SULFUR, CALCIUM and MAGNESIUM

Sulfur, calcium and magnesium are required in smaller quantities than other macronutrients nutrients and are less likely to be deficient for optimum plant growth. Thus, they are sometimes referred to as secondary nutrients. However, calcium, magnesium, and sulfur are very important and often are required as fertilizer or as soil amendments.

Most Kansas soils contain sufficient quantities of calcium and magnesium for optimum yields. Acidic soils are most likely to be calcium of magnesium deficient, but proper liming of these soils supplies sufficient amounts of these nutrients for crop production.

Sulfur is a secondary element that has been shown to be deficient in some Kansas soils. Most responses to sulfur have been observed on sandy, low organic matter soils, though occasional responses have been noted on other soils. Since sulfur is required in fairly large amounts by plants, it needs to be watched carefully

SULFUR

Sulfur (S) is one of 17 elements essential for crop growth. Although sulfur is considered a secondary nutrient, it is often called the fourth major nutrient ranking just below nitrogen, phosphorus, and potassium in terms of how widespread deficient soils are.

Deficiencies of sulfur are increasing in Kansas, most of North America and worldwide. The incidence of sulfur deficient soils has increased in recent years likely due to one or more of the following:

- Continued use of fertilizers that contain little or no sulfur
- More intensive cropping systems (double cropping, less use of fallow, more use of crop residue) that result in greater sulfur removal
- Higher yielding varieties and hybrids
- Less sulfur deposition from the atmosphere
- Stable or declining levels of organic matter

Plant Considerations

Sulfur is taken up by plants as the sulfate ion (SO_4^{-2}) and may be retained in this form in plant tissues and cell sap. Much of the sulfate is reduced and used in the formation of amino acids, proteins, and oils; in nitrogen fixation (root nodules); in structural components of protoplasm; and in activation of certain vitamins and enzymes. Sulfur is essential as a structural component of some amino acids found in both plants and animals, thus it is a part of the makeup of every living organism.

Sulfur Removal In Crops

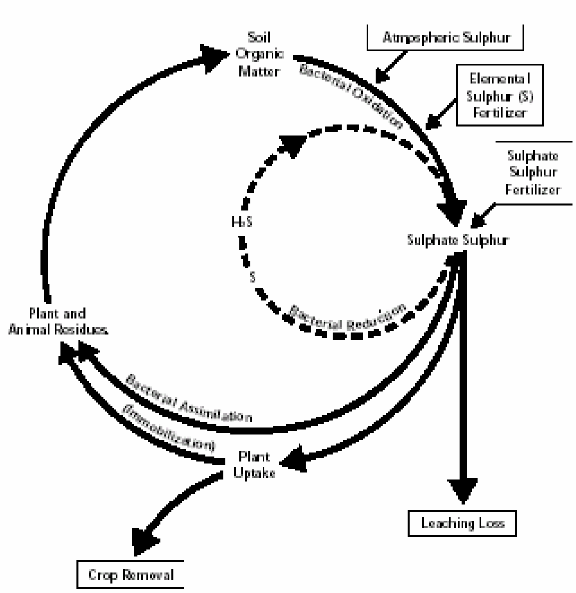
Crop	Yield	S
	- - lbs - -	
Corn	200 bu grain	15
	Stover	18
Grain Sorghum	150 bu grain	22
	Stover	16
Wheat	80 bu grain	7
	Straw	15
Canola (rapeseed)	35 bu grain	12
	Straw	9
Soybeans	60 bu grain	12
	Stover	13
Alfalfa	6 ton	30
Cool-season grass	4 ton	16
Sunflower	3,500 lb seed	6
	Stover	10

Chlorophyll formation also is dependent on proper sulfur nutrition. The amount of sulfur in plants is similar to phosphorus in many cases, thus removal by crops can be sizeable especially when the entire aboveground portion of the crop is harvested. Sulfur removal by various crops is summarized in Table 1.

Sulfur deficiency on growing crops is often mistaken for nitrogen deficiency. With sulfur deficiency, many crops become uniformly chlorotic. The pale yellow symptom of sulfur deficiency often appears first on the younger or uppermost leaves, while nitrogen deficiency initially appears on the older lower leaves. Deficiencies of sulfur are often difficult to identify because the paling in crop color is not always obvious. Crops lacking sulfur also may be stunted, thin-stemmed and spindly. In the case of cereal grains, maturity is delayed. On legume crops, nodulation may be reduced. In some crops, a reddish color may first appear on the underside of leaves and on stems.

