Basic Concepts of Soil Acidity and Liming

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Most midwestern soils require periodic applications of aglime or other liming materials for optimum crop production. Liming has several beneficial effects: I) it reduces harmhl or potentially tosic conditions which can develop in acid soils; 2) it increases the availability of some of nutrients: **3)** it replaces the supply of calcium and magnesium essential for plant growth which is depleted as soils become acid; 4) it ensures favorable conditions for the activity of certain herbicides; and 5) it provides a suitable environment for microbial activity.

What is Soil Acidity.

By definition, an acid is a proton or a hydrogen donor, while a base is a proton acceptor. In soils, that means that when a large portion of the cation exchange capacity (CEC) is satisfied by acids such as hydrogen $(H³)$ or aluminum $(Al³)$, the soil is acidic and is donating acidity. hydrogen. to the water which sur-rounds the soil particles. When the CEC is satisfied primarily by basic cations such as calcium, magnesium and potassium, the soil is basic, and it will accept hydrogen From the soil water and donate a basic cation in its place.

'The ion concentration in the soil water is a reflection of the cations which are held on the soils CEC. In soils that have a large proportion of the CEC satisfied by basic cations, a high base saturation, the concentration of basic cations (calcium, magnesium and potassium) in the water will be high, while the concentrations of acids in the soil water will be low. In soils where the CEC is primarily saturated by acidity (hydrogen and/or aluminum). low base saturation, the concentration of acidity in the soil water will be high and the concentration of bases in the water will be low. Thus the relative concentration of acids and bases on the exchange sites of the soil is what determines the relative acidity found in the soil water.

How Acidity Is Expressed.

The concentration of acidity in a solution is commonly expressed using pH, the negative log of the hydrogen ion concentration (activity) in solution. The pH scale runs from 1 (very acid) to 14 (very basic). The midpoint, pH 7 is neutral, with the concentration of acids in solution being equal to the concentration of bases.

The relative acidity of a soil is commonly measured by estimating the pH, or hydrogen ion activity/concentration in the soil water. This is nornially done by collecting a soil sample. mixing the soil with a standard volume of water and measuring the pH of the soi1:water mixture with a pH meter. The **pH** value obtained reflects both the chemical environment

in the soil water where plant roots reside, and also the relative misture of acids and bases on the soil cation exchange capacity, since the ions in the soil water are in equilibrium with the ions on the exchange sites. Tlius altering the soil pH requires changing the balance of acids and bases in both the soil water and on the cation exchange capacity. Figure **1** gives a graphical representation of the relationship between percent base saturation and soil pH commonly found in the midwest.

Figure 1. The relationship between percent base saturation and soil pH

Sources of Acidity

Some soils are acidic because of the composition of the parent material from which they were formed. Other soils become acid by a number of processes. Cropping and use of nitrogen fertilizers are two main sources of soil acidity while another contributor is rainfall. The net result is that hydrogen, and aluminum (acidic cations) replace calcium. magnesium, and potassium, (basic cations) on the soil cation exchange complex.

Crop Removal. Calcium, magnesium, and potassium are essential nutrients for plant growth. Their uptake by plants, and subsequent removal through harvest, can have an acidifying effect on soils. The amount of these nutrients removed by cropping depends on: a) crop growth, b) part of crop harvested, and c) stage of growth at harvest. Removal is greater for hay crops than for grain crops, as shown in Table 1.

Fertilizers. Nitrogen fertilizers have a greater acidifying effect on soils than any other source. Most commonly used nitrogen fertilizers contain ammonium nitrogen (urea is an ammonium forming material). Soil bacteria convert ammonium (NH_4^{\dagger}) to nitrate (NO_3^{\dagger})

through a biochemical process called nitrification. Hydrogen (H') is released in this process. and the freed hydrogen ions cause an increase in acidity.

 $2 NH_4$ + 40₂ -----> $2 NO_3$ + 2 H₂O + 4H

Nitrification

Table 2 shows the calculated amount of aglime needed to offset the acidity potential of several common nitrogen fertilizers. It is evident that applying more nitrogen fertilizer than a crop can take up is not only wastehl and expensive from the nitrogen standpoint but also increases the cost of a liming program and can be a pollution hazard.

