Sulfur Usage by Turfgrasses

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Of the six macronutrients, sulfur is undoubtedly the most neglected by turf managers. This is not because sulfur is the macronutrient required in the lowest amount by plants, which it is, but because no effort is generally required to insure that turf receives all the sulfur it needs.

Living in an industrial nation virtually insures that sulfur will be available to plants through atmospheric sulfur dioxide (SO_2), a major air pollutant. Also, sulfur is normally present in mineral and organic fertilizers. Common (single) superphosphate is manufactured by reacting rock phosphate with sulfuric acid; the resulting product contains 14 percent sulfur. Sulfur-coated urea, which is commonly used by turf managers as a slow-release nitrogen source, contains about 10 percent sulfur. Many commercial grade fertilizer materials contain small amounts of sulfur as a contaminant and all naturally derived organic fertilizers or soil conditioners will deliver some sulfur.

This ambivalence toward sulfur may be changing. More refined inorganic fertilizer ingredients contain less sulfur as well as other contaminants. For example, triple superphosphate contains only 1.5 percent sulfur, but 2.3

Figure 1. Path of sulfate transport and metabolism in roots of grass plants.

times as much phosphate as single superphosphate. The plastic coatings now being used to slow the release of urea and other soluble fertilizers might contain no sulfur.

More stringent air quality regulations are reducing the amount of atmospheric SO_2. In northern Europe, industrial emissions have been so reduced that many crop plants are currently exhibiting yield increases when fertilizer sulfur is applied (Marschner 1995). As turf managers remove clippings from ever larger areas of their turf and more sand-based greens are installed, the likelihood of sulfur supplies within the rooting medium becoming insufficient increases.

Sulfur in Turfgrasses

Compared to other macronutrients, sulfur also has received little attention from turfgrass researchers. In their comprehensive review on the nutritional requirements of turfgrasses, Turner and Hummel (1992) devoted less than one page to sulfur and cited only eight research reports extending back to 1962.

One of the few turf scientists who seriously considered the needs of turf for sulfur was Roy Goss at Washington State University. During the 1970s, he discovered that colonial bentgrass turf managed under high nitrogen fertility experienced a 71 percent growth increase (Table 1) when sulfur was applied (Goss et al., 1979). Working in the Pacific Northwest where air quality is normally very good, sulfur was not as readily provided through atmospheric SO_2 as would be the case in the more industrial Midwest and East.

Turfgrass clippings normally contain between 0.25 and 0.45 percent sulfur on a dry matter basis depending on fertility level and how much sulfur is provided (Turner and Hummel, 1992). Sulfur levels as low as 0.15 percent have been found to be adequate for several turfgrasses. This value is lower than that for any other macronutrient although not much below that for magnesium. These low sulfur levels can be deceiving because sulfur does not circulate very well within plants and this causes new growth to experience the greatest deficiency (Marschner, 1995). Because of this, **sulfur must be supplied throughout the growing season so its content in growing tissues will be maintained** at about 0.35 percent (Table 1). Otherwise, serious growth suppression may result.

The Availability of Sulfur

In a well aerated soil of moderate acidity, sulfur is absorbed by plant roots primarily as sulfate (SO_4^{-2}). If the soil fertility level is reasonably high, SO_4^{-2} can be carried to the root surface by water flow more rapidly than it can be absorbed. This results in an accumulation of SO_4^{-2} at the root surface and within the cell walls of root epidermal cells. Thus, under conditions of normal fertility, sulfur is not likely to be limiting due to soil supply. However, **during times of rapid growth in the spring, mild sulfur deficiencies may be encountered due to a limited rate of absorption by roots.**

Sulfate is a divalent anion (2 negative charges per ion) and as such its uptake by roots is not likely to be passive for the same reasons that we explained for nitrate uptake (Hull and Liu, 1995).

Table 1. Sulfur content and quality of colonial bentgrass putting green turf fertilized with various combinations of N and S

Nutrients Applied				Sulfur Content	Average Content
N	P	K	S		
1 lbs/1,000 sq. ft./yr.				%	10=dark green
0	0	0	0	0.35 b	4.8 c
20	0	6.6	0	0.30 c	4.9 c
12	1.8	6.6	1.2	0.40 a	7.8 b
20	1.8	6.6	1.2	0.40 a	7.6 b
20	1.8	6.6	3.4	0.42 a	8.7 a

Values followed by same letter are not statistically different.
Adapted from Goss et al. 1979

Table 2. Various oxidation forms of sulfur in soils and plants

| Chemical form of sulfur	Chemical notation	Oxidation/Reduction state
Sulfide	S^{-2}	S^{-2}
Sulfur-elemental	S	S^{0}
Sulfite	SO_3^{-2}	S^{+4}
Sulfate	SO_4^{-2}	S^{+6}

Sulfide is most reduced and sulfate is most oxidized.

