSb</u>
C	10	Ida sil	5	23	1.0	0.5	7.9	29	56	<u>CMMM</u>
C	11	Weller sil	4	21	1.3	--	5.2	25	235	<u>SbCCC</u>
D	12	Monona sil	3	26	1.5	0.0	7.0	26	103	<u>CSbC</u>
Missouri River Bottomland										
E	13	Sarpy l	45	12	0.8	5.0	8.2	15	42	<u>CMC</u>
E	14	Albaton sil	6	36	1.3	3.0	7.8	32	169	<u>CSbC</u>
<u>Iowa Subsoil (18-24") Samples</u>										
F	15	Clarion sil	54	21	0.6	1.1	6.6	15	38	See no. 6
F	16	Webster l	39	27	0.5	4.3	8.3	13	24	See no. 3
F	17	Fayette sil	7	23	0.2	--	5.7	22	46	See no. 5
G	18	Monona sil	3	24	0.4	0.7	6.8	26	46	See no. 12
H	19	Weller sil	2	40	0.4	--	5.2	32	25	See no. 11
<u>Out-of-State Surface Soil (0-6") Samples</u>										
O	N	Thurman s (Neb.)	86	6	0.1 0.2	0.4 --	7.1	5	74	--
O	M	Dorset sil (Minn.)	71	9	1.6	--	6.6	13	37	--

<sup>a/</sup> In this and subsequent tables, the soil samples are listed within groups in order of increasing sulfur uptake from the control samples by ryegrass (see table 3).

<sup>b/</sup> C = corn, F = fallow, G = native grass, M = legume meadow, O = oats, Sb = soybeans; Crop in 1968 underlined.

Table 2. Ryegrass yields on different soil samples with 0 and 45 mg S, as CaSO<sub>4</sub>, added per pot.

Sub-group	Soil		Plant dry-matter yield (g/pot)				
	No.	Soil series	1st Harvest		Harvests 2 & 3	Total, 5 Harvests	
			S <sub>0</sub>	S <sub>45</sub>	S <sub>45</sub>	S <sub>0</sub>	Increase due to S <sub>45</sub>
<u>Iowa Surface Soil (0-6") Samples</u>							
Upland							
A	1	Hamburg	1.41	2.32** <sup>a/</sup>	7.87	3.25	12.42**
A	2	Hagener	1.59	2.18**	6.95	3.77	8.20**
B	3	Webster	2.96	3.43**	7.69	6.86	8.97**
B	4	Sharpsburg	3.28	3.86**	7.95	7.73	11.06**
B	5	Fayette	2.98	3.39**	7.93	7.33	8.07**
B	6	Clarion	2.69	3.20**	7.90	7.17	8.59**
B	7	Tama	2.77	3.32**	8.37	7.68	9.71**
B	8	Marshall	3.63	4.03*	8.18	8.37	10.04**
C	9	Grundy	3.31	3.57	8.20	9.40	8.58**
C	10	Ida	3.07	3.50**	8.40	10.50	8.22**
C	11	Weller	4.93	5.18	7.71	11.62	6.07**
D	12	Monona	4.12	4.12	8.26	13.29	9.04**
Missouri River Bottomland							
E	13	Sarpy	2.73	3.08*	7.89	9.58	8.95**
E	14	Albaton	3.25	3.80**	9.13	11.65	11.84**
<u>Iowa Subsoil (18-24") Samples</u>							
F	15	Clarion	2.19	2.39	6.92	3.68	10.16**
F	16	Webster	2.55	2.51	6.40	4.11	9.53**
F	17	Fayette	2.30	2.41	7.40	3.95	10.16**
G	18	Monona	2.86	2.99	7.19	7.15	10.46**
H	19	Weller	2.42	2.61	7.74	16.87	2.51**
<u>Out-of-State Surface Soil (0-6") Samples</u>							
O	N	Thurman	2.87	2.94	7.33	5.70	6.50**
O	M	Dorset	2.81	3.05	6.88	6.24	7.47**

<sup>a/</sup> Yield increase significant at: \*\* = 1%, \* = 5%.



Table 3. Indexes of plant availability of sulfur in the different soil samples.

Sub-group	Soil		% S 1st harvest	Total S uptake <sup>a/</sup>		"a" Value <sup>b/</sup> mg S/pot	S uptake-70 to 202 days <sup>c/</sup>	
	No.	Series		2 harvests mg S/pot	5 harvests mg S/pot		b <sub>0</sub> <sup>a/</sup> mg S/pot	b <sub>1</sub> (Rate of uptake) mg S/pot· 100 days
<u>Iowa Surface Soils (0-6") Samples</u>								
A	1	Hamburg	0.15	0.1	1.1	2.2	-0.6	0.8 ± 0.8
A	2	Hagener	0.16	0.2	1.9	1.4	-0.8	1.4 ± 0.1
B	3	Webster	0.14	3.6	7.8	7.0	1.5	3.2 ± 0.4
B	4	Sharpsburg	0.18	5.0	8.1	6.6	3.2	2.4 ± 0.1
B	5	Fayette	0.19	5.3	8.7	5.8	3.6	2.5 ± 0.2
B	6	Clarion	0.19	5.0	9.8	6.6	2.9	3.5 ± 0.3
B	7	Tama	0.29	6.9	10.2	6.5	5.4	2.4 ± 0.3
B	8	Marshall	0.25	8.3	11.2	8.7	6.8	2.2 ± 0.1
C	9	Grundy	0.31	10.4	15.4	12.1	7.6	3.9 ± 0.3
C	10	Ida	0.38	12.4	18.6	16.0	9.1	4.8 ± 0.2
C	11	Weller	0.30	15.6	21.6	20.2	12.6	4.7 ± 0.4
D	12	Monona	0.50	24.6	35.2	29.2	19.1	8.0 ± 0.2
<u>Missouri River Bottomland</u>								
E	13	Sarpy	0.19	4.5	10.8	11.3	2.4	4.8 ± 0.2
E	14	Albaton	0.30	11.5	18.1	12.8	7.8	5.0 ± 0.4
<u>Iowa Subsoil (18-24") Samples</u>								
F	15	Clarion	0.31	4.8	5.3	5.6	5.7	0.3 ± 0.04
F	16	Webster	0.31	6.0	6.7	3.6	5.6	0.5 ± 0.1
F	17	Fayette	0.37	7.2	8.1	8.8	6.8	0.6 ± 0.1
G	18	Monona	0.37	11.9	13.6	11.5	11.3	1.2 ± 0.3
H	19	Weller	0.50	16.4	38.8	67.2	27.3	16.6 ± 3.4
<u>Out-of-State Surface Soil (0-6") Samples</u>								
O	N	Thurman	0.29	6.8	8.0	7.2	6.2	0.9 ± 0.1
O	M	Dorset	0.28	5.6	8.0	6.1	4.1	1.8 ± 0.1

<sup>a/</sup> Corrected for S uptake from basal sand layer.

<sup>b/</sup> Estimate of available S in soil in terms of S added as CaSO<sub>4</sub>. Derived from regression equations in table 4 ( $Y = b_0 + b_1 X$  where  $Y = \text{mg S taken up by plants in 5 harvests per kg of soil}$  and  $X = \text{ppm S added as CaSO}_4$ ).

<sup>c/</sup>  $Y = b_0 + b_1 X$  where  $Y = \text{cumulative S uptake in plants from 70 to 202 days of cropping}$ ,  $X = \text{days of cropping}/100$ .  $n = 4$ .

