Importance of sulphur in crop production*

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Abstract. Sulphur in agricultural soils occurs in organic and inorganic forms, with organic S accounting for > 95% of the total S. Analysis of a wide range of soils shows that from 25 to 75% of the organic S in soils is HI-reducible, from 7 to 30% is C-bonded, and from 11 to 22% is unidentified S. Nitrogen is associated with S in soil organic matter in a ratio of about 8:1, although the extreme ratios may vary from 5:1 to 13:1. Laboratory studies showed that humus S is depleted faster than humus N. Mineralization of S in crop residues varied with type of crop residue and soil studied. The amounts of S fertilizers (gypsum, elemental S, and sulfuric acid) used in the United States in 1981 and 1982 were 1.9×10^6 and 1.5×10^6 tons, respectively. Of the total amount used in 1982, 3, 5, 20, and 71% were used in the West North Central, Mountain, South Atlantic, and Pacific regions, respecitively. A survey of S deposition at about 100 sites in the United States and many other sites in Canada in 1980 showed that annual addition by precipitation in North America ranged from 0.5 to slightly above 10 kg/ha. The usual ranges of values in concentrations and spatial rates of N, P, and S in precipitation is well within the ranges of these elements in natural waters. Atmospheric sources are important components in meeting crops S requirements and should be considered in benefit-cost analyses relating to S emissions.

Introduction

Sulfur has been recognized as an essential element for plant growth and development for more than 100 years, and Liebig (1859) was aware of the close relationship between N and S in many plants. According to Hall (1909) and Juhalin-Dannfelt (1911), the beneficial effect of gypsum as a fertilizer was already known by the ancient Romans and Greeks. Alway (1940) has presented an interesting review of the history of S as a plant nutrient element. The history of the use of S fertilizers may be divided into three periods. The first period was the Reign of Gypsum (1760–1845). During this period gypsum was used widely and its beneficial effect generally overestimated. The second period was the Reign of Superphosphate (1845–1905) during which the need for any S additions to soils was ignored and

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the use of gypsum was discouraged by agricultural scientists. The third period is the Renaissance, or Modern Period. This last period dawned when a Russian chemist, Bogdanov, in 1899 questioned the assumption that the natural supply of S is everywhere sufficient for crops and three English agronomists (Dymond, Hughes, and Jupe) stationed at an Essex County laboratory, put the question to practical test on local fields from 1896 to 1901 with red clover, peas, cabbage, rutabagas, oats, barley, and permanent pasture, and published their work in the first volume of the Journal of Agrucultural Science in 1905 (Alway, 1940).

The use of gypsum as a fertilizer in modern times can be traced back to the middle of the eighteenth century. A field trial with gypsum applied to a clover field was reported in Switzerland in 1768 (Johansson, 1959). Application of gypsum increased the yield of clover by more than 2-fold. This resulted in a rapid increase of use of gypsum as a fertilizer. In the U.S. the introduction of gypsum was greatly encouraged by a classical experiment by B. Franklin, who applied gypsum to part of an alfalfa field situated beside a main road near Washington, D.C. Passing travelers on the road saw the effect of S in the gypsum in dark green letters against a light green background which read, 'This has been plastered'. The history of the use of S as fertilizer since the beginning of this century is reported by Johansson (1959), Evans (1975), and Alway (1940).

Interest in fertility-related aspects of the S cycle is increasing because S deficiencies on agronomic crops are observed with increasing frequency. Sulfur is considered the fourth important nutrient element after N, P, and K. Sulfur fertilization is now required in many areas in the United States to ensure satisfactory crop production. Other areas that have shown responses to S fertilization are in Australia, Africa, Asia, Canada, New Zealand, and South and Central America (Anonymous, 1982a). The factors responsible for the increased need for S fertilization has been discussed by Coleman (1966). They include increased use of high-analysis fertilizers that contain little or no S, increased crop yields, decreased use of S as a pesticide, more intensive cropping, and decreased gain of atmospheric S by soils and plants as a result of decreased combustion of coal and other S-containing fuels. This paper will deal primarily with the parts of the S cycle as they relate to crop production.

Sulfur requirements of crops

The importance of S in agriculture is obvious because plants require S for synthesis of an essential amino acid and proteins, certain vitamins and coenzymes, glucocide oils, structurally and physiologically important disulfide linkages and sulfhydryl groups, and activation of certain enzymes (Coleman, 1966). Generally, agronomic crops require about the same amount of S as they do of P. Although the S content of plants varies depending on the

| Table 1. Sulfur content of cro | .ps. | | | | |
|--------------------------------|---------|-----------------|--------------------|---------|-----------------|
| | Yield | Total S content | | Yield | Total S content |
| Crop | tons/ha | kg/ha | Crop | tons/ha | kg/ha |
| Grain and oil crops | | | Cotton and tobacco | | |
| Barley | 5.4 | 22 | Cotton (lint + | 4.3 | 34 |
| Corn | 11.2 | 34 | seed) | | |
| Grain sorghum | 9.0 | 43 | Tobacco | | |
| Oats | 3.6 | 22 | Burley | 4.5 | 21 |
| Rice | 7.8 | 13 | Flue cured | 3.4 | 50 |
| Wheat | 5.4 | 22 | | | |
| Peanuts | 4.5 | 24 | | | |
| Soybeans | 4.0 | 28 | | | |
| Hay crops | | | Fruit, sugar and | | |
| Alfalfa | 17.9 | 45 | vegetable crops | | |
| Clover-grass | 13.4 | 34 | Beets | | |
| Bermudagrass | | | Sugar | 67 | 50 |
| Common | 9.0 | 17 | Table | 56 | 46 |
| Coastal | 22.4 | 50 | Cabbage | 78 | 72 |
| Bromegrass | 11.2 | 22 | Irish potatoes | 56 | 27 |
| Orchardgrass | 13.4 | 39 | Onions | 67 | 41 |
| Pangolagrass | 26.4 | 52 | Oranges | 52 | 31 |
| Timothy | 9.0 | 18 | Pineapple | 40 | 16 |
| | | | Sugarcane | 224 | 96 |
| | | | | | |

Estimates by Potash/Phosphate Institute of North America (Terman, 1978).

