

## Indexes of Sulfur Deficiency in Alfalfa.

### I. Extractable Soil $\text{SO}_4\text{-S}$ <sup>1</sup>

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#### ABSTRACT

Sulfur deficiencies occur on many of the undeveloped agricultural soils found in the mountain valleys of the western United States; however, the majority of the S soil-test correlation studies have been conducted on leached and weathered soils. Identification of S deficiency on alfalfa (*Medicago sativa* L.) growing in three mountain valleys permitted the collection of S soil-test correlation data for these undeveloped soils. This paper reports the relationships found between extractable soil  $\text{SO}_4\text{-S}$  levels and the response of alfalfa to S fertilization.

Soil samples were taken from 13 experimental sites before active plant growth commenced in the spring in 30-cm depth increments to 92 cm. Soil  $\text{SO}_4\text{-S}$  was extracted by water, 0.1 M LiCl, and 0.032 M  $\text{KH}_2\text{PO}_4$ , and measured by the methylene-blue reduction method. Significant correlations were obtained between the  $\text{SO}_4\text{-S}$  extracted by all three extractants from the 0- to 30-cm soil layers and relative forage yields and total S uptake by the first harvest of alfalfa at early bloom. Critical soil  $\text{SO}_4\text{-S}$  levels of 3.0, 3.0, and 4.0 ppm in this soil layer were found when extracted by water, LiCl, and  $\text{KH}_2\text{PO}_4$ , respectively. Inclusion of  $\text{KH}_2\text{PO}_4$ -extractable  $\text{SO}_4\text{-S}$  to 92 cm did not improve the curvilinear regression relationships, nor did inclusion of percent soil organic matter. Increasing the soil:extractant ratio from 1:2 to 1:3 did not significantly change the amount of  $\text{SO}_4\text{-S}$  extracted by the  $\text{KH}_2\text{PO}_4$  solution. The 0.1 M LiCl solution is recommended for extracting  $\text{SO}_4\text{-S}$  from soils with relatively small amounts of absorbed  $\text{SO}_4\text{-S}$ .

*Additional index words:* S Uptake, Lucerne, *Medicago sativa* L.

by water and dilute salt or phosphate solutions or the  $\text{SO}_4\text{-S}$  extracted plus a fraction of the organic S. Water-extracted  $\text{SO}_4\text{-S}$  has generally not been well correlated to S uptake by plants except on relatively unweathered soils (3). The phosphate solution extracts adsorbed (1) as well as soluble  $\text{SO}_4\text{-S}$  and have been used successfully by many workers (2, 3, 4, 9). Attempts to account for the organic S contribution to the plant's S requirement have also been made by measuring the S released by heating (6, 14, 15), or the total S extracted by salt solutions (3).

A Washington study (7) showed that the S uptake by wheat (*Triticum aestivum* L.) from 53 soils in the greenhouse was correlated to the  $\text{SO}_4\text{-S}$  extracted by 0.1 M LiCl or 5 mM  $\text{MgCl}_2$ . The  $\text{SO}_4\text{-S}$  extracted by water or 0.1 M  $\text{CaCl}_2$  from the top 15 cm of soil was also related to the S available to legumes under field conditions in Canada (12). That study also showed that the ability to predict S deficiencies was increased by measuring  $\text{SO}_4\text{-S}$  to a 30-cm soil depth, sampling the soils in the spring before active growth commenced, and by air-drying the samples. A similar relationship between soil  $\text{SO}_4\text{-S}$  and plant response has been reported under Australian field conditions, except that adsorbed soil  $\text{SO}_4\text{-S}$  was measured (8).

Whereas some degree of correlation has been found for almost every index of soil S availability, the majority of the studies were not done under field conditions. In addition, most studies have been conducted primarily on leached and weathered soils, whereas many agricultural soils of the mountainous areas in the western United States are relatively undeveloped. These soils may be subjected to seasonal leaching from snow-melt but can become droughty during the growing season unless irrigated. Sulfur deficiency was identified on alfalfa (*Medicago sativa* L.) growing in the mountain valleys of southern Idaho and exploratory studies indicated that soil  $\text{SO}_4\text{-S}$  would be a good

**M**OST of the sulfur in soils is in the organic form, but neither total S nor organic S has proved to be a satisfactory index of soil S availability to growing plants (16). More promising methods measure some form of "available S" such as the  $\text{SO}_4\text{-S}$  extracted

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index of soil S availability. The present reports the relationships found between the extractable soil  $\text{SO}_4\text{-S}$  level and alfalfa response to S fertilization. A second paper in this series presents the relationships between plant analyses and the severity of S deficiency.