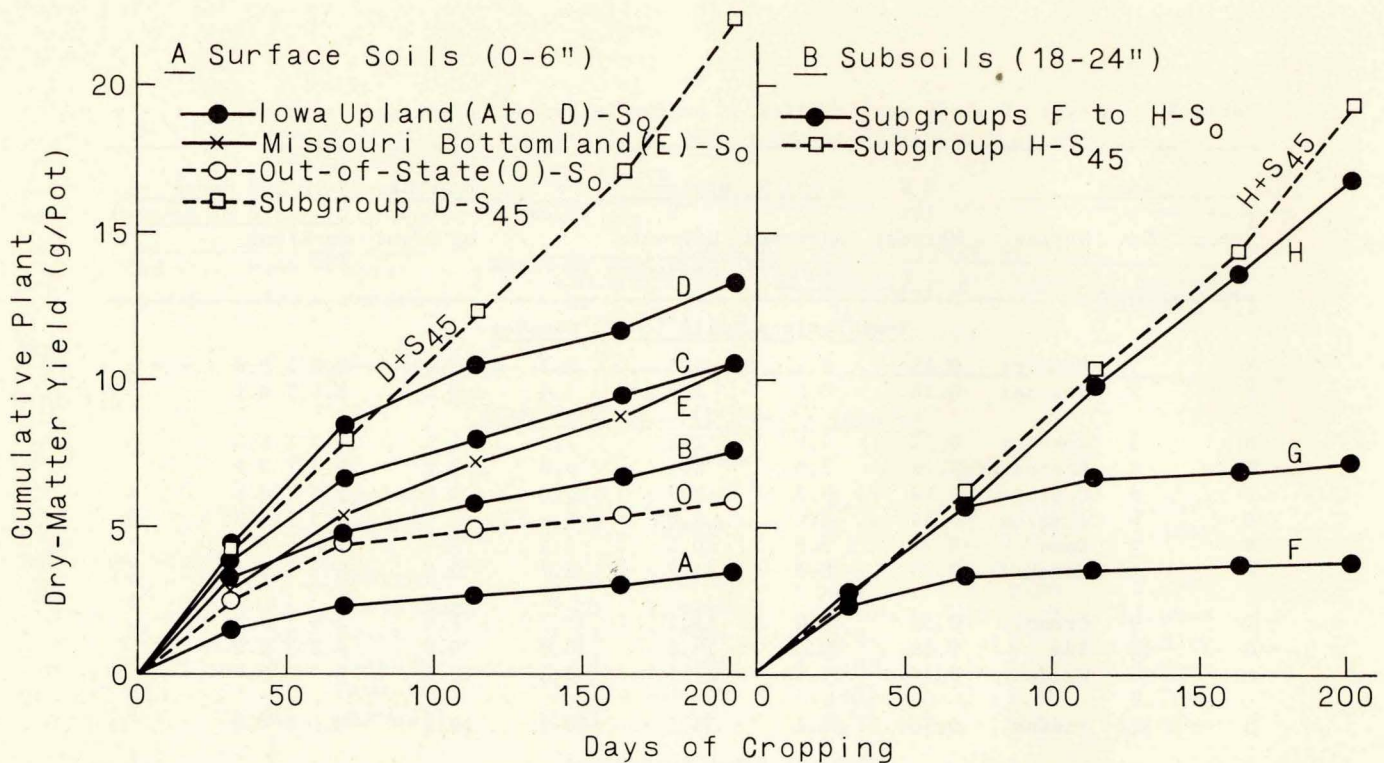


Fig. 2. Cumulative plant dry-matter yields on different subgroups (see table 2) of surface soils, A, and subsoils, B, without added fertilizer S (except on subgroups D and H).

Because nutrients, other than S, were supplied to the pot cultures in amounts sufficient to give optimum growth of ryegrass, differences in ryegrass yields among soils in the presence of adequate S should have been minimized. The similarity in yields for harvests 2 and 3 (table 2) from the different soils where 45 mg S/pot had been applied indicates that this was the situation for that treatment during that period of cropping. This S addition did not eliminate the yield differences among soils at the first harvest. Linear-regression analysis relating plant dry-matter yields from the  $S_{45}$  treatment to the log of inorganic N present in the soil samples showed that the yield differences among soils at this first harvest could be explained primarily by the differences in available nitrogen in the soil samples. The relationship was:  $Y = -1.05 + 2.45 \log X$ , where Y = the predicted dry-matter yield (g/pot) and  $X = NO_3-N + NH_4-N$  (pp2m) in the soil at potting,  $r^2 = 0.77^{**}$ . Because the additional nitrogen and other nutrients were added to the sand below the soil, they would be unavailable to the ryegrass until the roots had grown through the soil into the sand. Consequently, the rate and amount of ryegrass growth during this early period was directly related to the amount of available nitrogen in the soil. This effect was not present after the plant roots reached the sand layer, where all nutrients, except S, were present in adequate amounts.

The 45-mg addition of S per pot resulted in statistically significant increases in ryegrass yields at

the first harvest on all the undried Iowa surface soil samples, except on the Monona soil, which (as shown later) had a very high level of available S. Additions of S did not significantly affect the first harvest yields on Iowa subsoil samples or on the air-dried, out-of-state soil samples.

As shown by the dashed lines in fig. 2, dry-matter accumulation for soil subgroups D and H, plus 45 mg S/pot, continued at a high, nearly constant daily rate throughout the five cropping periods, indicating that, where the supply of soil plus added S was adequate, the rapid rate of dry-matter accumulation continued throughout the cropping period. For all soils without added S and for most soils even with added S, however, the rates of dry-matter accumulation decreased in later harvests, indicating the development of S deficiencies.

On most soils without added S, the rate of dry-matter accumulation decreased markedly after the second harvest. The daily rate of dry-matter accumulation during the later cropping periods generally was slow, but essentially constant with time for each subgroup. This rate varied markedly among the Iowa surface soils and generally was very slow for the subsoils (except Weller subsoil H) and the out-of-state soils. Growth on the Iowa subsoils ceased almost completely after the second harvest, and many plants died, especially on the Webster and Fayette subsoils.

The effect of added S on ryegrass yields characteristic of the effects obtained on 16 of the 21 soil samples tested is illustrated in fig. 3. The yield

response changed with successive harvests, fig. 3A. As the amount of added S increased, yields increased at a decreasing rate for the first two harvests, but increased at an increasing rate in harvests four and five. The cumulative yield with time as influenced by increasing rates of S addition (fig. 3B) changed progressively from a decreasing rate with time where no S was added to almost a linear rate with time where 45 mg S/pot was added. The higher rates of S addition resulted in additional yield increases only in the later harvests. At harvest five, the cumulative yield response to added S averaged 0.22 g of plant dry matter per mg S applied.

The results from the five soil samples not included in fig. 3 varied. The effect of added S on ryegrass yields from the two out-of-state soil samples was similar to that of most of the Iowa samples. Added S on the Albaton soil sample resulted in yield increases similar to the majority of the soil samples through the third harvest, but, for some unknown reason, the yield increases measured for the fourth and fifth harvests from this soil were unusually large. Added S resulted in no yield increase on the Monona surface soil sample until the third harvest or on the Weller subsoil sample until the fifth harvest, indicating that these soil samples were initially well supplied with plant-available S.

Three types of yield response to applied S are illustrated in fig. 4, which shows differences in plant growth before the fourth harvest. Fig. 4A is typical of surface soils, with S becoming progressively more limiting with each harvest and yields at lower levels of added S becoming similar to those of the control treatment, with a continuing, but very slow, growth of ryegrass plants. Fig. 4B is typical of most of the subsoils, with plants becoming severely S deficient and dying at low levels of added S. Fig. 4C illustrates the lack of response to added S, typical of a soil well supplied with available S.

*Percentage of S in ryegrass.* The S concentrations in the harvested ryegrass varied among soils, applied S levels, and harvests, as illustrated in fig. 5. Differences among soils in percentages of S in plants were most marked at harvest 1 in the absence of applied S. Percentages of S in these plants varied from 0.14 to 0.50 (table 3). The response of percentage S in the ryegrass to applied S was large and curvilinear in the first harvest. As successive harvests depleted both native and added S in the soils, the response to applied S disappeared, the differences among soils became minimal, and percentage S in the plants declined to a minimal value. The percentages of S in ryegrass plants grown on the S-deficient out-of-state soil samples were similar to the averages for the Iowa soils.

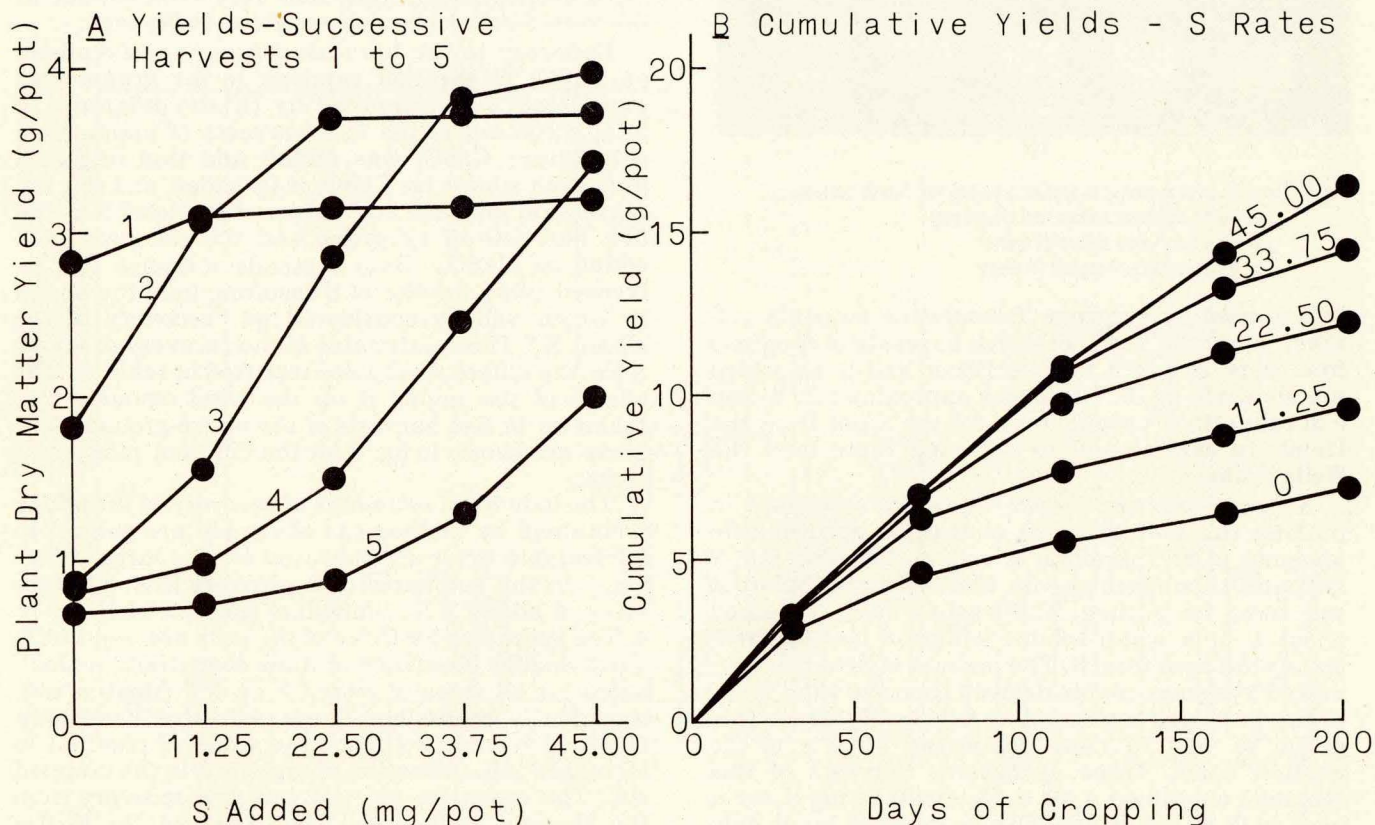
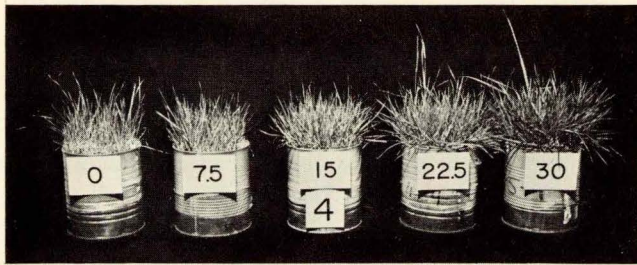


