

## Manganese Usage by Turfgrasses

By Richard J. Hull  
University of Rhode Island

**A**ny consideration of micronutrient use in turfgrass management is limited by a general lack of specific research aimed at defining turf needs for these essential elements. The age of turfgrass fertility research has long passed, leaving the present turf manager with little more than hype from fertilizer salesmen and anecdotal accounts of product effectiveness.

Unless a plant nutrient is viewed as a threat to surface or ground water quality and thereby a risk to human health, it is virtually impossible for a serious turf

researcher to obtain grant funds to study its role in turf physiology or management. This is unfortunate because turf is increasingly being grown on artificial substrates that often have little inherent nutrient content. If all mineral nutrients, including micronutrients, must be supplied as part of a management program, the questions of how much, in what form and when become critical. Research generated 30 or 40 years ago is poorly suited to address these questions because nutrient sources, turfgrass genotypes and end user expectations all have changed dramatically. This is a problem especially for less appreciated micronutrients such as manganese (Mn).

This is the third in our series on

*Many soil fungi that normally would not be pathogenic or only weakly so will cause disease in Mn deficient plants.*

**Table 1.** Manganese content in leaf tissues of several turfgrasses.

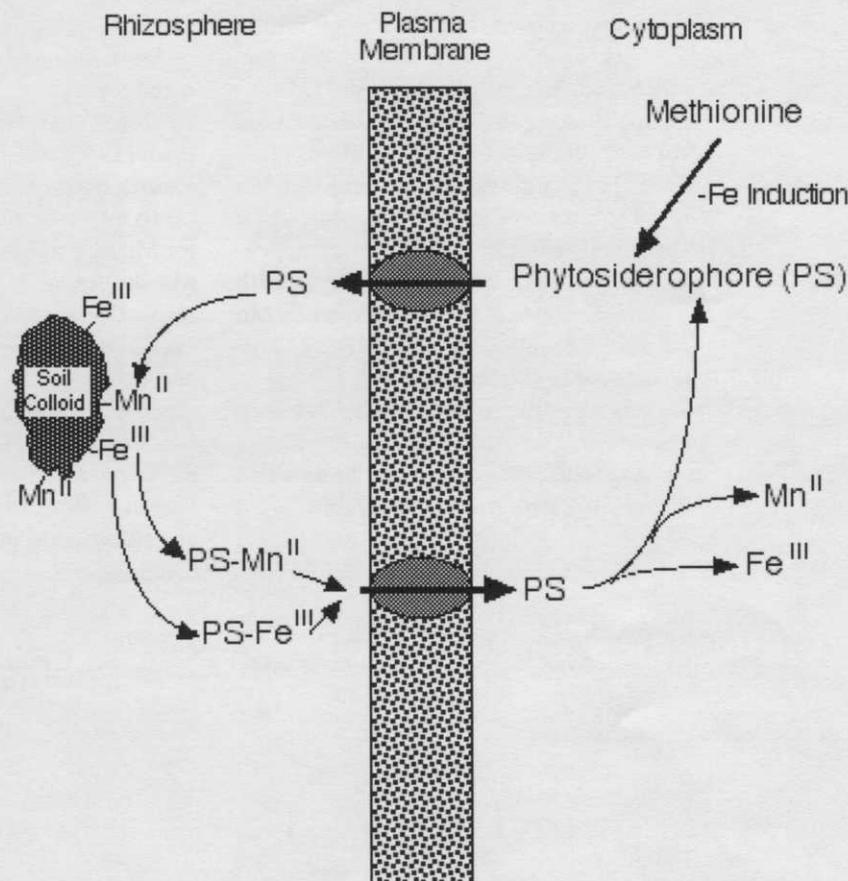
Turfgrass	Manganese content*	
	Waddington & Zimmerman (1972)	Butler & Hodges (1967)
	ppm (mg/kg)	
Annual bluegrass	250	—
Kentucky bluegrass	154	33
Colonial bentgrass	414	83
Creeping bentgrass	339	—
Tall fescue	434	71
Creeping red fescue	185	54
Perennial ryegrass	304	73
Bermudagrass	—	57
Zoysiagrass	—	29