Because the cytoplasm of root cells is normally less acid and more negatively charged than the cell walls, the anionic SO_4^{-2} tends to be retained within the walls and must be actively transported across the cell membrane (plasma membrane) into the cytoplasm. This requires the expenditure of metabolic energy by the root cells and the presence of a specific SO_4^{-2} transporter (Figure 1) within the outer cell membrane (Marschner 1995). Divalent ions also are generally absorbed less rapidly by roots than are single charged monovalent ions.

This places SO_4^{-2} within a group of nutrient ions that are absorbed by roots relatively slowly. The outcome of all this is that, even under the best of conditions, the rate of SO_4^{-2} transport through the roots is never very great. Thus, sulfur supply rate is not likely to push vegetative growth like nitrogen can.

Sulfur is in many ways similar to nitrogen with regard to its availability and activity in the soil. While the oxidized SO_4^{-2} ion is the form of sulfur most available to plant roots, sulfur generally enters the soil in its reduced sulfide (S^{-2}) form usually as a component of organic matter (Tisdale et al. 1985). In most noncalcareous soils, more than 90 percent of soil sulfur is in an organic form (mostly plant residues and humic substances). This organic matter is slowly utilized by soil microorganisms (bacteria and fungi) as an energy source and in the process sulfur is released (mineralized) into the soil as free S^{-2} along with carbon dioxide (CO_2), water and ammonium (NH_4^+). Within a well aerated soil of reasonable temperature, S^{-2} is readily oxidized to SO_4^{-2} by chemical processes or by bacteria (Table 2). Chemical oxidation can withdraw electrons from S^{-2} to produce elemental sulfur (S^{0}) and these two forms can be further oxidized by bacteria that use the energy

contained in reduced sulfur to fix CO_2 and make carbohydrates.

$$CO_2 + S + 1/2\ O_2 + 2H_2O > [CH_2O]_n + SO_4^{-2} + 2H^+$$
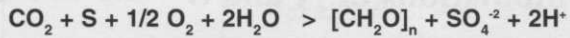
This reaction occurs within several bacterial groups, but the genus *Thiobacillus* is most involved. The soil nitrifying bacteria that oxidize ammonia to nitrate are similar chemolithotrophic organisms which use the energy and electrons present in NH_4^+ to reduce CO_2 rather than the light driven reactions of photosynthesis. *Thiobacillus* is tolerant of acid conditions which make sulfur oxidation less dependent on a narrow pH range than is NH_{4+} oxidation. There are many other microbial reactions involving sulfur but many of them occur under anaerobic conditions and probably are less important in soils on which turf is grown.

You might notice that one product of the reaction printed above is H^+, which has the effect of making the soil more acid: lowering its pH. This reaction explains how the addition of elemental sulfur can be used to make a soil more acid.

Unlike soil organic nitrogen, as much as 50 percent of organic sulfur may be present as SO_4^{-2} esters (SO_4^{-2} bound to carbon through an oxygen). The presence of sulfatase enzymes in the soil releases this SO_4^{-2} from organic matter and constitutes a major part of sulfur mineralization.

$$R\text{-}C\text{-}O\text{-}SO_3^- + H_2O > R\text{-}C\text{-}OH + SO_4^{-2} + H^+$$

