

### The pH Dilemma

Liming soils is among the oldest agricultural practices known. When scientists first began to perform chemical tests and study fertility of soils, the practice had been going on for over a thousand years. About 200 years ago, simple field tests showed infertile fields to be acid. Limestone raised pH and improved crops, and therefore the culprit was designated soil acidity by most soil scientists ever since.

The measurement of pH is an indicator of the 'power of hydrogen'. It is the inverse logarithm of the chemical activity of the  $H^+$  ion. The pH of solutions is valuable in chemical and biological reactions for everything from medicine to wine making. A pH of 6 has  $10^{-6}$  moles hydrogen ions; pH 8 designates there

are  $10^{-8}$  moles of  $H^+$  - a smaller number. Thus lower pH means more hydrogen.

The pH scale is based on the following reaction, which occurs in all water:



When the  $H^+$  ions are equal to the  $OH^-$  ions, the solution is called "neutral" and given the pH of 7. This is an oversimplification, and the reaction rarely occurs in isolation in nature. Soil pH is much more complex and variable because it results from the interaction of water, minerals, ions in solution, organic matter, plants, microbes, and cation exchange reactions.

Originally, simple measurements of the  $H^+$  ions in the soil solution were considered sufficient to understand soils. By 1926 researchers were finding many shortcomings of this method, suggesting that quantity and quality of cations were more important in determining soil fertility (Cooper, Wilson & Barron, 1929). However, mainstream agronomists continued to use the pH theory to recommend limestone. Farmers continued to use limestone to help raise crops, and most scientists continued to believe that acidity was the primary cause of infertility. Meanwhile, Albrecht (1932) conducted research that showed that pH alone does not always determine optimum plant growth - the balance of nutrients is the most important factor. Using his work with clays and other colloids, he was able to construct H-Ca clays, use them in bioassays, and prove that pH alone does not regulate soil fertility. The presence and ratios of major nutrients were found to be more important. Working with soybeans, which prefer "near neutral pH," he made sand-clay mixtures at a constant pH of 4.4 - an  $H^+$  concentration much too high for most crops, especially legumes. By increasing calcium-clay levels he showed that best growth and disease resistance occurred at the highest calcium (Ca) concentration - even though at pH 4.4 .

Albrecht then set up tests with soybeans in sand and Ca-H clay in pH increments of 0.5 from pH 4.0 to 6.5. As he increased the calcium content in the series of tests, the best growth occurred at lower pH levels. Each time Ca level was doubled, best growth dropped from pH 6.0 to 5.5 to 5.0. Again, the pH alone was not the determining factor of best growth. He concluded (p. 805):

The data point out clearly that the significance of calcium for the soybean plant rests on its function as an element in the plant's activities rather than on that of reducing the hydrogen-ion concentration.

Other researchers continued to show crop response to liming, although they only used calcium carbonate. This confounded their research. Limestone usually raises pH, but adds calcium at the same time. Albrecht demonstrated that Ca caused the improvement, with no change in pH. He remains one of the only researchers who made the distinction. Between 1940-1950, Albrecht published at least ten articles on the subject of soil acidity. The issue came to a head before the U.S. Senate Subcommittee on Agriculture, April 29, 1954. Changes in the federal cost-sharing program for liming and fertilizers were being debated, and a strong push was on that simple soil testing procedures, among them pH, be required. Albrecht (1975, p. 135 -136) testified:

Only recently have we recognized the fallacious reasoning behind the conclusion contending that it must be the presence of acidity in the soil that brings crop failure when liming lessens both the degree and the total of the soil acidity while making better crops at the same time. While the convenience of soil testing gadgets for refined points of pH was encouraging this erroneous belief about soil acidity as an enemy, it was the diligent study of the physiology of plants, of the colloidal behavior of the clays growing them, and of the chemical analyses of them that finally pointed out the errors of such hasty conclusions. It indicated that the presence of soil acidity is not detrimental, but that the absence of fertility, represented by the acidity, is the real trouble. On the contrary, some acidity can be, and is beneficial.

... Should you decide to demonstrate for yourself the truth for what has been said above, you might apply some soda-lime, or sodium carbonate, to acid soil. This will increase the pH of the soil. It will reduce its total

acidity. But while this soil treatment will rout the enemy, i.e. soil acidity, and raise the pH toward 7.0, it will still not give successful crops.