The need for sulfur is associated with amounts of nitrogen available to crop plants. This relationship is not surprising since both are components of protein and are associated with chlorophyll formation. Nitrogen and sulfur also are linked because sulfur plays a key role in the activation of the enzyme nitrate reductase, which facilitates conversion of nitrates to amino acids. Low activity of this enzyme due to sulfur deficiency depresses soluble protein concentrations in plant tissues. Significant economic forage and grain yield losses can occur with sulfur deficiency, even when deficiency symptoms are not obvious. This can be particularly true when high levels of nitrogen nutrition are not balanced with adequate sulfur. Nitrogen use efficiency can be significantly reduced when sulfur is deficient.

Figure 1. *The Soil Sulphur Cycle*



Soil Considerations

Sulfur is usually present in relatively small amounts in soils and a majority is in organic forms. Sulfur deficient soils are often low in organic matter, coarse-textured, well-drained, and subject to leaching. In recent years, an increasing number of finer textured soils have shown sulfur deficiency, however. Much like nitrogen, sulfur tends to cycle in the soil environment. The soil sulfur cycle is illustrated in Figure 1.

Soil organic matter is an excellent source of sulfur. Since organic sulfur is not plant available, sulfate must be released from reserves of organic matter through microbial mineralization. Nitrogen and sulfur mirror each other closely in terms of the transformations and reactions that occur in the soil. Mineralization of sulfate from soil organic matter is controlled by organic matter levels, temperature, and moisture. Generally, environmental factors that favor plant growth enhance sulfur release from organic matter.

Sulfur deposition from sulfur dioxide and other sulfur gases dissolved in rain or snow contribute to soil sulfur supplies. Some studies have indicated that 10 to 20 lbs S per acre are deposited annually in some parts of the U.S, but 5 to 15 lbs S per acre is likely more typical for Kansas and the Great Plains. Recent air quality studies indicate that sulfur deposited from the atmosphere in the U.S. is declining slowly over time. The amount of S received in precipitation varies from region to region in relation to distance from industrial areas and sources of air pollutants.

Sulfate ($SO4^{-2}$) is an anion (negatively charged ion) and as such is mobile in the soil though not as free moving as nitrate ($NO3^{-}$) or chloride (Cl^{-}). In well drained, coarse-textured soils, sulfate can be leached below the root zone especially in high rainfall areas or under irrigation. Supply of sulfate in soils can vary greatly from year to year, based on crop removal, environmental conditions, and the amount of sulfur deposition from the atmosphere.

The total sulfur concentration of soil varies widely from about 50 to 50,000 parts per million (ppm). As is the case with many other nutrients, however, total sulfur is not necessarily a good predictor of a soils ability to supply this nutrient. A soil test for available sulfate-sulfur has been developed. However, for proper interpretation of this test , soil organic matter, soil texture, the crop to be grown and the expected yield level also need to be factored in to accurately assess sulfur needs.

As with nitrate-N, soil samples should be collected from a deeper depth than for normal soil samples if the soil test is to be used. Since sulfate sulfur (SO4- S) is mobile, sampling to a 24-inch depth is suggested for best results. When sampling for routine analyses (pH, phosphorus, potassium) and organic matter and zinc a 0 to 6 inch and 6 to 24 inch sample is suggested.

Significant amounts of plant available sulfate-sulfur can be added to the soil via irrigation water. In Kansas, sulfur content of irrigation water varies, but in some cases enough sulfur could be added through irrigation to meet crop needs. The sulfur content of irrigation water should be determined by testing and factored into sulfur applications. However, it must be kept in mind that irrigation water must be applied before sulfur in irrigation water will help the crop. If it is well into the growing season before the first irrigation is made, the plant may be sulfur stressed early even though more than enough sulfur will eventually be applied during the growing season. Timeliness of the sulfur additions also needs to be taken into account. An example is irrigated corn production on sandy soils.

Fertilizer Sources of Sulfur

Liquid and dry sulfur-containing fertilizer materials are plentiful. In fact, more sulfur-containing fertilizer materials are available to the industry than any other major or secondary plant nutrient.