\* AS REPORTED IN TURNER & HUMMEL (1992)

micronutrient use by turf with iron (Hull 1999a) and zinc (Hull 2001) having been discussed earlier in this journal. As was the case with Zn, the literature on Mn use by turf is not extensive. Turner and Hummel (1992) summarized the few reports on Mn content in several turfgrasses and found that the values varied widely among grass species and between laboratories (Table 1). The Mn content of dried clippings reported by Waddington and Zimmerman (1972) for seven turfgrasses averaged 297 mg/kg (ppm) while that reported for another seven turfgrasses by Butler and Hodges (1967) averaged only 46 mg/kg.

Waddington and Zimmerman (1972) were concerned about these differences and compared the Mn content of creeping bentgrass leaves on several dates throughout a growing season. They found the Mn content ranged from 163 to 391 mg/kg. These differences could reflect the fact that Mn is not readily redistributed in plants so it pretty much remains in those leaves into which it is delivered by xylem transport from the roots.

During times of slow shoot growth, Mn would have more time to accumulate in leaves before they were sampled for analysis. Variation between analytical laboratories could reflect differences in methods utilized or differences in the amount of



**Fig. 1. Mechanism employed by grasses to recover Fe and Mn from soils having these ions in nonavailable form.**

Mn available to the turf (sand vs. soil based greens). Jones (1980) concluded that a Mn sufficiency range for turfgrasses was between 25 and 50 mg Mn/kg dry leaf tissue. The critical Mn concentration (plant tissue concentration that will support 90% of maximum growth rate) generally ranges from 10 to 20 mg Mn/kg dry weight (Marschner 1995). This makes the turfgrass requirement for Mn about the same as that for zinc.

### Soil manganese

Manganese is a reasonably abundant element with an average concentration in the earth's crust of 1000 ppm and a soil range of 20 to 3000 ppm averaging about 600 ppm.

Manganese is present in most Fe-Mg containing igneous rocks and when solubilized by weathering, forms several secondary minerals mostly pyrolusite ( $MnO_2$ ) and manganite ( $MnOOH$ ). Thus, most soil Mn is insoluble and not available to plant roots. The plant-available form of free Mn in soil solution is the divalent cation  $Mn^{2+}$ . Manganese solubility is very much dependent on soil pH, decreasing 100 fold with each unit increase in pH. Consequently Mn is much more soluble and available to plants in acid soils ( $pH < 5.5$ ).

However, for free  $Mn^{2+}$  to be released into the soil solution and occupy cation exchange sites, reducing power in the form of organic matter must be available.



Here, minerals containing Mn in oxidized form ( $Mn^{3+}$  or  $Mn^{4+}$ ) will be reduced to  $Mn^{2+}$  by acquiring electrons ( $e^-$ ) through the microbial oxidation of organic carbon.

To meet the nutritional needs of plants for Mn, the soil solution and exchangeable Mn should be 2-3 ppm and 0.2-5.0 ppm, respectively. In acid soils, soluble Mn may exceed these levels by substantial amounts and become toxic to plants. This is likely in situations where soil minerals contain Mn, the organic matter content is high, the pH is low and the soil is periodically waterlogged (low in free oxygen). Under such conditions, acid inhibition of plant growth