Mainstream agriculture continued to fight acidity, and as long as calcium amendments were used, the theory worked. During the 1940's quicklime, CaO, a by product of the cement industry, was promoted as a liming material. Because this material proved to be caustic and highly alkaline, water was added to create hydrated lime - less caustic and alkaline. This became known as 'agricultural lime', and the confusion between lime and limestone began. Most of the problems from over - liming came from application of either of the two highly alkaline materials, CaO or Ca(OH)<sub>2</sub>. Research continued, often using hydrated lime for pH maintenance, such as in a critical field study comparing BCSR and SLAN concepts (McLean, Hartwig, Eckert, & Triplett 1983). They continued the confusion of calcium and pH, using the two terms interchangeably, resulting in such statements as:

The primary objective was to determine whether an ideal BCSR (or range in ratios) exists in a soil...Additional objectives were 1) to examine the SLAN concept by determining the effects of three levels of Ca (pH), three levels of Mg, and two levels of K, in all combinations, on yields and compositions of important field crops...

Because of this confusion, well-meaning researchers never reached the BCSR levels promoted by Albrecht, Bear and the others, and they concluded that the BCSR theory was valueless.

In the early 1960's attention turned to refining pH testing methods, mostly from the recognition of two new facts of soil science: toxic aluminum concentration must be considered in acid soils, and soils have the capacity to buffer against changes in pH. This means that short term measurements do not correctly predict the dynamics of soil acidity. Various salt solutions that remove more hydrogen from the clay were developed, in attempts to further improve

accuracy. In 1970's, the addition of lime sufficient to remove  $Al^{+3}$  was proposed for achieving best crop yields, while others stressed using buffers to assess soil acidity. Volumes have been written on the subject of acidity and soil fertility, and the subject can become very complicated. In Soil Acidity and Liming (Pearson & Adams, 1967, p 36) the problem was summed up well. "In many ways, the uncertainties attendant to measuring lime requirement reflect the lack of information on the nature of the acid-soil system."

There are now several ways to measure pH and acidity, each with its own strengths and weaknesses. Distilled water is mixed with soil to make a saturated paste. The pH of this mixture shows the active hydrogen and aluminum in the soil solution. Various salts, such as CaOH, KCl or CaCl, are added for buffer pH tests, measuring potential hydrogen or aluminum, which is released by the clay after the soil solution has been neutralized. The buffer pH more accurately addresses the problem of acidity, and results in more limestone being recommended for a given acid soil. All of these tests are based on a fundamental assumption - "the idea that a 'good soil' has a pH value between 6.0 and 7.0 is still the opinion of many soil scientists, agronomists, and crop producers" (Brown, 1987, p. 66). However, according to Pearson & Adams, "...it is clear that appreciable and sometimes very large amounts of 'soil acidity' ...can exist in soils above pH 7" (1967, p 24). The pH theory often leads to the erroneous belief that many of our crop soils do not need calcium.

Defining "acid soil" can be difficult. Coleman and Thomas give two definitions for an acid soil (in Pearson & Adams, 1967): one states that the pH is <7, the other that the CEC is not totally saturated with basic (Ca, Mg, Na, K) cations. They state (p. 9) that "defining soil acidity in terms of base saturation would be simpler and more specific were there a uniform convention for

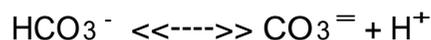
defining the CEC. Unfortunately, there is not." The BCSR system, along with knowledge of how natural waters and soils work, provides the answer.

The actual factors that determine pH in soils and bodies of water lie in the biochemistry of carbon dioxide. "In natural water systems, the carbonic acid buffering system is the dominant inorganic component of the water" (EPA, 1993). Ruttner, in Fundamentals of Limnology (1970) discussed the CO<sub>2</sub> cycle in water & soil. It begins with rain falling, picking up small amounts of CO<sub>2</sub> from the air. As it percolates through the soil, it picks up more from soil air and from humus - both rich in CO<sub>2</sub> from respiration of roots and microbes. Dissolved CO<sub>2</sub> forms carbonic acid H<sub>2</sub>CO<sub>3</sub>. The effect on soils is best summarized in Hunger Signs in Crops (Sprague, 1964):

The carbon dioxide in the soil solution makes it a potent solvent for calcium compounds; thus calcium is leached out of the soil as calcium bicarbonate and soil acidity is increased. Large amounts of calcium and sodium have been carried into the oceans. Sea water is salty from the accumulation of sodium salts; it would be milky from the accumulation of calcium salts, if most of the calcium had not been removed from the water and built into the shells of marine animals to be deposited on the ocean bottom.