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supply available, some crops have greater S requirements than others (Table 1). An average yield of forage crops removes 17 to 50 kg of S per ha and the cereal grains generally remove < 30 kg/ha. Other crops such as cabbage, turnip, and alfalfa have a particularly high requirement for S. Such crops commonly need from 45 to 70 kg of S per ha. One of the crops that require a very high amount of S is sugarcane. A yield of 224 tons per ha removes about 100 kg of S (Table 1).

Another factor that affects the S requirement of plants is the available N. Sulfur and N are closely associated in protein synthesis, thus S requirements vary with the supply of N to crops. Therefore, when S becomes limiting, additions of N do not increase the yield or protein level of plants (Dijkshoorn and Van Wijk, 1967).

The N:S ratio of many crops at maximum yields have been determined. Alfalfa requires one part of S with every 11 to 12 parts of N to ensure maximum production (Aulakh et al., 1976); with wheat, corn, beans, and sugar beet leaf blades, one part of S is required for every 12 to 17 parts of N (Stewart, 1966; Steart and Porter, 1969). During early growth, cereals are also very sensitive to S deficiency; the N:S ratios of grains such as oats and barley are 13:1 and 9:1, respectively (Saalbach, 1970). It has been suggested that many soils known to be deficient in S for alfalfa may also provide insufficient S for optimum cereal growth (Nyborg, 1968).

Crop plants obtain their S requirements from a number of sources. These are (1) soils, crop residues, and manures, (2) irrigation waters, (3) rainfall and the atmosphere, and (4) fertilizers and soil amendments. The order of importance of each of these sources varies with the type of crop, location, and management practices.

Sulfur in soils

Total S in mineral soils may range from < 20 ppm in sandy soils to > 600 ppm in heavy textured soils. Organic soils may contain as much as 0.5% S. Most soils in the United States, however, contain between 100 and 500 ppm of S.

Sulfur occurs in soils in organic and inorganic forms, with the organic S accounting for more than 95% of the total S in most soils from the temperate, humid, and semi-humid regions. The proportion of organic and inorganic S in soils, however, varies widely according to soil type and depth of sampling. While much of the organic S in soils remains unidentified, three broad fractions have been identified. The analytical methods currently in use permit differentiation between three broad fractions of organic S in soils: (1) HI-reducible S, (2) C-bonded S, and (3) unidentified S (residual or inert). The first fraction contains S compounds that are not directly bonded to C and it is believed to consist primarily of sulfate esters such as phenol sulfate, sulfated polysaccharides, choline sulfate, and sulfated lipids (Freney,

1967; Tabatabai and Bremner, 1972a; Chae and Tabatabai, 1981). Because the S in this fraction can be readily hydrolyzed to inorganic sulfate by acid and alkali, HI-reducible S is considered to be the most labile fraction of organic S (Spencer and Freney, 1960; Lowe, 1965; Freney et al., 1971; Cooper, 1972). Analyses of a wide range of soils have shown that, on the average, about 50% of the total organic S in soils of humid and temperate regions is present in the HI-reducible form, although the percentage may range from 25 to 75% (Table 2).

The second fraction, the C-bonded fraction, is determined by reduction to H_2S with Raney nickel (Tabatabai, 1982). Table 2 shows results obtained for the C-bonded S and the unidentified fractions in soils from different regions. Expressed as percentage of total S in soils, the means of the C-bonded S fraction range from 7 to 30; and the unidentified S fraction from 11 to 22.

The presence of large amounts of organic S in surface soils is indicated by the close relationship found between organic N and S. In many of the soils studied in North America and other parts of the world, these elements are associated approximately in the ratio of 8:1 for N and S, respectively, although this ratio may vary from 5:1 to 13:1 (Table 3). The N:S ratio appears to be the same for virgin soils as for their cultivated counterparts (Table 4), suggesting that organic N and S are mineralized in about the same ratio as they occur in soil organic matter. However, recent laboratory studies (will be discussed below) show that organic S is depleted faster than organic N.

As is true with N, when land is first cultivated the S content of the soil declines rapidly and an equilibrium level is reached which is characteristic of climate, cultural practices and soil type. At the equilibrium level, soil humus essentially ceases to act as a source of S for plant growth. Before reaching this equilibrium, the rate of mineralization of S will be so slow that it cannot cope with the plant's requirements. This results in the appearance of S deficiency symptoms on the plants. Recent studies show that most of the soils in the Midwest may be at or near the marginal levels of supplying S to plants. This is suggested from laboratory tests and greenhouse experiments showing that soils do not contain sufficient plant-available S and most respond to S fertilization when cropped under greenhouse conditions (Tabatabai and Bremner, 1972b; Widdowson and Hanway, 1974).

