## Is Reducing Soil pH Possible?

By Charles F. Mancino

**S** oil pH is probably the most outstanding characteristic of soil solution (Brady, 1990). Acidic soil conditions pose much greater problems in turfgrass management than alkaline soil conditions.

Acidity in the soil results from the leaching of exchangeable base-forming cations calcium  $(Ca^{+2})$ , magnesium  $(Mg^{+2})$ , potassium  $(K^{+})$  and sodium  $(Na^{+})$  from the upper soil horizon. Hydrogen  $(H^{+})$  and aluminum  $(Al^{+3})$  remain as the primary cations in these soils.

Under strong acidic soil conditions (a pH of less than 5) adsorbed  $Al^{+3}$  solubilizes and enters soil solution where it reacts with water to form aluminum hydroxide (Al(OH)<sup>+2</sup>) and H<sup>+</sup>.

#### $Al^{+3} + H_2O => Al(OH)^{+2} + H^{+}$

This hydrolysis generates a large amount of  $H^+$  ions. Similar reactions occur with iron (Fe<sup>+3</sup>), but the acidity generated by iron is much less than that of aluminum. Adsorbed  $H^+$  actually contributes little to the pH of acid soils because it's tightly bound to organic matter, Fe and Al oxides, and 1:1 type clays.

Aluminum also contributes to the pH of moderately acidic soils (a pH of 5 to 6.5). However, under moderate soil pH conditions, aluminum no longer exists as  $Al^{+3}$  ions. Instead, it exists as aluminum hydroxy ions  $(Al(OH)_2^{+}, Al(OH)_2^{+}$  and much more complex forms). An equilibrium is reached between hydroxy ions held on cation exchange sites and those in the soil solution. Solution aluminum hydroxy ions hydrolyze and generate H<sup>+</sup> ions.

 $Al(OH)^{+2} + H_2O => Al(OH)^{+} + H^{+}$ 

In addition, easily exchangeable H<sup>+</sup> and some of the less tightly bound H<sup>+</sup> ions are released into soil solution and also contribute to acidity.

#### **Alkaline soil**

Alkalinity occurs when aluminum and hydrogen have been predominately replaced by Ca<sup>+2</sup>,  $Mg^{+2}$ ,  $K^+$  and  $Na^+$  on the permanently charged cation exchange sites. Aluminum hydroxy ions in solution have been converted to insoluble gibbsite (Al(OH)<sub>3</sub>) while any H<sup>+</sup> that has been released has reacted with hydroxyl ions in soil solution to form water.

Alkaline soils are generally found in arid and semi-arid regions where leaching of base cations is low. However, they are also found in humid regions where soils have formed from calcium and magnesium carbonate parent materials, and where calcium and magnesium carbonates precipitate out as a result of irrigation with limestone aquifer water.

Calcareous sands can be found wherever sand is mined from ancient coral reefs, crushed limestone or the mixing of crushed seashells with quartz sand. Under all of these conditions, adsorbed  $Ca^{+2}$ , and often  $Mg^{+2}$ , dominate the permanent cation exchange sites.

Difficulties associated with naturally occurring alkaline soils, or in soils that have been overlimed, are predominately related to nutrient imbalances rather than from the direct effects of soil solution pH on plant growth. Carrow et al. (2001) point out that these nutritional problems include:

 phosphorus (P) deficiency due to the reaction of P with calcium carbonate and calcium sulfate to form insoluble calcium phosphates;

 the formation of insoluble iron and manganese oxides and hydroxides;

 the unavailability of zinc as it combines with applied phosphate to form zinc phosphate;

• boron deficiency as pH increases from 7 to 9 as it possibly becomes bound to soil colloids; and

• molybdenum toxicity for certain crops, but generally not turfgrass.

These conditions, which do not occur in all alkaline soils, can be corrected through the use of proper turfgrass nutrient management.

