Preface

This book has been written to serve as a text for a soil fertility course at the junior-senior level and at the master's level for students who have had an introductory course in soil science and several basic science courses. We have chosen to cover the most essential topics and not produce an all-inclusive text to serve as a reference book. The treatment is an evolutionary one which considers soils as dynamic, ever-changing bodies.

There has been major progress over the past three decades in the accumulation of new knowledge and development of theories in the fields of soil science, agronomy, plant physiology, and plant nutrition. Thus, the production of this book has been an exciting challenge to integrate the most recent information about soil fertility with the knowledge and theories about weathering and soil evolution, mineralogy, exchange chemistry, soil taxonomy, fertilizer technology, and plant growth and nutrition.

Soils are one of the world's most important resources. We hope that the information put forth in this book will help to increase the food supply for the world's expanding population.

We extend our special thanks to Mary Foth for the graphic art work and to Nate Rufe for photographing the mineral models.

Henry D. Foth
Boyd G. Ellis
East Lansing, Michigan
June 1988
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CHAPTER 1

Soil Fertility and Plant Nutrition

SOIL FERTILITY DEFINED

Soil fertility is the status of a soil with respect to its ability to supply elements essential for plant growth without a toxic concentration of any element. Thus, soil fertility focuses on an adequate and balanced supply of elements or nutrients to satisfy the needs of plants. Because plants have evolved in different climates and on different soils, plants have different needs for the essential nutrients and different tolerances of the toxic elements. Cassava is native to the humid tropics and grows well on strongly acid soils containing a large amount of soluble aluminum. Wheat, by contrast, originated on the steppes where soils are neutral or alkaline and contain very little soluble aluminum. As a consequence, a soil can be fertile for cassava and at the same time be infertile for wheat. In fact, many wheat cultivars have low tolerance for soluble aluminum, and their root growth is restricted in its presence.

Soil Productivity.

Soil productivity encompasses soil fertility plus all the other factors affecting plant growth, including soil management. Soil productivity is a measure of the soil's ability to produce a particular crop or sequence of crops under a specified management system. All productive soils are fertile for the crops being grown, but many fertile soils are unproductive because they are subjected to drought or other unsatisfactory growth factors or management practices. There is a strong positive correlation in productive soils between fertility and physical properties so that highly productive soils have desirable physical properties as well as high fertility.
HISTORICAL DEVELOPMENT

Interest in soil fertility likely originated with the development of agriculture. By Roman times many of today’s soil fertility management practices were used, including manuring, liming, crop rotations, and fallowing to build up the supply of available nutrients. For the next 2,000 years, till the end of the Middle Ages and the beginning of the Renaissance, the accumulation of knowledge and improvements in agricultural practice were slow. And even though the developed world uses high technology in agriculture today, about half of the world’s farmers still use methods similar to those of Roman times or of the Middle Ages (see Figure 1.1).

Search for the Nourishment of Plants

During the later years of the Middle Ages, the foundations of modern science were being laid, and much attention was focused on discovering how vegetation or plant growth was nourished. Many theories had evolved, variously proposing water, saltpeter, soil, and the juices of the earth as the primary constituents. Jan Baptista Van Helmont (1577-1644), a Belgian chemist, put 200 pounds of soil in an earthen vessel and grew a 169-pound willow tree in five years by adding only water. The soil lost only 2 ounces, so he concluded that the tree grew because of the water. John Woodward in about 1700 reviewed the findings of Van Helmont and others and set up an experiment with four water treatments including rain, river water, and two sewage water treatments. In all treatments the plants had an abundance of water and should have grown equally if water was the nourishment of vegetation. Plant growth, however, increased with an increase in the amount of terrestrial matter in the water. Soon after 1800 the analytical balance was invented and aided scientific discovery because it became possible to weigh very small quantities of chemicals and solutions. It was discovered that plants and animals respire by burning organic food, and the basic concept of photosynthesis was elucidated. Van Helmont’s willow tree increased in weight largely because it fixed carbon. It was proved that plants do not ingest particles of food as animals do, but that plant roots take up nutrient elements for the most part as ions. An analysis of the plant ash revealed elements commonly or abundantly found in soils. Justus von Liebig (1803-1873) summarized the major findings and brought an end to the search for the nourishment of vegetation. Liebig, a German chemist, wrote that plants get most of their carbon from carbon dioxide, that water is a source of hydrogen and oxygen, and that the soil is a source of elements in the ash. But he erroneously believed that plants absorbed their nitrogen as ammonia from the atmosphere. Liebig’s book Organic Chemistry in Its Application to Agriculture and Physiology, published in 1840, marks the beginning of agricultural science.

Fertilizer Development

Some of the earliest fertilizer materials used as sources of nitrogen, phosphorus, and potassium included sodium nitrate from Chilean mines, bones and guano to supply P, and wood ashes and evaporite salt deposits to supply K. The treatment of bones with sulfuric acid to increase the solubility of the P began about 1830, and soon the modern fertilizer industry was born. In 1842 Sir John Lawes of England started the first commercial manufacture of superphosphate, and in 1850 the first mixed fertilizer was made in Baltimore, Maryland. The famous Rothamsted Experimental Station north of London, England began field experiments in 1843, and in 1855 the station declared that soil fertility could be maintained for many years with artificial manures or chemical fertilizers. The first commercial mining of K salts occurred in Germany in 1861.

The discovery in the 1880s of nitrogen fixation by bacteria of the genus Rhizobium allowed agriculturists to understand why legumes grow much better than other plants. Work by Fritz Haber and Karl Bosch led to the development of an efficient process for the production of synthetic ammonia in Germany in 1913. The Haber-Bosch process gave Germany an advantage in World War I for the production of N used in explosives. Today, N is generally the most limiting nutrient for crop production, and nearly all the N in fertilizers is derived from ammonia synthesis. The most recent developments in fertilizers include more-concentrated and lower-cost materials, pesticide incorporation, and improved physical and chemical properties, which have increased the efficiency of application and utilization.
**Soil Fertility and Plant Nutrition**

**Discovery of Essential and Toxic Elements**

An element is essential for plant growth when the plant is unable to complete its life cycle without the element, when no other element can take its place, and when the element must be directly involved in the plant's nutrition. Although N, P, K, and some other nutrients have been recognized as essential for a considerable length of time, the date appears to be lost in antiquity. Iron was found essential for all plant life in 1860, and many other nutrients were found essential during the first half of the twentieth century, as shown in Table 1.1.

Research then centered on the forms of the essential nutrients in soils and the factors affecting their availability for plants. Soil tests were developed and used as the basis for making recommendations for fertilizers. More recently, the roles of aluminum in soil acidity and as a toxic element in acid soils have received much attention. The potentially disastrous consequences of applying sewage sludge to the land encouraged studies of the uptake of heavy metals by plants, their toxicity for plants, and their effects on food quality. Environmental concerns received public attention as application rates of N and P fertilizers increased. Current research in soil fertility continues to emphasize better soil- and plant-testing methods so that the best fertilizers can be ascertained and recommended. Research in fertilizer technology emphasizes the development of new manufacturing processes and materials for more efficient improvement of soil fertility.

**Genetic Improvement To Cope with Mineral Stress**

An estimated 22.5 percent of the world's land has some form of mineral stress, a nutrient deficiency, an element toxicity, or both. Historically, lime and fertilizers were used to remove the mineral stress in order to increase crop production. Now an exciting new area of research aims at modifying or improving plants so that they can better cope with mineral stress and be productive with minimal use of lime and fertilizers.

In ancient times grape growers observed the different abilities of grape cultivars to tolerate calcareous soils in Greece, Italy, and France. As a consequence, the grafting of desirable grape scions on efficient rootstocks became a common method of growing good wine grapes on calcareous and alkaline soils throughout the world. Today, most grapes and most fruit and nut tree tops are grafted onto efficient rootstocks to overcome mineral stress, especially micronutrient deficiencies associated with alkaline soils, as well as to provide protection against soil-borne root diseases. An example of the difference of soybean cultivars to grow in calcareous soil without developing iron chlorosis is shown in Figure 1.2. When the iron-efficient top is grafted onto the roots of the iron-inefficient plant (shown in Figure 1.2), Fe chlorosis develops. If the iron-inefficient top is grafted onto iron-efficient roots, chlorosis does not develop.

Scientists are now trying to identify the genes that account for the tolerance of certain cultivars for toxicities and for their effective uptake of

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**Table 1.1** Proof of Essentiality of Elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Need proved by</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>Sachs</td>
<td>1860</td>
</tr>
<tr>
<td>Manganese</td>
<td>McHargue</td>
<td>1922</td>
</tr>
<tr>
<td>Boron</td>
<td>Sommer and Lipman</td>
<td>1926</td>
</tr>
<tr>
<td>Zinc</td>
<td>Sommer and Lipman</td>
<td>1926</td>
</tr>
<tr>
<td>Copper</td>
<td>Sommer and others</td>
<td>1931</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Arnon and Stout</td>
<td>1939</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Broyer and others</td>
<td>1939</td>
</tr>
</tbody>
</table>

Source: Adapted from Viets, 1977.

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**Figure 1.2** The iron-efficient Hawkeye soybean on the left shows no iron chlorosis, but the iron-inefficient T203 cultivar on the right has severe iron chlorosis. Both were grown in the same calcareous soil. (Photograph courtesy John C. Brown.)
nutrients from infertile soils. Researchers are also making efforts to transfer these genes to other cultivars. Success in these efforts will have a great impact in developing countries where fertilizers and lime are expensive and of limited availability.

**SOIL AS A NUTRIENT RESERVOIR**

About 90 percent of most mineral soils, soils other than organic soils or Histosols, consist of oxygen, silicon, and aluminum. These elements are not important in plant nutrition because plants obtain their O from air and water, Al is not an essential element, and Si is also not considered an essential element, even though it is sometimes beneficial for rice and sugar cane grown on soils low in silicate. The fourth most abundant mineral soil element is Fe, which plants use in small amounts. Thus, chemically speaking, the essential nutrients that plants remove from the soil come from a relatively small percentage of the soil.

**Soil Nutrients versus Plant Needs**

There are great differences in the amounts of the various elements in both soils and plants. In the soil there are, for example, about 3,000 times more calcium and potassium than molybdenum, and plants take up annually from infertile soils. Researchers are also making efforts to transfer these genes to other cultivars. Success in these efforts will have a great impact in developing countries where fertilizers and lime are expensive and of limited availability.

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### TABLE 1.2 Typical Concentrations of Essential Nutrients in Mineral Soils, Annual Plant Uptake, and Ratio of Content in 10-cm Layer of Soil to Uptake

<table>
<thead>
<tr>
<th>Nutrient</th>
<th>Soil content, percent by weight</th>
<th>Annual plant uptake, kg/ha</th>
<th>Soil content, 10-cm layer, to annual uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>1</td>
<td>50</td>
<td>260</td>
</tr>
<tr>
<td>Potassium</td>
<td>1</td>
<td>30</td>
<td>430</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.1</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>0.08</td>
<td>7</td>
<td>150</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.6</td>
<td>4</td>
<td>2,000</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.05</td>
<td>2</td>
<td>320</td>
</tr>
<tr>
<td>Iron</td>
<td>4.0</td>
<td>0.5</td>
<td>100,000</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.08</td>
<td>0.4</td>
<td>3,000</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.005</td>
<td>0.3</td>
<td>2,000</td>
</tr>
<tr>
<td>Copper</td>
<td>0.002</td>
<td>0.1</td>
<td>1,000</td>
</tr>
<tr>
<td>Chlorine</td>
<td>0.01</td>
<td>0.06</td>
<td>200</td>
</tr>
<tr>
<td>Boron</td>
<td>0.001</td>
<td>0.03</td>
<td>400</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>0.0003</td>
<td>0.003</td>
<td>1,000</td>
</tr>
</tbody>
</table>

*Source: Adapted from Bohn, McNeal, and O'Connor, 1985.*

... of 50 for nitrogen to 2,000 for magnesium. For the remaining seven nutrients with uptake less than 1 kg/ha annually, the ratio of soil content to uptake ranges from 200 to 100,000. The nutrients absorbed in very small amounts are usually sufficient unless some factor like soil pH causes them to be insoluble or unavailable. In general, the greater the amount that plants use, the more likely that the soil supply will be insufficient for crop needs.