Ammonium Sulfate. (21-0-0-24S) is one of the oldest sources of ammoniacal nitrogen, manufactured as a by-product of the coking of coal from the steel industry. Ammonium sulfate is also manufactured as a byproduct from metallurgical and chemical operations. Nearly one-fourth of world production comes from caprolactam manufacture, a raw material for the production of synthetic fibers. Three to four pounds of by-product ammonium sulfate are formed for each pound of caprolactam produced. Ammonium sulfate accounts for 4 million tons of plant nutrient sulfur worldwide. This product can be blended with most other dry fertilizers or can be made into a liquid. Ammonium sulfate is a good source of both nitrogen and sulfur, has low hygroscopicity, and is chemically stable. Its use may be undesirable on acidic soils, due to the acid-forming potential.

Ammonium Thiosulfate. (12-0-0-26S) is a clear liquid material with no appreciable vapor pressure containing 12 percent nitrogen and 26 percent sulfur. Ammonium thiosulfate is the most popular sulfur-containing product used in the fluid fertilizer industry, as it is compatible with nitrogen solutions and complete (N-P-K) liquid mixes or can be used in suspensions. When ammonium thiosulfate is applied to the soil, it decomposes to form colloidal elemental sulfur and ammonium sulfate. Ammonium thiosulfate should not be used in starter fertilizers placed in direct seed contact, because of toxicity to seed.

Potassium Magnesium Sulfate (0-0-22S-11Mg) is sometimes referred to as K-Mag, is marketed as a dry material that is 22 percent K2O, 22 percent sulfur, and 11 percent Mg. It is used in mixed fertilizers or sometimes applied alone to supply sulfur and magnesium on soils deficient in these two elements.

Elemental Sulfur (typically 90 to 95% S) is marketed by several manufacturers. These products are usually 90 percent or higher sulfur content with a small amount of binding material and/or bentonite clay to facilitate blending, application and soil reaction. Concern exists about availability of elemental sulfur during the year of application. Before it becomes available for plant uptake, elemental sulfur must first be oxidized by soil microorganisms to sulfate-S and this can be a slow process when surface applied.

Many factors affect the rate of oxidation of elemental sulfur to sulfate. Particle size, rate, method, and time of application are important. Soil temperature and moisture are critical. Generally, anything that favors microbial activity (oxidation), fine particle size, incorporation, warm temperatures, and adequate moisture, favors quicker conversion to sulfate. Topdressing elemental sulfur on wheat or cool-season grasses is not recommended as conditions would not be favorable for conversion of elemental sulfur to sulfate in time to help the crop that year.

<u>Gypsum</u> (analysis varies) is calcium sulfate and is commonly available in a hydrated form containing 18.6 percent sulfur. This material is generally applied in a dry form and is available in a granulated form that can be blended with other materials.

<u>Potassium Thiosulfate</u> (0-0-20-17S) Is a relatively new product that is a clear liquid containing about 20 percent K2O and 17 percent sulfur. Potassium thiosulfate can be mixed with other liquid fertilizers and has potential for use in starter fertilizer mixes where both K and S are needed. This material should not be placed in direct seed contact. Potassium thiosulfate is not a commonly used product

<u>Ammonium Polysulfide</u> (20-0-0-40S) is a dark red to brown solution containing 20 percent nitrogen and 40 to 45 percent sulfur. Besides supplying nitrogen and sulfur, this material also is used for reclaiming high pH soils and for treating irrigation water. It is compatible with nitrogen solutions but is incompatible with phosphate-containing liquids. Ammonium polysulfide is a good source of sulfur, but is not as convenient or pleasant to handle as ammonium thiosulfate due to a strong hydrogen sulfide (rotten egg) odor. Not commonly used in Kansas or the Great Plains.

<u>Potassium Sulfate</u> (0-0-50-17S) is usually applied in a dry granular form, is often referred to as sulfate of potash. It contains 50 to 52 percent K2O and 17 to 18 percent sulfur. Potassium sulfate is used as a K and sulfur source in potato and tobacco production since these crops are sensitive to large applications of chloride. Potassium sulfate is not commonly available in the marketplace.

In the past, many fertilizers carried significant amounts of S as impurities. Today most fertilizers are more highly refined and no longer a major source of S. For example, normal superphosphate (0-20-0), a common P fertilizer of the past, contained about 13% S as an impurity. It is no longer on the market. Today the sulfur content of triple superphosphate (0-45-0) is less than 3% S, while DAP and MAP contain less than 2% S and 10-34-0 typically contains less than 1% sulfur.