Fig. 3. Effect of sulfur ( $\text{CaSO}_4$ ) additions on yield of ryegrass. Average of 16 Iowa surface and subsoil samples. Does not include Monona (0-6") or Albaton and Weller (18-24"). A: Yield of successive harvests 1-5. B: Cumulative yields as influenced by different amounts of added S.



(a)



(b)



(c)

Fig. 4. Three types of response to applied S before the fourth harvest.

- a. On a S-deficient surface soil (Hamburg)
- b. On a S-deficient subsoil (Fayette)
- c. On a S-sufficient subsoil (Weller)

**S uptake by ryegrass.** Cumulative amounts of S taken up in the five successive harvests of ryegrass from pots to which no S fertilizer had been added are shown in fig. 6. There was approximately a ten-fold range in S uptake, from 3.8 mg S/pot from the Hamburg surface soil to 41.5 mg S/pot from the Weller subsoil.

**S from basal sand layer.** The silica sand used in potting the soil samples contained appreciable amounts of S. Therefore, it was washed with 0.5 N HCl and then leached with distilled water before it was used for potting. The washed sand contained about 1 ppm water-soluble sulfate S and approximately 50 ppm total S. The amount of S in the harvested ryegrass plants derived from the sand layer in the pots was estimated as follows: Ryegrass was grown in no. 10 cans containing 4000 g of the washed sand. Three successive harvests of this ryegrass contained 4.69, 2.83, and 0.54 mg S, for a total of 8.06 mg S/pot. The basal sand layer contained 1330 g of sand for the fine-textured soils and 1875 g of sand for the coarse-textured soils. Therefore, it was estimated that the plants took up 2.68

and 3.78 mg S/pot from the basal sand layer of the fine-textured and coarse-textured soils, respectively. The estimated amounts of S derived from the basal sand layer are shown in fig. 6 and account for a major portion of the S taken up from the pots containing soil samples of subgroup A.

**S from soils.** S uptake by the plants from the soil samples with no added S generally consisted of two phases with time of cropping: a rapid rate of uptake gradually decreasing with time up to 70 days of cropping, followed by a slower rate that tended to remain relatively constant with time during the 70- to 202-day cropping period. This is illustrated for the different subgroups of soils in fig. 7. Data for the individual soil samples are reported in table 3. Within the group of Iowa upland surface soil samples, S uptake during the first 70 days increased from subgroup A to D, and the rate of S uptake from 70 to 202 days increased similarly. S uptake from soils of subgroup E, Missouri River-bottomland, was similar to that from subgroup C soils, except that S uptake from the Sarpy soil during the first 70 days was much less than that from the Albaton or group C soils. S uptake from subsoils of subgroups F and G was rapid, especially before 31 days of cropping, but the rate of S uptake after 70 days of cropping was extremely slow. Uptake of S from the Weller subsoil, subgroup H, was rapid throughout the cropping period. S uptake from the sandy out-of-state soils, subgroup 0, was rapid before 31 days but was very slow, similar to the very S-deficient subgroup A, after 70 days.

Recovery in the harvested ryegrass of S added as  $\text{CaSO}_4$  to the soil samples in the greenhouse experiment was estimated by (a) the difference in total S content of the five harvests of plants from pots where  $\text{CaSO}_4$  was added and that of plants from pots where no  $\text{CaSO}_4$  was added and (b) the regression for each soil between the total S in the five harvests of ryegrass and the amounts of S added as  $\text{CaSO}_4$ . Both methods measure the increased plant uptake of S resulting from the added S, which will be considered as "recovery of the added S." These estimates of the recovery of added S for the different soils are reported in table 4. The effects of the added S on the total amounts of S taken up in five harvests of the above-ground parts are shown in fig. 8 for the different subgroups of soils.

The individual estimates of recovery of the added S obtained by method (a) obviously are subject to appreciable error as indicated by the large differences in the estimates of S recovery from different rates of added S for individual soils shown in table 4. The estimates for three of the soils are especially questionable. Recovery of more than 100%, as indicated for all rates of added S on the Albaton soil, is obviously impossible. These estimates of recovery of added S could be high if the added S resulted in increased mineralization of organic S in the cropped soil. The estimates of relatively low recovery from the Monona surface soil (no. 12) and the Weller subsoil (no. 19) are not reliable estimates of the recovery of added S because of the initially high levels of plant-available S in these soil samples.

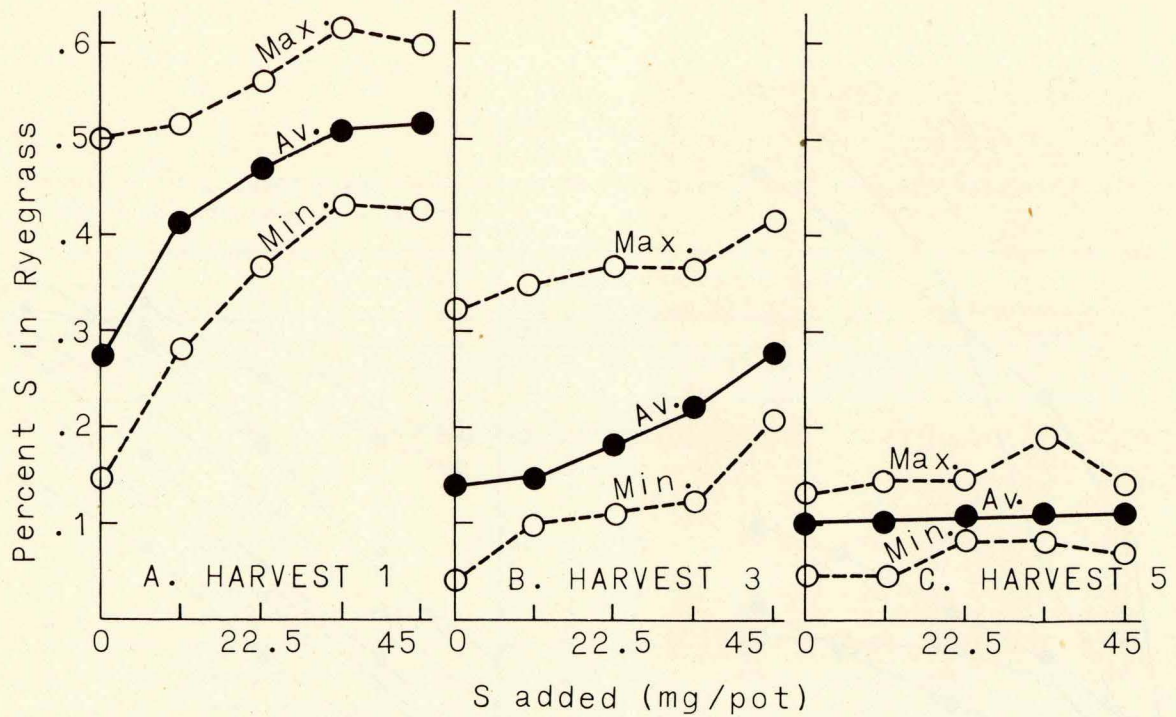


Fig. 5. Average (and range from minimum to maximum) S percentages in ryegrass plants at the first, third, and fifth harvests as influenced by S ( $\text{CaSO}_4$ ) additions. Data from 19 Iowa soil samples.