The second potential acidifying effect from nitrogen comes from nitrate that is not taken up by the growing crop. Nitrates are very soluble and if not taken up by plants. will move downward with soil water and be carried below the root zone. The negatively charged

nitrate ions take other positively charged ions, most likely calcium and magnesium since they are normally present in the largest quantities. with them and their removal in this manner has the same acidifying effect on soils as removal by a crop.

Rainfall. Soils will naturally become acid even in the absence of crop removal or fertilizer applications, because rainfall is a natural source of acidity. Natural rain, without any pollution from man, has a pH of about 5.6. The actual amount of acidity supplied through rainfall each year is very, very small. But over long periods of times, centuries in geologic time, this will cause soils in a humid climate, where rainfall exceeds the amount of water use by plants. to become acid. Most of the soils in humid parts of the United States are naturally slightly acid.

Acid rain receives considerable publicity but is not a significant factor in a farmers liming program. The present day acid rain of Indiana has a pH of about 4.3 to 4.5. about ten times more acid than natural rainfall. This additional acid is produced by the sulfur and nitrogen oxides in the air reacting with water, and it amounts to about half a pound of acid per acre in a years rain.

There may be as much as another half pound of acidity added by dry deposition (airborne particles or dust containing acid forming N and S compounds) deposited on Indiana soils each year. Thus up to 1 pound of total acidity per acre per year may be received each year. Neutralizing this would require about 50 pounds of limestone per acre per year. Thus a ton of lime every 40 to 50 years would neutralize the effect of both acid rain and dry deposition.

Note that this same N and S in rain and dry deposition producing a pound of acidity each year also provides about 10 pounds of N and 20 pounds of sulfur annually. This is the primary reason that many Midwestern farmers do not have to routinely fertilizer with sulfur.

Other Sources of Acidity. In addition to the acidifying effects of rainfall, organic acids, similar to vinegar, are produced in the soil when plant residues and organic matter decompose. These weak acids react and combine with nutrients such as calcium, magnesium, and potassium and move down through and below the root zone with rainfall. Hydrogen is released fiom these organic acids and replaces basic cations causing the soil in the leached zone to become even more acid. Examples of this process are found in South central Indiana soils where limestone rock is found just a few feet below an acid surface soil. The long-term leaching of these acids has dissolved sufficient limestone and caused a collapse of the surface soil creating sinkholes.

Surface runoff can also carry calcium, magnesium and other nutrients in solution, and these nutrients can be physically removed in the erosion process. Both actions leave the remaining soil more acid.

Beneficial Effects from Liming

Soil acidity has a direct effect on availability of most essential plant nutrients. Figure 2 shows the general effect of pH on plant nutrient availability. The pH range for highest availability of most nutrients is between *6.0* and 7.0. Deficiencies can be observed at both low and high pH's. Manganese and iron can also become toxic at low pH. Although aluminum is not an essential nutrient, its availability also increases rapidly as the soil pH drops below 5.0. Too much aluminum in solution will restrict root growth and plant development.

Soil pH

Figure 2. General relationship between soil pH and the availability of nutrients in the soil (adapted from Troug in USDA Yearbook of Agriculture)

Soil microorganisms do not function effectively in acid soils. As soil pH levels decline so does the activity of the organisms which decompose organic materials, releasing nutrients to plants. Although these organisms function best at soil pH levels of 8.0, their effectiveness does not drop rapidly until pH levels drop below 6.0. Decomposition of organic matter also contributes to aggregation of soil particles which provides for good soil tilth. aeration, and drainage.

l'he survival and effectiveness of the bacteria which enter legume roots and fix nitrogen (nodulation) is also highest at pH levels of 6.5 to 7.0 and declines rapidly when pH levels fall under 6.0.

The performance of some herbicides, particularly triazines, is effected strongly by soil pH. As pH levels drop below 6.0, the effectiveness of atrazine for example, is greatly reduced. On the other hand, the activity of some compounds may be greatly enhanced at high pH. Metribuzin, a common soybean herbicide is not labled for use on calcareous soils because it is too active and causes crop injury. Carryover or persistance of some materials is also effected by soil pH. Chlorimuron, Classic, is not used at high pH because the compound is persistant and carryover damaging to rotation crops is possible. Again, maintaining a soil **pH** in the range of 6.0 to 7.0 optimizes the performance of most commonly used herbicides and minimizes potential problems.

