Introduction

Soil pH is a measure of the soil solution’s (soil water) acidity and alkalinity. By definition, pH is the negative logarithm of the hydrogen ion concentration \([H^+]\), i.e., \(pH = -\log [H^+]\). Soils are referred to as being acidic, neutral, or alkaline (basic), depending on their pH values on a scale from 0 to 14. A pH of 7 is neutral, less than 7 acidic and greater than 7 alkaline. Because pH is a logarithmic function, each unit on the pH scale is ten times less acidic or basic than the unit above or below it. For example, a solution with a pH of 6 has a 10 times greater concentration of \(H^+\) ions than a pH of 7, and 100 times higher concentration than pH 8. Soil pH is influenced by both acidic- and basic-influencing ions in the soil. Common acidic cations (positively charged ions) are hydrogen (\(H^+\)), aluminum (\(Al^{3+}\)), and iron (\(Fe^{2+}\) or \(Fe^{3+}\)); whereas common basic cations include calcium (\(Ca^{2+}\)), magnesium (\(Mg^{2+}\)), potassium (\(K^+\)), ammonium (\(NH_4^+\)), and sodium (\(Na^+\)).

Many factors influence the pH of a soil or subsoil. These include parent material the soil was derived from; length of weathering and soil formation; climate; organic matter mineralization; \(NH_4^+\) fertilizer rate and nitrification to \(NO_3^-\); cropping system and crop harvest; and land use and management. Of the management practices for crop production, application of fertilizers or organic sources that contain ammonium (\(NH_4^+\)) or compounds that transform into \(NH_4^+\) once applied to the soil and the cropping system will have the largest influence on increasing soil acidity. Nitrification of \(NH_4^+\) to \(NO_3^-\) from any fertilizer or manure source, or mineralization of organic-N compounds such as from manure, produces \(H^+\) ions, thus lowering soil pH. Frequency of crops in a rotation that require N application, and frequency of crops with high N fertilization requirement, will affect acidification rate. An example is continuous corn versus corn-soybean rotation. Some manure sources contain liming materials, eggshells and limestone with poultry manure as an example, and may offset acidity from nitrification or even increase soil pH.
Most agricultural soils in dry climates have alkaline conditions with average pH values ranging from 7 to 8.5. This is primarily due to the presence of basic cations associated with carbonates and bicarbonates found naturally in those soils and irrigation water. When sodium (Na) is abundant, which sometimes is the case in dry climate areas, soil pH can be as high as pH 10. Due to relatively low precipitation, often less than evapotranspiration, there is little leaching of basic cations resulting in a relatively high degree of base saturation (percentage of the cation exchange complex occupied by basic cations) and pH values greater than 7. In contrast, acidic conditions occur in soil derived from parent material high in elements such as silica (rhyolite, granite, sandstone), high levels of sand with low buffering capacities (ability to resist pH change), and in regions with high precipitation. High precipitation causes increased leaching of basic cations, low base saturation and therefore low soil pH.

Soil pH affects plant growth directly and also indirectly by affecting availability of essential nutrients, levels of phytotoxic elements, and microbial activity. Figure 1 shows relatively how nutrient availability and microbial activity are affected by soil pH. The availability of Fe and zinc (Zn), for example, is severely reduced in high-pH soils. Even though Fe is present in large quantities in soils, much greater than Zn, its availability to plants (in a form plants can take up) is limited by reactions that form insoluble compounds at high pH.

Most plants have a wide range of pH where they can grow and survive, but have optimal growth and production in a fairly narrow range. For example, a legume crop like alfalfa can grow and survive in soil pH’s ranging from 5.0 to 8.1, however, forage yield will be greatly reduced in low-pH soils (less than 6.0) and is optimized with soil pH only slightly acidic to neutral. Other crops, like cranberries, for example, are adapted to acidic soils and will not grow well in soils with a pH above 6.0. Soil pH modification, therefore, must be tailored to the crop or cropping rotation. Optimum soil pH ranges, which depend on the crop and geographic region, have been established for crops. Examples are given in Figure 1.
Negative Effect of Acidic Soils