## METHODS AND MATERIALS

Experiments were conducted during 1970 and 1971 in mountain valleys in the Idaho counties of Camas, Custer, and Teton. These valleys are at elevations of 1,520 to 1,850 m, have 60 to 90 frost-free days, and receive 180 to 380 mm of annual precipitation, mostly as snow. Soils are acid to slightly alkaline and have formed from a variety of parent materials. The soil classification and chemical characteristics for each of the experiments are shown in Table 1. Experiments 9-71 through 13-71 were sprinkler-irrigated; the remaining were not irrigated although moisture was not limiting for the first harvest.

Sulfur, as  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , was applied on the soil surface the previous fall on the nonirrigated sites and before active growth commenced in the spring on the irrigated sites. Fertilization rates of S ranged from 22 to 67 kg/ha. Plant analyses indicated that all other essential plant nutrients were adequate. Soil samples were taken at each site prior to fertilization in depth increments of 0 to 30, 30 to 61, and 61 to 92 cm from each of four replications. The samples were air-dried and passed through a 2-mm sieve. The 0 to 30 cm samples were extracted by shaking for 30 min with cold water (22°C), 0.1 M LiCl, or 0.032 M  $\text{KH}_2\text{PO}_4$  (500 ppm P) with a soil:solution ratio of 1:2 by weight. Soil samples from all depths were extracted with the  $\text{KH}_2\text{PO}_4$  solution but with a soil:solution ratio of 1:3. The suspensions were filtered through a Whatman No. 42 paper and the  $\text{SO}_4\text{-S}$  in the filtrates was determined by the methylene-blue reduction method (5). All soil data given are based on the air-dried weight of the original soil samples and are the averages of the four replications.

Forage yields and plant samples for chemical analyses were taken at early bloom of the first harvest. The samples for chemical analyses were oven-dried at 55°C and ground to pass a 40-mesh screen. Total S was determined on the wet-ashed plant samples turbidimetrically (10). The plant data are the averages of four replications and are from the control and maximum yielding S treatments. Yields were also measured on the second harvest on the irrigated sites, but will not be

Table 1. Soil classification and chemical characteristics of the experimental sites.

Site-year of study	Series	Suborder classification	0- to 30-cm	
			pH*	Organic matter†
1-71	Riceton g 1	Typic Argixeroll	5.4	1.05
2-71	Riceton 1	Typic Argixeroll	5.6	2.01
3-71	Riceton 1	Typic Argixeroll	5.5	1.63
4-70	Brinegar 1	Pachic Argixeroll	5.7	0.87
5-70	Vodermaier g 1	Pachic Haploxeroll	6.0	1.89
6-70	Simonton g 1	Typic Argixeroll	5.6	1.38
7-70	Riceton 1	Typic Argixeroll	5.5	1.69
8-71	Riceton 1	Typic Argixeroll	5.6	1.80
9-71	Glin g 1	Typic Haplagid	7.4	1.42
10-71	Berenicaton si 1	Xeric Torriorthent	7.6	2.98
11-71	Driggs g 1	Aeric Cryoboroll	6.8	1.84
12-71	Tetonia si 1	Pachic Cryoboroll	6.4	2.38
13-71	Driggs si 1	Aeric Cryoboroll	6.4	2.58

\* Determined on a saturated paste. † Percent organic matter determined by method of Walkley and Black (13).

Table 2. Curvilinear regression equations and indexes of determination ( $R^2$ ) for the relationships between  $\text{SO}_4\text{-S}$  in the 0- to 30-cm soil layer and relative yield (R.Y.) or S uptake (kg S/ha) by the first harvest of alfalfa for each extractant.