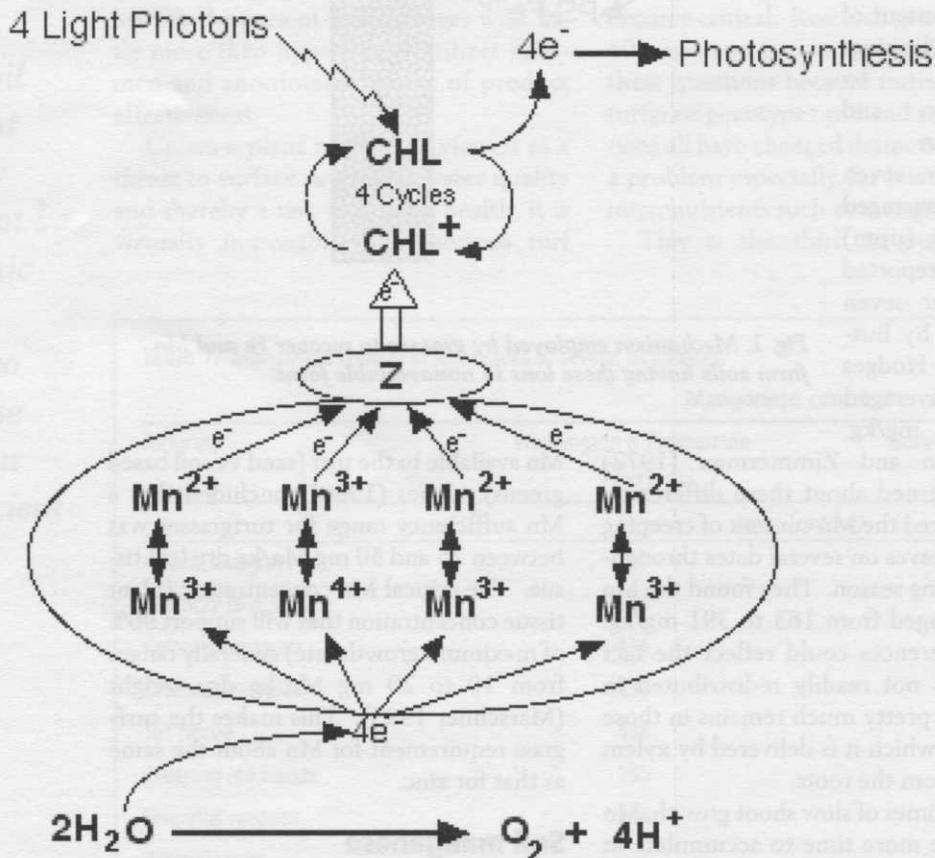


Fig. 2. Oxygen evolving mechanism of plant photosynthesis in which water replaces electrons driven by light from chlorophyll through the re-dox action of Mn.

may be due primarily to toxic levels of available Mn.

Under opposite conditions (parent minerals low in Mn, alkaline pH, low organic matter and good drainage) inadequate supplies of available Mn are likely. Some 13 million acres in 30 states of the US exhibit chronically inadequate levels of Mn (Tisdale et al. 1993). For the turf manager, Mn insufficiency is a more likely problem than its toxicity.

Soluble soil Mn is also present in the form of Mn-chelates. These organic chelates are excreted from plant roots or produced during the metabolism of organic residues. They will bind with  $Mn^{2+}$  but remain in solution as uncharged molecules. Much of the soluble Mn in organic soils will be present in a chelated form. Being soluble, Mn chelates are mobile in the soil and can be drawn to roots via mass flow when plants are removing water from the soil through transpiration. This process can assist in Mn uptake as we will see below.

### Manganese uptake

Plant roots can absorb Mn primarily as the divalent cation ( $Mn^{2+}$ ). It enters root cells by crossing their plasma membrane via a

specific transporter protein following an electrical gradient (cell interior is more negative than the cell wall). Other divalent micronutrient cations, such as Copper ( $Cu^{2+}$ ) and Zinc ( $Zn^{2+}$ ), do not compete with  $Mn^{2+}$  for membrane transport sites although they do compete with each other (Bowen 1969).

However, the abundance of several macronutrients on cation exchange sites within the cell walls of root cells (the apoplast) can influence Mn absorption by roots. Manganese is much less available from soils of high pH. This is in large part due to the high concentrations of Calcium and Magnesium ions ( $Ca^{2+}$  &  $Mg^{2+}$ ) in such soils. When  $Ca^{2+}$  and  $Mg^{2+}$  dominate cation exchange sites in root cell walls, there are few places for less abundant ions like  $Mn^{2+}$  to be retained.