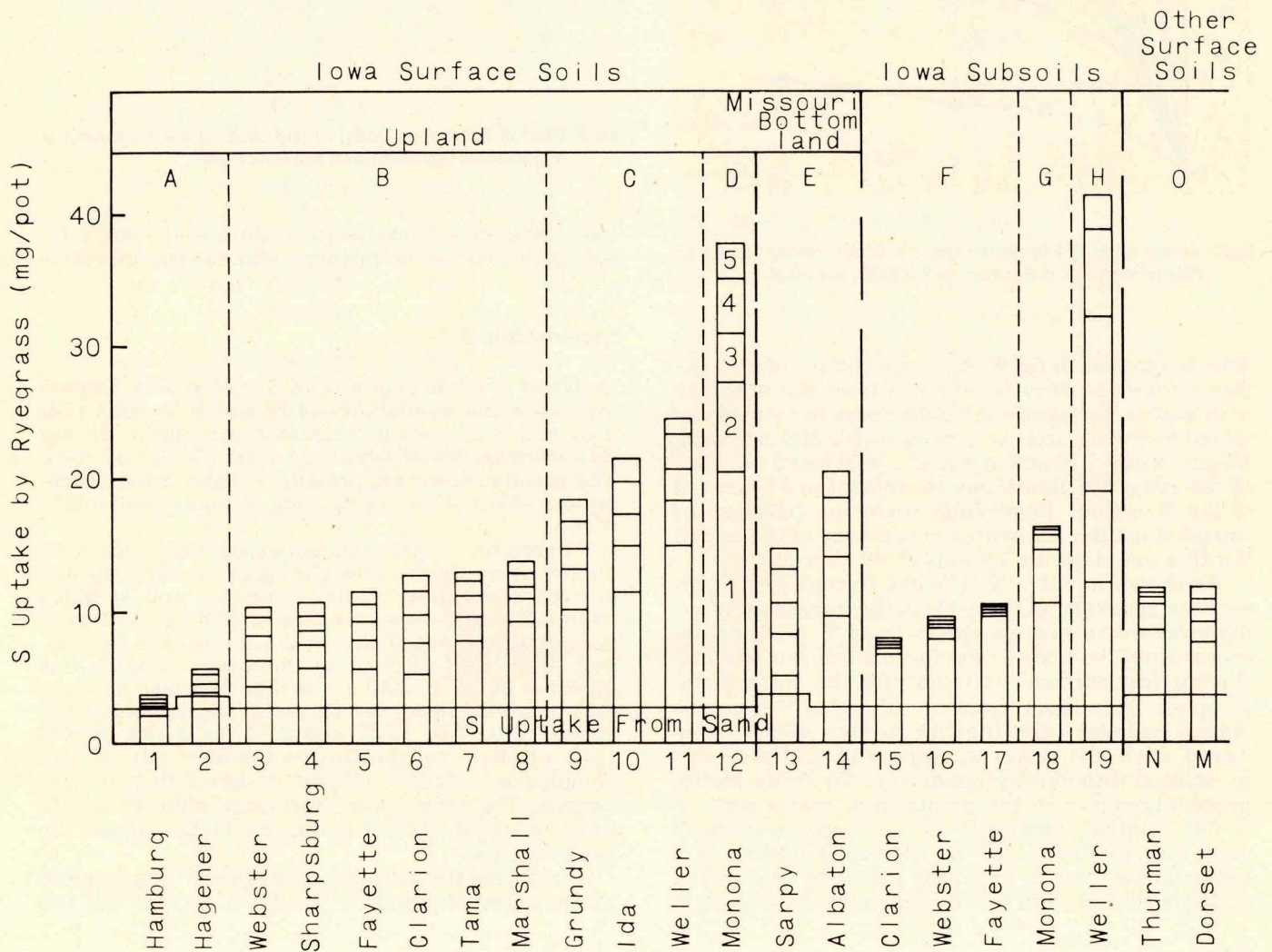


Fig. 6. Uptake of S by ryegrass over five harvests from different soils where no S was added.

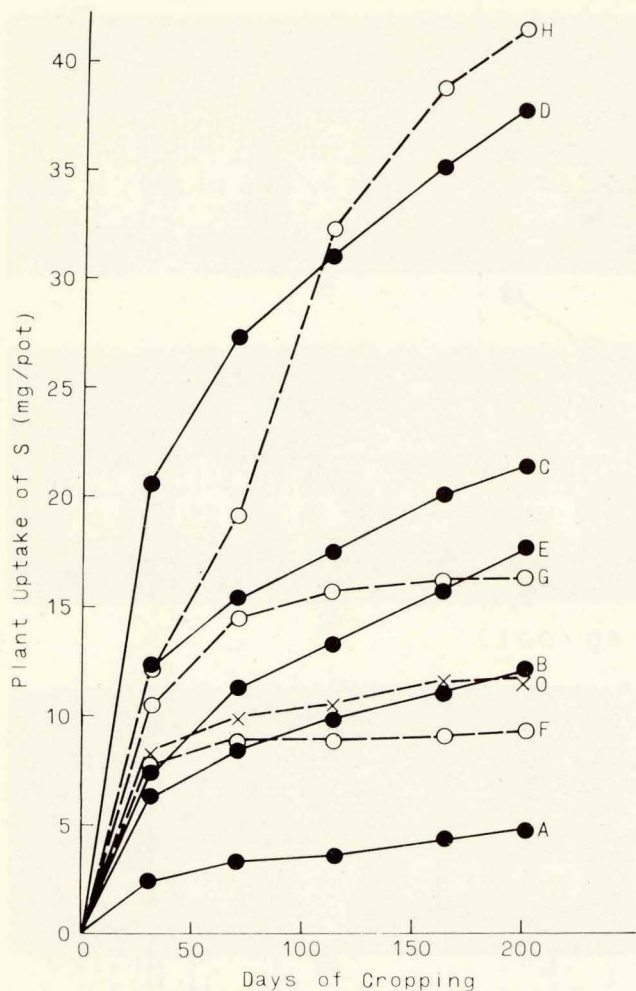


Fig. 7. Average uptake of S by ryegrass over the 202-day cropping period from different subgroups of soils where no S as  $\text{CaSO}_4$  was added.

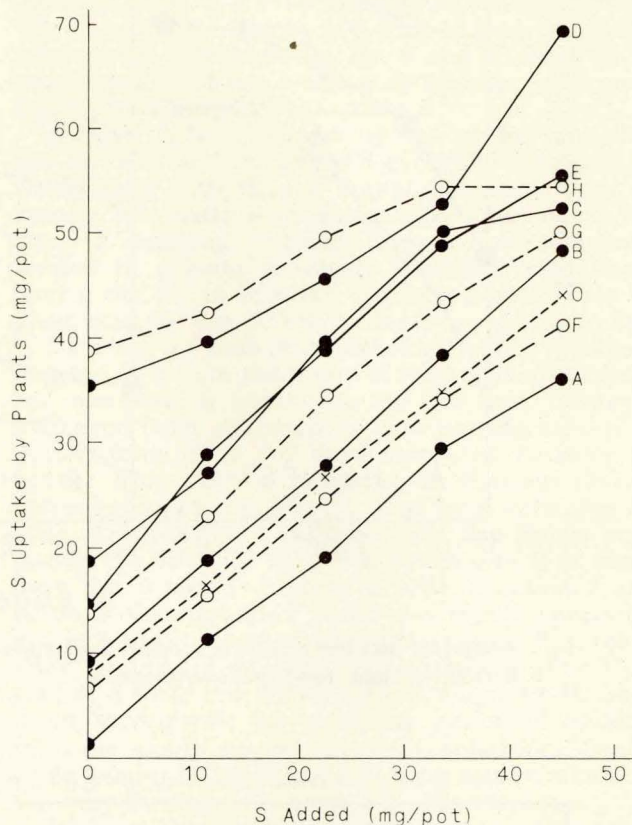


Fig. 8. Effect of added S (as  $\text{CaSO}_4$ ) on total uptake of S in five harvests of ryegrass plants from the different subgroups of soils.

This is obvious in fig. 8. Analysis of variance of the percentage recovery of added S from the other 18 soils shows no significant differences in recovery of added S among soils or among rates of S addition. Mean recovery of added S in the harvested portions of the ryegrass plants was equivalent to 84 percent of the S added. Regression analyses (method b) provided similar estimates of recovery of the added S with a mean for the 18 soils of 82 percent.

As shown in table 5, in early harvests, the percentage recovery of added S in the harvested plant material decreased as the rate of S addition increased and was lower for the subsoil samples (including Ida surface soil) than for the surface soil samples. This lower recovery of added S from the subsoil samples (and the Ida surface soil) as compared with the other surface soil samples was associated with lower plant dry-matter yields, higher percentages of S in the plants from pots where no S was applied, and little or no increase in plant yield due to the added S. Increased uptake of S between the fourth and fifth harvests due to the added S varied from 0 to 3 percent of the added S,

indicating that continued cropping would have resulted in little or no further uptake of the added S.

## Experiment 2

*Effect of air-drying soil on S availability.* Drying increases the availability of N and K in soils (24, 25), and increases in extractable S due to drying soil samples have been reported (5, 21, 57, 60). The results, however, provide no evidence concerning the effect of air-drying soils on plant availability of S.

Therefore, a greenhouse experiment was conducted to study the effect on growth and S uptake of ryegrass plants of air-drying the soil samples before potting in the greenhouse. Soil samples were collected from six of the field sites in late November 1968. Half of each of these soil samples was air-dried at 35 C until no further decrease in moisture content could be detected. Treatments consisted of 0, 7.5, 15.0, and 22.5 mg S (as  $\text{CaSO}_4$ ) /pot applied to the undried and air-dried soil samples in a split, split-plot design with two replications. The plants were harvested after 39 and 73 days of cropping by clipping 1¼ inches above the sand surface.