Studies on transformation of N and S under field conditions show mineralization patterns for N differ from those for S, with sulfate levels in uncropped soil undergoing much greater seasonal variation than levels of mineral N (Simon-Sylvestre, 1965). Recent laboratory work at Iowa State University to simulate field conditions showed that humus S is depleted faster than humus N. The data in Table 5 show that the rates of S mineralization from 12 Iowa surface soils are much lower than those of N mineralization. This observation is expected because soil humus contains more N

| | Percentage | of total S in forr | n specified | | | 1 | |
|-----------------------|-----------------|--------------------|-----------------------|------|-------------|------|-------------------------------|
| | HI-reducib. | le | C-bonded ^a | | Unidentifie | p | |
| Location ^b | Range | Mean | Range | Mean | Range | Mean | Ref. |
| Alberta. | | | | | | | |
| Canada (15) | 25-74 | 49 | 12-32 | 21 | 7-45 | 30 | Lowe (1965) |
| Australia (15) | 32-63 | 47 | 2254 | 30 | 3 - 31 | 23 | Freney et al. (1970) |
| Brazil (6) | 36-70 | 51 | 5-12 | 7 | 24-59 | 42 | Neptune et al. (1975) |
| Iowa, USA (24) | 36-66 | 52 | 5 - 20 | 11 | 21-53 | 37 | Tabatabai and Bremner (1972a) |
| Iowa, USA (10) | 42-58 | 51 | 7-14 | 11 | 33-44 | 38 | Chae and Tabatabai (1981) |
| Quebec, | | | | | | | |
| Canada (3) | 44–78 | 65 | 12-32 | 24 | 0-44 | 11 | Lowe (1964) |
| | | : | | | | | |
| Determined by rec | luction with Ka | nev NI. | | | | | |

| soils. | |
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| sulfur in | |
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beteinmen of reduction with range Mr. bFigures in paretheses indicate number of samples.

| Table 3. Mean ratios of nitrogen to sulfu | r in surface horizons of soils. | | |
|---|-----------------------------------|-----------|--------------------------------------|
| Location | Description ^a | N:S ratio | Ref. |
| | Virgin soils | | |
| Alberta, Canada | Brown Chernozems (4) | 7.1 | Lowe (1965) |
| | Black Brown Chernozems (4) | 7.7 | |
| | Grey Wooded (7) | 12.5 | |
| | Gleysols (6) | 5.0 | Lowe (1969) |
| U.S.A. (several states) | Not specified (10) | 8.7 | Stewart and Whitefield (1965) |
| | Cultivated soils | | |
| N.S.W., Australia | Pasture soils (5) | 8.5 | Barrow (1961) |
| | Clover pasture, podzolic (44) | 7.1 | Williams and Donald (1957 |
| Eastern Australia | Acid soils (128) | 8.3 | Williams and Steinbergs (1958) |
| | Alkaline soils (27) | 6.6 | 1 |
| Sao Paulo and Parana, Brazil | Agricultural, varied (6) | 7.7 | Neptune et al. (1975) |
| Canterbury, New Zealand | Grassland, unfertilized | 7.7 | Walker and Adams (1958) |
| North Scotland | Agricultural, non-calcareous (40) | 7.1 | Williams, Williams, and Scott (1960) |
| Iowa | Agricultural, varied (37) | 6.5 | Tabatabai and Bremner (1972a) |
| Iowa | Agricultural, varied (6) | T.T | Neptune et al. (1975) |
| Minnesota | Brown Chernozems (6) | 6.4 | Evans and Rost (1945) |
| | Black prairie soils (9) | 6.1 | |
| | Podzols (24) | 8.5 | |
| Mississippi | Podzols (4) | 13.1 | Nelson (1964) |
| Oregon | Agricultural, varied (16) | 9.9 | Harward et al. (1962) |
| Several states | Agricultural, varied (10) | 8.0 | Stewart and Whitefield (1965) |
| | | | |

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^aFigures in parentheses are number of soils examined.

| Location | | N:S ratio |
|------------------|---|-----------|
| Big Springs, TX | v | 12.0 |
| | С | 11.1 |
| Colby, KS | v | 6.5 |
| | С | 6.8 |
| Mays, KS | V | 8.0 |
| | С | 6.8 |
| Moccasin, MT | v | 7.6 |
| | С | 6.0 |
| Dalhart, TX | v | 9.6 |
| | С | 11.7 |
| Mandan, ND | v | 9.0 |
| | С | 9.6 |
| North Platte, NE | v | 9.9 |
| | С | 9.0 |
| Lawton, OK | v | 10.3 |
| | С | 10.4 |
| Archer, WY | V | 8.5 |
| | С | 8.0 |
| Havre, MT | v | 9.1 |
| | С | 8.2 |
| Average | | 8.7 |
| - | | 8.0 |

Table 4. Organic nitrogen and sulfur ratios in virgin soils (V) and their cultivated (C) counterparts^a.

^aStewart and Whitefield (1965).

| | Rate of | mineralizatio | n | | | |
|-----------|---------|---------------|----------------|----------|-----|-----|
| | at 20°C | | | at 35 °C | | |
| Soil | N | S | N : S | N | S | N:S |
| | | kg pe | er ha per weel | k | | |
| Lester | 6.7 | 1.6 | 4 .2 | 22.6 | 4.9 | 4.9 |
| Ackmore | 4.9 | 1.6 | 3.1 | 27.6 | 4.9 | 5.6 |
| Fayette | 5.6 | 1.8 | 3.1 | 23.5 | 5.2 | 4.5 |
| Downs | 8.1 | 2.7 | 3.0 | 35.9 | 7.0 | 5.1 |
| Clarion | 6.7 | 1.8 | 3.7 | 26.7 | 7.8 | 3.4 |
| Muscatine | 7.4 | 1.8 | 4.1 | 33.2 | 6.7 | 5.0 |
| Nicollet | 3.8 | 1.3 | 2.9 | 17.3 | 4.0 | 4.3 |
| Tama | 9.0 | 2.2 | 4.1 | 34.3 | 7.2 | 4.8 |
| Webster | 9.4 | 2.2 | 4.3 | 38.1 | 6.5 | 5.9 |
| Canisteo | 4.9 | 1.3 | 3.8 | 20.9 | 4.0 | 5.2 |
| Harps | 4.3 | 1.2 | 3.6 | 21.7 | 3.6 | 6.0 |
| Okoboji | 6.3 | 1.8 | 3.5 | 34.3 | 6.1 | 5.6 |
| Avg. | 6.4 | 1.8 | 3.6 | 28.0 | 5.7 | 5.0 |

Table 5. Comparison of rates of nitrogen and sulfur mineralization in Iowa surface soils.