Extractant	Regression equation	$R^2$ *
Cold water (1:2)	R. Y. = $52.26 + 13.14 (\text{ppm}) - 0.80 (\text{ppm})^2$	0.618
	kg S/ha = $0.50 + 1.90 (\text{ppm}) - 0.10 (\text{ppm})^2$	0.762
0.1 M LiCl (1:2)	R. Y. = $-95.69 - 42.79 (\text{ppm}) + 186.16 \sqrt{\text{ppm}}$	0.843
	kg S/ha = $-3.44 + 4.76 (\text{ppm}) - 0.42 (\text{ppm})^2$	0.807
0.032 M $\text{KH}_2\text{PO}_4$ (1:2)	R. Y. = $-85.97 + 28.82 (\text{ppm}) + 150.01 \sqrt{\text{ppm}}$	0.785
	kg S/ha = $-3.20 + 3.44 (\text{ppm}) - 0.21 (\text{ppm})^2$	0.780
0.032 M $\text{KH}_2\text{PO}_4$ (1:3)	R. Y. = $21.39 + 25.08 (\text{ppm}) - 1.94 (\text{ppm})^2$	0.696
	kg S/ha = $-4.65 + 3.90 (\text{ppm}) - 0.27 (\text{ppm})^2$	0.879

\* All  $R^2$ 's are significant at the 1% level.

discussed here since the results did not differ from the first harvest. The relative yield (R.Y.) is defined as (yield without S/yield with S)  $\times$  100.

## RESULTS AND DISCUSSION

Sulfur fertilization significantly increased forage yields on 9 of the 13 experimental sites where the control treatment yields ranged from 0.94 to 4.46 MT/ha. Yields on the S-fertilized treatments were from 1.68 to 5.57 MT/ha. Yields were generally higher on the irrigated sites, although the highest yielding site was not irrigated. Percent S in the plant tops ranged from 0.06 to 0.21 and from 0.18 to 0.24 on the control and S-fertilized treatments, respectively. The alfalfa plants at only one experimental site were below suggested critical levels of 0.20 to 0.22% S at early bloom (2) after S fertilization.

Good relationships between the  $\text{SO}_4\text{-S}$  in the 0- to 30-cm soil layer and relative forage yields were obtained with all extractants (Fig. 1 and Table 2). The highest index of determination was obtained with LiCl followed by  $\text{KH}_2\text{PO}_4$  (both 1:2 and 1:3) and cold water. In all cases, the presented curvilinear regression equation gave a better fit than linear regression. Attempts to improve the fit of the regression line to the data for the cold water extractant by dropping the highest soil  $\text{SO}_4\text{-S}$  value did not improve this relationship; however in this case a more realistic handdrawn line would give a soil  $\text{SO}_4\text{-S}$  level of approximately 3 ppm at the 100% relative yield level. A similar level is also suitable for LiCl, whereas slightly greater than 4 ppm  $\text{SO}_4\text{-S}$  would be necessary for both  $\text{KH}_2\text{PO}_4$  extractions. On the experimental sites with soil  $\text{SO}_4\text{-S}$  below these values no response to S fertilization was measured in 3 out of 12 for the  $\text{KH}_2\text{PO}_4$  and LiCl extracts and in 2 out of 11 for the cold water extract.

Measuring  $\text{SO}_4\text{-S}$  to a soil depth of 92 cm did not improve the relationship for the  $\text{KH}_2\text{PO}_4$  (1:3) extractant (Fig. 2). Appreciable amounts of  $\text{SO}_4\text{-S}$  below 30 cm were found only in the soils where there was not a response to S fertilization. Approximately 2 ppm of  $\text{SO}_4\text{-S}$  were found in each 30-cm depth increment below 30 cm in these soils.

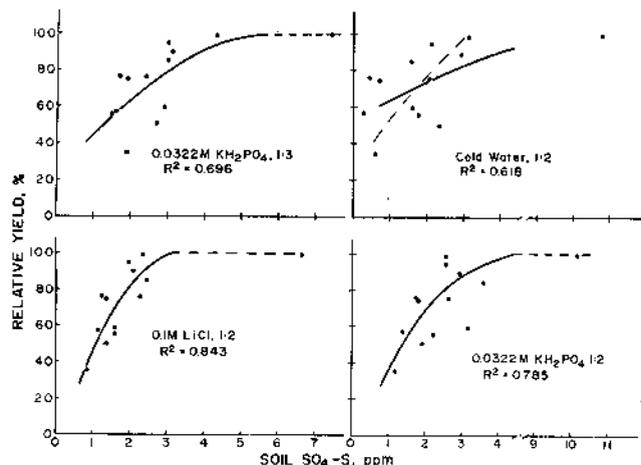


Fig. 1. The relationships between extractable  $\text{SO}_4\text{-S}$  in 0- to 30-cm soil layers for the respective extractant and relative yield. All relationships are significant at the 1% level. Dashed line is hand-fitted.