Air-drying the soil samples before potting resulted in increased dry-matter yields in each of the two

Table 4. Increased plant uptake of S in five harvests of ryegrass resulting from additions of S as CaSO<sub>4</sub>

Sub-group	Soil		Increased S uptake due to added S					Regression analyses <sup>a/</sup>	
			(as % of added S)				Mean	b <sub>1</sub>	r <sup>2</sup>
			mg S added/pot						
No.	Series	11.25	22.50	33.75	45.00				
<u>Iowa Surface Soil (0-6") Samples</u>									
Upland									
A	1	Hamburg	99	84	88	74	86	77 ± 7	0.98
A	2	Hagener	79	73	79	80	78	79 ± 6	0.99
B	3	Webster	61	85	86	71	76	76 ± 12	0.95
B	4	Sharpsburg	99	89	88	91	91	87 ± 4	0.99
B	5	Fayette	80	91	93	91	89	93 ± 6	0.99
B	6	Clarion	69	77	82	86	78	86 ± 7	0.98
B	7	Tama	93	77	85	96	88	93 ± 11	0.97
B	8	Marshall	95	80	84	88	87	86 ± 8	0.98
C	9	Grundy	73	94	89	83	85	86 ± 8	0.98
C	10	Ida	62	104	92	72	83	81 ± 17	0.90
C	11	Weller	94	83	101	72	88	78 ± 18	0.90
D	12	Monona	39	47	53	77	54	73 ± 22	0.83
Missouri River Bottomland									
E	13	Sarpy	124	89	95	78	87 <sup>b/</sup>	79 ± 13	0.94
E	14	Albaton	138	132	109	105	122	105 ± 12	0.97
<u>Iowa Subsoil (18-24") Samples</u>									
F	15	Clarion	92	91	95	76	88	79 ± 13	0.94
F	16	Webster	49	60	87	78	69	84 ± 14	0.94
F	17	Fayette	98	90	68	77	83	72 ± 15	0.91
G	18	Monona	85	93	89	87	87	84 ± 9	0.98
H	19	Weller	31	49	47	35	40	39 ± 11	0.84
<u>Out-of-State Surface Soil (0-6") Samples</u>									
O	N	Thurman	75	76	70	75	74	74 ± 10	0.96
O	M	Dorset	77	93	89	85	86	87 ± 8	0.98
Mean (excluding 12, 14, 19)			84	85	87	81	84	82	--

<sup>a/</sup>  $\bar{Y} = b_0 + b_1 X$  where Y = mg S/pot taken up in 5 harvests of ryegrass, X = mg S added (as CaSO<sub>4</sub>)/pot.

<sup>b/</sup> Mean of 3 values.

Table 5. Increased S uptake in above-ground parts of ryegrass plants as influenced by soils, S added, and time of cropping

Soils	S added (as CaSO <sub>4</sub> ) (mg S/pot)	Increased S uptake (as % of added S) Harvest no.				
		1	2	3	4	5
Surface <sup>a/</sup>	11.25	55	80	86	88	88
Surface	22.50	37	68	80	83	84
Surface	33.75	30	63	80	87	88
Surface	45.00	23	52	70	80	83
Subsoil <sup>b/</sup>	11.25	25	58	72	73	73
Subsoil	22.50	18	54	80	85	87
Subsoil	33.75	13	45	72	82	85
Subsoil	45.00	12	36	62	76	78

<sup>a/</sup> Includes soil samples 1-9, 11, 13.

<sup>b/</sup> Includes soil samples 10, 15-18.

harvests of ryegrass at all levels of added S, as shown in fig. 9A. The dry-matter yield increases over the two harvests varied from 0.19 to 0.77 g/pot for the different soils and averaged 0.54 g/pot. These increases in dry-matter yields were associated with increases in S uptake at the lower rates of added S for the first harvest and for all rates for the second harvest (fig. 9B). The increased S uptake due to drying the soils varied from 0.23 to 1.96 mg S/pot for the different soils and averaged 0.88 mg S/pot.

These data indicate that air-drying the soil samples resulted in increased yields of plants and increased S availability in the soil samples, but the yield increases were not due only to the increase in S availability. Increasing S availability by additions of CaSO<sub>4</sub> did not influence the increases in plant yields resulting from drying the soil samples.

## Laboratory Studies

Results of the laboratory analyses of the soil samples for different forms of S are shown in table 6. Total S averaged 268 ppm (range 78 to 452 ppm) in the Iowa surface soil samples and 140 ppm (range 85 to 210 ppm) in the subsoil samples. These values are similar to those of Tabatabai and Bremner (48, 49) for Iowa soil samples and are of the same order as those reported for Australian soils (44, 59, 60) and Minnesota soils (17). Total S in these samples was significantly correlated ( $r = 0.73^{**}$ ) with organic carbon.

HI-reducible S accounted for an average of 54 percent (range 46 to 61 percent) of the total S in Iowa surface soil samples and 72 percent (range 61 to 82 percent) in subsoil samples. This S is thought to consist of sulfated polysaccharides, phenolic sulfate, choline sulfate, and inorganic sulfate, and the results here are similar to those for Australian soils (23).

Carbon-bonded S accounted for an average of 8 percent (range 5 to 14 percent) of the total S in Iowa surface soil samples and 4 percent (range 4 to 6 percent) in the subsoil samples. In Canadian soils, carbon-bonded S accounted for 12 to 35 percent of the total S (34).

The amounts of S mineralized during a 70-day aerobic incubation averaged 3.3 ppm (range 0.7 to 9.4 ppm) for the surface soil samples, but were consistently less than 1 ppm for the subsoil samples.

The amounts of sulfate S extracted from the individual undried soil samples before cropping by a LiCl solution at a 1:5 soil:solution ratio varied from 1.6 to 10.4 ppm, table 7. This S accounted for an

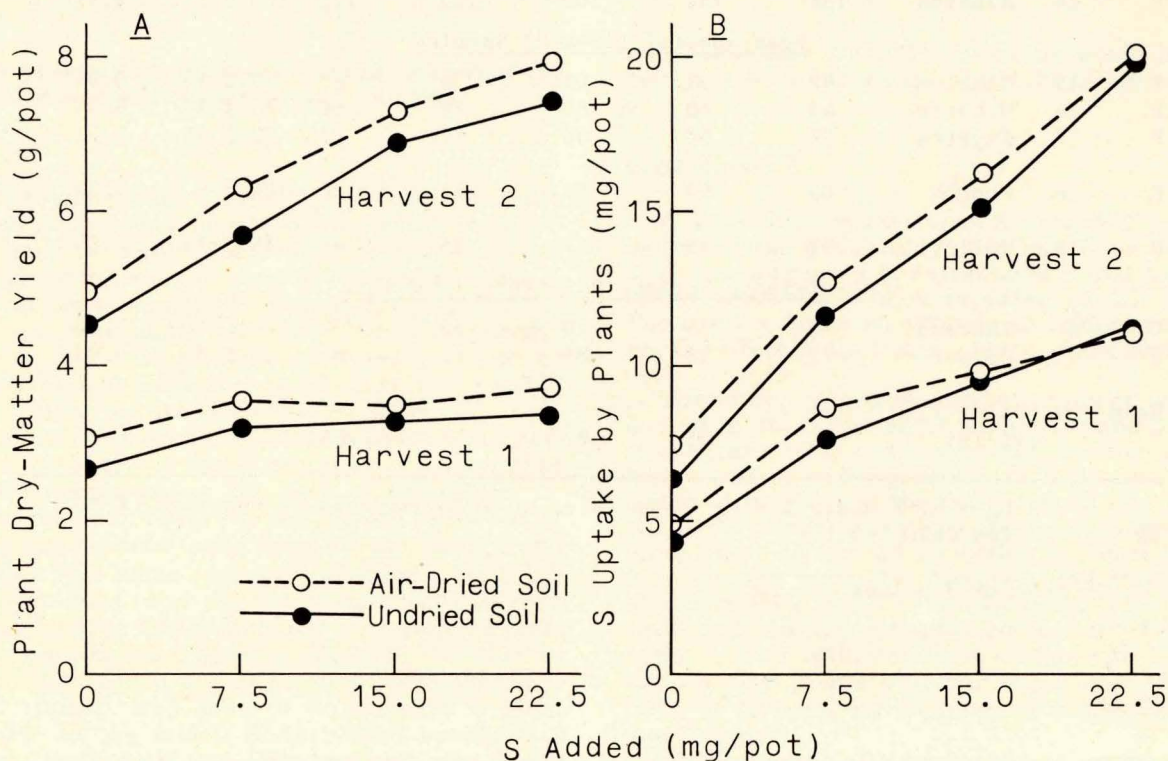


Fig. 9. Cumulative yields of dry matter and S in ryegrass harvests 1 and 2 as influenced by CaSO<sub>4</sub> additions and by air-drying the soil samples. Average of 6 soil samples.