Soil Sampling for Limestone Needs

Consider soil buffer capacity. The amount of lime needed to obtain a change in soil pH, (buffering capacity) varies with the soils cation exchange capacity. Cation exchange capacity refers to the amount of the soils negative charge and the amount of positively charged ions such as calcium and magnesium or hydrogen which can be held. Cation exchange capacity is a function of soil organic matter and clay content. The higher the organic matter content and the heavier the soil texture, the higher the soils CEC. Since soil pH is a reflection of the percent acids on the exchange sites, acidic soils with a high CEC contain more acidity than a low CEC soil of the same pH. Thus more lime will be required to get the same change in pH of a high CEC soil than a low CEC soil.

Many fields vary in organic matter content and texture. it is important that soil samples be taken to select and identify variations that exist in a field rather than mix everything together into one sample and then obtain an average. This process may require carefully selecting sample locations within a field to minimize the variation and more efficiently use lime. A detailed soil survey is available in most counties and provides a helpful guide to soil difference that can be expected in a field. Out in the field, soil samples should be separated primarily on the basis of soil color differences which reflect variations in organic matter. Separate soil samples should be taken also where the texture of soil surface varies widely.

Use the appropriate sampling depth. Soil samples for routine pH, P and K recommendations for grain crops are normally taken using an eight inch sampling depth. However. sample depth needs to be adjusted when working with conservation tillage systems or in forage fields. If a moldboard plow or chisel plow is used once every four or five years, take samples for fertilizer and lime recommendations at an eight inch depth. While most of the soil mixing occurs in the upper one half to two thirds of the chisel depth (depending on the type of chisel points used), and nutrient stratification is known to occur, enough mixing occurs to get lime and lime effects throughout most of the surface soil.

Where fields are in continuous no-till for four years or more, especially where nitrogen fertilizer is broadcast or sprayed on the soil surface, or in pastures and haytields. soil samples for pH and lime requirement should be taken from the top four inches of soil. This will identify the acidity stratified near the surface, which is also the acidity which a surface application of lime will neutralize. An adjustment of lime recommendations will be necessary in these situations also. Most soil testing laboratories make lime recommendations assuming that the lime will be mixed with eight inches of soil. Since lime is relatively insoluble. when applied on the surface the effects are limited to the top **3** to *5* inches of soil. Thus lime rates should be cut in half when surface applying lime to notill fields. pastures or hay fields.

\\'hen to saniple. Surface soil pH fluctuates during the growing season according to soil moisture levels. This is due to variations in salt content in the soil surface. As water evaporates from the soil surface, soil pH drops due to soluble salt accumulations. These salts are primarily calcium, magnesium and potassium salts of nitrate. sulfate and chloride. **As** the soil rewets and the salts move down through leaching, the soil pH goes back up. The lower the cation exchange capacity of the soil. the bigger this change in pH is likely to be. It is not unusual for the pli of a sandy. low CEC soil to drop as much as 0.5 pH units during the summer in Indiana, while dark colored silt loams may show little or no measurable change. It is recommended that soil samples be collected in the fall or spring. when soils are moist. to minimize variation from year to year. **An** alternative approach to get around seasonal variations in pH due to salts is to add a known amount of salt to the sample when measuring pH in the lab. Commonly refered to as salt pH, the technique is used in several states including Missouri and Indiana.

Measuring Acidity and Lime Requirement

Soil testing labs routinely use a two step process to measure soil acidity and determine lime requirement. The first step is to mix a sample of dry soil with deionized water and measure soil or water pH. If the soil: water pH falls more than 0.2 pH units below the recommended pli level for the crop being grown, lime is normally recommended. The recommended pH varies with both crop being grown and soil. The recommended pH for different crops grown in Indiana, Michigan and Ohio are summarized in Table 3.

Table 3. Recommended soii pH for the principle crops grown in Indiana.