Thus carbonic acid is the predominant acid in natural systems, and the pH of all natural water systems is determined almost entirely by the absorbed carbon dioxide and any salts it picks up en route to our use. The predominant anions in most natural waters are bicarbonates, associated mainly with calcium, to a lesser degree magnesium, and still lesser potassium and sodium. "The presence or absence of bicarbonates determines whether a water is alkaline or acid in its reaction" (Ruttner, 1970). Calcium bicarbonate serves as a major nutrient for life such as microbes and plants. Other cations are dissolved by the inherent acidity in most soil and water. These are used by organisms as needed and available. As the water sits in rivers, lakes, ponds or soil CO<sub>2</sub> can be lost in many ways - volatilization, use by organisms, or precipitation of CaCO<sub>3</sub>. The pH

of such waters rises "as to be expected when there are major withdrawals of CO<sub>2</sub>" (Rutner, p. 71). The pH of water and soil solutions is determined by the following balance:



The point at which bicarbonates change to carbonates, and thus from a net acidic (limestone consuming) reaction to a net basic (limestone precipitating) reaction, is pH 8.3. This is the true "neutral point" in soils. This important principle of natural systems explains such statements that "it is clear that appreciable and sometimes very large amounts of 'soil acidity', in terms of buffer capacity or pH-dependent charge, can exist in soils above pH 7" (Pearson & Adams, 1967, p. 25). The neutral point between acid and basic reactions in natural systems - lakes, rivers, and soils- does not occur at pH 7.0.

Soils in which free carbonates (CO<sub>3</sub>) exist are treated using various acidification strategies. Phosphoric, sulfuric, or nitric acids are commonly used, along with acid forming fertilizers. Several companies sell and service CO<sub>2</sub> injecting technology for irrigation of high carbonate soils. These have been used successfully on thousands of acres, and have been shown to increase organic matter (from the carbon in CO<sub>2</sub>), yields, and productivity in high carbonate soils (unpublished data, New Era Farm Service). Novero, Smith, Moore, Shanahan and d'Andria (1991) studied carbonated water additions to tomato fields and found increased yields and uptake of P, K, Ca, Mg, Zn, Fe, Mn, Cu and B. Cover cropping and compost additions with occasional sulfur amendments are now used with limestone in alkaline soil reclamation (R. Jurgens, personal communication, June 28, 1997). Acidity is natural and necessary for dissolving and taking up nutrients - and carbonic acid is the predominant acid in natural systems. A detailed account of the subject of

alkaline soils is beyond the scope of this project. However, the key to high pH soil management is recognition that pH is the symptom, not the cause of the problems. The effects of excess carbonates are the real culprits.

The Northern California area has acid soils, where calcium is a limiting factor and soils are rich in bicarbonates. I have summarized the effects of climate on soil formation, as originally proposed by Albrecht (1975) (see Appendix B). He outlined several important principles of soil science that are valuable in explaining many aspects of agricultural production. He divided soils into major groups, based on the climate and its effect on the soils, and the characteristics of each. Arid soils contain low organic matter, an abundance of minerals, excess harmful salts, and high carbonates of calcium, magnesium, potassium & sodium. They support low animal production. He termed these soils "UNDER CONSTRUCTION" - just add water for soil development and productivity to begin. He called areas of high rainfall "UNDER DESTRUCTION". These areas are usually forested. They are characterized by high organic matter content above the ground in biomass such as trees, with organic matter accumulation above the soil due to poor breakdown. Excess leaching causes deficiencies of calcium & magnesium, leaving acidity (large volumes of  $H^+$  and  $Al^{+3}$  in the soil), no sodium problems, and net bicarbonate production from organic matter breakdown. These soils support moderate populations of animals well, however plants that are high in carbohydrates predominate. The main crops are timber, grapes, pears, apples and other fruits - all woody or high in carbohydrates. Limestone and other major nutrients can be serious limiting factors. "WELL DEVELOPED" soils were found to receive low to moderate rainfall, have high organic matter accumulation in topsoil (roots of grasslands), good quantities & balance of major nutrients, just enough acidity to release minerals, and very

high animal production due to the high protein content of the native grasses & legumes. These soils support the highest production of corn, wheat, & legumes.