Knowing the soil pH helps identify the kinds of chemical reactions that are likely to be taking place. In general, the most important reactions from the standpoint of crop production are those dealing with solubility of essential and non-essential elements. As indicated in Figure 1, the relative availability of several essential nutrients is greatly reduced at low pH. Phosphorus (P) is an important example. Toxicity from Al$^{3+}$, Mn$^{2+}$, and H$^+$ is a major cause for crop failure in very acidic soils. Aluminum and Mn are a problem in acidic soils because they are more soluble at low pH. There are always large quantities of Al present in soils because it is a component of clays. When the soil pH is above 5.0 to 5.5, soluble Al$^{3+}$ is low and Al remains in a solid combination within clays and other elements, and therefore is not harmful to plants. As the pH drops below those levels, Al containing materials began to dissolve and Al$^{3+}$ increases in soil solution and on the soil cation exchange complex. Because of its nature as a cation
Soil pH and Lime Management

(Al$^{3+}$), the amount of dissolved aluminum is 1,000 times greater at pH 4.5 than at 5.5, for example. Toxic levels of Al$^{3+}$ harm the crop by negatively affecting root activity. As a result, plants are unable to absorb water and nutrients normally and will appear stunted and exhibit nutrient deficiency symptoms, especially such as those for P. Often the field also will appear to be under greater stress from pests, such as weeds, because of the poor crop growth and inability to compete.

The relationship between pH and dissolved Mn$^{2+}$ is similar to that just described for Al$^{3+}$, except that Mn$^{2+}$ only increases 100 fold when the pH drops from 5.5 to 4.5, and levels are greatly affected by the oxidation/reduction conditions of the soil. Toxic levels of Mn interfere with the normal growth processes of the above ground plant parts, usually resulting in stunted, discolored growth, and poor yield.

Iron reactions are similar to that for Al and Mn where Fe solubility increases as soil pH decreases and is very low at high soil pH (Figure 1). Iron toxicity, however, in low-pH soils is not a major problem for most crops (as it is for Al and Mn toxicity), but can be for some crops (rice, for example). Iron deficiency in high-pH soils is widespread for some Fe-sensitive crops (soybean, for example) and is therefore a cause of concern in many agricultural systems.

**Testing for Soil pH**

Soil pH is best measured in soil-water slurries, with soil to water ratios of 1:1 (most common in most of the U.S.), 1:2, or in a saturated soil paste. Soil pH values are measured with a pH electrode placed into either the slurry or paste. This pH is designated as the water pH and is an indication of what is called the active acidity or acidity in soil solution. Though most soil testing laboratories utilize water for pH determination, some will use a dilute salt solution (such as KCl or CaCl$_2$). The dilute salt is used to mask the effects of naturally occurring soluble salts or recent fertilizer application on pH measurement. By adding a slight concentration of salts, more exchangeable H$^+$ ions are brought into solution from the exchange complex, with the measured pH generally 0.5 to 1.0 units lower than measured using a water slurry. Also, differing soil-water ratios produce slightly different pH values; a reading obtained from a 1:1 soil:water ratio is generally 0.15 to 0.25 pH units higher than that of a saturated paste extract, but lower than a 1:2 ratio. Therefore, it is important to be aware of the soil pH test being used and to be consistent between methods to ensure comparable data over time. Soil testing laboratories typically denote the pH test method used on their soil test reports.
Table 1. Range and suggested optimum soil pH values for optimum growth of selected crops

<table>
<thead>
<tr>
<th>Crop</th>
<th>Optimum Soil pH range</th>
<th>Suggested optimum pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alfalfa</td>
<td>6.2-7.5</td>
<td>7.0</td>
</tr>
<tr>
<td>Barley</td>
<td>5.5-7.0</td>
<td>6.5</td>
</tr>
<tr>
<td>Corn</td>
<td>5.5-7.0</td>
<td>6.5</td>
</tr>
<tr>
<td>Soybean</td>
<td>5.5-7.0</td>
<td>6.5</td>
</tr>
<tr>
<td>Wheat</td>
<td>5.5-7.0</td>
<td>6.5</td>
</tr>
</tbody>
</table>


Soil sampling: Methods, Timing, and Frequency

Collecting an appropriate soil sample for pH determination is the first and most critical step in determining liming needs. Improper sample collection and handling can lead to incorrect recommendations. It is generally suggested to collect at least 12 cores from the recommended depth (this varies by region) at random locations across the area of interest and place them in a clean, plastic container for shipment to the lab. Timely soil sampling is important because limestone requires time to neutralize soil acidity. Sampling and limestone application should be completed several months in advance of crop growth to provide time for pH adjustment. In addition, soil pH fluctuates during the year, thus soil sampling should be conducted at the same time during the season.