Soil pti vs. Lime Index. The pH measured in water reflects the environment that plant roots are exposed to and is routinely used to determine if lime is needed. Water pH is not a good measure of the amount of lime needed to change soil pH. The water pH is a reflection of the percent base saturation of the soil. But it does not give any indication of the quantity of acids or bases that are present or the buffer capacity of the soil. To determine the amount of lime that will be required to neutralize the acidity on the exchange sites a buffer test is used. Buffers are solutions which are designed to resist change in pH. By mixing a buffer of known pH with an acid soil and measuring the drop in pH that results, one can calculate the amount of lime needed to reach the desired pH.

In most of the midwest, the SMP buffer is used to estimate the lime requirement of mineral soils. The **SMP** buffer is adjusted to an initial pH of 7.5, and upon mixing the buffer with an acid soil the pH drops. The more the pH drops, the more lime will be required. Most soil test reports will give the measured pH of the soi1:buffer mixture as either the **ShfP** Buffer pH or the Lime Index. Lime index is created from buffer pH by removing the decimal point i.e. a buffer pH of 6.4 is a lime index of 64 .

The lime reconimendations for mineral soils based on the SMP buffer test used in Indiana, Michigan and Ohio are summarized in Table 4. The rates given are based on limestone with a relative neutralizing value of 65, and assume that primary tillage such as moldboard or chisel plowing will be used to incorporate the lime to an 8-inch depth. If the limestone source being used deviates form RNV 65, then adjustments in rate must be made. For notill or established forages, the rates should be reduced 50%.

Buffer pH	Lime	-Desired pH level--				
	Index	Mineral soils			Organic soils	
		6.8	6.5	6.0	Soil pH	5.3
6.8	68	1.4	1.2	1.0	5.2	$\boldsymbol{0}$
6.7	67	2.4	2.1	1.7	5.1	$\boldsymbol{0}$
6.6	66	3.4	3.0	2.4	5.0	1.3
6.5	65	4.5	3.8	3.1	4.9	2.0
6.4	64	5.5	4.7	3.9	4.8	2.6
6.3	63	6.5	5.6	4.6	4.7	3.2
6.2	62	7.5	6.5	5.3	4.6	3.9
6.1	61	8.6	7.3	6.0	4.5	4.5
6.0	60	9.6	8.2	6.7	4.4	5.1

Table 4. Tons of Aglime needed to raise the soil pH to the desired level based on the **SNIP buffer test.**

If the lime recommendation is for 2 tons per acre or less, the lime can be applied at any time in a cropping sequence. When the lime recommendation exceeds 4 tons per acre. apply half the lime before primary tillage and the balance after to improve mixing with the total tillage zone. If lime recon~mendations exceed **5** tons per acre, apply **3** to 4 tons per acre and then re-test in 12 to 18 months to determine the remaining amount needed.

Low CEC Soils. Sandy soils have a low CEC and are very weakly buffered. In some cases the water pH may be below the recommended but the buffer pH may not indicate a need for lime. This occurs because these soils do not have enough acidity to lower the pH of the buffer solution. When this occurs apply 1 ton of lime per acre if the water pH is more than 0.3 pH units below desired or 2 tons of lime per acre if the pH is more than *0.6* pH units below desired.

Organic Soils. The SMP buffer test is not normally used to determine the lime requirement of organic soils. This is because soil organic matter is a weak acid and tends to react with the buffer and skew the test. For this reason water pH is used to make lime recommendations directly on organic soils. The lime recommendations for organic soils can also be found in Table 4.

Quality of Liming Materials.

How effective a liming material will be in correcting soil acidity is dependent on two factors - purity and fineness.

Purity. Liming materials vary in their composition and thus their capacity to neutralize acidity. Calcium carbonate equivalence (CCE) is the standard for measuring purity. Pure calcium carbonate has a CCE of loo%, while calcium magnesium carbonate has a CCE of 108%. Most aglime contains both calcium and magnesium carbonates along with varying levels of other impurities. The CCE of most midwestern limestone generally ranges between 85 and 107. **A** suggested minimum is a CCE of SO.

Fineness. This refers to particle size and is important because it governs how quickly acidity will be corrected. Most liming materials contain a mixture of particle sizes, from dust to fine-gravel like. Small particles dissolve rapidly and react quickly due to their high surface are. Coarse particles react very slowly and are of little value in correcting an acidity problem.

