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Small Amounts of Molybdenum Streamlines Nitrogen Uptake

By Dick Hull

Of all the mineral nutrients known to be essential for plants, molybdenum (Mo) is required in the least amount. To put this in perspective, for every Mo atom required by most plants, 1 million nitrogen (N) atoms are needed. Even with respect to those micronutrients generally recognized as being required in small amounts, such as copper (Cu) or zinc (Zn), a plant needs 100 Cu and 300 Zn atoms for every one of Mo present. Only nickel (Ni) comes close to being needed in amounts as low as Mo.

Little research has been conducted on the needs of turfgrasses for Mo. In their analyses of nutrient levels present in several turfgrasses, Butler and Hodges (1967) found a range of Mo concentrations from 1.77 to 8.45 parts per million (ppm) in common Kentucky bluegrass and perennial ryegrass, respectively (Table 1.). These values are the lowest among all mineral nutrients analyzed by these investigators.

However, no critical Mo concentrations have been published for turfgrasses so it's impossible to say if these values even approach the amounts actually required by turf.

Critical concentrations for Mo could be less than one-tenth the levels reported by Butler and Hodges. For several agricultural crops, critical Mo concentrations ranged from .1 to 1 ppm dry-leaf weight (Gupta and Lipsett, 1981).

Molybdenum in soils

The form of Mo most available to plants is the divalent molybdate anion (MoO_4^{-2}) where it exists in its most oxidized form (Mo^{+6}).

In some chemical properties, MoO_4^{-2} resembles other divalent oxyanions, especially sulfate (SO_4^{-2}) and phosphate (HPO_4^{-2}), that are the most available forms of sulfur and phosphorus, respectively. Because the sulfate content of the soil solution is vastly greater than that of molybdate, the two ions can compete for uptake sites on plant roots with molybdate invariably being the loser.

Plants are more likely to experience a Mo

TABLE 2

Molybdenum concentration in common turfgrass varieties

Grass	Concentration (ppm)
Kentucky bluegrass	1.77
Kentucky bluegrass (Merion)	3.35
Perennial ryegrass	8.45
Creeping red fescue	2.72
Tall fescue	4.05
Colonial bentgrass	2.25
Meyer zoysiagrass	1.77
Bermudagrass	8.20

SOURCE: BUTLER & HODGES (1967)

deficiency when fertilized with single superphosphate that contains substantial amounts of gypsum (CaSO_4), than with triple superphosphate that contains much less sulfate. Thus, the availability of molybdate to plant roots is heavily influenced by the concentration of other anions in the soil solution (Marshner, 1995).

Soil pH also exerts a strong influence over the availability of molybdate to plant roots. Unlike most metal micronutrients that increase in availability as the soil pH becomes more acid, molybdate acquires hydrogens and becomes less ionic as soil acidity increases.

The more acid forms of molybdate are not only less readily absorbed by plant roots but they can also form molybdate polyanions, (up to six molybdates per ion) rendering them completely unavailable to plants.

In addition, several metallic elements (iron, manganese and copper) become more ionized in acid soils and can form insoluble salts with molybdate rendering it unavailable to plant roots. Thus, liming a soil from pH of 4.5 to 6.5 will markedly increase the availability of Mo. This has been shown to preclude the need for applying Mo to some soils where plants had exhibited deficiency symptoms.

Mo functions in turfgrasses

Being required in such small amounts, Mo can't perform numerous essential functions in plants. It may be surprising then to realize that Mo is required for the efficient use of a plant's most abundant mineral nutrient, nitrogen.

Nitrogen can be assimilated into a plant's metabolism only in its reduced ammonium (NH_4^+) form (Hull, 1996a).

However, since nitrogen is generally available to plants in its oxidized nitrate (NO_3^-) form, it must first be reduced to NH_4^+ before a plant can use it. This process involves a gain of eight electrons and occurs in two steps. After a NO_3^- ion enters a root and while it is in the cell's cytoplasm, it is acted upon by the enzyme nitrate reductase (NR) that transfers two electrons from the electron donor NADH to form nitrite (NO_2^-).