Since cations absorbed by roots are drawn mostly from those present within the cell wall matrix, any less abundant ions (including most micronutrients) will have a difficult time reaching the plasma membrane when they are vastly outnumbered by basic divalent cations. This is the reason why most micronutrient metals are less available in soils of neutral or alkaline pH.

In acid soils, the principle competing cation is Hydrogen ( $H^+$ ) and it is not held on exchange sites as tightly as most divalent cations. However, if other cations such as aluminum ( $Al^{3+}$ ), potassium ( $K^+$ ) or other micronutrients greatly outnumber  $Mn^{2+}$  even in acid soils, Mn may become deficient. Even so, the most common method for increasing Mn availability to plants is to apply acid fertilizers such as  $(NH_4)_2SO_4$  or urea.

The availability and absorption of Mn from soils is more influenced by microbial activity than is any other

*Most soil Mn is insoluble and not available to plant roots.*

#### **TABLE 2.** **MANGANESE FUNCTIONS IN HIGHER PLANTS INCLUDING TURFGRASSES**

##### **Essential component of two enzymes:**

- $O_2$  evolving component of photosynthesis (PS II)
- Mn-containing superoxide dismutase (MnSOD)

##### **Activating cofactor for ~35 enzymes required for:**

- Respiratory metabolism of organic acids (TCA cycle)
- RNA synthesis in chloroplasts (RNA polymerase)
- Shikimic acid pathway (aromatic amino acid synthesis)
- Lignin synthesis in roots (cell wall peroxidases)
- Lipid synthesis including chlorophyll and carotenoids
- Regulating auxin levels and isoprenoid synthesis (GA)

##### **Required for root elongation and lateral root formation**

*To meet the nutritional needs of plants for Mn, the soil solution and exchangeable Mn should be 2-3 ppm and 0.2-5.0 ppm, respectively.*

micronutrient. To be absorbed by plants, Mn must be reduced to the divalent  $Mn^{2+}$  ion and this requires the action of microbial metabolism (Marschner 1995). Under acid conditions, Mn-containing minerals will slowly be solubilized and several ionic

forms of free Mn and  $Mn(OH)_n$  will be released to the soil solution. Under such conditions, most plant roots will discharge low molecular weight exudates (organic acids, sugars, amino acids and phenolics) to the soil immediately adjacent to the roots (rhizosphere). These exudates along with dead root cells (root cap cells, root hairs, epidermal and cortical cells) fuel microbial activity and, especially when the soil is waterlogged, supply electrons to reduce Mn ions to the plant-available  $Mn^{2+}$  form.

This ion can then be absorbed by root cells as described above.

In grasses, there is a cooperative mechanism for acquiring Mn by plants experiencing an Iron (Fe) deficiency. Because of its low solubility and the inability of membrane transporters to accommodate trivalent ions,  $Fe^{3+}$  poses some special problems in its availability to plants.

Grasses have a unique strategy for making  $Fe^{3+}$  ions available for root uptake (Marschner 1995; Hull 1999a). In response to low Fe stress, grass roots are induced to release special amino acids called phytosiderophores that chelate free  $Fe^{3+}$  allowing it to move to root surfaces and be absorbed (Fig. 1). While phytosiderophores have a very high affinity for  $Fe^{3+}$  and root cells have enhanced transporter capacity for the Fe-phytosiderophore complex, other micronutrient cations can also be chelated by phytosiderophores and become mobilized within the rhizosphere.

Thus when Fe is deficient,  $Mn^{2+}$  can be chelated by phytosiderophores and diffuse to the root surface where it is absorbed into the root. The Mn-phytosiderophore

complex is not absorbed as readily as is that formed with  $Fe^{3+}$ . However, this Fe deficiency induced mechanism for capturing micronutrient ions can make nutrients other than Fe more available to grasses.