Most of the usable or available nutrients originate from the weathering of minerals and the decomposition of organic matter. Many plow layers contain 2% to 4% organic matter, which results in about 0.1% to 0.2% N. As the amount of organic matter increases, there is a corresponding increase in N content and decreasing content of nutrients that exist primarily in the mineral fraction of the soil. About 0.9% of the world’s soils are organic soils or Histosols. These soils, compared to mineral soils, have a high percentage of nutrients that accumulate in humus, such as nitrogen, phosphorus, and sulfur. By contrast, Histosols are commonly very deficient in K for crop needs. The near absence of silicate minerals in Histosols may keep the amounts of soluble Si in the soil solution very small, which means that the yields of sugar cane and rice may increase when Si fertilizer is applied, even though, as mentioned earlier, Si is not strictly an essential element.

**NUTRIENT UPTAKE FROM SOILS**

*Movement of Nutrients to Roots*

Since nutrients are absorbed for the most part as ions from the soil solution at the root surface, a discussion of why nutrients occur along root surfaces in position for absorption is important.

As roots elongate through soil, the roots directly encounter some of the ions that exist in the soil solution. For most plants about 1% or less of the soil volume is composed of active roots, and about 1% to 2% of the nutrients taken up are positionally available at the root surface because roots intercept them. After a root becomes a resident in a soil region, ions in the soil solution are moved to the root by the mass flow of water. During mass flow both water and ions are moved to the root surface. The greater the ionic concentration in the soil solution, the greater the quantity that will be brought to root surfaces by mass flow. Ions in the soil solution are also in constant motion and move toward roots by diffusion. Diffusion is very important for moving ions to root surfaces when their concentration in the soil solution is very low and little is moved by mass flow. It has been estimated that the distance of diffusion per day through soil at field capacity to roots is 0.13 cm for K and 0.004 cm for the phosphate ion, $H_2PO_4^-$. Considering the slow diffusion rate of nutrient ions, it requires many days for some of the ions to diffuse only 1 cm through soil. This makes it necessary for roots to invade all soil regions from which significant nutrient uptake occurs. The relative importance of root interception, mass flow, and diffusion in the uptake of several nutrients by corn is shown in Table 1.3.
Root interception was 2 kg/ha of N or about 1% of the 190 kg absorbed to produce a high yield of corn on a fertile soil in Indiana (Table 1.3). Available N exists mainly as soluble nitrate in solution, and the water that was absorbed moved 150 kg/ha of N to roots by mass flow. The difference between 152 and 190 is considered the amount of N moved to roots by diffusion. Although mass flow is very important in N uptake, diffusion is the most important for P and K uptake because of their low concentrations in the soil solution. As for Ca, the corn absorbed only 40 kg/ha, 60 kg were intercepted by roots, and 150 kg were moved to the roots by mass flow. These calculated values are based on the assumption that there were 6,000 kg/ha of available (exchangeable) Ca, and that the solution concentration was 60 milligrams/liter. Thus, if roots intercept 1% of the available Ca, 60 kg will be intercepted. If the plants absorb 2.5 million liters of water per hectare, 150 kg/ha of Ca (2,500,000 L x 0.060 mg/L) will be moved to roots by mass flow. The amount from root interception and mass flow is 210 kg, which is over five times the amount absorbed. Under these conditions an excess of Ca is moved to the root surfaces by mass flow, and a concentration gradient for Ca is established away from the root. This results in no Ca being supplied by diffusion. The situation is similar for Mg and S.

Root Morphology and Nutrient Uptake

Roots elongate through the soil by the continued division and elongation of cells in the apical meristematic zone. Cell division and elongation occur both away from and toward the shoot, which means that root cap cells continue to form and the root elongates. The elongation zone is made up of immature cells near the root tip where nutrients and water can freely diffuse to the center of the root and enter the transpiration stream of the xylem. The cell walls contain much cellulose, which forms chainlike microfibrils. Ions and water molecules can readily diffuse into and through the intermicrofibrillar spaces. Ions absorbed into the cell walls of cortical cells can migrate centripetally by moving through the cell wall of one cell and into and through the cell wall of an adjacent cell. The cell walls are the apoplast, the part away from the plasma, and make up the apoplastic pathway. Thus, in the immature section of the root, ions and water can move across the cortex and enter the transpiration stream in the xylem vessels without crossing plasma membranes (see Figure 1.3). Ion uptake in this zone is rapid, and Ca uptake is restricted to this zone. Since plants are unable to translocate Ca toward the apex from older root sections, root elongation into calcium-deficient soil is inhibited. Most cations appear to be absorbed on newly formed roots, and their uptake is restricted when soils become dry because new root growth is greatly restricted.

Roots cells quickly mature a few centimeters behind the elongation

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**TABLE 1.3 Importance of Root Interception, Mass Flow, and Diffusion for the Production of 9,500 Kilograms of Corn Grain on a Fertile Alfisol**

<table>
<thead>
<tr>
<th>Nutrient</th>
<th>Amount absorbed</th>
<th>Interception, kg/ha</th>
<th>Mass flow, kg/ha</th>
<th>Diffusion, kg/ha</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>190</td>
<td>170</td>
<td>2</td>
<td>150</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>40</td>
<td>36</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Potassium</td>
<td>195</td>
<td>174</td>
<td>4</td>
<td>35</td>
</tr>
<tr>
<td>Calcium</td>
<td>40</td>
<td>36</td>
<td>60</td>
<td>150</td>
</tr>
<tr>
<td>Magnesium</td>
<td>45</td>
<td>40</td>
<td>15</td>
<td>100</td>
</tr>
<tr>
<td>Sulfur</td>
<td>22</td>
<td>20</td>
<td>1</td>
<td>65</td>
</tr>
</tbody>
</table>

Source: Adapted from Barber, 1984.
zone, and the Casparian strip forms in the endodermis that lies adjacent to the stele or central core of the root. The Casparian strip is a thickening surrounding the endodermal cells and forms a barrier at the inner cortex for the apoplastic movement of nutrients. The Casparian strip also inhibits the outward flow of ions from the xylem. Along the mature section of roots, nutrients and water may move freely through the cortex via the apoplastic pathway, but they eventually encounter the endodermis, which prevents further movement to the center of the root. Thus, to migrate across the endodermis, the nutrients must enter epidermal or cortical cells and move inward by the symplastic pathway, which consists of the cytoplasm and interconnections between cells, called plasmodesmata (see Figure 1.4).

A mucigel sheath surrounds the root cap and extends into the elongation zone. This material, along with root exudates, forms a substrate for microorganisms in the rhizosphere. The density of microbes in the rhizosphere may be 100 times greater than that in root-free soil. These organisms have an influence on nutrient availability and nutrient uptake near the root surface. Mycorrhizal fungus roots greatly extend the effective surface area of most roots and similarly influence nutrient uptake from soils.

**Carrier Theory of Ion Uptake**

Mass flow moves a large amount of Ca to root surfaces relative to plant needs. Calcium can be taken up passively along a concentration gradient between the soil solution and center of the root via the apoplastic pathway. For the other nutrients moving in the symplastic pathway, the concentration in the xylem is commonly greater than in the soil solution. Movement of ions against a concentration gradient, that is, by active uptake, requires metabolic energy. Energy appears to be needed to move ions across the plasmic membrane just inside the cell wall of epidermal or cortical cells and perhaps at other places along the symplastic route before the ions enter the transpiration stream in the xylem.

Research with large algal cells showed that cells could accumulate ions in greater concentration than in the external solution, while effectively excluding some ions in high concentration in the external solution. Plant roots also discriminate in ion uptake as shown in Table 1.4. The common crop plants excluded Na and accumulated K relative to the nutrient solution, which contained 25% equivalent concentrations of each cation. Magnesium and Ca uptake were more in line with solution concentrations. The halophyte is indigenous to saline soil areas and accumulated much more Na and much less Ca than the other plants. In general, as the concentration of an ion in the soil solution increases, uptake of this ion increases. Sometimes uptake of an ion increases with a simultaneous reduction in the uptake of some other ion. The uptake of Mg is commonly reduced when fertilization with K causes an increased uptake of K.

The carrier theory of ion absorption attempts to explain both the need for metabolic energy and the ability of plants to discriminate in ion uptake. Ions readily diffuse through cell walls and encounter the plasmic membrane. At or near the plasmic membrane, ions link up with ion-specific carriers that transport the ions across the membrane and deposit the ions into the cell's interior. Carrier transport requires energy, and the carriers exhibit specificity to account for their discriminatory behavior. As indicated earlier, the use of energy to accumulate ions against a concentration gradient is active uptake; most ion uptake by roots is active. In general, anions and cations are taken up simultaneously. When an excess of cations, compared to anions, is taken up, H+ are excreted to maintain electrical neutrality in both the soil solution and the cell. With excess uptake of anions, OH are excreted for the same reason. Small amounts of nutrients are absorbed as molecules, including N as urea and some micronutrients as chelated compounds.

![Diagram of (a) symplastic and (b) apoplastic movement of ions from the soil solution through the cortical cells. Ions that move apoplastically through the cortex must enter cortical cells and move from cell to cell symplastically (through a plasmodesma) to cross the Casparian strip in the endodermis. Plasmodesmata are cytoplasmic strands that pass through openings in some plant cell walls and provide living bridges between cells.](image)

### Table 1.4 Discrimination of Plant Roots in Uptake of Four Cations from a Solution Containing Equivalent Concentrations of the Cations

<table>
<thead>
<tr>
<th>Plant</th>
<th>Na</th>
<th>K</th>
<th>Mg</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Buckwheat</td>
<td>0.9</td>
<td>39</td>
<td>27</td>
<td>33</td>
</tr>
<tr>
<td>Sunflower</td>
<td>2.3</td>
<td>54</td>
<td>17</td>
<td>27</td>
</tr>
<tr>
<td>Corn</td>
<td>2.9</td>
<td>70</td>
<td>16</td>
<td>11</td>
</tr>
<tr>
<td>Potato</td>
<td>4.1</td>
<td>44</td>
<td>25</td>
<td>27</td>
</tr>
<tr>
<td>Halophyte</td>
<td>19.7</td>
<td>39</td>
<td>31</td>
<td>10</td>
</tr>
</tbody>
</table>

*Source: After Collander, 1941.*
Nutrient Uptake and Plant Growth

The first nutrients of a germinating seed come from the seed. After germination, the roots invade the surrounding soil in search of nutrients and water. As roots leave the immediate vicinity of the seed and elongate into the surrounding soil, nutrients and water are absorbed adjacent to the roots. Water uptake causes soil drying. The drying near the root surface decreases the soil's hydraulic conductivity, which reduces the movement of both water and ions to the roots by mass flow. Later-formed roots will tend to grow in unoccupied soil where water and nutrients are more available. As a consequence, roots tend to space themselves rather uniformly through the soil in a lateral direction as shown in Figure 1.5.

The penetration of small grain roots, such as oats and wheat, is typically less than for corn. By the end of the growing season, corn roots will usually have invaded the soil to depths of a meter or more. This is necessary to supply the water needs because the mobility of water held in soil between field capacity and the wilt point is limited. Available nutrients and roots tend to be in the highest concentration in the Ap horizon, which causes a greater proportion of the nutrients to be absorbed from the Ap horizon.

Early in the development of an annual plant, root growth is relatively more rapid than shoot growth. Growth rates vary with seasons, however. By the time corn roots have 50% of their weight, only 15% of the top corn growth may have occurred. In the shoots N, P, and K are taken up more rapidly, relatively speaking, than growth occurs or dry matter accumulates. This means that delaying the applications of fertilizer, after the period of normally rapid uptake, will reduce the opportunities for nutrient uptake and for increases in yield. Of the nutrients, K accumulates in corn more rapidly than N, and the N accumulates more rapidly than the P (see Figure 1.6). In addition, the amount of K in the corn shoot decreases late in the season.