This mineralization involves no reduction of sulfur but releases SO_4^{-2} directly into the soil solution where it can be absorbed by plant roots. Organic SO_4^{-2} esters arise from secondary plant metabolites formed by the direct assimilation of SO_4^{-2} into organic compounds. These sulfur compounds are among the first to become mineralized in the soil which makes their SO_4^{-2} most available for plant uptake.
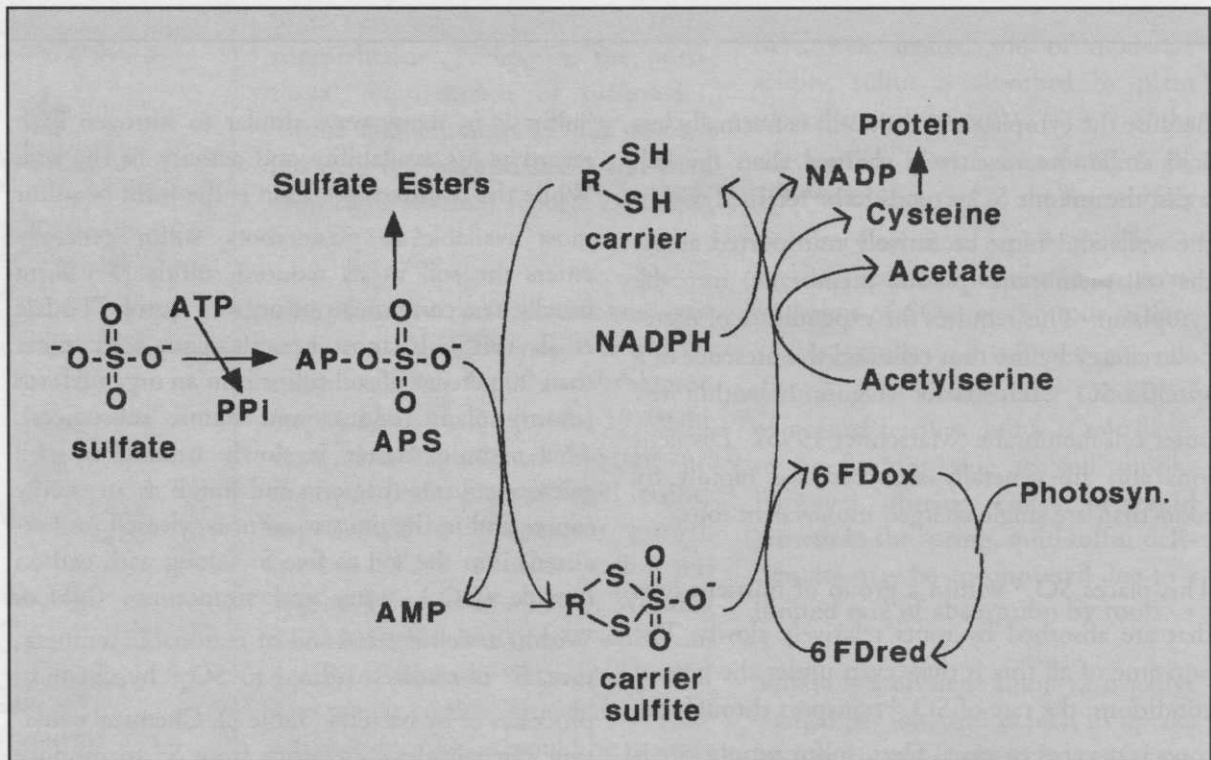

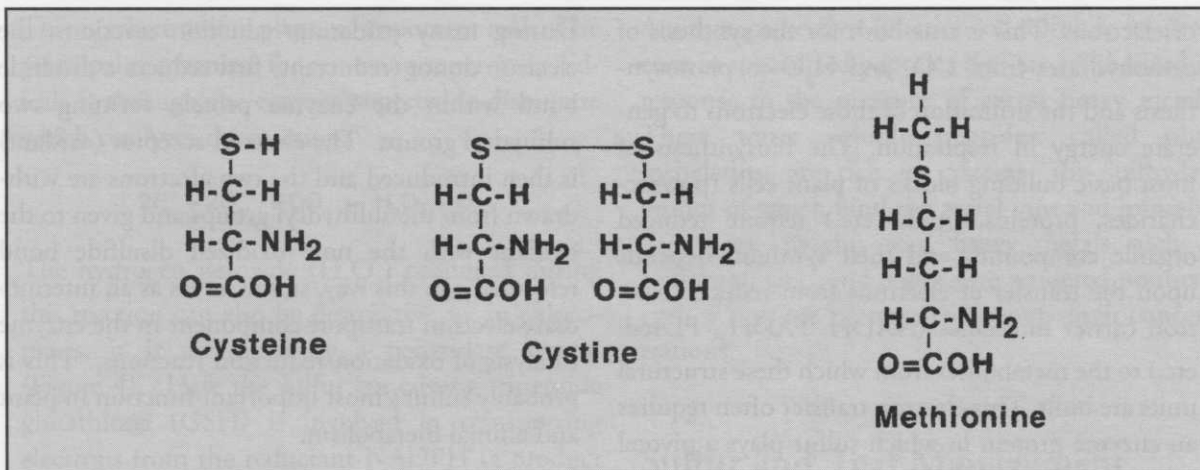Figure 2. The pathway of sulfate reduction and assimilation into cysteine.