Within the cell, the nitrate then enters a plastid and is reduced to NH_4^+ by the addition of six additional electrons through the action of the enzyme nitrite reductase (NiR). Thus, the whole process of NO_3^- assimilation begins with the enzyme nitrate reductase, an essential component of which is a Mo atom. This Mo is the business end of the enzyme because it transfers the two electrons to NO_3^- forming NO_2^- .

To accomplish this, the Mo must first be reduced to its Mo^{+4} redox form before it can transfer two electrons to NO_3^- with the Mo then being oxidized back to its original Mo^{+6} form. No element except Mo can function within the NR enzyme. Without Mo, plants could not use nitrate, causing extreme nitrogen deficiency. In very acid soils, where nitrogen is present in its NH_4^+ form, plants can absorb NH_4^+ and assimilate it directly without a need for NR and its Mo.

Mo has a unique ability to reduce nitrogen because it is also the functional component of the nitrogenase enzyme that transfers six electrons to a diatomic nitrogen molecule (N_2) reducing it to two NH_4^+ ions. Nitrogenase is present only in bacteria that have the ability to fix atmospheric N_2 to the biologically useful NH_4^+ form. This occurs in nodulated roots of legumes and some woody shrubs, in cyanobacteria of rice fields and in various free-living soil bacteria.

The process is not directly important as a nitrogen source for turfgrasses, so we will consider it no further here. It is worth considering, however, that most nitrogen that enters the biosphere through natural means does so

through the nitrogenase enzyme and thus depends on Mo.

Another role for Mo generally recognized in plants is its function in the enzyme xanthine dehydrogenase or xanthine oxidase. Here it also acts as a carrier of electrons during the oxidation of purines that are components of nucleic acids.

Mo draws electrons away from a nitrogen-con-

On sand-based greens and light soils, applications every two to three years constitute good insurance against micronutrient limitations.

taining organic ring structure and donates them to oxygen (oxidase) or NAD^+ (dehydrogenase). These enzymes are important in recycling nitrogen from degraded nucleic acids and in the synthesis of ureids that are important nitrogen transport molecules in some plants, especially legumes. The oxidative properties of these enzymes also make them important players in the antioxidative defense reactions of many plants.

Closely related to the purine oxidizing enzymes is another that oxidizes aldehydes to acids. This Mo-containing aldehyde oxidase is responsible for the oxidation of several plant aldehydes, but most significantly it catalyzes the final step in the synthesis of abscisic acid (ABA) and the auxin indole-acetic acid (IAA). In both cases, an aldehyde surrenders two electrons to the Mo^{+6} of aldehyde oxidase and in the process being oxidized to an acid.

These two acids are primary plant hormones that are essential for orderly growth and the plant's ability to react to environmental stresses.

Mo and plant stress

A new concept is emerging that places Mo at the center of a plant's ability to respond to stress conditions by signaling information between roots and shoots (Lips et al., 2000).

In an earlier article (Hull, 1996b), we discussed the ability of turf to sense the drying of shallow roots by producing abscisic acid that, when translocated to shoots, slowed leaf growth and closed stomates, thereby conserving water use. This enabled the grass to sense the onset of drought before the plants actually were experiencing any moisture stress. Now we have a bet-

Continued on page 44



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ter idea of how Mo-enzymes coordinate several processes to allow plants a more comprehensive response to the imposition of stress conditions.

Drought, salinity and even elevated ammonium levels, when perceived by roots, increase the activity of the aldehyde oxidase enzyme that promotes the synthesis of ABA from abscisic aldehyde. The ABA moves in the transpiration stream to leaves where it promotes stomates to close and reduce the rate of water loss.

At the same time, nitrate loading into the xylem of roots is reduced and this induces the activation of nitrate reductase, and more nitrate is then assimilated in the roots.

With less nitrate moving to the leaves, more photosynthetic product (sugars) are directed to roots because nitrate in leaves serves as a signal directing photosynthate toward amino acid synthesis and that promotes shoot growth. Also, higher ABA concentrations in the leaves will inhibit shoot growth.