The amount of  $\text{SO}_4\text{-S}$  extracted from the 0- to 30-cm soil layer was significantly related to the S uptake by the alfalfa at the first harvest (Fig. 3 and Table 2). Approximately 8 to 9 kg of S per ha was found in the first harvest at soil  $\text{SO}_4\text{-S}$  levels adequate for a maximum yield under the experimental growing conditions. Indexes of determination for S uptake were similar to those obtained for the relative yield relationships. Inclusion of the extractable  $\text{SO}_4\text{-S}$  below 30 cm did not improve the relationship between  $\text{KH}_2\text{PO}_4$  (1:3) and S uptake, but when included gave a set of regression curves similar to those shown in Fig. 2.

Nonsignificant differences in soil  $\text{SO}_4\text{-S}$  levels for the various extracting solutions indicate that significant amounts of adsorbed  $\text{SO}_4\text{-S}$  were not present in these soils. Similar results showing a lack of adsorbed  $\text{SO}_4\text{-S}$  in unweathered soils have been reported for some Nebraska (3), Iowa (11), and eastern Washington (7) soils. The  $\text{KH}_2\text{PO}_4$  solution generally extracted more  $\text{SO}_4\text{-S}$  from the acidic and less  $\text{SO}_4\text{-S}$  from the alkaline soils than did cold water;  $\text{SO}_4\text{-S}$  extracted by  $\text{LiCl}$  was intermediate except on the

two slightly alkaline sites where it was lower. Increasing the soil:solution ratio from 1:2 to 1:3 did not significantly change the amount of  $\text{SO}_4\text{-S}$  extracted by  $\text{KH}_2\text{PO}_4$  and it increased the difficulty of measuring the small amounts of  $\text{SO}_4\text{-S}$  extracted. Soil particle dispersion problems were also encountered when using cold water but were avoided by using the salt solutions.

The soil  $\text{SO}_4\text{-S}$  levels needed for maximum production of the first harvest of alfalfa in this study are identical to those reported by Spencer, Bouma, and Moye (8) for production of subterranean clover pastures and by Walker and Doornenbal (12) for legume production. The 3-4 ppm  $\text{SO}_4\text{-S}$  levels may not be too far from an earlier critical value of 7 ppm  $\text{SO}_4\text{-S}$  obtained on digested soil extracts that may have included some soluble organic S (3).

Nonsoil contributions of S to plant growth confound S soil test correlation studies unless they can be accounted for. In this study contributions from rainfall and atmospheric sources were not measured, but were assumed to be low because of a lack of industrial and dense population centers and a lack of rainfall. Measurement of  $\text{SO}_4\text{-S}$  in the irrigation waters also indicated insignificant amounts coming from that source. Attempts to account for the S mineralized from the soil organic matter by including percent organic matter in the regression equations did not improve the indexes of determination. This source of S may have been partially accounted for in the relationships presented here since air-drying has been shown to increase water-soluble  $\text{SO}_4\text{-S}$  (2).

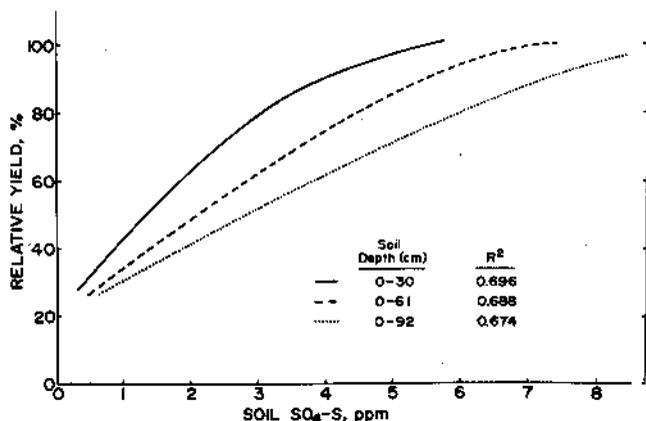


Fig. 2. The calculated regression relationships between relative yield and  $\text{SO}_4\text{-S}$  extracted by 0.0322 M  $\text{KH}_2\text{PO}_4$  with a 1:3 soil:solution ratio for the respective soil depths.