A pH range of 6 to 7 promotes the best availability of plant nutrients to higher plants (Brady, 1990). This is the pH range most suited to the availability of phosphorus in miner-*Continued on page 42* 

### QUICK TIP

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Fire ants, like all insects, require moisture. During hot and dry weather, fire ants will burrow deeper into the soil making control more difficult. Insecticide applications should be made during moderate temperatures and adequate soil moisture. Chipco® Topchoice<sup>™</sup>, with its revolutionary mode of action, can provide up to 52 weeks of control with a single application.

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al soils and is important for taller crops where this nutrient can't be applied after they have achieved some height. However, phosphorus can be applied at any time to turf and ornamentals. Most agronomic and horticultural crops actually grow well under a wide soil pH range, provided they are supplied with the correct amounts of nutrients. Alfalfa and sweet clover would grow well on slightly acidic soils provided they were supplied with calcium, and acid-loving plants could thrive under alkaline soil conditions if supplied with micronutrients (Tisdale et al., 1993). Many tree species also prefer acid soils because of their high micronutrient requirements. Adjustment of pH is important for disease control in some crops, primarily because of its influence on pathogen populations and activity, as well as its influence on micronutrient availability which is important for certain disease reductions.

Turfgrass and landscape managers are usually overly concerned about the pH of the alkaline soils that they are managing. Often they believe that plants will not perform to their genetic potential if not grown in moderately acidic to slightly acidic soil. As a result, the manager often requests a recommendation on how to reduce soil pH. However, acidification of alkaline soils is usually not necessary.

Problems due to alkalinity are less common than problems due to acidity. As mentioned previously, the primary problems are nutritional and, for turf and ornamentals, can usually be corrected at any time during the growing season.

The acidification of alkaline pH soils may not be practical or possible. A soil that is alkaline can also be calcareous, i.e., it contains inorganic carbonates. Often referred to as "free lime" inches or "free calcium carbonate" inches this term includes both calcite (CaCO<sub>3</sub>) and dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>). Calcite in soil is the size of coarse clay and fine silt particles. Dolomite (calcium and magnesium carbonate) is the size of silt and fine sand. These two minerals are sparingly soluble salts. Dolomite has a dissolution rate of about 100 times less than calcite because of its larger size (Loeppert and Suarez, 1996).

Calcite and dolomite are referred to as alkaline-earth carbonates. They are the primary forms of inorganic carbonate in soil with calcite being the most predominant. Their hydrolysis in the soil is an alkaline reaction that generates hydroxyl and bicarbonate ions that neutralize H<sup>+</sup>. The dissolution of the carbonates decreases as the H<sup>+</sup> concentration is reduced and the rate at which OH<sup>-</sup> is removed from solution decreases.

#### $CaCO_3 + HOH \leq = > Ca^{+2} + 2OH^- + HCO_3^-$

Alkaline conditions actually favor calcium carbonate accumulation in the soil by consuming H<sup>+</sup>ions and driving the following reaction to the right.

$$Ca^{+2} + H_2O + CO_2 \implies CaCO_3 + 2H^+$$

Calcium carbonate precipitates out of soil solution at pH 8.2, but calcareous soils can range in pH from 7.3 to 8.5 when averaged across the soil depth (Carrow et al. 2001). A pH of more than 8.3 is indicative of the presence of exchangeable sodium which hydrolyzes to form NaOH (sodium hydroxide), a strong base, in the soil solution.

Soil is a buffered system. It requires more acid or base to neutralize it than would be indicated by its pH value. Buffering occurs because weak acids, weak bases and salts (which give rise to weak acids or bases) have a low ionization rate when strong acids or strong bases are added. In other words, a weak acid or base does not give up all of its H<sup>+</sup> or OH<sup>-</sup> at any one time. For example, acetic acid (CH<sub>3</sub>COOH) will dissociate only 1 percent of its H+ while hydrochloric acid (HCl) will dissociate 100 percent of its H<sup>+</sup>. Acetic acid is a weak acid while hydrochloric acid is a strong acid. The dissociated H<sup>+</sup> is active acidity inches, the undissociated H<sup>+</sup> is potential acidity inches and the total H<sup>+</sup> is "total acidity. inches. If active acidity or basicity is nearly equal to total acidity or basicity, you have a strong acid or base.