Root growth in corn is especially interesting because late in the season, just before the ear develops, brace roots emerge from the lower stem nodes and branch profusely upon entering the soil. Research has shown that 1% to 36% of the P in plants was absorbed by brace roots. These secondary roots can be important for nutrient uptake when the Ap horizon is occasionally rewetted by late season rains.
Soil Fertility and Plant Nutrition

Root and Soil Interaction

It is a common observation that organisms are, in part, a product of their environment. So it is with roots. The soil environment affects the root, and the root responds with various strategies to cope with the existing soil environment. The differential excretion of $H^+$ and $OH^-$ ions with cation and anion uptake, which was mentioned earlier, modifies the pH in the immediate environment at the root surfaces. It has been observed that some plants growing in iron-stressed soils excrete additional $H^+$, which increases the acidity and solubility of Fe. Some plants excrete low-molecular-weight organic molecules that mobilize Fe, which is subsequently absorbed. These mechanisms are associated with plants that are iron-efficient. A wheat cultivar that is tolerant of soil with a high content of aluminum was found to increase the pH near root surfaces, which resulted in precipitation of the Al and reduced uptake. Thus, the interactions of roots with soils are very complex, and roots are not passive but are active in modifying their environment, the better to cope with nutrient deficiencies and element toxicities.

Importance of Fertilizers

Soils can sustain a low level of crop yields for centuries when soil management inputs are minimal. This level is in the range of 8 to 10 bushels/acre or about 1 000 to 1 200 kg/ha and is comparable to wheat yields in Britain between 1 100 and 1 350. Notice in Figure 1.7 that between 1 350 and 1 550 wheat yields increased slowly as grass was used to improve privately owned lands that had become exhausted during the feudal period. Over the next 350 years, yields were increased slowly through trial and error. The sharp rise in yields since 1900 reflects the application of scientific knowledge about pest control, improved varieties, and soil management.

Large increases in crop yields have occurred in many countries since World War II. Corn yields in the Corn Belt of the United States nearly doubled between 1939 and 1961. Partitioning of the factors that caused yields to increase showed that improvement of varieties accounted for 36% of the increase, followed by the use of fertilizer for 31%. Several studies have concluded that fertilizer use accounts for 25% to 50% of the grain production in the United States.

When a human community invades new land, the existing balance of nature is destroyed. In pioneer societies soil fertility tends to be exploited as nutrients in organic matter are mineralized, and the organic matter declines after the land is cultivated. Such an exploitative society may not have the wealth or means to improve soil fertility. Since the industrial revolution began about 500 years ago, the accumulation of wealth has resulted in investments that have increased soil fertility. A study by the Food and Agriculture Organization of the United Nations (FAO) of 41 countries found a positive relation between amount of fertilizer used and the value index (yield) of crops produced per hectare. The most developed countries tended to use fertilizer at the highest rates. Thus, it is seen that the fertility of soils and the use of fertilizers play an important role in world food production and are related to the overall economic activity in a country.

A Look to the Future

In 1876 the Morrow Plots were established at the University of Illinois to study both soil fertility depletion and improvement. The plots were established on Mollisols of high natural fertility, but when the fields were cropped to continuous corn without fertilizers or manure, yields quickly declined and were about 20 bushels/acre in 1954. In 1955 the plots were split in half, fertilizers were applied according to soil tests, and the yield was 86 bushels/acre. These dramatic results were published in a paper entitled "All the Way Back in One Year?" Because soil fertility is essentially an integration of the kinds and amounts of nutrient ions in the soil solution, it can be rapidly depleted. On the other hand, soil fertility can be restored almost instantaneously. For the future, knowledge of soil fertility and the use of fertilizers will play an increasingly important role in exploiting the soil's food production potential to improve the living standard of the world's people.

References

 Ion Exchange

The discovery of ion exchange in soils occurred about 1850 in England. Harry Stephen Thompson, a Yorkshire farmer, reported that leaching a soil with an ammonium sulfate solution produced leachate that was primarily calcium sulfate. The ammonium ions in solution were exchanged for calcium ions from the soil. The cation exchange reaction that occurred is represented as

\[(NH_4)_2SO_4 + CaX = (NH_4)_2X + CaSO_4\]  \hspace{1cm} (2.1)

where X designates the exchange surface. Calcium ions originally adsorbed by colloidal particles were exchanged by ammonium ions and leached from the soil along with the sulfate ions. This showed that the soil preferentially adsorbed cations as compared to anions, and that the soil was negatively charged. In cation exchange there is an exchange of cations in solution with cations adsorbed onto a surface-active material. The surface area and charge of the particles are large so that a single colloidal particle or micelle can be viewed as a giant anion with hundreds of thousands of adsorbed cations.

Within the past fifty years considerable knowledge has accumulated about the soil’s positive charge and anion exchange capacity. In most soils the negative charge is much greater than the positive charge. As soils become extremely weathered, however, the positive charge becomes more nearly equal to the negative charge and in certain soils may even exceed the negative charge.

**CATION EXCHANGE CAPACITY DEFINED**

The cation exchange capacity, CEC, is a quantitative expression of the amount of negative charge per unit quantity of oven-dry soil, or soil components. Or it is
the capacity to adsorb cations from solution. The CEC is expressed as milliequivalents per 100 grams (meq/100 g) of oven-dry soil. A soil with a CEC of 1 meq has 6.02 X 10^18 negative charges per 100 grams and can adsorb that many monovalent cations from solution. Since each divalent cation can neutralize two charges, the soil can theoretically adsorb 3.01 X 10^20 divalent cations from solution. If the monovalent cation is K, 0.039 gram will be adsorbed per 100 grams. If the divalent cation is Ca, 0.020 gram of Ca will be adsorbed per 100 grams. Thus, the CEC is a measure of the soil's ability to adsorb cations in terms of chemical equivalence rather than mass or weight.

**Determination of Cation Exchange Capacity**

The amount of CEC or negative charge of a soil is pH-dependent. For example, the H of various acidic groups of soil organic matter may be neutralized by OH^–, which results in the formation of water and an unsatisfied negative charge. As soil pH increases, so does OH^– concentration (or activity) and the formation of water and negative charge or CEC. For this reason the CEC must be determined at a standard pH to make valid comparisons between soils.

Commonly, the soil is treated with a normal ammonium acetate solution adjusted to pH 7.0. Ammonium replaces the adsorbed cations and occupies the exchange sites. The excess ammonium, along with the exchanged or displaced cations, is leached out with alcohol adjusted to pH 7.0. The amount of ammonium retained by the soil is then measured and equated to the CEC. Another procedure determines CEC at pH 8.2 using NaOAc and BaCl2 plus triethanolamine (TEA) solution. The NaOAc replaces exchangeable Ca, Mg, K, and Na, which are measured and added to the amount of acidity neutralized by the TEA. Another method uses an extracting solution of unbuffered KC1 or CaCl2 to replace the exchangeable cations and leach them from the soil. Then the amount of each exchangeable cation in the leachate is determined, and the sum of the cations is equated to the CEC. This method is very important for determining the CEC of soils at their present or natural pH, particularly, for acid soils.

**Source and Amount of Negative Charge**

Organic matter and clay fractions are the source of most of the negative charge. The negative charge of the soil organic matter, SOM, is pH-dependent, and the negative charge of the clay fraction is both pH-dependent and permanent.

**Negative Charge of Organic Matter**

Organic matter has several acidic functional groups that dissociate H^+ or deprotonate. About 85 percent or more of the negative charge is due to carboxyl and phenol groups. In the pH range of most soils (pH less than 8.0), carboxyl groups provide most of the CEC of SOM:

\[
\text{COOH} = \text{COO}^- + \text{H}^+
\]

A small amount of charge comes from enolic and imide N groups. An increase in hydroxyl concentration of the soil solution, accompanying an increase in pH, brings about a greater dissociation of adsorbed \( \text{H}^+ \); more water forms, and the CEC increases. As a result, the CEC of organic matter is pH-dependent or variable (CEC).

Both living roots and dead organic matter have CEC. As organic matter decomposes in the soil, there is an increase in acidic groups, which in turn increases the CEC. Histosols are composed mainly of organic matter and have relatively high CEC, typically between 100 and 200 meq/100 g. Fibrists are fibrous Histosols and are the least-decomposed or most peaty Histosols with a CEC of about 100. The Saprist, the most-decomposed Histosols, have a CEC more nearly 200. The bulk of humus in mineral soils is generally well decomposed and has quite high CEC averaging about 200 and ranging from 100 to 400. Thus, the degree of decomposition of soil organic matter greatly affects the CEC.

**Negative Charge of Mineral Fraction**

The minerals of the clay fraction are the source of most of the negative charge of the soil’s mineral fraction. The negative charge is both pH-dependent and permanent. Isomorphous substitution produces permanent CEC (CEC), and the CEC is due mainly to deprotonation of edge or exposed hydroxyls.

**Origin of Clay Minerals in Soils**

Clay minerals are formed by the weathering and alteration of existing minerals or by neogenesis, the crystallization of ions from solution. Soils formed from sediments and sedimentary rocks inherit clay minerals present in these materials. In the glaciated North Central region of the United States, the major clay mineral in the loess is montmorillonite (a smectite) and in the till hydrous mica (illite). Many of the till-derived soils of this region have a significant amount of hydrous mica inherited from the till and vermiculite that was produced by the alteration of hydrous mica. Mollisols of the Corn Belt that developed from loess have clay fractions dominated mostly by montmorillonite, for this clay was inherited and has not been substantially altered or destroyed. Vertisols of the Deccan Plateau in India, by contrast, contain montmorillonite that formed from the weathering of underlying basalt (neogenesis). Thus, the formation and alteration of clay minerals in soils are complex. Our consideration of the origin of the negative charge will focus on the generally accepted weathering sequence of mica to hydrous mica to vermiculite and smectite to kaolinite and, finally, to gibbsite. The weathering sequence approach provides a unifying concept about the origin of clay minerals and the source and amount of their negative charge.
Muscovite and biotite are micas that are 2:1 layer minerals and are ubiquitous in soils. Biotite is trioctahedral with Mg\(^{2+}\) and Fe\(^{2+}\) as the dominant cations in the octahedral sheet. Muscovite is dioctahedral with Al\(^{3+}\) in the octahedral sheet. Both have isomorphous substituted Al\(^{3+}\) in the silica tetrahedral sheet that produces one negative charge for every Si\(^{4+}\) replaced by Al\(^{3+}\). About one in four of the silicon atoms in the tetrahedral sheets is replaced by Al\(^{3+}\), resulting in a high permanent negative charge. In unweathered mica this charge is balanced by K ions that fit between adjacent layers. The interlayer K ions balance the charge and act as a bridge holding the layers together so that the layers do not expand (see Figure 2.1).

During weathering, interlayer K is lost along the particle edges. The loss of K creates voids where unsatisfied negative charge develops, thereby creating CEC. The loss of K parallels the increase in CEC and results in about 10 to 40 meq/100 g. The loss of K also results in expansion or separation of the 2:1 layers along the edges of the mica particles. This altered mica is hydrous mica (see Figure 2.2).

When the concentration of hydrated K is high near CEC sites where interlayer K has been lost, these ions reenter the voids and become fixed. This fixation is related to the low energy of hydration and the easy loss of hydrated water when K ions reenter the interlayer space. The fixation of K lowers the CEC and causes the expanded edges of layers to collapse. Potassium may become fixed when K fertilizer is applied and then protects K from being lost by leaching.

When loss of the interlayer K is complete or nearly complete, the layers expand, and hydrous mica alters into vermiculite with CEC of about 120 to 150 meq/100 g. This is about the highest CEC found in soil clay minerals. The surface area of vermiculite is 600 to 800 m\(^2\)/g compared to only 70 to 120 m\(^2\)/g for nonexpanding hydrous mica (see Figure 2.3).

The high charge near the interlayer space produced by the adjacent tetrahedral sheets favors K fixation, similar to that for hydrous mica; in the

FIGURE 2.1 Model of the 2:1 mica mineral (muscovite) with two layers slightly offset to show the location and arrangement of the interlayer potassium ions (nonhydrated) that neutralize the tetrahedral sheet charge and hold the layers together.

FIGURE 2.2 Model of hydrous mica with two layers slightly offset to show four interlayer potassium ions (nonhydrated) exposed along the edges. The loss of interlayer potassium produces cation exchange sites on the exterior planar surfaces and edges that absorb hydrated cations, which are exchangeable. Three are shown.

FIGURE 2.3 Model of 2:1 expanding clay vermiculite showing hydrated cations (each with six water molecules) in the interlayer space. These cations are exchangeable and move freely into and out of the interlayer space. In effect, the interlayer distance is equal to the thickness of two layers of water molecules. Drying causes a loss of water and contraction of the interlayer distance, and rewetting causes reexpansion. Cation exchange sites also occur on the exterior planar surfaces and edges.
Ion Exchange

laboratory vermiculite can be converted to hydrous mica by treatment with a solution containing a large number of K ions. The treatment results in much K fixation, loss of CEC, and collapse of the layers.