Table 6. Forms of sulfur in the soil samples<sup>a</sup>

Soil sample			Total S	HI-reducible S <sup>b</sup>	Carbon- bonded S <sup>b</sup>	S Mineral- ized
Sub- group	No.	Soil series				
----- ppm -----						
<u>Iowa Surface Soil (0-6") Samples</u>						
Upland						
A	1	Hamburg	279	168 (60)	15 (5)	--
A	2	Hagener	78	42 (54)	7 (9)	2.3
B	3	Webster	336	179 (53)	30 (9)	0.7
B	4	Sharpsburg	264	148 (56)	25 (10)	2.4
B	5	Fayette	203	112 (55)	28 (14)	4.4
B	6	Clarion	283	162 (57)	20 (7)	2.5
B	7	Tama	241	143 (59)	21 (9)	9.4
B	8	Marshall	292	177 (61)	24 (8)	2.4
C	9	Grundy	289	164 (57)	30 (10)	2.0
C	10	Ida	300	163 (54)	15 (5)	1.7
C	11	Weller	189	96 (51)	15 (8)	2.0
D	12	Monona	333	184 (55)	26 (8)	4.2
Missouri River Bottomland						
E	13	Sarpy	211	101 (48)	19 (9)	5.5
E	14	Albaton	452	209 (46)	24 (5)	3.5
<u>Iowa Subsoil (18-24") Samples</u>						
F	15	Clarion	160	115 (72)	9 (6)	<1
F	16	Webster	110	67 (61)	5 (5)	<1
F	17	Fayette	85	70 (82)	3 (4)	<1
G	18	Monona	210	155 (74)	8 (4)	<1
H	19	Weller	135	95 (70)	5 (4)	--
<u>Out-of-State Surface Soil Samples</u>						
O	N	Thurman	68	36 (53)	3 (4)	--
O	M	Dorset	168	82 (49)	10 (6)	--
Mean Iowa Surface Soils			268	146 (54)	21 (8)	3.3
Mean Iowa Subsoils			140	100 (72)	6 (4)	<1

<sup>a</sup> Results provided by Dr. M. A. Tabatabai.

<sup>b</sup> Percentage of the total S is given in parentheses.

Table 7. Effect of extractant (at 1:5 soil:solution), air-drying, and cropping on sulfate-S extracted from individual soil samples

Soil			Sulfate-S Extracted (ppm)						
			Before cropping			Air-dried LiCl	After cropping		
Sub-group	No.	Series	Field-moist		NaHCO <sub>3</sub>		LiCl	Field-moist	
			LiCl <sup>a/</sup>	Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>		LiCl			
							S added (ppm) <sup>b/</sup>		
							0	15	30
A	1	Hamburg	2.0 (1)	1.6	9.1	4.7	1.9	--	--
A	2	Hagener	1.6 (2)	2.0	12.1	3.2	1.1	--	--
B	3	Webster	3.2 (1)	4.9	18.4	5.5	0.5	0.6	0.4
B	4	Sharpsburg	4.0 (2)	4.9	25.5	5.8	0.5	0.5	0.4
B	5	Fayette	3.6 (2)	4.6	25.5	4.7	0.7	--	--
B	6	Clarion	4.6 (2)	5.7	37.8	6.7	0.9	--	--
B	7	Tama	5.1 (2)	4.6	30.4	5.7	0.7	--	--
B	8	Marshall	7.4 (3)	8.1	29.2	8.8	0.6	--	--
C	9	Grundy	5.7 (2)	5.3	28.8	8.8	0.3	--	--
C	10	Ida	7.4 (2)	5.5	15.4	8.0	0.7	--	--
C	11	Weller	5.8 (3)	3.8	25.7	8.9	0.8	--	--
D	12	Monona	7.9 (2)	8.0	25.5	11.1	0.9	1.4	3.7
E	13	Sarpy	3.4 (2)	3.7	7.1	3.8	0.4	--	--
E	14	Albaton	7.9 (2)	8.3	12.1	8.4	1.3	--	--
F	15	Clarion	5.5 (3)	5.9	27.2	6.2	0.2	--	--
F	16	Webster	5.9 (5)	5.7	8.6	6.6	0.2	--	--
F	17	Fayette	4.1 (5)	5.6	12.4	4.1	0.1	0.3	0.1
G	18	Monona	5.0 (2)	4.2	14.9	5.7	0.1	--	--
H	19	Weller	10.4 (8)	14.1	29.2	11.7	0.4	1.7	4.5
O	20	Thurman	--	--	--	3.5	0.2	--	--
O	21	Dorset	--	--	--	5.5	0.6	--	--
Mean Iowa Surface Soils			5.0 (2)	5.1	21.6	6.1	0.8	--	--
Mean Iowa Subsoils			6.2 (4)	7.1	18.5	6.9	0.2	--	--

<sup>a/</sup> Percentage of total S is given in parentheses.

<sup>b/</sup> S added as CaSO<sub>4</sub> before cropping.

average of 2 percent (range 1 to 3 percent) of the total S in the surface soil samples and 4 percent (range 2 to 8 percent) in the subsoil samples. The amounts of sulfate S were not highly correlated with the amounts of the other forms of S in these samples.

Air drying the soil samples increased the amount of sulfate S extracted, resulting in a range of from 3.2 to 11.7 ppm sulfate S extracted by a LiCl solution. The increases were greater for some soils than for others.

The LiCl-extractable sulfate S in the soil samples was reduced by cropping to very low levels in all soils to which no CaSO<sub>4</sub> was added before cropping. The residual sulfate was especially low in the subsoil samples, being below the limit of detection in some of the samples. The residual sulfate S was less than 1 ppm in all except three soils and was less than 2 ppm in all soils. Residual sulfate S was determined on five of the soils to which 15 and 30 ppm S (22.5 and 45 mg S/pot) had been added before cropping. All this added S had been removed by cropping in three of the soils, and most of the added S had been removed from the other two soils (nos. 12 and 19), which were the soil samples with the highest initial levels of plant-available S.

Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> extracted slightly more sulfate S from some soils and slightly less from others than did LiCl. These differences generally were very small,

however, except for soil no. 19, Weller subsoil, pH 5.2.

NaHCO<sub>3</sub> generally extracted much more sulfate S than did the other two extractants. But differences between the amounts of sulfate S extracted by NaHCO<sub>3</sub> and the other two extractants were extremely variable among soils.

The average effects of air-drying the soils and of the soil:solution ratio on the amounts of sulfate S extracted by the different extractants are shown in table 8. The amounts of sulfate-S extracted from soil samples by a 0.1 M LiCl solution and a Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> solution were very similar, but the amounts varied with the soil:extractant ratio and were increased by air drying the soils before analysis. These results are similar to those reported (48) for extractions of Iowa soils with LiCl, CaCl<sub>2</sub>, and Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> solutions. The NaHCO<sub>3</sub> solution extracted 3 to 4 times as much sulfate S as did these other solutions, but was less affected by the soil:solution ratio or by air drying of the soil samples.

Sulfate extracted by a solution of KH<sub>2</sub>PO<sub>4</sub> or Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> additional to that extracted by solutions of NaCl, CaCl<sub>2</sub>, or LiCl is considered to provide a measure of adsorbed sulfate (14). Such adsorbed sulfate is normally found in very acid soils. In this study, the Weller subsoil (no. 19), pH 5.2, was the only soil sample that possibly contained an appreci-

Table 8. Effect of air-drying soil samples and of soil:solution ratio on the amount of sulfate S extracted from Iowa soils by different extractants. Av. of 19 surface and subsoil samples

Extractant	Field-moist soil Soil:solution ratio		Air-dried soil Soil:solution ratio	
	1:5	1:10	1:5	1:10
0.1 M LiCl	5.3	6.3	7.0	8.3
Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> (500 ppm P)	5.7	6.3	7.3	8.5
0.5 M NaHCO <sub>3</sub>	21.5	24.7	25.0	26.9

able amount of adsorbed sulfate. The Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> solution extracted about 4 ppm more sulfate S from this soil than did the LiCl solution.

The amounts of sulfate S extracted from soils that adsorb sulfate have been shown to be influenced by the pH of the soil-extractant suspension (31, 39). Therefore, five undried soil samples (nos. 5, 6, 8, 11, and the Weller subsoil no. 19) were extracted at a 1:5 soil:extractant ratio with a KH<sub>2</sub>PO<sub>4</sub> solution containing 500 ppm P adjusted to pH 3.3, 4.6, and 6.7. The pH of the extractants had no effect on the amounts of sulfate S extracted. The 4 ppm adsorbed sulfate S was extracted from the Weller subsoil regardless of the pH of the extractant. It seems that, if the Weller subsoil contains sorbed sulfate, the Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> solution (pH 3.3) is a satisfactory extractant of adsorbed sulfate and has the advantage of producing clear extracts.

The relationships between the results of the different methods used to extract sulfate S were further examined by correlation analysis, table 9. Correlations between the amounts extracted from field-moist or air-dried soils at either 1:5 or 1:10 soil:solution ratios within an extractant were very similar. The amounts extracted by Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> were highly correlated with the amounts extracted with LiCl. The relationships between the amounts extracted by NaHCO<sub>3</sub> and by LiCl were not significant.

Correlation coefficients also were computed between soil S fractions (HI-reducible S, carbon-bonded S, and total S) and sulfate S extracted with LiCl, Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> and NaHCO<sub>3</sub>. In general, the relationships were not significant. LiCl extractable S in air-dried soils was correlated with HI-reducible S ( $r = 0.46^*$  and  $0.47^*$ ). NaHCO<sub>3</sub> extractable sulfate was correlated with carbon-bonded S ( $r = 0.44^*$  to  $0.49^{**}$ ).