The greater nitrate assimilation in roots and additional photosynthate being delivered through the phloem from the shoots stimulates deeper root growth and makes additional water available. The greater nitrate assimilation in roots also induces xanthine dehydrogenase that promotes ureide biosynthesis. Ureides are transported to leaves where they provide nitrogen for shoot function and growth without diverting sugars from transport to roots.

Xanthine oxidase/dehydrogenase in leaves may also contribute some antioxidative protection from drought and high-temperature stress experienced by the shoots. Many details of this stress response sequence are still poorly understood, but the general process has been observed in several plants including perennial ryegrass (Lips et al., 2000).

You will note that many of the key enzymes involved in this complex plant response contain Mo, which places the micronutrient at the center of plant tolerance responses to stress conditions.

Mo in turfgrass management

In turfgrass culture, where soils are normally limed to a pH of more than 6, any Mo present will likely be available to the turf. However, on a sand-based green or turf growing on a light soil, additions of micronutrients such as iron or manganese could form insoluble salts with molybdate making it less available.

In general, grasses have a lesser requirement for Mo than legumes or other plants that depend on N₂ fixation so deficiencies are rarely if ever observed. However, turf managers are not normally looking for Mo deficiencies and likely would not observe the subtle reduction in growth or chlorosis that could result from inadequate Mo.

The best approach to insuring adequate Mo for turf is similar to that for most other micronutrients: periodic applications of a commercial mixture of such elements. On sand-based greens and light soils, applications every two to three years constitute good insurance against micronutrient limitations.

Molybdate is an oxyanion and like phosphate and sulfate is mobile in both the xylem and phloem of turfgrasses. This makes a foliar application of ammonium molybdate especially effective because it can be translocated to all plant organs once absorbed by leaves. If soils are acid or high in sulfate and likely to immobilize Mo, foliar treatments can be the most practical means of insuring adequate levels in turfgrasses.

Normally the turf manager need not be concerned about Mo adequacy. However, if clippings are regularly removed and organic topdressings are not applied, Mo along with other micronutrients should not be ignored. Mo offers a large safety margin in plants so toxicity problems are not likely. Even if reclaimed water is used for irrigation, problems with Cu, Mn or B toxicity are more likely than injury from excess Mo.

Hull, a professor of plant sciences at University Rhode Island in Kingston, R.I., specializes in plant nutrition.

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CIRCLE NO. 125

Herbicide-treated Mulches Address Some Environmental Concerns

Editor's Note: Note that herbicide-treated mulches are experimental and are not registered products.

By Hannah Mathers

Weed control with mulch is the main reason cited for mulch use. In this article, we will discuss our research with herbicide-treated mulches.

A variety of organic mulches have been advocated for weed suppression in ornamentals. Organic mulches control weeds in two ways: inhibition of germination and suppression of weed growth (Skroch et al., 1992, Borland, 1990 and Duryea et al., 1999). The effects of mulches on weed control are greatest when the mulch is fresh (Duryea et al., 1999). The most commonly used mulches in ornamentals are barks. This article will focus on the research I did while at Oregon State University.

A study of three bark mulches and two pine needle mulches found that even when applied at a depth of 3.5 inches the mulches only reduced weed counts by 50 percent over untreated controls. This level of control was well below commercially acceptable levels.

As a result of increasing financial and environmental concerns, reducing the amount of herbicide used in ornamental weed control while still maintaining profitable maintenance has been the recent focus of considerable research.

Beyond suppression

Mulching with products such as bark, hazelnut shells and corn gluten meal or oyster shells has been advocated for suppression of serious weed problems. The most commonly used mulches in ornamentals are still barks. The level of weed control provided by bark mulch alone, however, is well below commercially acceptable levels.