### Functions of manganese

Manganese serves a number of functions in plants (Table 2). Its most important roles are as an essential component of the oxygen ( $O_2$ ) evolving complex in photosynthesis and as an activator cofactor of several major enzymes involved in numerous metabolic sequences. Manganese also plays a role in root elongation and lateral root initiation possibly by regulating the auxin levels along the root axis. Some of these functions that are most significant for turfgrass performance will be discussed in this section.

### Oxygen evolution in photosynthesis

Because of the central role played by photosynthesis in the life of all green plants, the requirement for Mn in the oxygen evolving complex of Photosystem II in the photosynthetic electron transport chain assumes primary importance. Virtually all oxygen in the atmosphere is derived from photosynthesis and its Mn requiring oxygen evolving complex. Thus, all aerobic life including human life is absolutely dependent on this Mn facilitated biochemical process.

The electrons used in photosynthesis to reduce carbon dioxide ( $CO_2$ ) to carbohydrates  $[(CH_2O)_n]$  ultimately are taken from the oxygen in water ( $H_2O$ ). When two molecules of water are so



oxidized (lose  $4e^-$ ), one molecule of oxygen gas ( $O_2$ ) is produced as a byproduct and the  $4e^-$  reduce an electron carrier that eventually will reduce the C of one  $CO_2$  to one carbohydrate C. The oxygen of water does not easily surrender its electrons and it will only do so in the presence of a very strong oxidant (substance having a powerful affinity for electrons). This strong ox-

dant forms when a special chlorophyll molecule receives a quantum of light energy that drives off an electron from the excited chlorophyll to a nearby electron acceptor (Fig. 2). This begins the photosynthetic electron transport pathway.

The chlorophyll that has lost an electron must obtain another or it will become further oxidized and destroyed. Electrons are provided from a near by protein that contains a cluster of four Mn atoms each capable of donating an electron to the oxidized chlorophyll. When each Mn atom has donated an electron (become oxidized from Mn<sup>2+</sup> to Mn<sup>3+</sup> or Mn<sup>4+</sup>), these four oxidized Mn atoms together represent an oxidant so strong that they can strip electrons from the oxygen of water.

To reduce the four Mn atoms, four electrons are needed and that requires the oxidation of two water molecules.



The Mn cluster is now ready again to deliver electrons to chlorophyll when it becomes oxidized through photoactivation. Thus, the Mn-containing oxygen evolving complex allows the flow of electrons to continue as light drives electrons from chlorophyll ultimately to reduce CO<sub>2</sub>.

### Manganese-containing superoxide dismutase (Mn-SOD)

Like Fe and Zn (Hull 1999a & 2001), Mn is the core atom (prosthetic group) in an enzyme that catalyzes the destruction of a potentially damaging oxygen free radical, superoxide (O<sub>2</sub><sup>-</sup>). Wherever O<sub>2</sub> is involved in biochemical reactions and a source of electrons is present (reducing agents), the probability of O<sub>2</sub><sup>-</sup> being formed is great. To eliminate this toxic radical, a family of SOD enzymes has evolved each employing a different metal as its prosthetic group.

The Fe-SOD and CuZn-SOD are most active in chloroplasts with the latter also found in mitochondria. The Mn-SOD is not so widely distributed among plant families and is most active in mitochondria and in peroxisomes that are involved in photorespiration (Hull 1999b). The Mn-

SOD enzyme is the major SOD in several groups of rhizosphere bacteria. Plants transformed to over-produce Mn-SOD experienced less chlorophyll degradation and mitochondrial leakage when grown in high light. These enzymes permit most grasses to grow in full sunlight without experiencing photo-oxidative damage.

### Mn and phenol biosynthesis leading to lignin

Lignin is a complex polymer of unsaturated six-sided ring structures that are produced in cell walls and give plant tissues great strength. The highly lignified vascular cells and fibers of trees enable them to reach great heights and withstand considerable mechanical stress.