Soil-glass beads columns were incubated at 20 or 30° C and the mineral N and S produced were determined after leaching every 2 weeks with 0.01NKCl for a total of 26 weeks.

than S. The weakly amounts of N, in the form of nitrate, produced in soils will not be completely available to plants because some of it is lost by leaching to ground water and another portion is lost to the atmosphere by denitrification. Similarly, not all the sulfate produced from the soil organic matter is available to plants because of its loss to ground water. No significant amount of S gases, however, are evolved from soil humus (Banwart and Bremner, 1976). As is the case with the amount of N mineralization, the sulfate produced from soil organic matter is not enough to cope with the crop requirements. Therefore, S fertilization is needed in some soils, especially in areas where the levels of atmospheric S are very low.

Although the N:S ratio of the 12 soils studied ranged from 5.8 to 7.4 (avg. 6.8) (Tabatabai and Al-Khafaji, 1980), the ratios of mineral N to mineral S produced during incubation ranged from 2.9 to 4.8 (avg. 3.6) and from 3.4 to 6.0 (avg. 5.0) at 20 and 35 °C, respectively (Table 5). Similar results recently were reported by Maynard et al. (1983) for three Canadian Prairie soils. These results clearly show that the pattern of N mineralization in soils differs from that of S mineralization and that the two elements are not mineralized at the same proportion as they occur in soil organic matter.

The data reported in Table 6 show the percentage of depletion of N and S in Iowa surface soils during the 26 weeks of incubation at 20 and 35° C. Generally, the rates of depletion of S are about 1.5 times those of N. The generally greater rates of depletion of organic S relative to that of organic N in soils supports the conclusion made by Fitzgerald (1978) that the belief held by some ecologists that S is nonlimiting in the environment requires reevaluation. This is especially true if the proposed transfer and use of N-fixing genes to improve plant growth becomes a reality. Because of the continued use of fertilizers that are free of or low in S and the proposed restriction on SO₂ emission into the atmosphere, a greater demand will be made by plants on the release of inorganic S from soil organic matter than in the past. Atmospheric sources are an important component in meeting crops S requirements and should be considered in benefit-cost analyses relating to S emissions.

Effect of soil management on sulfur mineralization

Soil management practices have been changing in recent years and minimum or no-till systems are becoming common methods. It is of considerable agronomic significance to know the extent to which the S returned in crop residue becomes available to succeeding crops. The release of plant available S from decomposing crop residue depends primarily on the rate of decomposition and the type and S content of the residue. To assess the effect of the type of residue on S mineralization in surface soils, crop residues (cornstalks and cobs, soybean residues, alfalfa, and sawdust) were applied at the rate of 50 mt/ha to five Iowa surface soils and soil-glass beads-crop residue mixtures

| | Percentage | depletion after 26 w | veeks | |
|-----------|------------|--|----------|------|
| | at 20 °C | ······································ | at 35 °C | |
| Soil | N | S | N | S |
| Lester | 6.0 | 12.5 | 22.6 | 32.7 |
| Ackmore | 4.2 | 9.3 | 25.1 | 27.3 |
| Fayette | 4.3 | 9.5 | 18.7 | 27.2 |
| Downs | 6.7 | 13.3 | 26.8 | 32.9 |
| Clarion | 4.7 | 9.5 | 18.3 | 34.9 |
| Muscatine | 3.6 | 7.0 | 16.3 | 24.1 |
| Nicollet | 2.0 | 5.6 | 8.3 | 14.7 |
| Tama | 4.6 | 8.4 | 18.0 | 25.7 |
| Webster | 4.3 | 8.1 | 17.8 | 22.6 |
| Canisteo | 1.9 | 4.2 | 9.1 | 10.9 |
| Harps | 2.0 | 3.5 | 9.1 | 8.9 |
| Okoboji | 1.8 | 4.0 | 9.3 | 11.4 |
| Avg. | 3.8 | 7.8 | 16.6 | 22.8 |

Table 6. Comparison of depletion rates of organic nitrogen and sulfur in Iowa surface soils.

Soil-glass beads columns were incubated at 20 or 30° C and the mineral N and S produced were determined after leaching every 2 weeks with 0.01N KCl for a total of 26 weeks.



Figure 1. Effect of crop-residue treatment on sulfur mineralization in soils.

were incubated in columns as described by Tabatabai and Al-Khafaji (1980). The mineral S, present initially, was removed by leaching with $5 \text{ m}M \text{ CaCl}_2$ and the columns were incubated at $30 \degree \text{C}$. The soil columns were leached with the same solution every two weeks for a total of 26 weeks. The sulfate-S thus released was determined by ion chromatography (Dick and Tabatabai, 1979). The crop residues used contained 174, 719, 1285, and 460 ppm of organic S in corn, soybeans, alfalfa, and sawdust, respectively. The soil studied contained 168, 249, 377, 396, and 612 ppm of organic S in the Lester, Downs, Webster, Harps, and Okoboji soils, respectively.