Mulches that have been pretreated with pre-emergent herbicides may offer extra advantages for weed control over untreated mulches. The only calibration required would be monitoring the mulch depth to ensure the optimum rate of

application. Herbicide treated mulches could be added as a top layer to landscape beds in the spring. Depending on the herbicide mulch combination used, it could provide weed control for more than 250 days after treatment (Case and Mathers, 2003).

Preliminary studies have shown excellent control of certain weeds with a layer of pine bark mulch containing pre-emergent herbicides. One study observed increased efficacy with pine bark mulch treated with pre-emergent herbicide vs. mulch alone. Waste paper mulch pre-treated with Casoron and covered by an additional layer of waste paper mulch, which sealed in the Casoron, gave excellent control of several weed species with no observed phytotoxicity in nursery field plantings of deciduous trees (Hogue).

Regardless of whether you are selecting the herbicide for weed control, for application on bare soil or on to mulch, the key selection criteria remain the same. These criteria are:

- matching the weeds to be controlled against the weeds listed on the product label;
- choosing a material that is labeled for application to both the turf and site; and
- choosing the right herbicide formulation (either sprayable or granular).

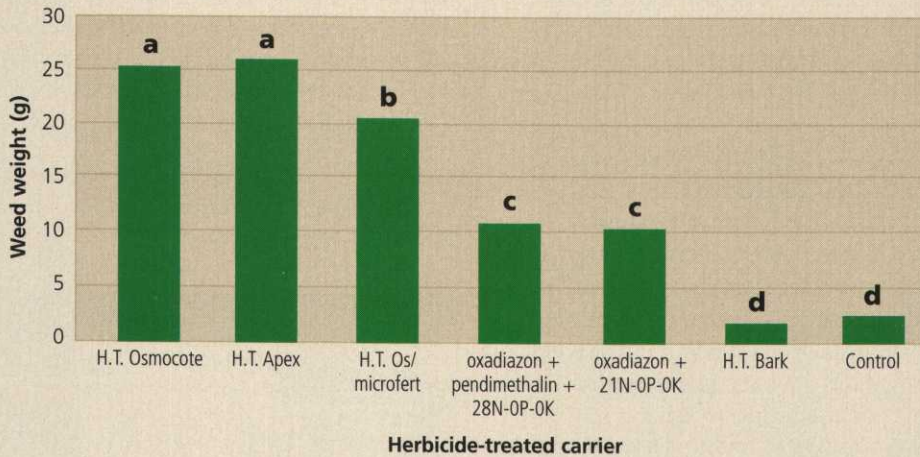
The sprayable formulations can be liquids (L), dry flowables (DF), wettable dispersible granulars (WDG), wettable powders (WP) or emulsifiable concentrate (EC). Many container stock nursery growers prefer pre-emergent granular materials that are applied with cyclone spreaders or belly grinders. Granulars work well when treating rectangular areas. In container production, three to five applications of pre-emergent herbicides may be required to keep the chemical barrier on the container surface because of the large amounts of water that are applied each season.

Many landscapers, however, who work with irregular shaped beds of flowers, shrubs or ground covers, prefer to use a sprayable herbi-

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TABLE 3

Efficacy of various pre-emergent carriers (1998) expressed as grams of weed weight. Different letters signify the LSD $P=0.05$. Bars represent the means of five replicates averaged over three herbicides and two evaluation dates, 70 and 150 DAT. The control received no fertilizer or pre-emergent. The control bar represents five replicates averaged over two evaluation dates. Abbreviation is H.T. = herbicide treated, os/microfert = Osmocote micro-fertilizer.

cide. In landscape culture, two applications of pre-emergent herbicides are recommended: one in fall and one in spring. Supplemental hand weeding during the growing season will be required to provide commercially acceptable weed control in landscape beds.

Because landscapers are accustomed to using mulch and sprayable formulations, herbicide-treated mulches could be easily integrated into most operations.

Research findings

The application of pre-emergent herbicide-treated bark nuggets resulted in increased efficacy in 1998 (Fig. 1) and 2000 (Fig. 2) compared to the herbicides or mulches applied alone. Efficacy was also extended from 35 days after treatment (DAT) to 130 DAT in 1998 and in 2000. The pre-emergent herbicide-treated bark nuggets resulted in increased and extended herbicide efficacy regardless of whether oxyfluorfen, oryzalin or isoxaben were applied to the bark.