The frequency of soil sampling to determine lime requirement will depend on soil properties, crop, the source and amount of N applied, and the quality and type of liming material used. Under intense cereal production using high rates of N fertilizer, sandy soils will rapidly increase in acidity. Finely ground liming materials will result in a more rapid increase in pH, but also a more rapid decrease in pH over time. Sampling at least every three to five years is recommended.

There is increased interest in within-field site-specific pH measurement and variable rate lime application due to the often large variation in soil pH. This is especially true in fields with variable soils, for example, fields where acidic soils are intermixed with carbonate containing (basic) soils. Dense grid soil sampling approaches and variable rate technologies are being adopted at a rapid rate by producers. Results from samples collected from producer’s fields and field-scale research have shown very high pH variation within fields and even within soil map units. Figure 2 shows soil pH spatial variability from a very dense grid sampling for a field having several soil types in central Iowa. Taking into account the degree of the spatial variability for most agriculture soils in the U.S. and cost of sampling, soil analysis, and limestone, the 2.5-acre soil sampling approach is the one most frequently recommended for making prescription maps for variable rate liming. However, less dense
grid sampling schemes or zone sampling, for example by soil type, are also used in areas where soil property variation dominates soil pH spatial variability. Also, remote sensing sometimes can be used to establish sampling zones for pH. For example, soybean iron deficiency chlorosis in high-pH, calcareous soils can be used to verify the pH is calcareous and map calcareous areas within fields.

![Figure 2. Example of soil pH spatial variability using a zone or grid soil sampling approach for a central Iowa field with several soil types. Adapted from Bianchini and Mallarino, 2002. Agron. J. 94: 1355-1366.]

**Managing Soil pH for Alkaline Soils**

Alkaline soils have pH above 7.0, which means the exchange complex is saturated with basic cations. In soils with pH 7.2 to 8.5, pH is controlled by dissolution of free lime (calcium and magnesium carbonates). In soils with pH 8.5 to 10.5, pH is controlled by exchangeable Na and dissolution of sodium carbonate. Therefore, decreasing pH of alkaline soils is difficult due to the need to neutralize free lime (carbonates) or Na salts and reduce base saturation. In field situations, this is impractical (except perhaps for high-value horticultural crops) due to the high cost for large application of acidifying amendments and potential salt buildup from those applications. For example, a soil containing 1% lime (carbonates) in the top 7 inches would require 68 ton/acre of concentrated sulfuric acid to neutralize the carbonates before
alkalinity could be reduced. In most cropping situations, alkaline soil pH is not modified, but instead crop, nutrient sources and production practice decisions are based on knowledge of field conditions.

Soil pH reduction can be achieved in localized (small areas); for example garden or landscape areas for plants that require low pH. In such cases, a common amendment to acidify soil is elemental sulfur (S). Elemental S is oxidized by microbes to sulfate ($\text{SO}_4^{2-}$), with production of $\text{H}^+$ ions which then neutralize free lime or lower base saturation on the exchange complex. Ferrous sulfate ($\text{FeSO}_4$) and aluminum sulfate [$\text{Al}_2(\text{SO}_4)_3$] can also be used to lower pH by contributing acidic cations. The amount of an acidifying material required depends on the volume of soil to be treated, free lime content, soil cation exchange capacity, desired pH and acidifying effect of the material applied. Salt issues can develop if the amount of acidifying material applied is large, and element toxicity is possible when materials containing Al are used.

**Managing Soil pH for Acidic Soils**

Soil acidification is one of the most common agronomic problems in humid and highly productive areas of the U.S. In non-alkaline soils, application of N fertilizers and many manure sources continually causes a steady increase in soil acidity. The most common method for neutralizing soil acidity and increasing soil pH is to apply limestone. Liming materials are most often carbonate containing materials, such as $\text{CaCO}_3$, and $\text{MgCO}_3$. Limestone (and other liming materials) react with carbon dioxide and water in the soil to yield bicarbonate ($\text{HCO}_3^-$), which reacts with $\text{H}^+$ and $\text{Al}^{3+}$ to form either water (for $\text{H}^+$) or insoluble compounds (for $\text{Al}^{3+}$). These reactions take acidic cations off the exchange complex and out of solution, thereby increasing base saturation and raising soil pH.