Figure 1 shows the effect of the crop residues on S mineralization in Lester and Okoboji soils. Only alfalfa residue additions released more mineral

| | Total amo | ount of S miner | alized in soil spe | ecified ^a | |
|--------------|-----------|-----------------|--------------------|----------------------|---------|
| Crop residue | Lester | Downs | Webster | Harps | Okoboji |
| | | | $\mu g S/g soil$ | | |
| None | 38 | 34 | 48 | 32 | 46 |
| Corn | 20 | 29 | 31 | 15 | 35 |
| Soybean | 25 | 26 | 40 | 17 | 37 |
| Alfalfa | 49 | 48 | 49 | 57 | 57 |
| Sawdust | 17 | 31 | 28 | 12 | 21 |

Table 7. Total amounts of S mineralized in crop residue treated soils.

^aSoil-glass beads columns were incubated at 30° C and the mineral S produced was determined after leaching every 2 weeks with 5 mM CaCl₂ for a total of 26 weeks.

S than the control on incubation with the five soils. Addition of corn residue, soybeans, and sawdust to the five soils resulted in reduction in the amount of S mineralized. This is expected because of the high C:S ratios of such materials. The amount of sulfate-S produced after 26 weeks of incubation with and without crop residue treatment are shown in Table 7. The amounts of S mineralized in the soils ranged from 32 ppm with Harps soil to 48 ppm with Webster soil. The magnitude of the reduction of mineral S production from incorporation of crop residue varied with the type of crop residue and soil used.

With the increased use of N and P fertilizers containing little or no S, immobilization and S and yield reductions accompnaying decomposition of crop residues have become more prominent. In humid regions S immobolization due to crop residue application should aid the retention of fertilizer S in surface soils. According to Jones et al. (1971) heavy additions of straw to soils in California failed to reduce leaching losses of sulfate, but reduced leaching losses of nitrate.

In a field experiment where crop residues were added for 11 consecutive years to a silty clay loam in Iowa, cropped to corn and well fertilized with N, Larson et al. (1972) reported that soil organic S increased linearly in proportion to the amount of residues added. After 11 years, organic S had increased by 16% at 2 tons/ha/yr and by 49% at 16/tons/ha/yr with alfalfa, and by 9% and 40% at the corresponding application rate with cornstalks. The increases in the organic S content were similar to those for C but greater than the gains in organic N and P. These results indicate that S levels can be maintained or increased, even under intensive cropping, when adequate quantities of crop residues are regularly returned to the soil. Addition of crop residues to soils under the minimum or no-till system, however, may significantly reduce the plant-available S, and consequently may lead to increases in application of S fertilizers.

Significance of atmospheric sulfur

Rainfall and the atmosphere constitute a third important source of plantnutrient S, and in any discussion about agricultural S balance, the contribution

of S by the air and atmospheric deposition must be considered. Unfortunately, this subject is difficult to quantify. Data on the S content of rainfall indicate wide variations by geographical locations. Several reports on S in precipitation as it relates to agriculture have been published (Terman, 1978; Tabatabai et al., 1981; Tabatabai, 1983a, b). The annual rates of S deposition by precipitation in North America for 1980 ranged from 0.5 to slightly above 10 kg/ha (Cowling, 1983). Other reports show that individual sites may receive annual S deposition $\ge 10 \text{ kg/ha}$ (Terman, 1978; Tabatabai, 1983a, b). As is true of N, the data available for S in precipitation in Iowa indicate that between 60 and 80% of the S is deposited during the crop growing season, the spring and summer (Tabatabai and Laflen, 1976). Therefore, the amounts of S added in precipitation in most rural areas of the United States are important for crop production. Laboratory and greenhouse experiments have shown that many soils of the United States do not contain sufficient plantavailable S to meet crop requirements for this element, yet no S deficiency symptoms have been reported (Tabatabai and Bremner, 1972b). Since it is known that soils and plants absorb SO₂ directly from the atmosphere, it is believed that other S gases are also absorbed in this manner (Ulrich et al., 1967). Thomas and Hill (1935) showed that lucerne could take up a substantial portion of its S as SO₂ from the atmosphere without injury, and this finding has been subsequently confirmed for other crop plants such as cotton (Olsen, 1957) and rape (Bromfield, 1972). In certain areas, uptake of atmospheric SO_2 is able to compensate for soil S deficiency (Cowling et al., 1973). Indeed, SO_2 and H_2S can be used by sunflowers as their only source of S without affecting their normal growth (Faller, 1972). Studies in Wisconsin showed that under optimum yield 44% of the S in alfalfa is derived from atmospheric sources (Hoeft et al., 1972).

Water pollution by sulfate from nonpoint sources is usually not of concern; water pollution by nitrate and phosphate from leaching, runoff, and erosion, especially from managed land, can contribute to quality of lakes and streams, and therefore have received the most attention. Thus, numerous reports are available on the concentration of N, P, and S in waters and sediments. This makes comparison of these elements in waters derived from managed and unmanaged lands with those in precipitation possible. The usual ranges of values in concentrations and spatial rates are presented in Figures 2 and 3.

Losses of S by leaching vary widely, some drainage waters contain more S than the rain supplies even though little or none is added in fertilizer. The extra quantity may be deposited directly on plants and soils from the atmosphere or released from soil organic matter or minerals. Whitehead (1964) reported annual losses from unfertilized fallow soils in Illinois ranged from 1.5 to 65 kg S/ha. West German soils also lost an average of 33 kg S/ha. Freney et al. (1962) consider annual losses by leaching to average 15 kg S/ha in Europe and North America, 4.5 kg in South America, and < 1 kg/ha in



Figure 2. Range of inorganic nitrogen, sulfur and phosphorus concentrations in natural waters. Source: Tabatabai (1983b).



Figure 3. Range of spatial rates of inorganic nitrogen, sulfur and phosphorus (total for sediments) in natural waters and sediments. Source: Tabatabai (1983b).

some areas of Australia. It has been estimated that between 3 and 32 kg S/ha are lost by tile drainage in Iowa (Baker et al., 1975). In general, loss of S from soils by leaching varies from insignificant amounts to as much as 320 kg S/ha annually from soils treated with S fertilizers (Harward and Reisenauer, 1966).