Figure 3. Structures of the three sulfur containing protein amino acids.

Sulfur Utilization Within Plants

Once absorbed by roots, SO_4^{-2}, can follow one of several paths similar to those available to NO_3^- (Figure 1). Sulfate can be transported into the large central vacuole of epidermal cells where it can be stored for some time. Sulfate can also be transported radially from cell to cell through plasmodesmate (cytoplasmic pores which connect adjacent cells) and deposited into xylem elements where it will be moved via the transpiration stream to leaves. Either in leaves or roots, SO_4^{-2} can be reduced to S^{-2} and assimilated into the amino acid cyseine which is a component amino acid of all proteins.

The process of SO_4^{-2} reduction also has many similarities with NO_3^- reduction. Initially SO_4^{-2} is activated by replacing the terminal two phosphates of ATP forming adenosine phosphosulfate (APS). This bound form of SO_4^{-2} is more chemically reactive and is necessary for its reduction and eventual assimilation into organic molecules (Figure 2). There is no comparable reaction required for NO_3^- reduction in plants. APS can undergo a further reaction and donate its SO_4^{-2} to the synthesis of SO_4^{-2} esters, a process that does not require sulfur reduction. Nitrate does not do this. To be assimilated into cysteine, however, SO_4^{-2} must be reduced to S^{-2} and for this to occur, APS must give up its SO_4^{-2} to a carrier molecule where it is bound to a pair of sulfhydryl (R-SH) units. In this reaction, each sulfhydryl group gives one electron to the SO_4^{-2} reducing it to sulfite (SO_3^{-2}). This is sort of analogous to the reduction of nitrate to nitrite (Hull and Jiang, 1998).

While bound to the disulfide carrier, SO_3^{-2} acquires an additional six electrons from the reduced form of ferredoxin (FDred) which is a product of photosynthesis. The SO_3^{-2} is not released from its carrier until it is fully reduced to S^{-2}. Again this reaction is similar to the reduction of NO_2^- to NH_4^+. Once fully reduced, S^{-2} binds to the serine part of an acetylserine molecule forming a cysteine and an acetate (Figure 2). The cysteine can then be utilized for protein synthesis or serve as the sulfur source for all other sulfur-containing amino acids (Figure 3) or sulfur metabolites. Plants, bacteria and fungi can carry out these reactions but, just as with nitrogen reduction and assimilation, animals cannot do so being dependent upon their food as sources of these essential amino acids.

The roles of sulfur within plants are many and varied and most are well beyond the scope of this article. However, their participation in electron transfer as a component of enzyme proteins deserves at least some consideration. Metabolism in all living things depends on the orderly transfer

of electrons. This is true both for the synthesis of carbohydrates from CO_2 and H_2O in photosynthesis and the utilization of those electrons to generate energy in respiration. The biosynthesis of most basic building blocks of plant cells (polysaccharides, proteins, lipids, etc.) require reduced organic compounds and their synthesis depends upon the transfer of electrons from reduced electron carrier molecules (NADH, $FADH_2$, FDred, etc.) to the metabolites from which these structural units are built. This electron transfer often requires an enzyme protein in which sulfur plays a pivotal role.

There are three sulfur containing amino acids in proteins: cysteine, cystine and methionine (Fig. 3). When the protein amino acid chain (polypeptide chain) folds on itself a disulfide bond (-C-S-S-C-) can form wherever sulfhydryl groups of two cysteines come together forming a cystine. This covalent bond links the chain at that point and stabilizes the protein's folded (tertiary) structure. This is important to insure the proper structure of the enzyme so it can do its catalytic work. The formation of a disulfide bond involves the oxidation of sulfhydryl groups of two cysteines where each sulfur loses one electron. The shared remaining electrons form the disulfide bond of a cystine. This bond can be reduced, given an appropriate electron donor, reforming the two sulfhydryl groups and eliminating the disulfide bond.