Fineness of aglime is determined by passing the material over a set of sieves (screens) of different sizes. Sieve size is expressed in terms of the number of openings per linear inch, an 8 mesh sieve has 8 openings per inch (64 per square inch). Table 5 shows the relative effectiveness of different size particles . In Indiana. 8 and 60 mesh sieves are used to determine fineness. In the absence of a lime law it is suggested that a minimum of 80% pass an 8 mesh sieve and *25%* pass a 60 mesh sieve.

Table 5. Relative effectiveness of different size limestone particles.

Estimating lime quality. The ultimate effectiveness of aglime is determined by a the interaction of purity and fineness. Since both fineness and purity vary from one producer to another. there have been several systems devised to compare limes for the purpose of economics and adjustment of recommended rates for quality. The Relative Neutralizing Value (RNV) is a system developed at the University of Kentucky that utilizes an 8 and 60 mesh sieve value and the purity (CCE) factor to calculate a single comparative number. Based on the assumption that particles larger than 8 mesh have little value in changing the soil pH, while particles finer than 60 mesh are very effective in the first year after application (see information in Table 5), the following formula is used to calculate the RNV:

(% passing 8 mesh 4- % passing 60 mesh CCE RNV = **A'** pp 2 1 00

This formula gives pure calcitic limestone ($CCE = 100$) ground so that all particles pass a 60 mesh sieve an RNV of I00 as indicated in the example below:

$$
RNV = \frac{(100 + 100)}{2} \times \frac{100}{100} = 100
$$

Many states have laws which specify minimum standards for lime quality. At least two states in the region, Indiana and Illinois. do not have lime laws however, so no standards exist for lime quality. Traditionally the minimum standards for payment through government farm programs were 80% passing an 8 mesh, 25% passing a 60 mesh and a CCE of 80%, giving an RNV of 41. Lime quality has improved dramatically in the past decade, and the current lime recommendations, given in Table 4, are based on an RNV of *65,* a value commonly found with good quality aglimes being sold today. **An** example of an aglime with an RNV of 65 would be:

$$
RNV = \frac{(90+50)}{2} \qquad x \qquad \frac{93}{100} = 65
$$

Adjusting rates when using lime products whose RNV differs from 65 can be done using the following formula:

Adjusted rate:

6 **5** Recommended rate $x =$ $+$ \cos of Aglime be applied RNV of Aglime

An example is a recommended rate of 2.5 Ton/A and applying an aglime with an RNV of 41, the traditional standard;

> 65 Recommended rate 2.5 $x - 4$ tons actual rate of lower RNV lime 41

Liming Sources

Several liming materials are marketed, and it is important to recognize differences among them.

Ground Aglime (dry). Limestone rock is crushed and ground into a material known by several names including: Aglime, Agridime, Ag stone, Ground Agricultural Limestone and Lime. Ground aglime is the most widely used liming material in the midwest, as it is easy to transport and apply. The calcium in limestone is in the carbonate form and most Indiana limestones also contain some magnesium carbonate. Calcium content ranges From 15 to 40% and magnesium content ranges from 0 to 15%. Limestone with less than 5% magnesium is designated as "calcitic limestone". Limestone with more than 5% magnesium is referred to as "dolomitic limestone.

Fluid Lime (liquid lime). In recent years a product called fluid or liquid lime has been marketed in some areas. The product is prepared by mixing very finely ground aglime (1 00% passing a 100 mesh sieve and 80-90% passing a 200 mesh sieve) with either water or liquid nitrogen fertilizer along with a suspending agent (attapulgite clay). The material is then applied with a liquid fertilizer applicator. Aglime content of liquid lime normally varies form 50 to 70%. with the lower value most common.

The main advantage for liquid lime is that a more uniform application can be made in the suspension form. Claims are also made that liquid lime will raise the soil pH faster than standard dry aglime and that much less material is needed because it is very finely ground. Both statements are only partially true. For the first few months after application, the soil pH will rise faster where liquid linie is applied. But, within one year soil pH changes will normally be equal for liquid and dry sources applied at equivalent rates.