Sulfur fertilizers

The sources of plant-nutrient S discussed in the other sections of this paper are generally beyond the control of the farmer. The last source of plantnutrient S, which can be deliberately and easily controlled, is S added in fertilizers and soil amendments. Until about three decades ago, most fertilizers were formulated using large amounts of normal superphosphate and ammonium sulfate. Both of these materials contain appreciable amounts of S, 12 and 24%, respectively. With the introduction of high-analysis N and P fertilizer materials, the S included incidentally in fertilizers has been gradually decreasing. This trend, which began around 1950, is expected to continue until S is deliberately reintroduced into the fertilizer.

There are many fertilizer materials, both liquid and solid, which can be and are being used to supply S to growing crops. The one selected for any particular situation is determined by the crop to be grown, the S level of the soil, the cost of the material, and the ease with which its use can be fitted into a particular fertilizer program. As a general rule, all of the soluble sources (sulfates, thiosulfates, polysufides) are about equally effective and immediately available to growing plants. Elemental S must be converted by soil microorganisms to the sulfate form before being absorbed by plants. The rate of this conversion is generally quite rapid in warm, moist, well-aerated soil provided that the S is in a finely divided form or in granular forms which disintegrates quickly to finely divided particles.

Gypsum has been widely used for many years as an S- and Ca-bearing material for fertilization and soil reclamation. It is a constituent of normal superphosphate and therefore, S deficiencies seldom occur on land adequately fertilized with this material. In the manufacturing of concentrated superphosphate, however, the gypsum is largely removed and, thus, this material contains little or no S.

Another source of S is sulfuric acid. When added to soils, sulfuric acid is immediately available to neutralize alkalinity and to supply plant-nutrient S. Its use has largely been limited to metering into irrigation waters. However, more recent developments in equipment suggest that it may be directly applied to the soil by injection.

| | Kind of sulfur fertilizer used (tons) | | | | | |
|--------------------|---------------------------------------|-------------|---------------|--------------------|--|--|
| Region | Gypsum | Elemental S | Sulfuric acid | Total ^a | | |
| New England | 122 | 5 | 0 | 127 | | |
| Middle Atlantic | 589 | 757 | 6 | 758 | | |
| South Atlantic | 287 866 | 3 607 | 277 | 291 750 (20) | | |
| East North Central | 6 357 | 839 | 0 | 7 1 96 | | |
| West North Central | 24 837 | 25 737 | 0 | 50 574 (3) | | |
| East South Central | 2624 | 30 | 128 | 2682 | | |
| West South Central | 0 | 543 | 369 | 912 | | |
| Mountain | 54 428 | 11 900 | 637 | 66 965 (5) | | |
| Pacific | 993 368 | 29 933 | 26 166 | 1 049 467 (71) | | |
| Alaska, Hawaii, | | | | | | |
| Puerto Rico | | | | | | |
| Total | 1 370 191 | 72 757 | 27 583 | 1 470 531 | | |

Table 8. Sulfur fertilizers consumed in regions of the U.S. in year ending June 39, 1982.

^aFigures in parentheses are S fertilizers used in the region expressed as percentage of the total amount used in the U.S.

The amounts of S fertilizers (gypsum, elemental S, and sulfuric acid) used in the United States in 1981 and 1982 were 1.9×10^6 and 1.5×10^6 tons, respectively. Of the total amounts used in 1982, 3, 5, 20, and 71% were used in the West North Central, Mountain, South Atlantic, and Pacific regions, respectively (Table 8). The amount of S fertilizer used in each region is an indication of the plant-available S status of the soils and cropping conditions. Another factor is the contribution of atmospheric S and S added by precipitation to the S requirements of the crops in the region.

Conclusions

Sulfur is required in large amounts by crops. Many crops contain as much S as P. Sulfur is ranked in importance with N and P in the formation of proteins. The increased use of more concentrated fertilizers which contain little or no S, combined with less S from rainfall in many areas, have decreased the supply of S to the crops. At the same time, higher crop yields have increased the uptake of S from soils. Soil which originally contained sufficient S often becomes deficient as agriculture is intensified, unless S-containing fertilizers are used.

Although the analytical methods available allow fractionation of soil organic S into three broad groups, little information is available about the specific S compounds present in each fraction. Among the various aspects of the S cycle, the factors affecting the mineralization and immobilization of S in agricultural soils deserves further investigation.

Despite the concern about atmospheric S deposition, significant amounts of S are added to agricultural soils as fertilizers. Of the total amount $(1.5 \times 10^6 \text{ tons})$ used in 1982, 3, 5, 20, and 71% were used in the West North Central, Mountain, South Atlantic, and Pacific regions, respectively. The current rates of S additions by wet deposition should be beneficial to crop production. The annual rates for 1980 in North America ranged from 0.5 to slightly above 10 kg S ha^{-1} , which are much below those required by agronomic crops. Therefore, atmospheric sources are important components in meeting crops S requirements and should be considered in benefitcost analyses relating to S emissions.

References

Alway, I. J. 1940. A nutrient element slighted in agricultural research. J. Am. Soc. Agron. 32: 913-921.

Anonymous 1982a. The fourth major nutrient. The Sulphur Institute, Washington, D.C.

Anonymous 1982b. Commerical fertilizer consumption for year ended June 30, 1982. Crop Reporting Board, Statistical Reporting Service, U. S. Department of Agriculture, Washington, D. C., SpCr 7(11-82).