During many oxidation/reduction reactions, the electron donor (reductant) first reduces a disulfide bond within the enzyme protein forming two sulfhydryl groups. The electron acceptor (oxidant) is then introduced and the two electrons are withdrawn from the sulfhydryl groups and given to the oxidant with the now oxidized disulfide bond reformed. In this way, sulfur serves as an intermediate electron transport component in the enzyme catalysis of oxidation/reduction reactions. This is probably sulfur's most important function in plant and animal metabolism.

Stress Tolerance and Sulfur

Another highly important function of sulfur, especially in plants, is its role in neutralizing dangerous oxygen radicals that are produced as a natural consequence of biochemical pathways involving the transport of electrons. Two of the most harmful oxygen radicals are superoxide ($O_2.-$) and the hydroxide free radical (OH.). If these radicals accumulate at metabolic sites, they will destroy lipids of membranes and kill the cells. These radicals form most readily in chloroplasts during photosynthesis. When the light is strong and CO_2 concentrations are low, O_2 free radicals are readily formed (Figure 4). If not destroyed, these radicals will cause much damage to leaves.
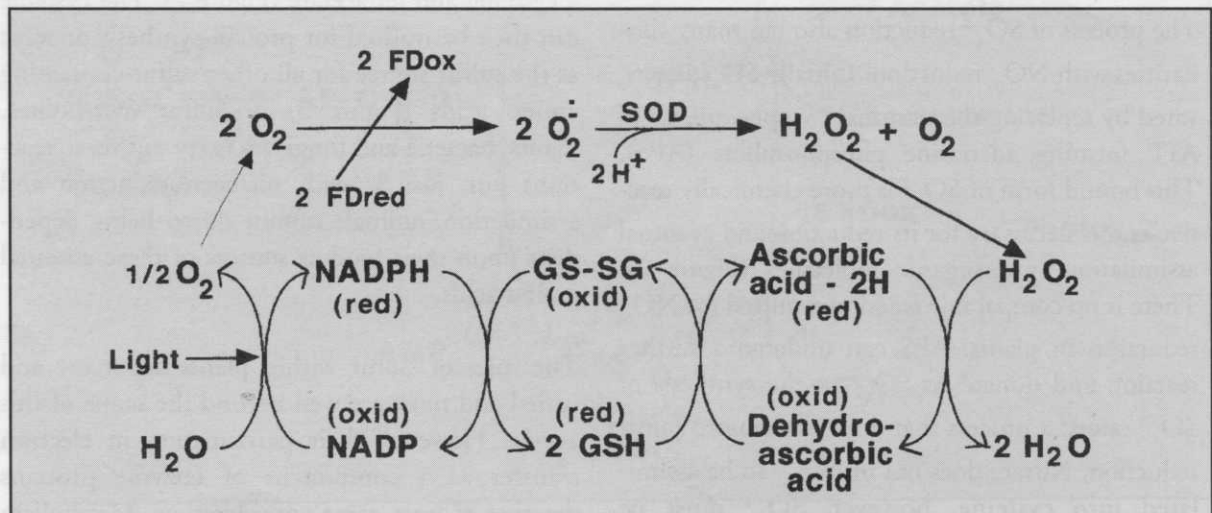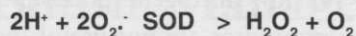

Figure 4. The role of glutathione in the detoxification of hydrogen peroxide.

This is where sulfur plays an important role. The principal mechanism for removing superoxide radicals is through the enzyme superoxide dismutase which catalyzes the reaction:

$$2H^+ + 2O_2^{-} \ SOD \ > H_2O_2 + O_2$$

The hydrogen peroxide (H_2O_2) produced during this reaction can also be destructive so, in chloroplasts, it is destroyed by a peroxidase system (Figure 4). Here the sulfur containing tripeptide glutathione (GSH) is involved in transporting electrons from the reductant NADPH (a product of photosynthesis) through ascorbate to H_2O_2, degrading it to two water molecules (Figure 4). Here again the sulfhydryl groups of two glutathione molecules each lose an electron forming a disulfide bond between them (GS-SG). This bond is broken when NADPH donates two electrons to re-reduce the two sulfurs and regenerate sulfhydryl groups of the two glutathione molecules.