Sulfur Summary

Sulfur, often called the fourth major nutrient, is essential for plant growth and sulfur deficiencies are becoming more widespread in Kansas and other states. Sulfur is essential for the formation of certain amino acids, proteins, and oils; is a structural component of protoplasm; and is necessary for activation of certain vitamins and enzymes. Sulfur cycles in the soil environment, much like nitrogen. Soil organic matter is an excellent source of sulfur. Plants take up sulfur as the sulfate (SO4) ion. Sulfate in the soil is leachable. If supplemental sulfur is needed, several sulfur fertilizers are available. Recent Kansas research has verified a need for sulfur fertilization in some instances. Sulfur recommendations can be determined based on several considerations. Crop grown, yield goal, soil organic matter levels, level of sulfur in irrigation water, manure application, and soil test sulfur levels are all important factors to consider when developing sulfur recommendations.

Over the past 15 to 20 years, considerable research with sulfur fertilization has been conducted in Kansas. Positive yield responses have been noted on corn, wheat, grain sorghum, alfalfa, and cool-season grasses (brome grass and tall fescue). Yield responses on irrigated crops have been limited to cases where the irrigation water was low in sulfur. In dryland situations, responses to sulfur fertilization have been most consistent on coarse-textured, low organic matter soils. Consistent responses, however, have been obtained on brome grass and many of these sites had organic matter levels of 3.0 percent or higher.

Calcium

Calcium is an essential nutrient that has varied functions within plants. and is absorbed by plants as the Ca^{++} ion. Inside the plant it performs several functions:

- Maintains strength of cell walls and reduces lodging.
- Regulates uptake of other elements.
- Regulates cell sap pH and neutralizes acids produced by plants.
- Essential for activity of Rhizobium.

Plant deficiency symptoms are rarely observed under field conditions. Deficiencies of calcium have not been observed in Kansas. a deficiency of calcium affects the growing points of both tops - leaf tips may stick together and unfold abnormally – as well as roots.

Calcium is the predominant positively charged ion (Ca^{++}) on soil particles because it is held more tightly than magnesium (Mg^{++}) and potassium (K^{+}). Also, the soil parent material usually contains much more calcium than magnesium or potassium.

Calcium does not leach through soils to any appreciable extent because it is held on the surface of clay particles. In addition, soils inherently contain large amounts of exchangeable calcium (1000-10,000 lbs/a.) Therefore, soils are very seldom deficient in calcium. Soils with a favorable pH (6.0 or above) will always contain adequate levels of calcium.

Limestone used to correct soul acidity is the predominant source of applied calcium. The amount of calcium added in limestone plus the relatively large amounts of exchangeable calcium in the soil far exceeds the 50-100 lbs/a of calcium commonly removed by crops.

Magnesium

Magnesium is absorbed and utilized by plants as the Mg^{++} ion. Magnesium and nitrogen are the only soil nutrients that are a part of chlorophyll and is also involved in phosphorus metabolism and several plant enzyme systems.

When deficient, Mg is transferred in the plant from older to new tissue. As a result, deficiency symptoms occur first in older leaves. Tissue between the veins becomes light green to whitish in color. In corn and other cereals this leads to striping between veins that may be intermittent rather than continuous. With severe deficiencies, purple coloration may follow. Cotton leaves turn purplish between the green veins.

The importance of adequate magnesium for both plant growth and nutrition of animals being fed grass forages is now recognized. Animals grazed on pastures low in magnesium sometimes develop hypomagnesia or grass tetany. Grass tetany is a nutrient deficiency disease of beef, dairy and sheep associated with low magnesium levels in the blood serum. Several incidents of grass tetany have been reported in the southeastern part of Kansas. Grass tetany has also been associated with cattle grazed on wheat pasture. Magnesium fertilization of forages has not proven effective in correcting grass tetany. Magnesium supplementation of livestock is the best way to manage grass tetany.

Magnesium is a positively charged cation (Mg^{++}) and as such is held on the surface of clay and organic matter particles. Magnesium is immobile in soils since it is held by soil exchange sites.

Acid soils often contain relatively low levels of magnesium, especially sands. Neutral soils or those with a high pH usually contain in excess of 1000 lbs/a of exchangeable magnesium.

Dolomitic lime is an economical source of Mg for acid soils. Potassium-magnesium sulfate (K-Mag, 11% Mg) is an excellent source of magnesium that also supplies sulfur and potassium. It is also the most common fertilizer source used in Kansas and the Great Plains. Other magnesium containing fertilizers include magnesium sulfate (epsom salt, 10% Mg) and magnesium oxysulfate (variable analysis).Sulfate forms of magnesium are more soluble than dolomitic lime and are preferred on soils where a immediate crop response is expected.