Lignin also contributes to the strength of grass stems and leaves and its presence in root cell walls helps resist pathogen

**TABLE 3.**

#### SOURCES OF FERTILIZER MANGANESE

Source	Formula	% Mn content
Manganese chloride	MnCl <sub>2</sub>	17
Manganese oxide	MnO	41-68
Manganese sulfate	MnSO <sub>4</sub> ·4H <sub>2</sub> O	26-28
Manganese chelates	MnEDTA	5-12

ADAPTED FROM TISDALE ET AL. 1993 PAGE 337.

attack. Manganese serves as activator for several enzymes of the shikimic acid pathway that leads to the synthesis of aromatic (phenolic) amino acids (phenylalanine and tyrosine). These are the starting products for the synthesis of phenolic acids and alcohols that are produced in response to attack by pathogenic fungi and constitute a major disease defense mechanism.

These substances are also the building blocks of lignin molecules that are assembled in cell walls through the action of Mn-containing peroxidases. Manganese plays a central role in several reactions required for the synthesis of phenolic compounds and its function cannot be substituted by any other element.

*Manganese insufficiency results in dull chlorotic leaves that do not grow rapidly.*

### **Manganese deficiency and toxicity**

As is the case for most micronutrients, deficiency symptoms of Mn are subtle and not easily recognized. For turfgrasses, physical deficiency symptoms are almost useless for diagnosing problems. Such symptoms are poorly defined and their presence invariably indicates that substantial damage has already occurred. Consequently I will not attempt to describe the appearance of Mn deficient turf but rather concentrate on the impact insufficient Mn can have on turfgrass growth and performance.

The most common turf response to inadequate Mn is a markedly reduced growth rate of both shoots and roots. This occurs because the oxygen evolving complex of photosynthesis is highly sensitive to low Mn levels and when it malfunctions, photosynthetic rates decline sharply. This results in a reduced supply of carbohydrates that in turn depress amino acid and protein synthesis and the growth of cells. As a result, nitrate, phosphate and other nutrients may accumulate because they cannot be utilized in plant growth. Root growth is also inhibited because photosynthetic energy from shoots (sugars) is not available to support root growth. Thus, even though roots are the first to receive whatever Mn might be available from the soil, resources from the shoots are not sufficient to support much growth.

Increased disease incidence is another symptom of Mn deficiency. Because Mn plays many critical roles in the biosynthesis of phenolics and lignin, grasses deficient in Mn are unable to respond to pathogen attack by producing phytoalexins that would inhibit spore germination and block fungal invasion. As a result, disease outbreaks are more frequent and difficult to control.

Many soil fungi that normally would not be pathogenic or only weakly so will cause disease in Mn deficient plants. This makes disease identification more difficult and reduces the effectiveness of fungicides. In short, the grass is unable to do its part in resisting infection and has no chance of growing out of an infection.

You might suspect that Mn supplies are low when turf receiving acid generating fertilizers exhibits less disease. Fertilizer materials such as  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$  and urea tend to acidify the rhizosphere making Mn more soluble and available to grass roots. If liming promotes an increase in disease incidence, again you might suspect that Mn supplies are marginal.

Because Mn is not readily mobilized within a plant (it does not translocate well in the phloem), new leaf growth is most likely to become chlorotic when Mn is deficient. This symptom can easily be confused with that resulting from an Fe deficiency. Iron deficiency causes emerging new leaves to be bright yellow and continue growing at a reasonable rate.

Manganese insufficiency results in dull chlorotic leaves that do not grow rapidly. Soil conditions that would promote Mn deficiency (elevated pH, high organic matter and carbonate enrichment) would also tend to reduce the availability of Fe. However, deficiencies of Mn are less common in turf than are those of Fe.

Turf grown on soil may experience Mn toxicity. Any program that would acidify soils ( $\text{NH}_4$ -fertilizers, sulfur sources) could make Mn increasingly available and reach toxic levels. As mentioned above, Mn toxicity is part of the acid soil toxicity syndrome but this can usually be avoided by maintaining the soil at pH 5.5 or higher.