Carbonates are salts of weak acids. As a result, they contribute to the buffering capacity of a calcareous soil, along with the organic and inorganic colloids, bicarbonates, phosphates and other salts present in the soil. The hydrolysis of these salts gives rise to hydroxyl ions that can be neutralized by an acid. However, neutralized hydroxyls are immediately replaced through further hydrolysis of the salt because *Continued on page 44* 

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only a small portion of the salt will dissociate at any one time.

$$Ca_{50}X + 5H_2SO_4 \implies Ca_{45}H_{10}X$$

The partially neutralized salt still contains an excess amount of calcium. Therefore, the buffering capacity of a calcareous soil is greatly supplemented by the presence of carbonates. As such, a calcareous soil will require large amounts of an acidifying amendment to neutralize all of the free lime before a permanent reduction in pH is achieved.

#### **Getting started**

Before embarking on a pH reduction program it is important for the turf manager to determine if the soil is alkaline or alkaline-calcareous. If a soil test shows a pH greater than 7.5, exchangeable calcium greater than 5,000 pounds per acre and a cation exchange capacity greater than 15, you are most likely dealing with an alkaline-calcareous soil (personal communication, Dr. Charles Darrah, CLC Labs, Westerville, Ohio).

The total amount of inorganic carbonates must be determined in an alkaline-calcareous soil to correctly determine how much acidifying amendment must be used to reduce pH. In many ways, this is equivalent to determining the lime requirement of an acid soil. There are numerous procedures that can be used to determine the quantity of total inorganic carbonate. For the most part they all require the complete acid dissolution of the carbonates in the soil (Loeppert and Suarez, 1996). In Ohio, the Ohio EPA Neutralization Potential Test is often used (Ohio EPA, 1978).

In this procedure either .1 nitrogen (N) or .5 N HCl is added to 2 grams of soil (less than .25 millimeters). The volume and concentration of the acid are dependent on a visual fizz rating with concentration and volume increasing as the fizz becomes stronger. The soil:acid solution is heated to nearly boiling until no gas evolution is visible. The sample is then boiled with distilled water to complete the reaction. The remaining unconsumed acid is measured by titrating with standardized .1 N or .5 N NaOH until the pH of the solution return is 7. The results are expressed as tons  $CaCO_3$  equivalent per 1,000 tons of soil.

Elemental sulfur (S<sup>0</sup>) is the most common amendment used to reduce soil pH. When sulfur is added to the soil it undergoes oxidation with the general reaction being:

 $S^{0} + H_{2}O + 3/2 O_{2} <=> 2 H^{+} + SO_{4}^{2-}$ 

Two classes of bacteria carry out this reaction. *Thiobacilli* uses the energy released during the oxidation of S<sup>0</sup> to fix CO<sub>2</sub> from organic matter (Tisdale et al., 1993). It is usually considered the most important class of S oxidizer in the soil. The second class includes many heterotrophic bacteria that are particularly important in the root rhizosphere. Most S<sup>0</sup> oxidizers are aerobic and require soil conditions favoring plant root growth.

It requires only 32 pounds S<sup>0</sup> to neutralize 100 pounds CaCO<sub>3</sub>. However, a soil with 1 per-CaCO<sub>3</sub> contains 230 cent pounds CaCO<sub>3</sub>/1,000 square feet/3 inches depth. Therefore this soil would require 74 pounds S/1,000 square feet. Alkaline calcareous soils can contain 40 percent or more of inorganic carbonates, but even amounts as low as only 2 percent or 3 percent can make pH reduction impractical, if not impossible. This is because surface applications of sulfur are usually limited to 5 or 6 pounds S<sup>0</sup>/1,000 square feet twice per year. It would take 6 to 7.5 years to apply enough S<sup>0</sup> to dissolve this limestone and cause a permanent change in pH. One-half this annual amount is recommended for low CEC sandbased putting greens.