Smectites—Beidellite and Montmorillonite

Smectites are 2:1 expanding clays with significantly less CEC than vermiculite and little or no ability to fix K. The CEC is about 80 to 120 meq/100 g. Vermiculite can be altered into smectite by dealumination, resulting in a loss of lattice charge. This is a likely means of forming beidellite, which has a significant amount of tetrahedral Al. Montmorillonite has little if any tetrahedral Al, and its formation by neogenesis and persistence is favored by an environment with limited leaching and a soil solution enriched with Si and Mg. Negative charge originates in the octahedral layer by the isomorphous substitution of Mg$^{2+}$ for Al$^{3+}$. Smectites have small-sized particles, a large surface area, and moderate to high permanent CEC. The model in Figure 2.3 is representative of both vermiculite and smectite, which are both 2:1 expanding clays with high and predominately permanent charge. The interlayer distance of the smectites, however, is highly variable and may be two or more times greater than that of vermiculite.

Hydroxy-Al-Interlayered Vermiculite and Smectite

For 2:1 expanding clays, vermiculite and smectite, to form and continue to exist they need an environment that has little or only moderately intensive weathering; pH should be about 6 or more, and there should be limited leaching, which will keep the soil solution enriched with Si and Mg. When the pH drops below 6, the amount of Al$^{3+}$ in solution increases, and large polymerized hydroxy-Al cations with a high charge are formed and are strongly adsorbed. Polymerization is enhanced near the surfaces of clay particles. Strongly adsorbed hydroxy-Al is not exchangeable, and adsorption reduces CEC. The smallest polymer believed to be nonexchangeable has a six-member ring structure and the formula Al$_6$(OH)$_{15}$$. Adsorption in the interlayer space causes the layers to remain permanently expanded. The clay becomes nonexpanding owing to the attraction of the positively charged hydroxy-Al interlayer and the negatively charged 2:1 layers (see Figure 2.4).

Hydroxy-Al interlayering is favored by pH of about 5.0, the release of significant Al by weathering, low content of organic matter, and frequent wetting and drying of the soil. The hydroxy-Al occurs first as islands (as shown in Figure 2.4) and in time may form a continuous interlayer. The clays are referred to as 2:1:1 clays. They have a CEC ranging from 10 to 40 meq/100 g and a surface area of 70 to 150 m$^2$/g, comparable to those of hydrous mica. Hydroxy-Al interlayer clays have great resistance to weathering and are an important component of both moderately weathered and intensely weathered soils, including Alfisols and Ultisols and some Oxisols.

Kaolinite

Kaolinite readily forms by neogenesis from the ions released by the weathering of micas, feldspars, 2:1 and 2:1:1 clay minerals, and other minerals. In an acid-leaching environment preferential loss of Si relative to Al, which is called desilication, favors the formation of kaolinite. The Si: Al ratio decreases from about 2:1 to 1:1 during the formation of kaolinite from 2:1 clays. Equation 2.3 represents the neogenesis of kaolinite from orthoclase and the formation of soluble silica (silicic acid) and K$^+$:

$$2\text{KAISi}_3\text{O}_8 + 2\text{H}^+ + 9\text{H}_2\text{O} = \text{orthoclase} + 4\text{Si(OH)}_4 + 2\text{K}^+.$$  \hspace{1cm} (2.3)

Kaolinite is nonexpanding and has low CEC, 3 to 10 meq/100 g. There is uncertainty whether or not kaolinite may inherit some isomorphous substitution charge. The particles have one planar surface that is all OH; however, the CEC is generally due to deprotonation of edge hydroxyls coordinated with Al along the edges and is pH-dependent (see Figure 2.5). The expanding clays, by contrast, may have a 90% permanent charge and a 10% pH dependent charge at pH 7. These charges are produced by the extent of isomorphous substitution and the limited deprotonation of edge hydroxyls.
FIGURE 2.5 Model of 1:1 nonexpanding kaolinite showing two offset layers whose upper surfaces are hydroxyl-coordinated, with aluminum in the octahedral sheet. The cation exchange sites occur along the edges, and the hydrated exchangeable cation is shown to be adsorbed on a site created by the deprotonation of a hydroxyl coordinated with aluminum.

Deprotonation of edge Si—OH groups usually occurs at very high pH and contributes little to the CEC, of most soils. Most of the variable charge of silicate clay comes from the more acidic Al—OH groups along the particle edges. The hydroxyls of planar surfaces deprotonate at too high a pH to make an important contribution to the charge of layer silicate clays in soils.

Gibbsite and the Oxidic Clays

As long as soils contain significant soluble silica, the formation of silicate clay is favored and that of gibbsite is inhibited. Over time, however, continued desilication removes the tetrahedral sheets of kaolinite. Kaolinite is thus transformed into gibbsite:

\[
\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 5\text{H}_2\text{O} = 2\text{Al}(\text{OH})_3 + 2\text{Si}(\text{OH})_4
\]

The gibbsite structure is similar to the Al octahedral sheet of the aluminum silicate clays with Al in sixfold coordination with OH. The mineral is dioctahedral with Al occupying two of every three cation positions. At the edges some of the hydroxyls are not fully coordinated with Al, and the exposed hydroxyls deprotonate to create CEC, or the hydroxyls can protonate to produce a positive charge, depending on pH. Gibbsite is crystalline and has relatively little surface area and CEC. A model of gibbsite is shown in Figure 2.6.

In all soils Al and Fe are released in weathering, and much of the Al enters into the formation of clay minerals along with Si, as we have just noted, and gibbsite formation is inhibited. Some of the Al and some Fe exist as free amorphous hydroxides with idealized formulas of Al(OH), and Fe(OH). In soils the hydrous oxides range from those that are freshly formed and amorphous to those that have varying degrees of crystallinity and a variable composition. The Al oxides tend to be positively charged because of incomplete coordination of OH with Al in an acid weathering environment, and their composition is related to soil pH. The Al is in six coordination, with the sum of the OH molecules and H₂O equal to six. The Al-to-OH ratio is commonly in the range 2.5 to 2.7, resulting in a positive charge. The positively charged hydrous oxides are adsorbed and coat the negatively charged surfaces of layer silicate clays. As a result, the total negative charge or CEC of the silicate clay is reduced. For clays with permanent charge, the adsorption of an oxide coating will increase the percentage of charge or CEC that is pH-dependent. The ubiquitous presence of hydrous oxides in soils causes the layer silicate clays to have exchange properties different from the ideal. Aluminum and Fe form complexes with organic matter and, in an analogous manner, decrease the CEC of the SOM.

The amorphous hydrous oxides have greater surface area and CEC as compared to their crystalline counterparts. Over time these amorphous minerals are converted into crystalline gibbsite, Al(OH), and goethite, FeOOH. Both the amorphous and crystalline forms are oxidic clays. Soils with abundant gibbsite tend to have a significant amount of kaolinite because these two clays tend to form near the end of the weathering sequence.

Allophane

Allophane is an amorphous, hydrous aluminum silicate that is formed by the weathering of volcanic ash and other amorphous volcanic materials. It
is a dominate component of soils developed from volcanic ash such as Andepts. Allophane has been reported to have a high amount of surface area per gram and moderate to high pH-dependent CEC owing to hydroxyl deprotonation. Over time allophane crystallizes into kaolinite with greatly reduced CEC.

Low-Activity Clay Soils
In intensely weathered soils, Ultisols and Oxisols, the dominant clay minerals are kaolinite and gibbsite or other oxidic clays. Frequently, the negative charge properties of the kaolinite in these soils are greatly modified by oxidic clays because they tend to coat the surfaces of kaolinite and mask the effects of the kaolinite. The soils dominated by these clays with low variable charge have been called low-activity clay (LAC) soils. The upper limit for the CEC of LAC can be considered to be 16 meq/100 g determined at pH 7. This is the upper limit for the clay fraction of oxic horizons of Oxisols. Soils dominated by LAC have distinctly different fertility characteristics and require distinctly different soil management practices compared to soils with a much greater CEC that is mostly permanent charge. These differences will be emphasized in the material covering ion exchange and soil pH.

Positive Charge and Zero Point of Charge
Hydroxyl replacement by other anions, called ligand exchange, is a significant source of positive charge or anion exchange capacity (AEC) of oxidic clays. The replacement is pH-dependent and increases with increasing acidity or decreasing pH. Thus, AEC is related to both the extent of ligand exchange and the protonation of exposed hydroxyls, which are both pH-dependent. In most soils AEC is minor, however; soil with abundant goethite and gibbsite may have a CEC-to-AEC ratio approaching 1.0, as do some oxic horizons or subsoils of Oxisols. The CEC and AEC of some clay minerals recovered from a soil are given in Table 2.1.

If increasing acidity causes a decrease in the negative charge and an increase in positive charge, theoretically, a soil can have a zero point of charge (ZPC) where the AEC and the CEC are equal. In most soils the CEC greatly exceeds the AEC. In some the subsoil or oxic horizon of Oxisols may contain little organic matter and have little negative charge contributed by SOM, resulting in a net charge of zero or a small positive charge.

Summary Statement
The negative charge of soils is strongly associated with the SOM and clay minerals. The charge is partly pH-dependent and variable (CEC) and is usually caused by hydroxyl deprotonation; part of the charge is permanent (CECP), owing to isomorphous substitution. In summary,

1. Soil organic matter has high CEC.

<table>
<thead>
<tr>
<th>Material</th>
<th>Cation exchange capacity, meq/100g</th>
<th>Anion exchange capacity, meq/100g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite</td>
<td>112</td>
<td>6</td>
</tr>
<tr>
<td>Vermiculite</td>
<td>85</td>
<td>0</td>
</tr>
<tr>
<td>Hydrous mica</td>
<td>11</td>
<td>8</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Gibbsite</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>Goethite</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>Allophanic colloid</td>
<td>10</td>
<td>41</td>
</tr>
</tbody>
</table>

Source: Data on Kenya soils adapted from Sanchez, 1976.

2. The 2:1 and 2:1:1 clays tend to have moderate to high CEC, and low CEC.
3. Kaolinitic clay has low CEC, and allophane has high CEC.
4. Oxidic clays have low CEC.
5. The ion exchange properties of layer silicate clays in soils are modified by coatings of oxidic clays.
6. According to the concept of a mineral-weathering sequence, the CEC of mineral soils tends to increase until soils become moderately weathered and the clays are predominately 2:1 expanding types. Then the CEC decreases to a minimum in intensely weathered soils, such as Ultisols and Oxisols, which are dominated by kaolinite and oxidic clays (LAC).
7. The CEC and AEC approach equality as the pH approaches the zero point of charge in the most weathered soils, the Oxisols.

CATION EXCHANGE CAPACITY OF SOIL
The CEC of soils is mainly a function of the amount and kind of clay and SOM, their interaction, and soil pH. A soil may occasionally have some clay minerals in the silt fraction or contain some silt-sized micaceous minerals that have a significant effect on the CEC.

Role of Organic Matter and Clay
A study of the A and B horizons of five Chernozemic soils or Mollisols on the Great Plains of western Canada showed that the average CEC of the clay was 57 meq/100 g with a range of 55 to 59. The SOM had an average CEC of 250 with a range of 214 to 297. In both the CEC was determined at pH 7. The data indicated similar clays in both horizons, but the SOM was more decomposed and had greater CEC in the B as compared to the A.
horizon. Assuming that the CEC of the clay is 57 and of the SOM is 250, an A horizon with 20% clay and 4% organic matter would have a CEC of 21.4 meq/100 g. About half of the CEC is due to the clay and about half to the SOM. For a B horizon with 30% clay and 1% organic matter, the estimated CEC would be 19.6, with 87% attributable to the clay and only 13% to the SOM.

Histosols commonly have a CEC between 100 and 200 meq/100 g. This does not mean, however, that plant roots have many times more CEC in a given volume of root environment than do mineral soils. A kilogram of an organic soil may represent a volume that is ten or more times larger than that filled by a kilogram of mineral soil. Thus, it is useful to compare the CEC on a weight and volume basis as shown in Table 2.2. The data in the table reflect both a greater CEC and bulk density of muck as compared to those of peat. On a volume basis, about the same amount of lime is required for a loam soil and for woody peat to make a similar change in calcium saturation of the CEC. Muck soils, however, require about four times more lime per unit volume of soil than do loamy soils.