The herbicide-treated Douglas fir represented four of the six most efficacious treatments in 2000 at 130 DAT (Fig. 2), specifically — little (less than 1 inch in diameter) Douglas fir nuggets treated with oryzalin at the one-time rate, large (more than 1 inch in diameter) and little Douglas fir nuggets treated with oryzalin at the .5-time rate, little Douglas fir nuggets treated with oryzalin at the .5-time rate, and large Douglas fir nuggets treated with flumioxazin WDG at the one-time rate. The corresponding phytotoxicities of these four top efficacious treatments were commercially

acceptable (Fig. 3).

In our experiments in 1998 and 2000, the herbicide-treated mulches were superior in reducing phytotoxicity, increasing efficacy and extending efficacy. We have found that the herbicide-treated bark provides a 1.5 time increase more efficacy compared to the herbicide applied alone, a 1.8 fold increase compared to the bark alone, a 2.8 times increase in duration of efficacy, and a 2.2 times reduction in phytotoxicity compared to the herbicide alone treatments.

Even though greater efficacy is achieved with the herbicide-treated bark, phytotoxicity is reduced, probably because the herbicide is never directly applied on or near the plant material.

Bark nuggets and herbicides

Present data indicates that the bark nuggets may bind the herbicides and possibly act as slow release carriers for the herbicides or reducing their leaching potential. Recent studies indicate that the application of pre-emergent herbicides onto organic mulches reduced herbicide leaching by 35 percent to 74 percent compared with bare soil pre-emergent herbicide applications (Knight et al., 2001).

Recent studies have also indicated that the controlled release of herbicides using lignin as the matrix offers a promising alternative technology for weed control (Oliveira et al., 2000).

Weed control has become a leading issue in ornamentals for four reasons. First, the increase in irrigation water restrictions and necessity of recirculation ponds means fewer and fewer her-

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bicides are being registered because of chemical company fears of reapplication onto stock.

Second, with the Food Quality Protection Act (FQPA) of 1996 becoming law, two existing acts were amended — the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) and the Federal Food Drug, and Cosmetic Act (FFDCA). These amendments changed the way the Environmental Protection Agency (EPA) regulates pesticides. As a result of these changes, the industry faces the loss of pesticide registrations. The loss of herbicide registrations will have a greater impact on the industry than fungicide or insecticide losses.

Third, the cost of traditional weed control, chemical applications plus hand-weeding, is already the largest pest-management cost that superintendents encounter. In fact, weed control costs far surpass any other form of pest control.

Fourth, the EPA recently announced the new Storm Water Phase II (SWII) regulations (1999) that will regulate quantity and quality of storm water. SWII will have an impact on superintendents. The SWII regulations may make it necessary for all golf courses to have catchment ponds. The impact of these new SWII regulations is not completely known. Each state and county will deal with the regulation in different ways.

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With increased run-off restrictions, superintendents are interested in better managing their irrigation practices and in optimizing their herbicide applications. New weed control methods that are effective and economical and which exhibit reduced environmental impact are needed.