Aulakh, M. S., G. Dev, and B. R. Arora. 1976. Effect of sulphur fertilization on the nitrogen-sulfur relationships in alfalfa (Medicago sativa L. Pers.), Pl Soil 45: 75-80.

- Baker, J. L., J. M. Laflen, H. P. Johnson, and J. J. Hanway. 1975. Nitrate, phosphorus, and sulfate in subsurface drainage water. J. Environ Qual. 4: 406-412.
- Banwart, W. L. and J. M. Bremner. 1976. Volatilization of sulfur from unamended and sulfate-treated soils. Soil Biol Biochem. 8: 19-22.
- Barrow, N. J. 1961. Studies on mineralization of sulphur from soil organic matter. Aust. J. Agric Res 12: 306-319.
- Bromfield, A. R. 1972. Absorption of atmospheric sulphur by mustard (*Sinapus alba*) grown in a glasshouse. J. Agric. Sic. 78: 343-344.
- Chae, Y. M. and M. A. Tabatabai. 1981. Sulfolipid and phospholipid in soils and sewage sludges in Iowa. Soil Sci. Soc. Am. J. 45: 20-25.
- Coleman, R. 1966. The importance of sulfur as a plant nutrient in world crop production. Soil Sci. 101: 230-239.
- Cooper, P. J. M. 1972. Aryl sulphatase activity in northern Nigerian soils. Soil Biol. Biochem. 4: 33-337.
- Cowling, D. A., L. H. P. Jones, and D. R. Lockyer. 1973. Increased yield through correction of sulphur deficiency in ryegrass exposed to sulphur dioxide. Nature (London) 243: 479-480.
- Cowling, E. B. 1982. The North American acid rain situation. In: Ecological Effects of Acid Deposition, National Swedish Environment Protection Borard-Report PM 1636, pp. 53-73.
- Dick, W. A. and M. A. Tabatabai. 1979. Ion chromatographic determination of sulphate and nitrate in soils. Soil Sci. Soc. Am. J. 43: 899–904.
- Dijkshoorn, W. and A. L. Van Wijk. 1967. The sulphur requirements of plants as evidenced by the sulphur-nitrogen ratio in the organic matter-A review of published data. Pl. Soil 26: 129-157.
- Evans, C. A., and C. O. Rost. 1945. Total organic sulfur and humus in Minnesota soils. Soil Sci. 59: 125-137.
- Evans, L. T. 1975. Sulphur in agriculture. In: McLachlan (ed.), Sulphur in Australasian Agriculture, pp. 3-8, Sydney University Press, Australia.
- Faller, N. 1972. Schwefeldioxide, schwefelwasser, nitrose gase und ammoniak als ausschliesslich s-bzw. n-quellen der höheren pflanze. Zeitschr. Pflanzenernahr. Bodenk. 131: 120-138.
- Fitzgerald, J. W. 1978. Naturally occurring organosulfur compounds in soil. In: J. O.
- Nriagu (ed.), Sulfur in the environment. Part 2, pp. 391-443. John Wiley & Sons, New York.
- Freney, J. R. 1967. Sulfur-containing organics. In: A. D. McLaren and G. H. Peterson (ed.), Soil Biochemistry, Volume 1, pp. 229–259. Marcel Dekker, New York.
- Freney, J. R., N. J. Barrow, and K. Spencer. 1962. A review of certain aspects of sulphur as a soil constituent and plant nutrient. Pl. Soil 17: 295-308.
- Freney, J. R., G. E. Melville, and C. H. Williams. 1970. The determination of carbon bonded sulfur in soil. Soil Sci. 109: 310-318.
- Freney, J. R., G. E. Melville, and C. H. Williams. 1971. Organic sulphur fractions labeled by addition of ³⁵S-sulphate to soils. Soil Biol. Biochem. 3: 133-141.
- Hall, A. D. 1909. Fertilizers and Manures. London, p. 266.
- Harward, M. E. and H. M. Reisenauer. 1966. Movement and reactions of inorganic soil sulfur. Soil Sci. 101: 326-335.
- Harward, M. E., T. T. Chao, and S. C. Fang. 1962. The sulfur status and sulfur supplying power of Oregon soils. Agron. J. 54: 101-106.
- Hoeft, R. G., D. R. Keeney, and L. M. Walsh. 1972. Nitrogen and sulfur in precipitation and sulfur dioxide in the atmosphere in Wisconsin. J. Environ. Qual. 1: 203-208.
- Johansson, O. 1959. On sulfur probelms in Swedish agriculture. Ann. Royal Agric. Coll. Sweden 25: 57-169.
- Jones, M. B., W. A. Williams, and W. E. Martin. 1971. Effect of waterlogging and organic matter on the loss of applied sulfur. Soil Sci. Soc. Am. Proc. 35: 542-546.
- Juhlin-Dannfelt, H. 1911. Gips verkan som gödselmedel. Kungl. Lantbruksak. Handl. Och Tidskr. 50: 87-91.
- Larson, W. E., C. E. Clapp, W. H. Pierre, and Y. B. Morachan. 1972. Effects of increasing amounts of organic residues on continuous corn: II. Organic carbon, nitrogen, phosphorus, and sulfur. Agron. J. 64: 205-208.