Virtually all soil textbooks and most practices in the field use pH theory as a base for limestone and fertilizer recommendations. Unfortunately, this theory is based on the solution chemistry of distilled water, and natural situations are not that simple. The reactions in soils are complex interactions of colloids, solutions, and biochemical processes. The pH theory really only works well if calcium amendments are used. The theory breaks down under several agricultural situations. Soils with pH levels from 6.5-7.5, which are low or deficient in calcium, are commonly found in the northern California. Agronomists using pH theory would recommend no limestone in these cases. High pH, non-sodic soils are often commonly called 'limestone soils' with no supporting soil or rock data. Excess magnesium and carbonates in irrigation water can drive pH up in such cases, yet the soils respond positively to high levels of calcium amendments. The BCSR is the only method that addresses specific nutritional, biological and structural conditions optimum for soil productivity.

The measurement of soil pH can be misleading. Approximations of continued release of hydrogen (buffering capacity) are needed just to get a better estimate of  $H^+$  concentration. Gascho, Parker and Gaines reported seasonal changes in pH in soils (but did not explain why), and I have observed this same trend. In this area, winter leaching acidifies soils with rain water rich in  $CO_2$ . In the summer, higher temperatures cause lakes, reservoirs, rivers, and streams to lose  $CO_2$  to the air. This leaves higher concentrations of carbonate salts and higher pH levels. In wells, groundwater levels drop during summer, increasing concentration of salts, including carbonates, and pH levels can increase. In ponds, lagoons, and other aquatic systems, pH levels can vary from

day to night. Algae take up  $\text{CO}_2$  during the day, resulting in pH levels above 10. At night, photosynthesis stops, plants respire, produce  $\text{O}_2$  and pH drops. Many researchers from Hoagland (1925) to Warfvinge & Sverdrup (1989) have cautioned against using pH alone to draw conclusions about soil fertility. Albrecht (1975) repeatedly warned that pH was the symptom of soil conditions, not the cause. Others, as I discussed previously, recommended BCSR to get the full picture.

Jurgens (1985, p. 9) in Positive Influences of  $\text{CO}_2$  on Soil, provides a clear explanation for the what actually occurs:

Carbon dioxide ( $\text{CO}_2$ ) occurs naturally in all soil and water systems. It is formed wherever plants grow and organic matter is decomposed. Plants utilize  $\text{CO}_2$  in their metabolism and release oxygen to the atmosphere.

Dissolved in water,  $\text{CO}_2$  becomes carbonic acid ( $\text{H}_2\text{CO}_3$ ). In areas of high rainfall and subsequent lush plant growth, carbonic acid becomes excessive to the point where limestone is required for productive agriculture on these acid pH soils. Conversely, in arid soil regions, plant growth and  $\text{CO}_2$  are often limiting. In these areas, top agricultural production requires additional  $\text{CO}_2$ . This is accomplished by the breakdown of organic matter, whether it be compost, manure, or mowed cover crop and where necessary additions of limestone. Through this process, carbonic acid and other weak humic acids release mineral nutrients from the soil and stimulate microbial activity.

Albrecht & Smith (1952) emphasized the importance of soil acidity in mineral breakdown, clay formation, and nutrient delivery to plants. Again, the primary source of carbon for plant and soil microbial growth is the bicarbonate ion. Jurgens gave the best true indication of soil reaction for our agricultural situations (1985, p. 9):

Alkalinity can be defined as a deficiency of  $\text{CO}_2$  and is measured in terms of pH. The pH scale corresponds to the amount of  $\text{CO}_2$  dissolved in water. At pH 8.3 no  $\text{CO}_2$  will be present. At pH values above 8.3 a theoretical negative amount of  $\text{CO}_2$  indicates an alkali solution of carbonate ions. At pH values below 8.3 carbonic acid is present..

Several researchers worked on developing models for recommending

limestone that compensates for the problems with the measurement of pH.

Warvinge and Sverdrup (1989) suggested lumping together  $H^+$  and  $Al^+$ , along with evaluating cation exchange reactions and  $H_2O-CO_2$  equilibrium. Marion, Schlesinger and Fonteyn (1992) pointed out the problems with the validity of pH measurements, and found inorganic C alkalinity correlates with total alkalinity. I suggest, to get the accurate picture, we determine the presence of carbonate or bicarbonate, and calculate the excess or deficiency of  $CO_2$ . Pounds per acre of appropriate amendments can then be quantified. Using the true soil reaction with BCSR method will then give optimum pH and cation ratios, with all the benefits that these conditions provide.