The relative speed at which a particle reacts is a function of surface area. The smaller the individual particles, the faster the panicle will react and change pH. Particles that are smaller than 60 mesh are considered to be 100% available and will be effective in changing soil pH within a year of application. Grinding particles finer than 60 mesh may speed the rate of reaction, but it will not alter the overall effectiveness of the lime. Research comparing liquid or finely ground lime products to good quality aglime indicates that fine lime rates should not be reduced more than one-third to one-half of those of standard lime products.

Higher cost is the main disadvantage of liquid lime. This is primarily due to the additional cost of grinding the material fine enough to keep it in suspension. the cost of the suspending agent and transportation costs for the water used in the suspension. A common application rate is 1000 pounds per acre-500 pounds water and 500 pounds aglime. This rate would be adequate for a maintenance program to offset acidity caused by N fertilization. but it could not be used as a corrective remedy where lime recommendations are 2 ton or greater. .

Pelletized Lime (pel lime). To avoid the dust problems associated with spreading very fine particles, finely ground aglime can be compressed into pellets or granulated using a binding agent. The resulting product can then be spread similar to dry fertilizers. Individual pellets are readily dispersible in water and like liquid lime, will react very quickly in soil. Application rates can also be reduced one-third to one-half because of the fineness of the particles used to make the granule. Claims that a few hundred pounds can substitute for a ton of aglime have not been substantiated by land grant university research. Likewise, the practice of banding 200 to 400 pounds per acre of pelletized lime in the row as a starter fertilizer may be a means of supplying calcium or magnesium to the crop, but would have no effect on other key processes controlled by soil pH, and has only a limited potential for creating a yield increase capable of paying for the product.

Marl. This liming material is soft, unconsolidated lime material made up of marine shell fragments and calcium carbonate and found under many shallow organic soils. Marl also commonly contains clay and organic matter as impurities and is mined wet and sold by the cubic yard because of the high moisture content. **As** a general rule, two cubic yards of marl has a neutralizing value equivalent to one ton of aglime. Uniforni spreading is difficult unless the material is dried and ground, which increases the cost of the product. Use is generally confined to areas very near marl deposits. Since marl contains no magnesium, repeated applications of marl may result in soils deficient in magnesium. Deficiencies can be prevented by occasional reliming using dolomitic limestone.

Burned lime (Quicklime). Limestone rock is heated at high temperatures to drive off carbon dioxide to produce calcium oxide, CaO. It is a fast acting liming material. but is also corrosive, disagreeable to handle and more expensive than aglime. It is usually used for special non-ag purposes.

Slacked Lime(Hydrated Lime). It is produced by adding water to burned lime to produce calcium hydroxide, $Ca(OH)$. It has many of the same characteristics and limitations as burned lime.

Industrial Byproducts as Lime Sources.

A number of industrial byproducts or coproducts have been used successfully as liming materials. Key factors to evaluate when considering the use of these products include cost, transportation, easy of spreading and neutralizing value. In many states the state EPA or Department of Environmental Management regulates the land application of these products. Always check that the rnaterial is properly registered or permitted before using these products.

Lime Sludge. Some water soffening plants produce a soft lime sludge containing fine lime particles precipitated in the softening process. Lime sludges vary in their calcium carbonate equivalent **(CCE)** and water content which will influence the amount of sludge needed to equal dry aglime. Since the particles are very tine. it reacts quickly in soils similar to liquid lime.

Fluid-bed Ash, Fly Ash and Stack dust. Modern electrical generating plants mix limestone into ground coal as a means of controlling burn rates and enhancing efficiency of operation. Much of the ash produced in these fluidized or plasma bed generators contains large quantities of calcium oxide and has neutralizing value. Ashes and dust collccted from smoke stacks and cement kilns also can have lime value, though the neutralizing value can vary widely. Many of these products can also contain heavy metals and other environmental hazards. Thus, these products are closely regulated and application rates can be limited by metal content.

Agricultural Slags. One of the steel industry by-products is a magnesium silicate or slag. Air cooled slag must be ground the same as limestone when used as a liming material. Water cooled slag is a porous granular material produced by applying water to the hot slag. Usually it is screened and the fines are used as a liming material.

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