The Effective Cation Exchange Capacity

The CEC of soils has typically been determined at pH of 7.0 or 8.2, depending on the method. Determination of the CEC at the soil’s current or natural pH is called the effective CEC, ECEC. The ECEC more accurately reflects conditions encountered by plant roots than does the CEC determined at some standardized pH such as 7 or 8.2.

An extensive study was made of the relation between the CEC and the pH of the Ap horizons of 60 Mollisols and Alfisols in Wisconsin. The soils averaged 13.3% clay, which can be expected to consist mostly of 2:1 types plus lesser amounts of 2:1:1 clay and minor amounts of hydrous oxides (oxidic clay). The SOM averaged 3.38%. The study covered the pH range from 2.5 to 8.0, but since soils seldom have a pH less than 3.5, the data in Figure 2.7 cover the range of about 3.5 to 8.0. As soil pH increases, the CEC of both the clay and the SOM increases with the SOM showing the largest increase. At pH 3.5 the CEC was 8.58 meq/100 g with 71% of the CEC contributed by the clay and 29% by the SOM. At pH 8.0 the CEC was 14.8 with 54% of the CEC contributed by the clay and 46% by the SOM. Liming soils increases soil pH, which in turn increases the CEC.

TABLE 2.2 Comparison of Cation Exchange Capacity on a Weight and a Volume Basis

<table>
<thead>
<tr>
<th>Soil</th>
<th>Cation exchange capacity</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight basis, meq/100 g</td>
<td>Volume basis, meq/100 cc</td>
</tr>
<tr>
<td>Loam, mineral soil</td>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td>Sphagnum peat</td>
<td>100</td>
<td>8</td>
</tr>
<tr>
<td>Woody peat</td>
<td>90</td>
<td>14</td>
</tr>
<tr>
<td>Muck</td>
<td>200</td>
<td>60</td>
</tr>
</tbody>
</table>

Source: Data from Lucas, 1982.

ION DISTRIBUTION NEAR CATION EXCHANGE SURFACES

The soil particles are surrounded by water films that contain hydrated cations and anions which are in constant motion. As a cation randomly approaches the surface where a negative charge is located, the closer the cation approaches to the surface, the more strongly it is attracted. Outward from the surface the strength of the negative charge decreases very rapidly with increasing distance. Within a certain sphere or volume that is centered on the charged site, the cation moves or oscillates but is under the influence of the negative charge and is considered to be an adsorbed or exchangeable cation. When an adsorbed cation is at the extremity of the sphere of charge influence and another cation from the solution moves in behind it, the adsorbed cation will be exchanged and then become a cation in solution. There is no sharp line of demarcation, however, between cations considered adsorbed or exchangeable and those in solution.

The rapid decline in the strength of the negative charge as its distance from the exchange surface increases causes the adsorbed cations to concentrate near the surface. The concentration of cations decreases rapidly with increasing distance from the surface. The negative-charged exchange surfaces repel anions. The net effect is to produce an ion distribution as shown in Figure 2.8. The net charge of the system is zero with the negative charge of the CEC plus the anions counterbalancing the positive charge of the cations and the AEC.
CHARACTERISTICS OF CATION EXCHANGE REACTIONS

In general, cation exchange reactions are rapid, reversible, and stoichiometric and obey the mass action law. The greater the concentration of any cation, the more likely is the cation to cause desorption of competing cations and be adsorbed.

Effects of Valence and Hydration

Valence is the major factor affecting the likelihood that a cation will be adsorbed on colloid surfaces. A trivalent ion like Al\(^{3+}\) is more strongly adsorbed than Ca\(^{2+}\), which is more strongly adsorbed than K\(^+\). It requires two K ions to replace one Ca ion. Divalent cations are held with about twice the energy as monovalent cations. For cations of similar valence, the smaller cation will have the greater charge density per unit volume and, therefore, attract more water molecules. These attracted water molecules cause the hydrated radius of a smaller cation to be larger than the hydrated radius of a larger cation. For this reason Ca is more strongly adsorbed than Mg and K is more strongly adsorbed than Na. The general order of selectivity or replaceability of some important hydrated exchangeable cations is Al\(^{3+}\) > Ca\(^{2+}\) > Mg\(^{2+}\) > K\(^+\) = NH\(_4\)^+ > Na\(^+\).

Complimentary Ion Effects

Exchange of one cation for another, in the presence of a third or complimentary cation, is easier if the complimentary cation has greater valence or energy of adsorption. During uptake of cations by roots, the root excretes H\(^+\), which is monovalent and weakly adsorbed. Thus, when the H\(^+\) diffuses to the colloid surfaces, it is more likely to exchange K than Ca\(^+\) if the soil is acid and many trivalent Al\(^{3+}\) ions are adsorbed. By contrast, the H\(^+\) would less likely exchange for K than Ca\(^{2+}\) under the following conditions: (1) if the soil was alkaline, and (2) if there was no exchangeable Al, (3) but much exchangeable Mg and Na as the complimentary cations. In effect, as soils become more acid and increase in exchangeable Al below pH 5.5, the exchangeable K is more likely to be in solution or to be more available. The immediate effect is good because these soils tend to be low in exchangeable K. However, the longtime effect is greater leaching of K.

Unique Cation Selectivities

Cation selectivity is sometimes affected by unique space and charge environments. The greater the charge density per unit of surface area, the greater the preference for cations of higher valence or energy of adsorption. Vermiculite has greater surface charge density than montmorillonite and preferentially adsors more Ca\(^{2+}\) relative to Na\(^+\) from a mixed solution than does montmorillonite. Hydrated Mg ions fit well into the water network between partially expanded layers of vermiculite, resulting in preferential adsorption of Mg over Ca, especially when Mg is fairly abundant. The weathered edges of micas, which become hydrous mica, contain voids that can collapse around a K ion and fix it so that it is no longer exchangeable. Such K fixation is enhanced by the easy loss of hydration water before entry of K into the voids. This process is the reverse of weathering and occurs when K fertilizers are used. The strong adsorption of large hydroxy-Al cations between the layers of 2:1 expanding clay minerals prevents interlayer collapse and decreases K fixation and cation adsorption in the interlayer space.

EXCHANGEABLE CATION SUITES

The compliment of exchangeable cations or the exchangeable cation suite of natural soils is a function of their parent material and the changes that occurred during their genesis. The dominant exchangeable cations are Al, Ca, Mg, K, and Na. An exchangeable cation is written with an X before the ion. For example, XAl means exchangeable Al and XMg means exchangeable Mg. Further, XAL..Na refers to the five dominant exchangeable cations (Al, Ca, Mg, K, Na), and their sum in milliequivalents per 100 g is equated to the CEC. When XCa..Na is used, it refers to exchangeable Ca, Mg, K, and Na (also called exchangeable bases). Since exchangeable cations represent the major available supply of many plant nutrients, their absolute and relative amounts are important in affecting plant growth.

Calcareous Soils

Young soils inherit from the parent material a particular chemical and mineralogical composition, including the clay mineral suite, the exchangeable cation suite, and pH. Many parent materials are calcareous and contain
an abundance of CaCO₃ and smaller amounts of other salts. From the
dissolution of the salts come the cations for adsorption. As salts dissolve, the
cations entering solution are attracted to the exchange sites usually accord­
ing to valence and mass action. Except for very small amounts of micronu­
trient cations and some NH₄⁺, it is the Ca, Mg, K, and Na ions that
dominate the exchange sites. Their abundances parallel the energy of
adsorption sequence, with Ca the most abundant and Na the least. The
CEC of a calcareous C horizon developed from loess in Iowa was reported
to be saturated 67% by Ca, 30% by Mg, 2% by K, and 1% by Na. The
exchangeable Ca plus Mg plus K and Na, or XCa..Na, as milliequivalents
per 100 g is equal to the CEC and the soil is 100% XCa..Na saturated. The
pH of calcareous soils is in the range 7.5 to 8.3.

Calcareous soils are common where young soils have formed from
calcareous parent material. They are prevalent in arid and subhumid re­
regions because leaching of carbonate salts is limited, and the Ca released by
weathering forms carbonate.

**Acid Soils**

Leaching of calcareous soils removes the carbonate, sulfate, and chloride
salts of Ca, Mg, K, and Na. Additional leaching results in the progressive
removal of XCa..Na and increasing adsorption of hydroxy-Al. Below pH
5.5, adsorption of Al³⁺ (XA1) becomes significant. The permanent charge
in acid soils becomes increasingly aluminum-saturated. More discussion of
the exchangeable cation suite of acid soils is given in Chapter 3.

**Saline and Sodic Soils**

Saline soils contain salts more soluble than the carbonate salts found in
calcareous soils. In arid and subhumid regions, water moves from one part of
the landscape to another, depending on topography. In some parts of the
landscape, runoff water collects in depressions and forms ponds. Subse­
quently, water evaporates and the salts that were in the water are deposited.
The upward movement of water from a shallow water table to the soil
surface may also cause water to evaporate and salts to deposit. Since the
most soluble salts are moved to the greatest extent, soils may become saline
from the infusion of soluble salt. Saline soils have sufficient soluble salt to
impair plant growth.

The exchangeable cation suite of saline soils is highly variable, depend­ing
on the amount and kind of salts. Sodium salts are the most soluble, and
their preferential accumulation over time may result in over 15% XNa and
the formation of sodic soils. The structure of sodic soils tends to disintegrate
because Na is weakly adsorbed and is inefficient in neutralizing the negative
charge. The dispersion of clays and humus greatly reduces permeability
and tilth. With the addition of gypsum, CaSO₄ • 2H₂O, and the leaching of
sodic soils, Na is desorbed by Ca and removed, and the soil becomes nonsodic.

---

**Serpentine Soils**

The mineralogical uniqueness of the parent material sometimes gives soils
an unusual exchangeable cation suite. This is the case with soils that have
developed from serpentine parent materials. Serpentine minerals have a
1:1 structure similar to kaolinite and contain considerable isomorphous
Mg and Fe. Weathering releases large amounts of Mg relative to the other
cations. Montmorillonite is a common clay formed from serpentine
weathering.

Four soils formed from serpentine rock in California were found to have
C and Cr horizons with average exchangeable cation ratios (in milliequiva­
Ients) of Ca: Mg: K: Na of 26:410:1:1. The A horizons were more
weathered and leached, but even so, they had high imbalance of Mg relative
to Ca for plant growth, with ratios of 61:174:3:1, respectively. Most
plants cannot tolerate a cation suite that is particularly unbalanced in Ca
and Mg. Calcium deficiencies are common. Lands with serpentine soils have
unusual floras and sparse plant growth and are referred to as serpentine
barrens. Serpentine soil materials exposed by mining are very difficult to
revegetate.

**Summary Statement**

In summary, we can state that

1. Soils develop from a wide variety of parent materials and have great
variation in degree of development. The exchangeable cation suite, however,
shows much less variability.

2. The order of exchangeable cations is Ca > Mg > K > Na in most soils
with a pH of 5.5 or more. Exceptions occur in sodic and serpentine soils;
in sodic soils Na may dominate the exchange, and in serpentine soils Mg.

3. Aluminum becomes an important exchangeable cation below pH 5.5
and increases in abundance as soil pH declines.

---

**Exchangeable Cations as a Source of Plant Nutrients**

In general, the greater the amount of an exchangeable cation, the greater
its concentration in the soil solution. As a consequence, the exchangeable
cations represent an available supply of Ca, Mg, K, and Na for meeting the
immediate needs of plants. It has been mentioned that a calcareous C
horizon developed from loess in western Iowa had a CEC that was 67%,
30%, 2%, and 1% saturated with Ca, Mg, K, and Na, respectively. The soil
has a CEC of 16 meq/100 g. We will consider next the adequacy of such
soil for supplying the annual needs of crops.