The amount of limestone material to apply depends on the amount of reserve soil acidity to be neutralized and the quality of the liming material. The quality of liming materials is determined by two factors. One factor is the ability to neutralize acid (purity), called the calcium carbonate equivalent (CCE). As CCE increases, the material purity increases and the acid neutralizing ability increases. The second factor is the particle size analysis. Finer limestone particles react faster due to increased surface area. The combination of these two factors is the effective neutralizing value (ENV). This quality factor has different names in different states, but in all cases is providing the ability of liming materials to be effective in neutralizing acidity and raising soil pH. In some states regulations require this quality measure to be supplied with the product label.

Most agricultural limestones are ground Ca and Mg carbonates, and have a mix of particle sizes from small to large. For example, in Iowa, the particle sizes effective in neutralizing soil acidity and used for
the quality measure (effective calcium carbonate equivalent, ECCE) are 60, 8 and 4-mesh screen sizes (mesh size is the number of screen wires per inch; the larger the number, the finer the screen opening). The quality measure (ECCE as in Iowa) is then a combination of the fineness efficiency from the percent of material passing each mesh size, the CCE and moisture content. The mix of particle sizes is important so there are adequate fine materials (passing the 60 mesh) and coarser materials (passing 8- and 4-mesh) to ensure rapid pH improvement and stabilization of pH for several years.

**Rate of Limestone Application**

The amount of limestone needed to adjust soil pH depends on the desired level for a particular crop, the initial soil pH and the soil cation exchange capacity (the soil clay and organic matter content which determine the soil buffer capacity or resistance to pH change). Although, soil pH is used to determine whether or not soil acidity limits crop growth and liming is needed, it does not directly estimate lime requirement (amount of lime to apply). Several analytical methods have been developed to determine lime requirement. These methods include soil incubation, direct titration and use of buffer solutions. Long-term soil incubations with CaCO$_3$ have been used for research studies and to calibrate other lime requirement methods, but are impractical for use by routine testing laboratories. Direct titrations are laborious and may require days to complete, so they are not practical for use in routine soil testing.

Buffer pH methods were developed to provide a faster assessment of lime requirement in a routine lab setting. A buffer solution resists pH change when exposed to acidity, and provides a linear decrease in pH when the soils potential acidity (acidity on the exchange complex) reacts with the buffer. The decrease in pH of the buffer solution is what is measured after mixing the buffer with soil and provides an estimate of the amount of lime required to neutralize the acidity of the soil in order to reach a desired pH. There are several buffer pH solutions in use. In the Midwest U.S., the Shoemaker-McLean-Pratt (SMP) buffer has been the method adopted in many states. However, that buffer solution contains hazardous chemicals and needs special and expensive disposal by soil testing laboratories. Therefore, new buffers, such as the Mehlich and Sikora buffers, were developed and are currently being used because they do not contain hazardous chemicals and are more environmentally friendly.

In some states, instead of using a buffer pH method, the lime requirement is calibrated from measured soil pH and the soil cation exchange capacity (CEC can be determined by lab measurement or knowledge of the soil’s textural class and color, both reflect the soil clay and organic matter content).
The liming rate need is estimated from the measured water pH and relationship to lime rate for various soil types.

In addition to these methods, some states (especially in the southeast U.S.) have developed fast direct titrations methods that use a single addition of a strong base to determine lime requirement. These methods are based on the assumption that the relationship between the addition of a liming material and soil pH is linear between pH 4.5 and 6.5.