Limitations on S<sup>0</sup> applications are based on the potential for excessive acidity to occur at the soil surface or in the thatch layer. Excess acidity can be as low as pH 2.5 in this zone and can cause direct injury to the crown and roots, as well as Al<sup>+3</sup>, Mn<sup>+2</sup> and H<sup>+</sup> toxicity (Carrow et al., 2001). Low S application rates reduce the possibility that large amounts of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) can be produced at the same time.

#### When to make a move

The question then is: Under what conditions should soil acidification of alkaline pH soils be attempted?

First, consider soil acidification if the soil is alkaline and contains no free lime. Then the pH of the soil can be significantly and permanently reduced over a period of time. However, the actual need to reduce pH may not exist if plants



The Andersons offers a wide variety of snow mold protection products in both granular and sprayable formulations. For more information, please visit our Web site at *www.andersonsgolfproducts.com* or contact your local Andersons distributor. are well adapted to alkaline soil conditions and their nutritional needs are being met.

In the book *Turfgrass soil fertility and chemical* properties, Carrow et al. (2001) present a table showing the approximate amounts of elemental sulfur (99 percent purity) necessary to reduce the top 6 inches of soil to pH 6.5 (see Table 1). These S0 rates are based on assumptions about how soil texture influences cation exchange capacity and the final amount of H+ saturation on the cation exchange sites. S0 rates can range from a low of 2 pounds to 5 pounds/1,000 square feet to as high as 70 pounds/1,000 square feet

Even with non-calcareous soil, it can take many years to apply enough sulfur to reduce pH. Therefore, the best time to reduce pH of an alkaline soil is prior to establishment when larger quantities of sulfur can be incorporated into the soil. Under these conditions it has been recommended that rates as high as 70 pounds S<sup>0</sup>/1,000 square feet can be safely incorporated into the upper 6 inches of soil (Carrow et al., 2001). However, S<sup>0</sup> rates up to 20 pounds/1,000 square feet/4 inches soil are usually considered safe when incorporated pre-planting incorporated. Rates over 25 pounds/1,000 square feet incorporated into the upper three to four inches of soil should be used with caution.

The pH reduction of alkaline-calcareous soils should occur only under specific conditions. Each 1 percent calcium carbonate in the soil requires that an additional 130 pounds S<sup>0</sup>/1,000 square feet be added to the amounts recommended in the table by Carrow et al. (2001). This essentially makes it impossible to change the pH of a calcareous soil in a reasonable time frame. Fry et al. (2002) reported that no significant change in pH occurred following the application of 40 pounds S<sup>0</sup>/1,000 square feet over a two year period to a calcareous (1.5 percent free lime) sand green.

In lieu of pH reduction, routine soil testing should be performed to determine if any nutritional imbalances are present. Bicarbonateextractable P should be determined to insure adequate plant available P levels in the soil. Magnesium levels should be monitored to insure a Ca:Mg ratio of more than or equal to 8.5:1 and exchangeable Mg levels should be in sufficient quantities to optimize plant growth.

Soil micronutrient levels should also be monitored, particularly for iron. Chelated iron

#### TABLE 1

# Approximate quantities of elemental S (99 percent purity) required to lower the pH of the top 6 inches of a non-calcareous soil to pH 6.5.

Soil pH	Sand to loamy sand	Loam	Clay or organic soil
8.5	30 to 50	50 to 60	60 to 70
8	15 to 25	25 to 35	35 to 50
7.5	10 to 15	15 to 20	20 to 25
7	2 to 5	3 to 6	5 to 10

(Adapted from Carrow et al. 2001)

products (especially EDDHA) have the longest lasting effects when applied to soil, but ferrous sulfate sprays may provide a more cost-effective way to provide foliar-fed and some rootabsorbed iron. Acidification of irrigation water to reduce high bicarbonate levels can also improve Fe availability in the soil.