The data in Table 2.3 show that a layer of soil about 7 or 8 inches thick
(20 cm) would contain enough exchangeable Ca to meet the needs of
productive crops for 86 years. For Mg and K the supply would last 38 and
TABLE 2.3 Amounts of Exchangeable Cations versus Plant Needs

<table>
<thead>
<tr>
<th>Cation</th>
<th>Furrow Slice</th>
<th>Supply,* years</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pounds/acre</td>
<td>kg/ha</td>
</tr>
<tr>
<td>Ca</td>
<td>4 280</td>
<td>4 798</td>
</tr>
<tr>
<td>Mg</td>
<td>1 152</td>
<td>1 291</td>
</tr>
<tr>
<td>K</td>
<td>234</td>
<td>262</td>
</tr>
</tbody>
</table>

*Based on an average value of the annual uptake of productive crops and data for Ida silt loam, as reported in Soil Survey Investigations Report 3, USDA, 1966.

1.2 years, respectively. The soil can be expected to supply the Ca and Mg needs for many years because weathering constantly releases additional Ca and Mg. On the other hand, the large annual demand for K and the low exchangeable supply relative to annual requirements means that K fertilizer is likely to be needed each year to produce high yields. The very small amounts of exchangeable Fe, Mn, Cu, and Zn are also important in meeting the nutrition needs of plants and microorganisms. Thus, it is difficult to overemphasize the importance of there being exchangeable cations in soils to serve as a source of plant nutrients.

ANION EXCHANGE

The pH is high enough in most agricultural soils that the CEC is much greater than the AEC. As soils become more acid and more dominated by low-activity clays, the CEC decreases and the AEC increases. Acid soils dominated by oxidative clays may have AEC about equal to, and in rare cases, greater than, the CEC. Positive charge originates from protonation of hydroxyls and by ligand exchange or the replacement of hydroxyls by other anions. A recent report indicates that there can be positive permanent charge in oxidative clay through the isomorphous substitution of Ti⁺⁺⁺ for Fe⁺⁺⁺. Nitrate and chloride ions are very weakly adsorbed and readily leach from soils. Phosphate ions involved in ligand exchange are so strongly adsorbed that they are fixed. Sulfate adsorption is intermediate.

REFERENCES


CHAPTER 3

Soil pH and Its Management

Soil pH is an indicator of soil acidity and basicity. Most soils have a pH in the range of 4 to 10. The pH of a particular soil, such as 5 or 8, reflects a certain chemical and mineralogical environment in that soil, and thus the pH is of great importance to plant roots and microbial activity. For these reasons soil pH is one of the most important factors affecting soil fertility and so is commonly managed to increase crop yields.

pH DEFINED

Chemically, the pH is an expression of the H ion activity, \( [H^+] \). Hydrogen ions hydrate similarly to other cations in the soil solution. The water molecules of hydration are not shown for simplicity. In solutions with low ionic concentrations, the activity of ions approaches the molarity, allowing molar concentration to be interchangeable with activity in the following discussion. The pH scale was devised to simplify the expression of \( [H^+] \) and is the logarithm of the reciprocal of the \( [H^+] \) or H ion concentration:

\[
pH = -\log [H^+] \quad (3.1)
\]

where \( [H^+] \) is \( H^+ \) in moles per liter, or

\[
pH = -\log (H^+) \quad (3.2)
\]

The pH of normal or pure water is 7.0 calculated as follows:

\[
pH = -\log \frac{1}{0.000001} = \log 1000000 = 7.0 \quad (3.3)
\]

or

\[
pH = -\log 10^{-7} = (-7) = 7 \quad (3.4)
\]

The pH of water is 7 because of the degree of dissociation or ionization of water. Water ionizes as

\[
H_2O = H^+ + OH^- \quad (3.5)
\]

The ionization constant \( K_w \) at 25 degrees C, is

\[
K_w = (H^+)(OH^-) = 10^{-14} \quad (3.6)
\]

Since the ionization of each molecule of water produces one \( H^+ \) and one \( OH^- \), the activity of each ion is the same. Thus

\[
K_w = 10^{-7} \times 10^{-7} = 10^{-14} \quad (3.7)
\]

In summary,

1. The effective concentration or molar activities of \( H^+ \) and \( OH^- \) in normal or pure water is 10^{-7} or 0.0000001, and the pH is 7.0.
2. Whenever the concentration or activity of \( H^+ \) increases, that of the soil decreases, and vice versa, to maintain the equilibrium constant.

DETERMINATION OF SOIL pH

Soil pH is commonly determined in the United States by mixing soil and water together in a 1:1 ratio. Fifty grams of air-dry soil that has passed a 2-mm screen is placed in a 100-ml beaker, and 50 ml of distilled water is added. The soil and water are stirred occasionally for an hour. Then the pH of the slurry is determined with a glass electrode and pH meter while the slurry is stirred. There are inexpensive kits that use indicator dyes to determine soil pH. These are accurate to about a half pH unit, which is sufficiently accurate to diagnosis many soil-fertility-related plant growth problems in the field.

Several factors affect the determination of soil pH. The concentration of \( H^+ \) near the exchange surfaces may be 100 to 1,000 times greater than in the bulk solution. If a soil-water suspension is allowed to settle, the pH as measured in the supernatant liquid will be higher than in the sediment layer. Because the pH value is affected by the extent to which the calomel electrode encounters clay and humus particles, the pH of the stirred suspension is measured.

Two other factors importantly affect the pH value of soils: the soil-water ratio and the presence of salts. An increase in each causes pH values to lower. In general, the more water added to a given amount of soil, the greater the dilution of the \( H^+ \), resulting in an increase in pH.

The soluble-salt content of the soil can affect the pH value, and this may be overcome by using CaCl_2, or KCl solutions instead of distilled water. When salt solutions in the range of 0.07 to 1 M are used, soil pH values may be 0.5 to 1.5 units lower than when they are measured with distilled water. The cations from salt solutions effectively put \( XA^+ \) (and perhaps some \( XH^+ \)) in solution along with some hydroxy-Al, depending on the degree of soil acidity. Subsequent hydrolysis of the exchangeable Al^3+ and hydroxy-
Al contributes to an increase of solution H⁺ (see equations 3.14 and 3.15). Soils with a net positive charge, however, will have a higher pH when KCl solutions are used, for hydroxyl ions are replaced by the chloride ions.

When the pH values of various soils are compared, it is important that they were determined by the same method. The KCl method is popular in tropical areas; in the tropics the values have been used to estimate lime needs. Soil pH values determined with water are popular in the United States. It must be realized, however, that the pH of an air-dry soil sample in the laboratory will be different from the pH that exists in the same soil in the field during the growing season. There will be differences in water and salt content, and roots and microorganisms will produce CO₂.

**THE SOIL pH CONTINUUM**

Many parent materials and young soils are alkaline, but old and intensely weathered soils are typically acid. This change in soil pH is related to and parallels the changes in the mineralogical and chemical properties that occur over time, as discussed in Chapter 2. A number of major processes account for the development of soil acidity: the loss of any lime (essentially CaCO₃) that may have been in the parent material, the loss of XCa..Na by leaching, the natural inputs of acidity from precipitation, nitrification, S oxidation, the production of CO₂, and the accumulation of hydroxy-Al, Al-organic complexes, and XA₁. Weathering of primary minerals is the major contributor to alkalinity through consumption of H⁺ and production of OH⁻ and the release of Ca⁺, Mg⁺, K⁺, and Na⁺.

**Alkaline Soils**

Sodic soils have 15% or more of XNa, and soil pH is controlled by the hydrolysis of XNa, of Na salts, or of both to produce a pH in the range of 8.5 to about 10. For example,

\[ \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} = 2\text{Na}^+ + \text{HCO}_3^- + \text{OH}^- \] (3.8)

When soils are calcareous and contain a few percent or more of CaCO₃, hydrolysis of CaCO₃ produces OH⁻ in a process similar to that shown in equation 3.8. The slow rate of dissolution of CaCO₃ produces fewer OH⁻ in calcareous soils compared to sodic soils. This means that calcareous soils have a maximum pH of about 8.3 when they are in equilibrium with the normal CO₂ content of the atmosphere. The dissolution of CO₂ released by respiring roots and microorganisms can produce sufficient carbonic acid to form local pockets of acidity in alkaline soils.

Nitrification, S oxidation, and other processes continually produce H⁺. The precipitation is naturally acidic when in equilibrium with the normal CO₂ content of the atmosphere, having a pH of 5.67. The precipitation is also a continuous source of acidity for soils. These additions of acidity are neutralized in alkaline soils; in calcareous soil, for example, the reaction is

\[ \text{CaCO}_3 + 2\text{H}^+ = \text{Ca}^{2+} + \text{H}_2\text{O} + \text{CO}_2 \] (3.9)

The H⁺ is converted to water. The alkaline nature of calcareous soils is maintained.

**Formation and Nature of Acid Soils**

Soil pH is strongly correlated with precipitation; that is, soils of arid and subhumid regions tend to be alkaline or neutral, and most soils of humid regions are acid. Let us look at the natural forces and processes that produce acid soils.

In a humid region the dissolution of salts in calcareous and other alkaline soils and their removal by leaching cause the soils to become nonsaline and noncalcareous. The soil at this point is 100% XCa..Na-saturated and will have a pH of about 7.5. Such soils, compared to calcareous soils, have lost much of their ability to neutralize acids. The H⁺ from the acids, which are constantly and naturally being added to the soil, gradually replace XCa..Na, and these cations are leached out of the soil with accompanying acid anions. In the situation shown in the following equation, there is leaching of Ca(NO₃)₂:

\[ \text{CaX} + 2\text{HNO}_3 = 2\text{HX} + \text{Ca(NO}_3)_2 \] (3.10)

The loss of some of the XCa..Na and the accumulation of some hydroxy-Al from weathering are accompanied by a decrease in pH. It is interesting that certain agricultural practices contribute to the development of soil acidity in a manner similar to natural processes. Nitric acid is produced in significant quantities by nitrification of the N that is fixed by legumes and the N that is added to soils in manure and ammonium fertilizers.

The natural inputs of acidity from precipitation, respiration, nitrification, and so forth continue after an alkaline soil has become acid through leaching. The greater the precipitation, the greater the acidic input both from precipitation and from associated biological activity. Acidity, on the other hand, stimulates weathering of primary minerals. Such weathering tends to generate alkalinity, as illustrated by the weathering of albite feldspar:

\[ \text{NaAlSi}_3\text{O}_8 + 4\text{H}_2\text{O} + 4\text{H}^+ = \text{Na}^+ + \text{Al}^{3+} + 3\text{Si(OH)}_4 \] (3.11)

Alkalinity increases because H⁺ is consumed and OH⁻ is produced. The Na (and Ca, Mg, and K) released by weathering can be adsorbed as XNa, and the Al is likely to be incorporated in silicate clay or to accumulate as hydroxy-Al. The abrasion pH, the pH of the ground mineral in water, that is, of albite, is 9 or 10. The abrasion pH of most of the weatherable minerals of the sand and silt fraction is between 7 and 11, and their weathering supplies the soil with alkali and alkaline earth cations (Na, K and Ca, Mg), which contribute to the maintenance of neutrality or alkalinity. At this point in soil evolution, the soil may be about neutral, and the soil may maintain a pH that fluctuates near 7. The longtime result of continued
leaching and weathering, however, is an acid soil. Most of the soils that
developed from late Wisconsin glacial materials were calcareous at the
surface about 10,000 years ago and are now acid at the surface and have
been leached of carbonates (lime) to a depth of about 1 to 2 meters where
the soil moisture regime is udic.

Most of the acidity of acid soils is associated with Al. The development
or accumulation of soil acidity parallels the mineral-weathering sequence in
which Al is released and accumulates in the soil. It was noted in Chapter 2
that hydroxy-Al accumulates in soils as they become acid, first as interlayer
Al, as coatings on clays and as complexes with organic matter, and, sec­
ondly, as exchangeable Al when soil pH declines below 5.5. The forms of
Al, without the hydration water, and their average charge as a function of
pH are shown in Figure 3.1.