**Timing of Limestone Application**

Although limestone can be applied at any time, several factors should be considered when planning an application. Most importantly is the length of time required for pH correction to take place. Crops with more sensitivity to low pH, such as forage legumes, should have pH corrected well in advance of seeding. Soil moisture is critical for the reaction of limestone with soil acidity, thus rainfall patterns can also be used as a guide for application timing. Soils should be sufficiently firm to support heavy equipment and minimize compaction. If subsoil pH is low, a long period will be required for the limestone to effect a change in the soil pH with depth. Coarse limestone particles react more slowly and may take several months to correct pH. Incorporation into the soil will provide faster reaction and pH adjustment within the tillage zone. Surface application, for example in no-tillage, will have most impact on pH near the soil surface. When a more rapid pH correction is needed, the use of finely ground limestone or an agricultural ground limestone with good quality (considerable fine materials) should be considered.

**Liming Method**

Dry bulk limestone is typically applied using fertilizer spreader trucks. The density of the spreading pattern declines with increasing distance from the truck. In addition, minimizing dust and achieving a uniform spreading pattern can be increasingly difficult with finely ground limestone products. A moisture content of 7 to 10% in fine limestone helps minimize dust and achieve a uniform spreading pattern.

**Variable Rate**

Application of lime using variable rate technology has grown in popularity over the last decade, because it helps growers avoid applying liming products in field areas having lower-than-optimum pH and reduces or avoids application in areas with high pH. This methodology increases liming efficiency and therefore profitability.
Liquid, fluid, or suspension lime is a combination of very fine limestone (100 mesh or smaller) in water with 1 to 2% clay to form a suspension that is about 50 to 60% solids. Some drinking water treatment byproducts are similar as they result from rapid throughput of water treated with finely ground calcium oxides. These materials are typically spread using a tank truck equipped with a boom and high-volume nozzles. With proper calibration, this enables very uniform product application with no dust. Fluid lime does not react differently than finely ground dry limestone, but because of the fineness of grind the rate of application should be adjusted to avoid over-liming and resulting too-high pH.

**Liming Materials**

A variety of agricultural liming materials, most frequently calcitic and dolomitic limestone, are readily available in the U.S. (Table 2). Agricultural liming materials are defined as follows:

1. Agricultural liming materials mean a product whose Ca and Mg compounds are capable of neutralizing soil acidity.
2. Limestone means a material consisting essentially of Ca carbonates or Ca and Mg carbonates capable of neutralizing soil acidity.
3. Dolomitic limestone means those materials of which sixteen percent or more of the neutralizing value expressed as Ca carbonate is derived from Mg carbonate.

<table>
<thead>
<tr>
<th>Liming Material</th>
<th>CCE</th>
<th>Equivalent to one ton pure limestone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium carbonate</td>
<td>100</td>
<td>2000</td>
</tr>
<tr>
<td>Calcitic limestone</td>
<td>85-100</td>
<td>2350-2000</td>
</tr>
<tr>
<td>Dolomitic limestone</td>
<td>95-109</td>
<td>2100-1830</td>
</tr>
<tr>
<td>Burned lime</td>
<td>150-175</td>
<td>1330-1140</td>
</tr>
<tr>
<td>Hydrated lime</td>
<td>120-135</td>
<td>1670-1480</td>
</tr>
<tr>
<td>Basic Slag</td>
<td>50-70</td>
<td>4000-2900</td>
</tr>
<tr>
<td>Baked oyster shells</td>
<td>80-90</td>
<td>2500-2200</td>
</tr>
</tbody>
</table>
There are other liming materials, such as CaO or Ca(OH)$_2$, but they are not commonly used due to high reactivity and corrosiveness. Also, there are drinking water treatment by-products and other by-products that provide liming capability.

Summary

- Soil pH is considered the single most important chemical property of soil because it affects plant growth and nutrient availability in many different and complex ways.

- Limited solutions exist for reducing pH in high pH soils because they are impractical or uneconomical.

- Soil acidity reduces plant nutrient availability and increases toxicity of some elements. Therefore, neutralization of soil acidity has positive effects on crop productivity.

- Lime application is the most common way to neutralize acidity in soils and there are many lime sources that vary in type, neutralization capacity (purity) and particle size. Agricultural ground limestone is the most commonly used liming material.

- Although several methods can be used to determine liming rates to achieve optimum pH for crop growth, buffer solutions, single titrations with a base and indexes that include soil characteristics such as soil pH and organic matter, clay, or CEC, are the most widely used approaches.

- The large within-field spatial variability in soil pH and lime requirement commonly found in many U.S. regions greatly justifies dense soil sampling and variable rate technology for limestone application.