Table 9. Correlations between sulfate-S extracted by LiCl from field-moist soil samples at a 1:10 soil:solution ratio and sulfate-S extracted from field-moist and air-dried samples with other extractants and at other ratios

Extractant	Soil:Soln. ratio	Correlation coefficient <sup>a/</sup> Soil treatment	
		Field-moist	Air-dried
		LiCl	1:5
LiCl	1:10	1.00	0.89
Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	1:5	0.83	0.77
Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	1:10	0.83	0.80
NaHCO <sub>3</sub>	1:5	0.34	0.30
NaHCO <sub>3</sub>	1:10	0.32	0.27

<sup>a/</sup> Values of  $r = 0.55$  and  $0.43$  are significant at  $P = 0.01$  and  $0.05$ , respectively.

## Laboratory-Greenhouse Relationships

Plant availability of S in the soil samples was not related to the laboratory measurements of total S, HI-reducible S, or carbon-bonded S. Therefore, only the relationships between the amounts of sulfate S extracted and the plant indexes of S availability will be discussed here. Major attention is devoted to relationships involving sulfate S extracted by LiCl from field-moist soil samples at a 1:5 soil:solution ratio. LiCl extractions of either field-moist or air-dried soil samples or at a 1:10 soil:solution ratio would provide comparable relationships. Results of Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> extractions also provided comparable relationships, but generally were not as highly correlated with the plant indexes as were the results of the LiCl extractions. Correlations between sulfate S extracted with 0.5 M NaHCO<sub>3</sub> and plant indexes of S availability were not significant and will not be discussed further.

The percentages of S in the ryegrass plants of the first harvest from pots where no CaSO<sub>4</sub> was added were highly linearly correlated with the amounts of sulfate S extracted by LiCl (fig. 10A). This occurred despite the fact, as shown previously, that dry-matter yields of the first harvest were markedly influenced by the inorganic N content of the soil samples. The percentages of S in two of the subsoil samples, nos. 17 and 18, with the highest inorganic N contents of subsoil samples were appreciably higher than the normal of the other samples.

The total plant dry-matter yields of five harvests from pots where no CaSO<sub>4</sub> was added were directly related to and highly correlated with the amounts of sulfate S extracted by LiCl (fig. 10B). The plant yields of three subsoil samples, nos. 15, 16, and 17, were especially low relative to the other soil samples.

S uptake in the ryegrass plants of the first two harvests was highly correlated with the sulfate S extracted by LiCl (fig. 11A). Plant uptake of S in these first two harvests from a majority of the soil samples approximated the amounts of sulfate S extracted by LiCl. However, S uptake from two surface soil samples, nos. 11 and 12, and, to a lesser extent, from one subsoil sample, no. 18, markedly exceeded the amount of sulfate S extracted by LiCl.

Total plant uptake of S in the five harvests was highly correlated with LiCl-extractable sulfate S (fig. 11B), but generally exceeded the sulfate S extracted by LiCl, as indicated by the regression equation. Except for the results of two surface soil samples, nos. 1 and 2, with very low levels of available S, the results of only three soil samples deviate markedly from the general relationship. These were the results for surface soil sample no. 8 and subsoil samples nos. 15 and 16, which are encircled with dashed lines in figs. 11B and 11C. As shown in fig. 11C, S uptake from these soil samples and from two other subsoil samples was very low in harvests 3 to 5. Evidently, very little additional S became available after the sulfate S extracted by LiCl from these subsoil samples, and this one surface soil sample, was depleted by plant uptake. Plants continued to take up S from the

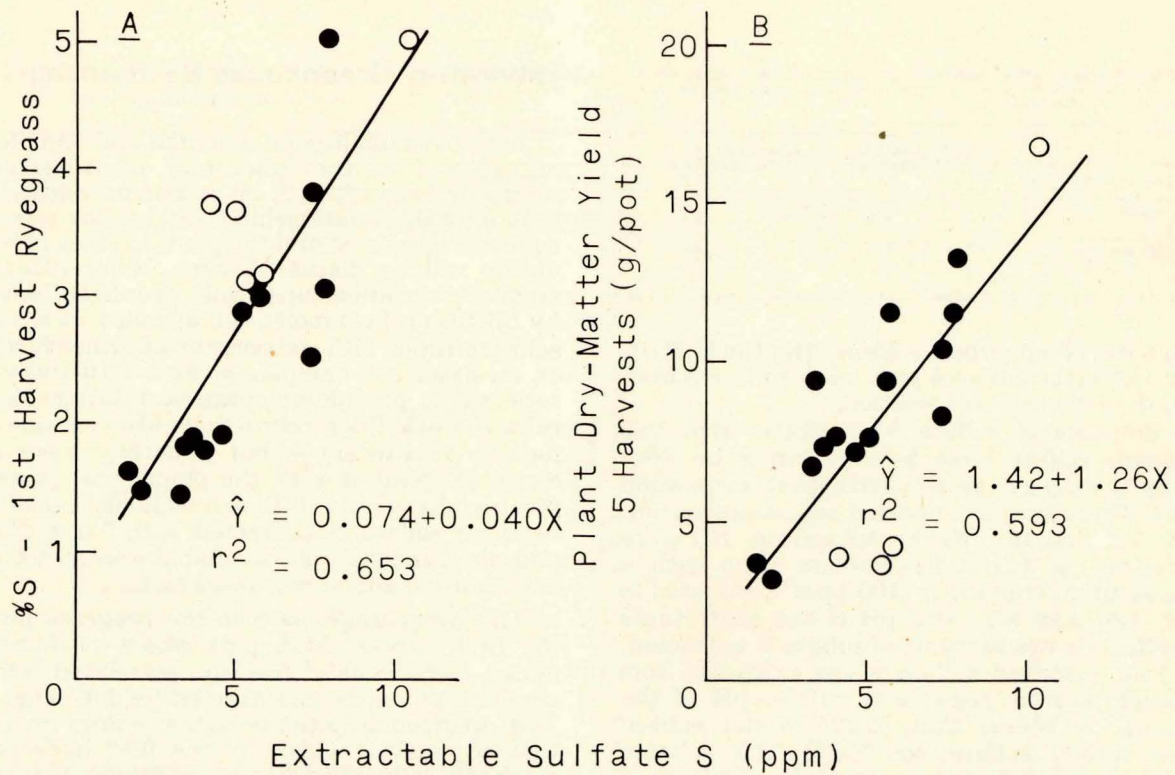


Fig. 10. Relation between sulfate S extracted with 0.1 M LiCl from field-moist soil samples at a 1:5 soil:solution ratio and (A) percent S in ryegrass plants at the first harvest and (B) total dry-matter yields of ryegrass plants in five harvests from pots with no  $\text{CaSO}_4$  added.