The Al is in six coordination with H₂O, with OH⁻, or with both
(H₂O + OH⁻ = 6). When equations are written with Al fully hydrated, it is
easier to follow the changes that occur with pH changes. As pH declines
from 7 and as the hydroxy-Al is protonated, the Al serves as a sink for the
accumulation of H⁺ (acidity):

\[
\text{Al(OH)₃(3H₂O)} + 3\text{H}^+ = \text{Al}^3+(6\text{H₂O}) \quad (3.12)
\]

The increase in the average charge of the Al is associated with a decrease in
ECEC. An increase in pH, by contrast, causes the neutralization of acidity, a
decrease in the average charge of Al, and an increase in ECEC:

\[
\text{Al}^3+(6\text{H₂O}) + 3\text{OH}^- = \text{Al(OH)}₂⁺(3\text{H₂O}) + 3\text{H₂O} \quad (3.13)
\]

The hydrolysis of both forms of Al produces H⁺ ions that contribute to
the acidity of the soil solution:

\[
\text{Al}^{3+} + \text{H}_2\text{O} = \text{Al(OH)}^2⁺ + \text{H}^+ \quad (3.14)
\]

\[
\text{Al(OH)}^2⁺ + \text{H}_2\text{O} = \text{Al(OH)}_3^+ + \text{H} \quad (3.15)
\]

The acidity of acid soils is commonly divided into the weak and strong
fractions. The strong acidity is the exchangeable acidity that is composed
mainly of XAl and makes up a small part of the total acidity. The weak
acidity is strongly adsorbed Al associated with the hydroxy-Al of the clay
fraction and organic-Al complexes and makes up the great bulk of the total
acidity. The weak acidity is slow to neutralize and gives the soil its buffering
characteristics. During the natural development of acid soils from alkaline
parent material, there is a progressive accumulation of hydroxy-Al followed
by the accumulation of XAl as soil pH declines. When acid soils are limed,
this sequence of events is reversed and the strong or exchangeable acidity is
neutralized first, followed by the neutralization of hydroxy-Al as soil pH
increases.

**Exchangeable Cation Suite of Acid Soils**

The exchangeable cation suite of acid soils varies with pH. Acid soils with
pH 5.5 or more will have little, if any, XAl. The CEC will be saturated with
XCa..Na and typically Ca > Mg > K > Na. Monovalent hydrogen competes
very poorly for adsorption on the exchange sites of clays, and little, if any, is
present. Some H ions are adsorbed on the acidic groups of the SOM.
Adsorbed H is so strongly bonded onto pH-dependent charge sites that it
plays little, if any, role in soil acidity.

When the pH declines below 5.5, XAl becomes increasingly abundant
and Al saturation (XAl as a percentage of XAl..Na) increases. By contrast,
XCa..Na become increasingly less abundant, and saturation with XCa..Na
decreases. When these acid soils are leached with an unbuffered 1 N KCl
solution, the cations removed are for the most part Al, Ca, Mg, K, and Na
(see Table 3.1). Notice in Table 3.1 that the Al saturation of some horizons

**Table 3.1 Exchangeable Cations, Effective Cation Exchange Capacity,**

| Horizon | Exchangeable cations, meq/100g | ECEC, meq/100g | Al percent | pH |
|---------|--------------------------------|----------------|------------|
| Ap      | Ca  2.3 Mg 1.1 K 0.1 Na 0.3 Al 2.4 | 6.2            | 39         | 4.5 |
| Bt21    | Ca 3.2 Mg 1.4 K 0.2 Na 0.4 Al 8.1 | 13.3           | 61         | 4.6 |
| Bt22    | Ca 2.0 Mg 1.1 K 0.5 Na 0.2 Al 9.2 | 13.0           | 71         | 4.7 |
| C1      | Ca 1.3 Mg 1.5 K 0.7 Na 0.2 Al 10.7 | 14.4           | 74         | 4.7 |

*Source: Data for pedon 121, Soil Taxonomy, Soil Survey Staff, 1975.*
is over 70%. Sometimes Al saturation can exceed 90%, and XCa..Na saturation is less than 10%. These conditions produce a small supply of available XCa..Na and the likelihood of an Al toxicity.

An increase in soil acidity and the accompanying changes in two soil properties are shown in Figure 3.2. Notice that the decrease of XCa..Na was small compared to the large increase in titratable (buffer) acidity, which reflects the accumulation of hydroxy-Al with decreasing soil pH. Thus, the amount of lime needed to increase soil pH is greatly increased as soils become highly acid.

Soils with pH less than 4 are usually affected by the formation of strong acid, sulfuric acid for example, owing to the oxidation of S and the formation of H$_2$SO$_4$ as in mine spoil soils and in cat-clay soils that contain sulfides.

Summary Statement

In summary, the major factors controlling soil pH over the range of about 4 and less to 10 are

1. Below 4 and 3.5 to as low as 2, pH is controlled largely by the formation of strong acids.
2. In the range 4 to about 7.5, the hydrolysis of exchangeable and hydroxy forms of Al is the major source of H$^+$; exchangeable H is minor.
3. In the range 7.5 to 8.3, the pH in calcareous soils is controlled mostly by hydrolysis of CaCO$_3$.
4. In the range 8.5 to 10, pH is controlled largely by hydrolysis of Na$_2$CO$_3$ and exchangeable Na.
5. The production of CO$_2$ from root and microbial respiration may locally and temporarily lower the pH of alkaline soils a significant amount.

FIGURE 3.2 Titratable acidity and quantity of XCa..Na (exchangeable bases) as a function of pH in the Ap horizon of an Alfisol. (Data from Wolcott et al., 1965.)

**EXTREME WEATHERING EFFECTS ON pH AND CATION EXCHANGE**

The concept of increasing soil acidity over time through soil evolution and the generalized relationships between soil pH and some soil properties have been given. Two acid soils, however, can have the same pH and have greatly different soil fertility parameters. Thus the need to elaborate on the effects of extreme weathering on soil pH, ECEC, and the exchangeable cation suite as they relate to the fertility of soils.

**Low-Activity Clay versus Permanent-Charge Clay Soils**

Soils with clay fractions dominated by permanent charge 2:1 and 2:1:1 clay minerals have a high CEC that is due mostly to isomorphous substitution. Low-activity clay (LAC) soils have low CEC because kaolinite (1:1 clay), gibbsite, and other oxidic clays have a small pH-dependent charge. LAC soils have also been called variable-charge soils. Generally, Ultisols and Oxisols are LAC soils and the product of intensive or extreme weathering. The exchange properties of most of the mineral soils of the other soil orders are dominated by permanent-charge clays. Soils dominated by permanent-charge clays may evolve into LAC soils. It is commonly recognized that Alfisols may over time evolve into Ultisols, which may evolve into Oxisols. The CEC, the amount of XCa..Na, and the amount of XAl and Al saturation of the most weathered members of these three orders will be compared to illustrate their important differences.

Some of the oldest Alfisols in the glaciated regions of the United States have been sufficiently weathered and leached to have horizons with a pH of 5 or less and some Al saturation in all horizons to a depth of 2 meters or more. Clays are mostly 2:1 and 2:1:1 types, and the weathering of primary minerals still releases a significant quantity of alkali (Na and K) and alkaline earth cations (Ca and Mg). These soils, compared to LAC soils, have high CEC and a considerable quantity of XCa..Na. These Alfisols are moderately but not extremely weathered, and as a rule they have moderate to high fertility for agriculture and forestry.

With a significant increase in weathering and leaching, the pH may remain the same or actually increase, but other soil fertility parameters may change significantly as Alfisols evolve into Ultisols (LAC soils). Many Ultisols (pale great groups) have less than 10% weatherable minerals in the 20- to 200-micron fraction (coarse silt and fine sand) that can weather and release alkali and alkaline earth cations. There is a small ECEC that is highly Al-saturated, which means that there is a very small amount of XCa..Na. Notice in Figure 3.3 that the pH of the Ultisol is similar to that of the Alfisol, but the Ultisol has much less ECEC, a smaller amount of exchangeable Ca, Mg, and K, and a much greater Al saturation. Ultisols are naturally infertile soils with a tendency to have Al toxicity and to be deficient in Ca and Mg. They are extensive in the southeastern United States on the Piedmont and Coastal Plains where some landscapes are over 5 million years old.
Straddling the equator in the humid tropics of South America and Africa are large areas of Oxisols (Orthox). Oxisols are the most-weathered soils and have an oxic subsoil horizon that has a clay fraction with a CEC, determined at pH 7, of 16 meq/100 g or less. The oxic subsoil horizon consists of a mixture of oxidic clays with varying amounts of 1:1 clay and accessory, highly insoluble minerals such as quartz. Only a trace of feldspars, micas, and other weatherable minerals are present. In the most-weathered Orthox, the great group Acrorthox, weathering has virtually come to an end. Some part of the oxic horizon contains 1.5 meq or less of exchangeable cations (including Al) per 100 grams of clay that can be removed by leaching with unbuffered KC1. The A horizons of natural Acrorthox have enough organic matter to produce a net negative charge. The low content of organic matter in the lower part of the oxic horizon means that it may have a net positive charge. When soils become this weathered, the pH is higher than that of less-weathered soils, like Alfisols and Ultisols, for example. Such soils, however, have a very small amount of XCa...Na, and they may have an insufficient quantity of XA1 to produce Al toxicity. A comparison of three Oxisols with five Ultisols in Puerto Rico showed similar Al saturation but, because of the lower ECEC, the Oxisols contained only one-tenth as much XA1. This difference in amount of XA1 explains why Al toxicity is less of a problem for crop production on Oxisols than on Ultisols. Crop production on Oxisols is commonly limited by Ca and Mg deficiencies. A comparison of these important soil fertility parameters of an Oxisol with those of an Ultisol and an Alfisol is given in Figure 3.3. Shifting cultivation or slash-and-burn agriculture are popular systems for crop production on naturally infertile Ultisols and Oxisols. Some of the world’s most productive soils, however, are intensively or extremely weathered. Examples include the Ultisols of the Coastal Plains of the southeastern United States for production of cotton and corn; Oxisols in Hawaii for sugar cane and pineapples; Oxisols in Brazil for soybeans, wheat, sugar cane, and a wide variety of other crops (see Figure 3.4).

On the basis of the degree of weathering, mineral soils can be classified into (1) LAC soils with very low ECEC and very low XCa...Na, (2) LAC soils with low ECEC and low XCa...Na, and (3) permanent-charge soils with high ECEC and high XCa...Na. Thus, three different soils with the same pH can have greatly different fertility parameters and need different soil management, including liming practices. In summary, as soils evolve from being moderately weathered, as represented by Alfisols, to becoming extremely weathered, as represented by Oxisols, there is

1. A decrease in 2:1 and 2:1:1 clays and weatherable minerals and an increase in 1:1 and oxidic clays.

2. A decrease in ECEC and an increase in Al saturation.

3. An increase in soil pH.

4. A decline in soil fertility for production of most food crops.

These generalizations apply to soils developed in parent material of
mixed mineralogy because some young soils inherit low-activity clays. Some Oxisols, of the suborders Torrox and Ustox, may have a good supply of XCa..Na. Even so, the concept of a mineral-weathering sequence is well established and is useful in relating the differences in soil pH and cation exchange relations of several of the soil orders.

**SOIL FERTILITY AND SOIL CLASSIFICATION**

In *Soil Taxonomy* (Soil Survey Staff, 1975) the Alfisols and Ultisols are differentiated, in part, by whether base saturation as determined at pH 8.2 is less than 35% for Ultisols versus 35% or more for Alfisols in the lower part of the root zone (1.8 meters below the soil surface or 1.25 meters below the upper boundary of the argillic horizon). Base saturation in this context is defined as the sum of exchangeable Ca plus Mg plus K plus Na (XCa..Na) divided by the CEC as determined at pH 8.2. About forty years ago, when work on soil taxonomy was started, this criterion was developed because it was commonplace to determine the CEC at 7.0 or 8.2 and calculate the percentage of base saturation. The role of Al and the importance and nature of pH-dependent charge in soils were poorly understood. Now we recognize that in soils with permanent charge, the CEC varies much less with changes in pH, relatively speaking, than it does in soils with pH-dependent charge (LAC soils). If both an Alfisol and an Ultisol had a pH of 5.5 and neither had any XA1, both soils would have the ECEC saturated with XCa..Na and would be 100% XCa..Na-saturated, or base-saturated, according to the ECEC. At pH 8.2 the Ultisol would have a lower percentage of base saturation than the Alfisol because the relatively greater increase in CEC of the Ultisol would mean a relatively larger denominator in the equation. This criterion, then, which uses a base saturation percentage determined at a pH of 8.2, differentiates the less-weathered, permanent-charge and more naturally fertile Alfisols from the more-weathered and less naturally fertile Ultisols dominated by variable charge.