Whenever plants are subjected to stress conditions and the normal flow of energy through photosynthesis is impeded, oxygen radicals are formed. If they are not destroyed as described above, damage occurs and the leaves become chlorotic and exhibit dead spots. Large increases in glutathione are often observed in leaves of evergreen plants during the stressful conditions of winter (Marschner, 1995). When sulfur is in short supply, glutathione synthesis occurs slowly and leaf injury occurs.

Another protective function of sulfur is its presence in specialized peptides that are synthesized in response to the presence of excess heavy metals. These water soluble peptides, called phytochelatins, are rich in cysteine; the sulfhydryl groups of which bind the metal ions and immobilize them. In this way, heavy metals such as cadmium, zinc, and copper are rendered nontoxic even if they are present in relatively high concentrations.

Sulfur and Turf Management

An understanding of how sulfur functions in plants can provide some insight into its role in turfgrass growth. Like nitrogen, sulfur is a component of three essential amino acids required for protein synthesis. Consequently whenever turf is expected to respond to a stress or to grow vigorously, sulfur must be available.

Goss (1979) noted that **turf lost more sulfur in clippings when its growth was stimulated by high applications of nitrogen** (Table 3). Even when no sulfur was applied, more was present in clippings of nitrogen stimulated turf. Under such conditions, sulfur deficiency symptoms became evident. **This suggests that intensively managed turf that is expected to recover from injury and fill in after being damaged must have adequate supplies of sulfur.**

Table 3. Influence of fertilization with and without sulfur on the volume of clippings and the sulfur contained in them.

Nutrient treatment N-P-S	Dry clipping yield/year lbs/1,000 sq. ft.	Total S removed in clippings lbs/1,000 sq. ft.
0-0-0	45.3	0.16
20-0-0	78.5	0.23
12-2-1	118.2	0.51
20-2-1	134.6	0.54
20-2-3	127.1	0.50

Adapted from Goss et al. 1979.

As mentioned at the beginning of this piece, sulfur is often taken for granted and in the past this often caused no problems. Today, I am not sure we can be so indifferent to sulfur. Turfgrasses are pushed more than ever before. Play is more intense and mowing heights are frequently lower than is agronomically sound. These are themselves or they directly contribute to stresses on the grass. For grass to respond effectively to stress, it must have adequate supplies of sulfur. It is not wise to leave this important ingredient in turf management to chance. Thus, **it makes sense to supply sulfur as part of a normal fertilizer program.**

Mechanical injury and climatic extremes are not the only stresses to which turfgrasses are exposed and must tolerate. Disease organisms also induce a response from turf which often prevents serious disease development. Such responses normally involve the synthesis of new enzymes and that requires sulfur. A low sulfur supply may delay the reaction of turfgrasses to pathogen attack providing time for disease to become established. Turner and Hummel (1992) describe several accounts of turf disease incidence being suppressed following the application of sulfur fertilizers.

Sulfur deficiency in turfgrasses is not well documented. Generally it appears as a light green coloration of new growth and might be confused with early iron deficiency. Once sulfur is assimilated into organic molecules (proteins) it becomes relatively immobile and is not readily redistributed from old leaves to new growth. By comparison, SO_4^{-2} is quite mobile moving readily from roots to shoots and from leaves to roots. Therefore, newly acquired sulfur is much more mobile within a plant than is sulfur that has been reduced and assimilated. **It is critical for sulfur to be available to the grass throughout its growing season.** Young leaves tend to exhibit yellowing first along the margins starting at the tip. This continues along the leaf as it grows and gradually advances toward the center of the blade. Dead tissue (necrosis) does not occur normally but can become evident if the grass is exposed to high light or other stresses. Inability to destroy oxygen radicals because of low glutathione levels probably explains this stress induced injury.

Because it is difficult to grow turf in the field under the complete absence of sulfur, deficiency symptoms are rarely extreme or even evident. They are also not so specific that they cannot be mistaken for low nitrogen, potassium or iron. Deficiency symptoms are not useful indicators of plant nutrient needs. By the time you can observe symptoms, considerable damage has already been done. This is especially true of sulfur which is required for so many metabolic functions.

Before a sulfur deficiency can be observed, much growth suppression has already occurred, disease has probably been more serious than normal, insects have fed more freely and high light, and drought and temperature extremes have been more damaging. Much of this, the turf manager will write off as bad luck when in fact it was easily avoided. That is the devious aspect of nutritional disorders, they can do so much damage before they are ever detected. When it comes to sulfur, one can easily assume that an ounce of prevention is worth a ton of cure.

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