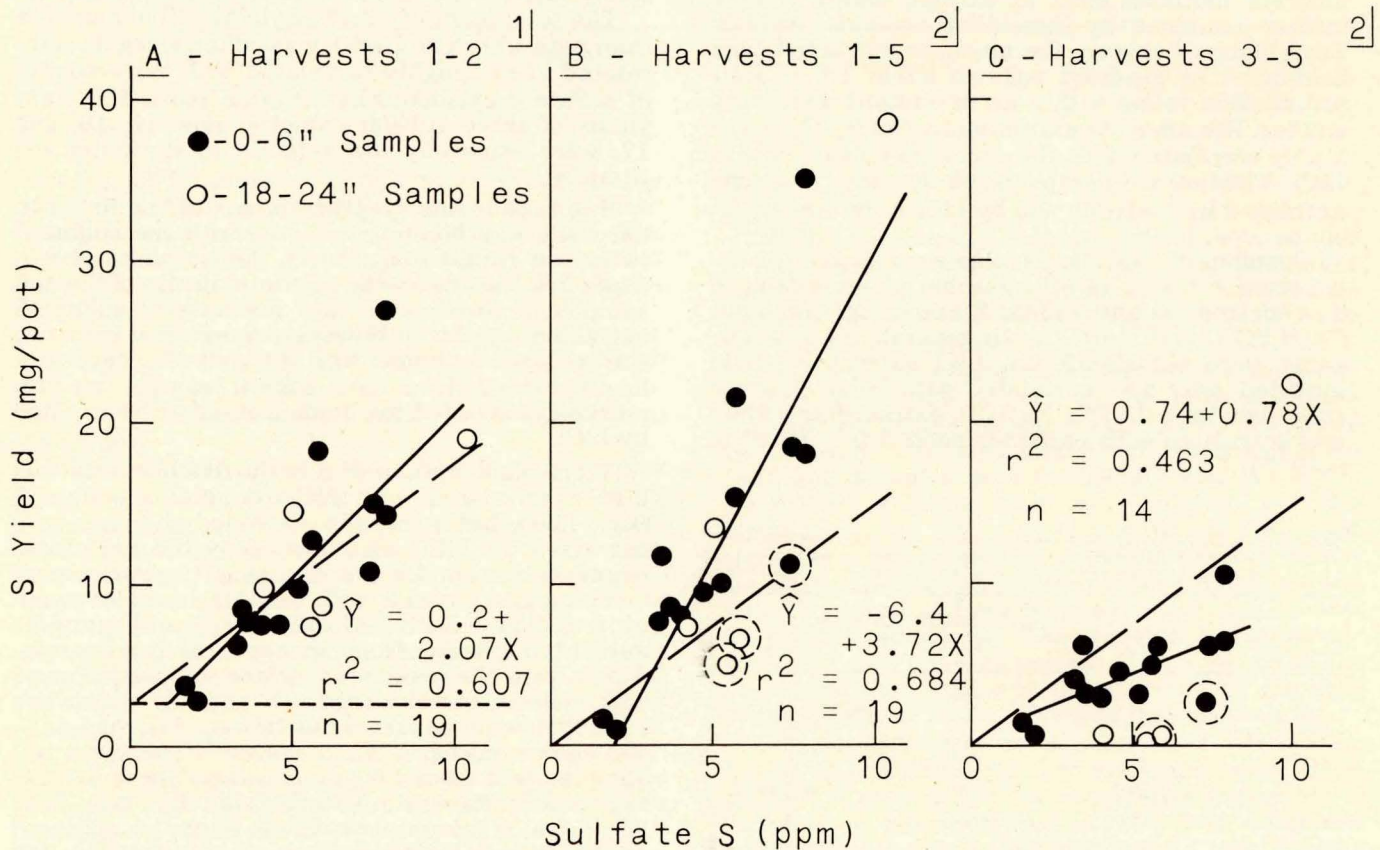


Fig. 11. Relation between sulfate S extracted from field-moist soil samples at a 1:5 soil:solution ratio and the cumulative S uptake in the harvested ryegrass plants of (A) harvests 1 and 2, (B) harvests 1 to 5, and (C) harvests 3 to 5 from pots with no  $\text{CaSO}_4$  added. (1 not corrected for S from sand layer, 2 corrected for S from sand layer.)

other surface soil samples and from subsoil sample no. 19, however, in proportion to the amount of LiCl-extractable sulfate S initially present in the soil samples.

### Field Time and Depth-of-Sampling Study

Six of the sites sampled in 1968 for the greenhouse-laboratory study were sampled to a depth of 48 inches at three times during 1969 to estimate the supply of S available to crops during the growing season (table 10).

The sulfate S concentrations were low, averaging 4.2 ppm (when expressed on an oven-dry soil basis). There was a threefold range in concentration between that in the Hagerer loamy sand, in fallow following corn, 1.9 ppm, and that in the Clarion loam in corn following soybeans, 6.1 ppm. The sulfate S concentration in the Sharpsburg soil was low, especially in the lower depths, as compared with the other medium-textured soils. This site had been in a legume meadow in 1968. The sulfate S concentration decreased with depth in the Fayette and Sharpsburg loess upland soils, but was relatively constant with depth in other soil profiles.

Between May and September, the mean sulfate S content of the soils to a depth of 48 inches decreased from 5.0 to 3.6 ppm. This is equivalent to about 21 lb S/acre. The average amounts of sulfate S in the profiles to a depth of 48 inches varied from 28 lb/acre in the Hagerer soil to 90 lb/acre in the Clarion soil.

### DISCUSSION AND CONCLUSIONS

Greenhouse experiments as reported in this paper are indispensable for: (a) the evaluation of laboratory tests for assessing nutrient availability to plants; (b) comparing the relative nutrient-supplying capacity for various soil horizons; and (c) comparing the relative response of crop plants to added fertilizer nutrients on the different soils. The results of these greenhouse studies should not be used to predict the response to S of field-grown crops, however, until the laboratory and greenhouse tests have been calibrated against the results of *field experiments*.

The greenhouse and associated laboratory studies did provide valuable guides concerning the availability to growing ryegrass plants of S from the following potential sources:

Table 10. Sulfate S<sup>a/</sup> in six Iowa soils in relation to time and depth of sampling, 1969

Sample depth (In)	Time of sampling	Sulfate-S extracted						Avg.
		Soil						
		Hagerer	Sharpsburg	Fayette	Hamburg	Webster	Clarion	
ppm (oven-dry soil base)								
0-6	Avg.	2.0	4.3	5.1	5.1	6.4	5.7	4.8
6-12	of	2.1	3.7	4.0	3.0	5.3	5.7	4.0
12-24	May,	1.6	2.9	5.0	3.9	4.8	6.1	4.0
24-36	July, &	1.8	2.1	3.6	5.9	5.9	7.4	4.4
36-48	Sept.	2.2	1.6	2.3	5.5	6.1	5.7	3.9
Avg. of all depths	May	2.3	3.6	4.3	5.3	7.1	7.1	5.0
	July	1.8	2.8	3.7	4.8	5.1	6.4	4.1
	Sept.	1.6	2.4	4.0	4.0	4.9	4.9	3.6
Average		1.9	2.9	4.0	4.7	5.7	6.1	4.2
lb/acre <sup>b/</sup>								
0-12	Avg. of	7.4	14.4	16.4	14.6	21.0	20.5	16
12-24	May,	5.8	10.4	18.0	14.0	17.3	22.0	14
24-36	July, &	6.5	7.6	13.0	21.2	21.2	26.6	16
36-48	Sept.	7.9	5.8	8.3	19.8	22.0	20.5	14
0-48		28	38	56	70	82	90	60
Cropping <sup>c/</sup>								
		C,F	M,C	C,C	G	Sb,C	Sb,C	

<sup>a/</sup> Sulfate S extracted with 0.1M LiCl from air-dried soil samples at 1:5 soil:solution ratio.

<sup>b/</sup> Assuming a bulk density of 1.32 g/cm<sup>3</sup> or 1.80 x 10<sup>6</sup> lb per acre 6 inches.

<sup>c/</sup> 1968, 1969 crop, respectively. C = corn, Sb = soybeans, M = legume meadow, G = grass, F = fallow.

1. Water-soluble inorganic S initially present in the soil samples in forms readily available to plants.
2. S in the soil samples that was initially insoluble and unavailable to plants but that was mineralized or dissolved during the cropping period.
3. Sulfur added as  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .
4. Sulfur in the basal sand layer in each pot.
5. Sulfur present as an impurity in the water or nutrient solution added to the pots.
6. Sulfur sorbed by the plants or soils from the air.

In the following discussion, attempts will be made to assess the contributions from each of these sources to the sulfur taken up by the plants. Only the sulfur in the above-ground plant parts was measured; S taken up but retained in the plant roots was not measured. Part of the soluble inorganic S added may have been precipitated in an insoluble form or immobilized through incorporation into organic compounds.

That growth of the plants in subsoil samples (nos. 15, 16, 17, and 18) without added S ceased almost completely after the second ryegrass harvest (and that many plants died, so acute was the S deficiency) provides good evidence that only minimal and insignificant amounts of S were obtained from the water or nutrient solutions or from the air.

The plants obviously took up appreciable amounts of S from the basal sand layer in each pot even though the sand had been washed with HCl. The separate experiment in which plants were grown on samples of the sand should, however, have provided reliable estimates of the amounts of S taken up by the plants from the basal sand layer, 2.015 mg S per 1000 g of sand. But, no reliable estimate of S uptake from the soil can be made for the first ryegrass harvest because the plant roots were not fully exploiting the soil or the sand at that time and variable amounts of the S would have been taken up depending on the extent of root development. The correction for S from the sand should be reliable for the results of the fifth harvest and reasonably accurate for the results of the cumulative S yield at the second harvest. The mean estimate of 84-percent recovery of the added fertilizer S in the harvested above-ground plant parts indi-

cates that almost complete recovery of the S added as  $\text{CaSO}_4$  would have been observed if the S in the plant roots had been included. The sulfate S extracted by LiCl solution after cropping substantiates this. Essentially complete recovery of the added S obviously occurred from all the soil samples except the two with very high initial levels of available S. A longer cropping period would have been required to effect complete recovery from these two soils. The possibility of some immobilization of added S by the soils, as found by Freney and Spencer (22), cannot be dismissed, but any such immobilization in these soils would seem to be very small.

The high degree of correlation between plant uptake of S and the water-soluble sulfate extracted by LiCl suggests that plant uptake of S was largely dependent on the water-soluble, inorganic fraction in the soils, source no. 1. This is similar to results reported in California soils (3). The relationships developed clearly indicate, however, that plant uptake of S from many of the soil samples exceeded the amount of water-soluble sulfate S initially present in the soil samples. Obviously, plant uptake of S after the depletion of the water-soluble sulfate S initially present in the soil samples was S derived from mineralization of organic S or dissolution of relatively insoluble inorganic S compounds.

Availability of soil S to a crop growing in the field depends on the S status, not only of the surface horizons, but also of the soil profile throughout the entire crop-root zone. Lack of response of alfalfa on soils with low levels of available S in the surface soil has been explained by accumulations of sulfate S in subsoils (9, 43). Unlike soils of semi-arid regions, however, that accumulate soluble sulfate S with depth (8, 40) or red-yellow podzolic soils that accumulate adsorbed sulfate S in the B horizon (2, 9), these Iowa soils showed no accumulation down the profile. Nevertheless, all the soil profiles sampled, except possibly the Hagener loamy sand, seem to contain adequate available S for the needs of most crops. In fact, the annual S needs of corn and soybeans, which range between 15 and 25 lb S/acre for both grain and stover (50), can be met from the top 24 inches of soil.

Field experimentation is needed to provide information concerning S availability in field soils and field-crop response to additions of S fertilizer.

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