Turf grown on artificial media (sand based greens) is prone to suffer from inadequate Mn unless it is applied in fertilizer or top dressing. The materials from which artificial greens are constructed will contain very little Mn and sufficient amounts will not likely be provided as contaminants in fertilizers or most other soil amendments. Thus, Mn should be considered as part of a micronutrient management program.

### **Sources of manganese**

When a Mn insufficiency is suspected, it should be confirmed by a tissue test to determine if it is approaching the critical concentration of 25 ppm. If an addition of Mn is indicated, there are several sources

available (Table 3). The material most widely used for the correction of Mn deficiency is  $MnSO_4 \cdot 4H_2O$ . It can be applied through the soil or as a foliar spray.  $MnO$  is largely insoluble but it can be used effectively as a Mn source if ground finely and incorporated throughout the root zone. There are a number of natural organic Mn complexes and synthetic Mn chelates that are effective sources of Mn when applied as a foliar spray. Manganese application rates generally range from 1 to 25 lbs/acre with the lower rates used as foliar treatments. When soils have a high capacity for binding and immobilizing soluble Mn, foliar applications are strongly recommended.

Because Mn will not translocate from leaves to perennial plant organs, several foliar applications may be needed to provide season-long benefits. Frequent mowing and clipping removal will reduce the effectiveness of foliar applications to greens or other intensively managed turf. For such areas, Mn and other micronutrients should be incorporated into a comprehensive turf management program. This could involve an application of Mn with selected pesticide treatments, top dressings, syringings or other appropriate opportunities throughout the season.

On sand-based greens, Mn immobilization within the root zone should not be a problem and less expensive granular Mn sources can be applied during aerification or when the turf is being established.

Broadcast topical applications can be made to established turf and incorporated via irrigation.

As turf is managed ever more intensely, the chances of micronutrients becoming deficient increase sharply. For elements such as Mn, deficiencies are not easily detected and the turf manager can spend much time and effort trying to identify the cause of problems that are indirectly related to a nutrient deficit. To avoid such problems, a preventive approach might be best.

Micronutrient treatments are not costly and if applied properly rarely can cause injury. Thus, the management of Mn in turf might best be guided by the saying: an ounce of prevention is worth a pound of cure.

— *The author is on the Editorial Review Board.*

## REFERENCES CITED:

- Bowen, J.E. 1969. Absorption of copper, zinc and manganese by sugar cane leaf tissue. *Plant Physiol.* 44:255-261.
- Butler, D.J. and T.K. Hodges. 1967. Mineral composition of turfgrasses. *HortScience* 2:62-63.
- Hull, R.J. 1999a. Iron usage by turfgrasses. *TurfGrass Trends* 8(2):1-11.
- Hull, R.J. 1999b. Summer decline: can cool-season turf-grasses take the heat? *TurfGrass Trends* 8(10):1-7.
- Hull, R.J. 2001. Zinc usage by turfgrasses. *TurfGrass Trends* 10(7):7-11.
- Jones, Jr., J.R. 1980. Turf analysis. *Golf Course Management.* 48(1):29-32.
- Marschner, H. 1995. *Mineral Nutrition of Higher Plants*, Second Edition. Academic Press, London. 889 pages.
- Tisdale, S.L.; W.L. Nelson; J.D. Beaton and J.L. Havlin. 1993. *Soil Fertility and Fertilizers*, Fifth Edition. MacMillan Pub. Co., New York. 634 pages.
- Turner, T.R. and N.W. Hummel, Jr. 1992. Nutritional requirements and fertilization. Chapter 11, pages 385-439. IN D.V. Waddington et al. eds. *Turfgrass, Agronomy Monograph No. 32*, ASA, CSSA & SSSA, Madison, WI.
- Waddington, D.V. and T.L. Zimmermann. 1972. Growth and chemical composition of eight grasses grown under high water table conditions. *Commun. Soil Sci. Plant Anal.* 3(4):329-337.