Some situations actually do warrant the use of acidifying amendments on alkaline-calcareous soils. The first is when inorganic carbonates precipitates near the soil surface. This caliche layer is a weakly or strongly cemented layer of soil particles and carbonates. It can develop in both sand and finer-textured soils. It usually forms when soils are irrigated yearround with water high in Ca<sup>+2</sup>, Mg<sup>+2</sup> and bicarbonate. It is not uncommon for the pH of a soil to increase when irrigation is initiated with this type of water.

Unlike sodium bicarbonate and potassium bicarbonate, calcium and magnesium bicarbonates only exist in solution. The following reaction illustrates what happens when a soil dries following irrigation with a hard and alkaline water:

#### $Ca(HCO_3)_2 \Longrightarrow CaCO_3 + CO_2 + H_2O$

These precipitates form the caliche layer that can act as an impediment to soil water movement (Soil Improvement Committee — California Fertilizer Association, 1985). The use of pH reduction, along with cultivation, is recommended in this situation to prevent or reverse caliche formation (Carrow, 2001). An advantage to a shallow layer of caliche is that the depth of soil that needs to be affected by added acidifying amendments is usually only 1 inch to *Continued on page 48* 

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2 inches. Guidelines for the amounts of acidifying amendments still need to be followed even if core cultivation is performed at the same time. An annual pH acidification program should be considered when irrigation water is the primary source of free lime.

### Elemental sulfur (S<sup>0</sup>) is the most common amendment used to reduce soil pH.

A turf manager can also consider following a long-term pH acidification program for alkaline-calcareous soils if the total inorganic carbonate level is 2 percent or less. Routine applications of sulfur can be made in conjunction with routine testing for soil pH. However, this program will require time for any permanent change in soil pH to occur. Soils with 2 percent to 3 percent free lime may also respond to acidifying amendments if they are mixed into the soil as a pre-plant treatment. However, it's my guess that soils that respond dramatically to sulfur are alkaline rather than alkaline- calcareous in nature.

Typical safe rates are 20 pounds S/1,000 square feet per 4 inches of soil. An annual acidification program can then be carried out after the turf or landscape is established and a longterm acidification program is acceptable to the landscape manager.

Carrow et al. (2001) recommend that a pH monitoring program be initiated when soil acidification is attempted. They recommend that two sets of samples be taken. The first set represents the top 0 inches to 1 inch depth of soil while the second set is from 0 inches to 4 inches. If turf crowns are located in the thatch layer, include the thatch with the shallower soil sample. Sample the thatch separately if it is less than or equal to 1 inch thick. Do not allow the thatch and surface soil pH to drop below 5. Neutralize it with 2 pounds to 4 pounds  $CaCO_3/1,000$ square feet if it does.

#### Summary

In summary, alkaline and alkaline-calcareous soils conditions, unlike acidic soil conditions, rarely pose a problem in turfgrass management. Any problems associated with alkaline pH are usually nutritional and can be overcome effectively with alterations in fertilizer practices. While alkaline soil pH can be changed using acidifying materials, the pH of alkaline-calcareous soils is very resistant to change due to the buffering capacity of calcium and magnesium carbonates. The amount of total inorganic carbonate in the soil must be determined in order to know how much sulfur is required to neutralize it.

Limitations on annual application amounts of acidifying materials may essentially make pH reduction impractical, if not impossible. Therefore, only a few situations exist where pH reduction should be attempted. They include the reduction of an alkaline soil with very little or no inorganic carbonates present; the establishment phase when large quantities of acidifying material can be incorporated into the soil and total inorganic carbonates are less than 3 percent; when irrigation water is the primary source of carbonates and a caliche layer can or has formed in the top 1 inch to 2 inches of soil; and, if soil carbonates are 2 percent or less and a long-term soil acidification program is acceptable.

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