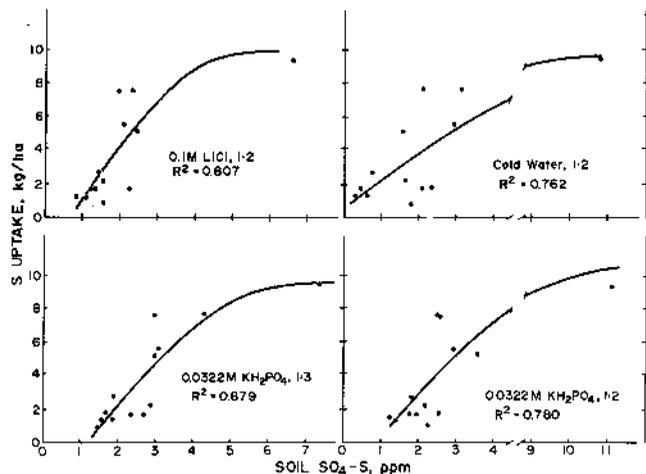


Fig. 3. The relationships between  $\text{SO}_4\text{-S}$  extracted from the 0- to 30-cm soil layer for the respective extractant and S uptake by the first harvest of alfalfa. All relationships are significant at the 1% level.

## LITERATURE CITED

- Ensminger, L. E. 1954. Some factors affecting the adsorption of sulfate by Alabama soils. *Soil Sci. Soc. Amer. Proc.* 18:259-264.
- , and J. R. Freney. 1966. Diagnostic techniques for determining sulfur deficiencies in crops and soils. *Soil Sci.* 101:283-290.
- Fox, R. L., R. A. Olsen, and H. F. Rhoades. 1964. Evaluating the sulfur status of soils by plant and soil tests. *Soil Sci. Soc. Amer. Proc.* 28:243-246.
- Hoeft, R. G., L. M. Walsh, and D. R. Keeney. 1973. Evaluation of various extractants for available soil sulfur. *Soil Sci. Soc. Amer. Proc.* 37:401-404.
- Johnson, C. M., and H. Nishita. 1952. Micro-estimation of sulfur in plant materials, soils, and irrigation waters. *Anal. Chem.* 24:736-742.
- Reddy, C. S., and B. V. Mehta. 1970. Fractionation of sulphur in some soils of Gujarat to evolve a suitable method for assessing available sulphur status. *Indian J. Agr. Sci.* 40:5-12.
- Roberts, S., and F. E. Koehler. 1968. Extractable and plant available sulfur in representative soils of Washington. *Soil Sci.* 106:53-59.
- Spencer, K., D. Bouma, and D. V. Moye. 1969. Assessment of the phosphorus and sulphur status of subterranean clover pastures. 2: Soil tests. *Aust. J. Exp. Agr. Anim. Husb.* 9:320-328.
- , and J. R. Freney. 1960. A comparison of several procedures for estimating the sulphur status of soils. *J. Agr. Res.* 11:948-959.
- Tabatabai, M. A., and J. M. Bremner. 1970. A simple turbidimetric method of determining total sulfur in plant materials. *Agron. J.* 62:805-806.
- , and ———. 1972. Distribution of total and available sulfur in selected soils and soil profiles. *Agron. J.* 64:40-44.
- Walker, D. R., and G. Doornenbal. 1972. Soil sulfate. II. As an index of the sulfur available to legumes. *Can. J. Soil Sci.* 52:261-266.

13. Walkley, A., and I. A. Black. 1934. An examination of the Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. *Soil Sci.* 37:29-38.
14. Virmani, S. M. 1971. Comparative efficacy of different methods for evaluating available sulphur in soils. *Indian J. Agr. Sci.* 41:119-125.
15. Williams, C. H., and A. Steinberg. 1959. Soil sulphur fractions as chemical indices of available sulphur in some Australian soils. *Aust. Res.* 10:340-352.
16. ———, and ——— 1964. The evaluation of plant available sulphur in soils: II. Availability of adsorbed and insoluble sulphates. *Plant Soil* 21:50-52.