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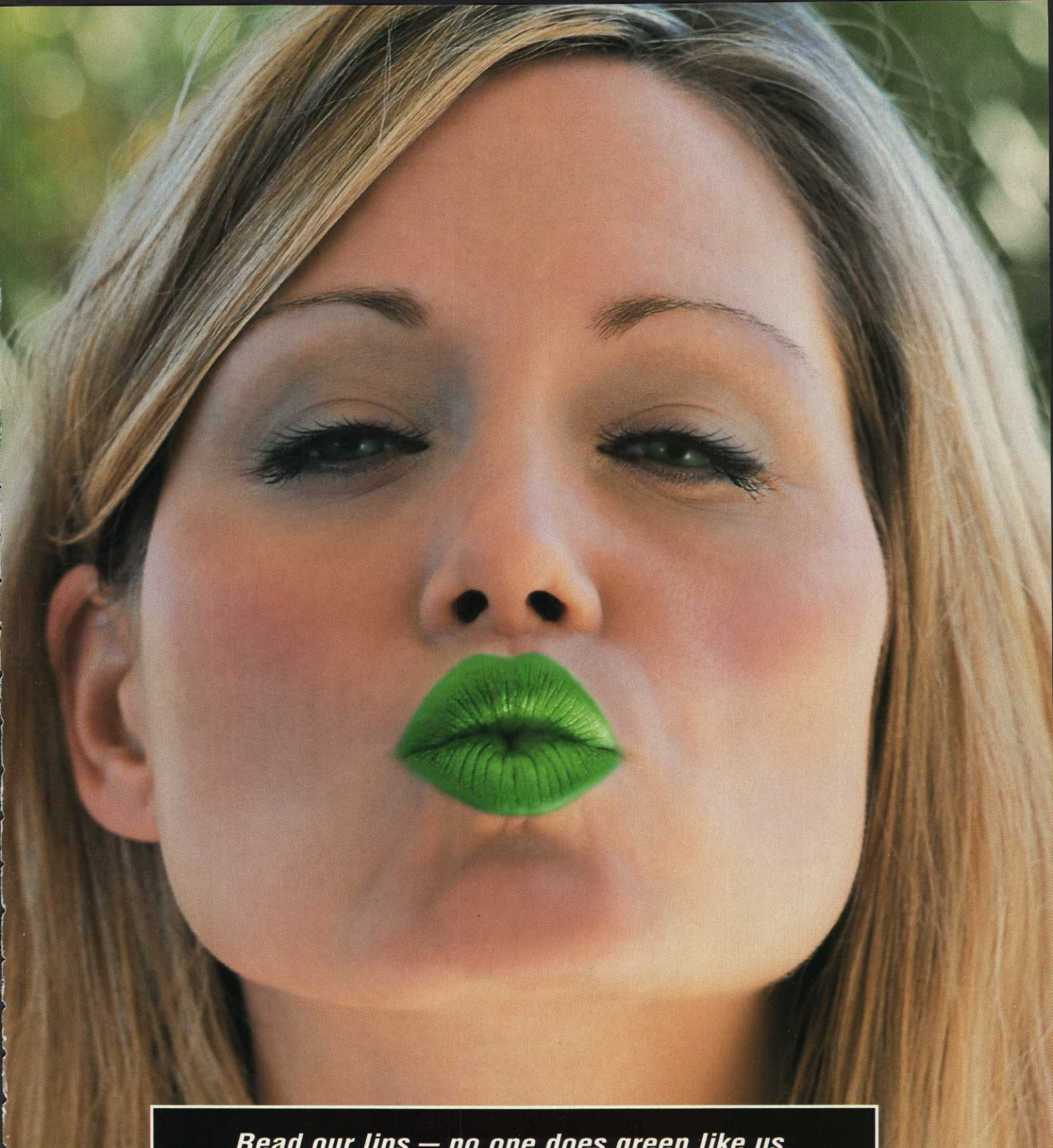
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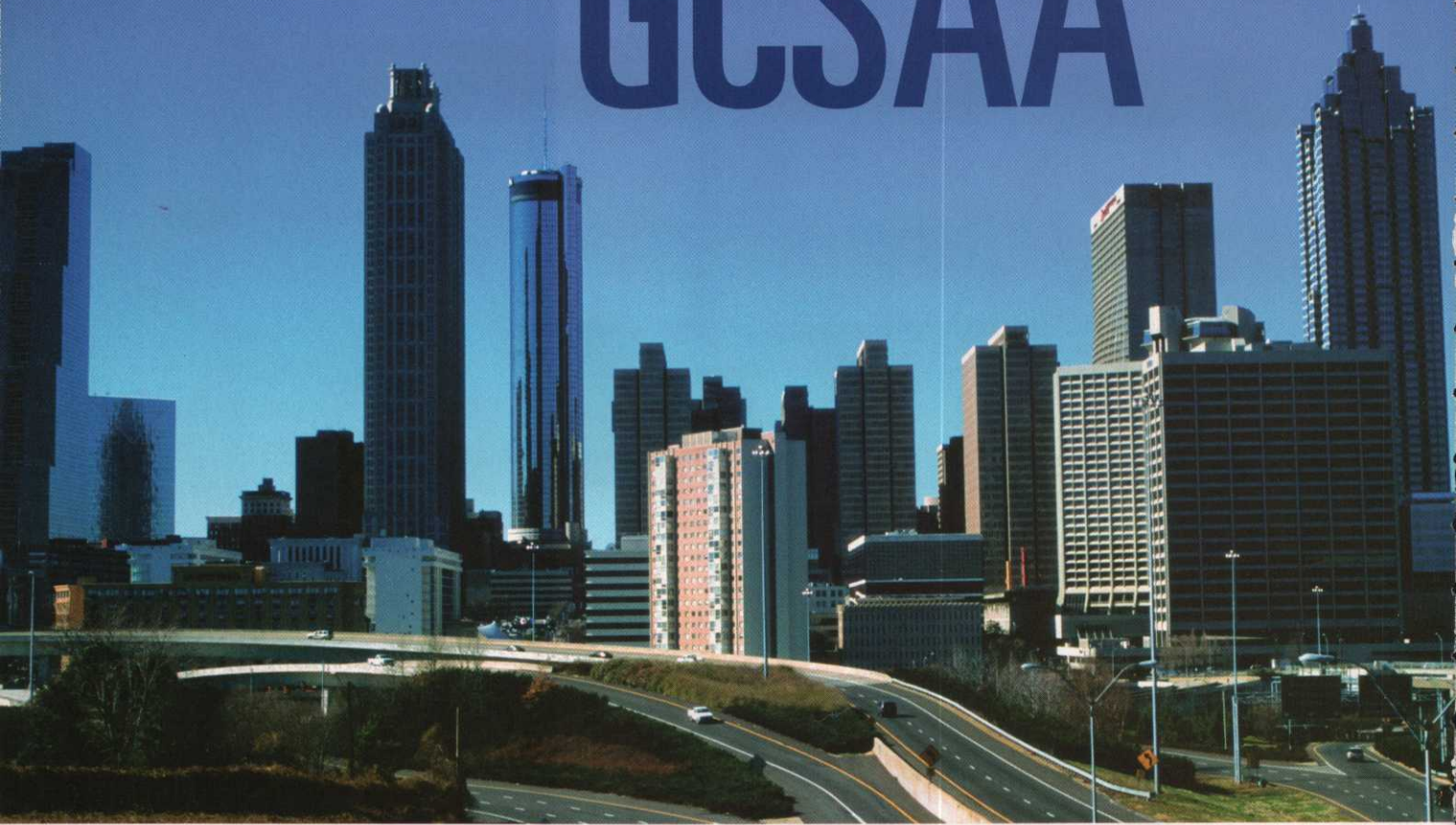
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CIRCLE NO. 126

Into the Deep South With the GCSAA



As long as you don't mention the Civil War or drink Pepsi products, you should be able to have a good time at this year's show

BY MARK LUCE



Before we begin our look at the town called "Hot-lanta," here are a couple of no-no's for visiting the city during the GCSAA show.

First, don't you dare be caught in public with a Pepsi product, as Atlanta is the world headquarters of Coca-Cola, so the city has long been a Coke town. Second, it's probably best not to

mention anything about the Civil War (or as some down there may say, the War of Northern Aggression). Those a bit rusty on their history may do well to recall that in 1864, Union General William T. Sherman torched the railroads, all businesses and two-thirds of Atlanta's homes on his infamous "March to the Sea." Atlanta remains the only major American city ever destroyed in a war.

Those Yankees among you might not know this either, but in the last two decades Atlanta has risen from those

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