- Liebig, J. 1859. Letters on Modern Agriculture, Blyth, J. (ed.). Walton and Maberly, London.
- Lowe, L. E. 1964. An approach to the study of the sulphur status of soils and its application to selected Quebec soils. Can. J. Soil Sci. 44: 176-179.
- Lowe, L. E. 1965. Sulphur fractions of selected Alberta soil profiles of the chernozemic and podzolic orders. Can. J. Soil Sci. 45: 297-303.
- Lowe, L. E. 1969. Sulfur fractions of selected Alberta profiles of the gleysolic order. Can. J. Soil Sci. 49: 375-381.
- Maynard, D. G., J. W. B. Stewart, and J. R. Bettany. 1983. Sulfur and nitrogen mineralization in soils compared using two incubation techniques. Soil Biol. Biochem. 15: 251-256.
- Nelson, L. E. 1964. Status and transformation of sulfur in Mississippi soils. Soil Sci. 97: 300-306.
- Neptune, A. M. L., M. A. Tabatabai, and J. J. Hanway. 1975. Sulfur fractions and carbon-nitrogen-phosphorus-sulfur relationships in some Brazilian and Iowa soils. Soil Sci. Soc. Am. Proc. 39: 51-55.
- Nybrog, M., 1968. Sulfur deficiency in cereal grains. Can. J. Soil Sci. 48: 37-41.
- Olsen, R. A. 1957. Absorption of sulfur dioxide from the atmosphere by cotton plants. Soil Sci. 84: 107–111.
- Saalbach, E. 1970. Sulphur requirements and sulphur removals of the most important crops. In: International Symposium on Sulphur in Agriculture, pp. 23-55. Sulphur Institute (London).
- Simon-Sylvestre, G. 1965. Further observations on the yearly cycle of soil sulphur and soil nitrogen. C. R. Hebd. Seances Acad. Agric. 53: 90-97.
- Spencer, K., and J. R. Freney. 1960. A comparison of several procedures for estimating the sulphur status of soils. Aust. J. Agric. Res. 11: 948-959.
- Stewart, B. A. 1966. Nitrogen-sulphur relationships in plant tissues, plant residues, and soil organic matter. Proc. Int. Soc. Soil Sci. Tran. (Comm II and IV) 131-138.
- Stewart, B. A., and L. K. Porter. 1969. Nitrogen-sulfur relationships in wheat (*Triticum aestivum* L.), corn (*Zea mays*), and beans (*Phaseolus vulgaris*). Agron. J. 61: 267-271.
- Stewart, B. A., and C. J. Whitefield. 1965. Effects of crop residue, soil temperature, and sulfur on the growth of winter wheat. Soil Sci. Soc. Am. Proc. 29: 752-755.
- Tabataóai, M. A. 1982. Sulfur. In: A. L. Page, R. H. Miller, and D. R. Keeney (eds.), Methods of Soil Analysis, Part 2--Chemical and Microbiological Properties, 2nd ed., pp. 501-538 American Society of Agronomy, Inc., Madison.
- Tabatabai, M. A. 1983a. Atmospheric deposition of nutrients and pesticides. In: G. W. Bailey and F. W. Schaller (eds.), Agricultural Nonpoint Sources and Pollutant Processes, pp. 92-108. Iowa State University Press, Ames.
- Tabatabai, M. A. 1983b. Effect of acid rain on soils. CRC Crit. Rev. Environ. Cont. (in press).
- Tabatabai, M. A. and A. A. Al-Khafaji. 1980. Comparison of nitrogen and sulfur mineralization in soils. Soil Sci. Soc. Am. J. 44: 1000-1006.
- Tabatabai, M. A. and J. M Bremner. 1972a. Forms of sulfur, and carbon, nitrogen and sulfur relationships, In Iowa soils. Soil Sci. 114: 380-386.
- Tabatabai, M. A. and J. M. Bremner. 1972b. Distribution of total and available sulfur in selected soils and soil profiles. Agron. J. 64: 40-44.
- Tabatabai, M. A. and J. M. Laflen. 1976. Nutrient content of precipitation over Iowa. Water Air Soil Poll 6: 361-373.
- Tabatabai, M. A., R. E. Burwell, E. G. Ellis, D. R. Keeney, T. J. Logan, D. W. Nelson, R. A. Olson, G. W. Randall, D. R. Timmons, E. S. Verry, and E. M. White. 1981. Nutrient concentrations and accumulations in precipitation over the North Central Region. Iowa Agric. Home Econ. Exp. Stn. Res. Bull. 594 (North Cent. Reg. Res. Publ. No. 282).
- Terman, G. L. 1978. Atmospheric sulfur-The agronomic aspects. Tech. Bull. No. 23. The Sulphur Institute, Washington, D. C.
- Thomas, M. D. and G. R. Hill. 1935. Absorption of sulphur dioxide by alfalfa and its relation to leaf injury.. Plant Physiol. 10: 291-307.

- Ulrich, A., M. A. Tabatabai, K. Ohki, and C. M. Johnson. 1967. Sulfur content of alfalfa in relation to growth in filtered and unfiltered air. Pl. Soil 26: 235-252.
- Walker, T. W. and A. F. R. Adams. 1958. Studies on soil organic matter: 1. Influence of phosphorus conent of parent materials on accumulation of carbon, nitrogen, sulfur and organic phosphorus in grassland soils. Soil Sci. 85: 307-318.
- Whitehead, D. C. 1964. Soil and plant-nutrient aspects of the sulphur cycle. Soils Fert. 27: 1-8.
- Widdowson, J. P. and J. J. Hanway. 1974. Available-sulfur status of some representative Iowa Agric. Home Econ. Exp. Stn. Res. Bull. 579.
- Williams, C. H. and C. M. Donald. 1957. Changes in organic matter and pH in a podzolic soil as influenced by subterranean clover and superphosphate. Aust. J. Agric. Res. 8: 179-189.
- Williams, C. H. and A. Steinbergs. 1958. Sulphur and phosphorus in some eastern Australian soils. Aust. J. Agric. Res. 9: 483-491.
- Williams, C. H., E. G. Williams, and N. M. Scott. 1960. Carbon, nitrogen, sulphur, and phosphorus in some Scottish Soils. J. Soil Sci. 11: 334-346.