In Mollisols the mollic horizon must have 50% or more base saturation determined at pH 7.0. In effect, this means that Mollisols also consist mostly of permanent-charge clays, that there is less leaching of XCa..Na as compared to Alfisols, and in general, that Mollisols are naturally more fertile than Alfisols for the crops commonly grown. This does not negate the fact, however, that fertilization and liming may enable the Ultisols and Alfisols to become as productive as Mollisols. Because *Soil Taxonomy* uses percentage base saturation, it is important to understand the historical development of base saturation and its significance for soil classification. Now there is much less emphasis on percentage base saturation because the CEC of soils at their current pH is essentially 100% base-saturated unless there is some XA1. Below pH 5.5, XA1 saturation increases, and the XCa..Na (base) saturation decreases with decreasing pH. This feature can be expressed with reference to Al saturation.

**EFFECTS OF SOIL pH ON PLANT GROWTH**

Within the pH range of 4 to 10, the primary effect of soil pH on plant growth is not the (H+) or (OH-) per se but the associated chemical environments. In general, the major influence of pH is on ion activities that affect the toxicity of elements like Al and Mn or on nutrient availability as shown for mineral soils in Figure 3.5.

Nitrogen availability is maximum between pH 6 and 8 because the mineralization of N is maximum in this range. The availability of P in acid soil is reduced by precipitation and adsorption by Fe and Al. Calcium carbonate in calcareous soils reduces the solubility of calcium phosphorus compounds by increasing the activity of Ca2+ or by adsorption on CaCO3 surfaces. These examples specifically show how pH affects nutrient availability. More complete discussions for the various nutrients appear in later chapters. Here the goal is to focus on the specific causes of acid and alkaline soil infertility.

**Acid Soil Infertility**

Adsorbed hydroxy-Al is so strongly adsorbed that it is inactive and does not directly influence plant growth. The XA1 is less strongly adsorbed and, when Al saturation exceeds 60% in soils with a significant ECEC, there is likely to be 1 ppm or more of Al in solution. Many crop plants will suffer from Al toxicity. Soluble Al also reacts with P to reduce its availability. Dissolution of Mn at low pH may cause Mn toxicity, especially in soils with a high percentage of Mn minerals. In highly acid Ultisols, plant growth is
commonly limited by toxic levels of Al and Mn before Ca and Mg deficiencies occur. In Oxisols, however, the reverse tends to be true.

Molybdenum anions are strongly adsorbed on pH-dependent clays, and Mo tends to become less available and deficient in some acid soils. The availability of Mo is important for legumes because of the role Mo plays in N fixation.

Although a pH of less than 4 is generally considered to affect plant growth directly, the infection process of some Rhizobium strains is acid-sensitive, and only moderate acidity may limit the growth of certain legumes.

A summary of the toxic factors found to limit the growth of alfalfa in some acid soils from Arkansas and Georgia is given in Table 3.2. Plants show great diversity in tolerance to and resistance to toxic factors; the results for a crop like cowpeas, which is more tolerant of high levels of soluble Mn, would be different from those shown for alfalfa.

Studies have indicated that for a given pH, acid soils have less XA1 if they contain more organic matter. The Al is complexed or chelated by the SOM. Notice that in Table 3.1 the pH of the A and B horizons are similar, but Al saturation of the A horizon is only 39% compared to 60% to 70% for the B horizon. Many acid surface soils allow for good root development, although in subsoils with the same pH root growth is poor because of Al toxicity. This has been confirmed by adding organic matter to mixes of acid and mineral soils, noting the reduction in XA1, and observing that plants can grow well, as shown in Figure 3.6. In acid Histosols plants are unlikely to suffer from Al toxicity because of the high content of organic matter and the complexing of Al. Histosols also have a low content of mineral matter. These factors contribute to the availability of plant nutrients as affected by pH in Histosols, as shown in Figure 3.7.

Alkaline Soil Infertility

Calcareous soils are frequently productive for a wide range of crops including cotton, corn, sugar beet, potato, and many legumes. On the other hand,
Soil pH and Its Management

Soil pH

FIGURE 3.7 The relation between soil pH and the relative availability of plant nutrients in organic soils or Histosols. The wider the bar, the greater the availability. (From Lucas, 1982.)

many plants, including roses, pin oak, grapes, sorghum, and maple, are susceptible to Fe or Mn deficiencies. Zinc and P may also have low availability at high pH. Some alkaline soils with soluble salts may contain enough soluble B to produce B toxicity. The low availability of P in calcareous soils is discussed in Chapter 5.

USE OF LIME

Agricultural lime is a soil amendment consisting principally of CaCO₃ and to a lesser extent MgCO₃. It is used to neutralize soil acidity and furnish Ca and Mg for the growth of plants. Lime is commonly ground limestone with varying amounts of CaCO₃ and MgCO₃. Other liming materials include marl, chalk, basic slag, and basic oxygen furnace slag from iron and steel manufacturing, flue dust from cement plants, and refuse from sugar beet and paper mill plants.

Neutralization Reactions

The CaCO₃ and MgCO₃, in lime hydrolyze to produce OH⁻ as follows:

$$\text{CaCO}_3 + \text{H}_2\text{O} = \text{Ca}^{2+} + \text{OH}^- + \text{HCO}_3^- \quad (3.16)$$

The H⁺ in the soil solution comes for the most part from Al hydrolysis. The H⁺ reacts with the OH⁻ to form water. The overall reaction representing the neutralization of Al-derived soil acidity can be written as

$$2\text{AlX} + 3\text{CaCO}_3 + 3\text{H}_2\text{O} = 3\text{CaX} + 2\text{Al(OH)}_3 + 3\text{CO}_2 \quad (3.17)$$

If a soil with a pH less than 5 is limed to a pH of 7, there will be a progressive series of reactions. The exchangeable Al, hydrated as Al(6H₂O)³⁺, will hydrolyze first, followed by the hydroxy-Al forms, as follows:

$$\text{Al(6H}_2\text{O)}^3+ + \text{H}_2\text{O} = \text{Al(OH)(5H}_2\text{O)}^{2+} + \text{H}_3\text{O}^+ \quad (3.18)$$

$$\text{Al(OH)(5H}_2\text{O)}^{2+} + \text{H}_2\text{O} = \text{Al(OH)(4H}_2\text{O)}^{+} + \text{H}_2\text{O}^- \quad (3.19)$$

$$\text{Al(OH)(4H}_2\text{O)}^{+} + \text{H}_2\text{O} = \text{Al(OH)(3H}_2\text{O)}^2 + \text{H}_3\text{O}^+ \quad (3.20)$$

Each reaction is driven to the right as the H⁺ or H₃O⁺ is neutralized by the OH⁻ supplied by the lime. At pH of about 7, the hydroxy-Al is precipitated as Al(3H₂O)(OH). The various forms of Al that are in solution for neutralization, which depend on the pH, are given in Figure 3.1. The reduction of Al saturation with increasing pH is given in Figure 3.8.

The neutralization of acidity and the increase in pH cause an increase in the CEC and an average reduction in the charge of the various forms of

FIGURE 3.8 The effect of liming on soil pH and the percentage of aluminum saturation of an Ultisol. (Data from the annual report on tropical soils research of North Carolina State University, 1976.)
Soil pH and Its Management

Soil pH and Plant Growth Response

As we have noted, the pH of most soils is in the range of 4 to 10 and depends on the soil parent material and the changes that have occurred during soil genesis. The plants that have evolved in desert regions have adapted to thrive on neutral and alkaline soils, and many desert plants have great tolerance for soluble salts and soluble Na (halophytes). Plants that are native to the humid tropics, such as cassava, have a tolerance for soluble Al. Some temperate region plants that do well on highly acid soils, such as rhododendron, appear to be Al accumulators. Great genetic variation exists between species and cultivars, and this fact is used to develop new varieties that can better cope with stressful soil conditions related to soil pH. For example, moderately Al-tolerant wheat varieties have been developed for production on Oxisols in Brazil. The pH preferences of over 1500 plants were published by Spurway (1941).

From Table 3.3 it can be noted that oats grew quite well at pH 4.7 and about as well at 5 as at 5.7, 6.8, or 7.5. Corn or maize grew well over the range of 5.0 to 7.5. By contrast, barley failed to yield at 4.7 and attained maximum yield only when the pH was 6.8 or higher. Legumes, like clover and alfalfa, needed a pH of about 6.5 or higher to produce maximum yields. For all crops the relative average yields at pH 4.7 were only 32% compared to 98% at pH 6.8. Data of this nature are the basis for recom-mending lime to increase the pH of some acid soils to a particular value. For example, the pH may be 6.0 for the production of continuous corn. However, if corn is included in a rotation with alfalfa, the pH should be increased for profitable production of the alfalfa. The yield responses shown in Table 3.3 are, in part, related to the fact that the soil had high CEC and high XCa..Na. Thus, liming strategies and lime requirements depend, in part, on the chemical and mineralogical properties.

The Lime Requirement

The amount of lime required is affected by both crop and soil. Three different liming strategies or lime requirement methods can be recognized for three different kinds of mineral soil situations: very low ECEC and very low XCa..Na, low ECEC and low XCa..Na, and high ECEC and high XCa..Na.

Soils with Very Low ECEC and XCa..Na

The most weathered soils with both very low ECEC and XCa..Na tend to be most deficient in the Ca and Mg needed for cropping. Even though there may be high Al saturation, there tends to be too little XA1 to produce Al toxicity. The lime requirement is the amount needed to correct the deficiency of Ca and Mg and is essentially a fertilization problem. The goal is one of adding enough lime to correct the deficiency without adding so much that the availability of some other nutrients, like Zn and B, is reduced enough that the soil becomes deficient in them. Small applications of lime are desirable where lime materials are scarce and must be transported a long distance. The effects of very small lime applications, however, are short-lived.

Soils with Low ECEC and XCa..Na

Most LAC soils have both low ECEC and XCa..Na. There is sufficient ECEC and Al saturation to make Al toxicity the primary limitation in cropping. The lime requirement is the amount needed to remove the threat of Al toxicity for Al-intolerant cultivars. Experience has shown that this is an amount of lime equivalent to one and a half to two times the XA1, and the pH will be increased to about 5.5. This situation is common for most Ultisols and many Oxisols, which require only small amounts of lime. The total and available amounts of some micronutrients in LAC soils tend to be very small, and yields may be very sensitive to increases in pH that affect the availability of micronutrients. Notice in Figure 3.9 that a small amount of lime, 0.5 ton/ha or about the amount needed to neutralize the XA1, increased the yield of all four cultivars. Additional lime sharply decreased yield for two cultivars, but two others were little affected. The LAC soils tend to have small ECEC, and liming may produce a significant increase in the ECEC, as shown in Figure 3.10.

<table>
<thead>
<tr>
<th>Table 3.3 Relative Crop Yields versus Soil pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crop</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Alfalfa</td>
</tr>
<tr>
<td>Barley</td>
</tr>
<tr>
<td>Corn (maize)</td>
</tr>
<tr>
<td>Oats</td>
</tr>
<tr>
<td>Red clover</td>
</tr>
<tr>
<td>Soybeans</td>
</tr>
<tr>
<td>Sweet clover</td>
</tr>
<tr>
<td>Wheat</td>
</tr>
</tbody>
</table>

FIGURE 3.9 The response to liming of four different cassava cultivars grown on Oxisols in Colombia. Type 1, normal response; type 2, little response; type 3, little positive response followed by marked negative effect; type 4, marked initial response followed by drastic negative effect.

Soils with High ECEC and XCa Na

Deficiencies of Ca and Mg and aluminum toxicity are seldom a problem in acid-mineral soils with high ECEC and high XCa Na. These soils are typically no more than moderately weathered and have a significant content of primary minerals that can weather and supply both macronutrients and micronutrients. The soils are buffered against changes in availability of micronutrients with changes in soil pH, although an increase in pH may significantly affect micronutrient availability, commonly the case for Mo. For these soils a considerable change in pH may be associated with little change in yield, as indicated by the data in Table 3.3, and injury through overliming is unlikely. Thus, the lime requirement is the amount that will adjust the soil to some selected pH, based primarily on the needs of the crops that are produced.

Theoretically, the best way to determine the amount of lime to add to achieve a particular pH is to add varying amounts of lime and then determine the equilibrium pH (see Figure 3.11). A rapid method is needed in soil-testing labs where a large number of samples are tested. Commonly, a known amount of buffer solution with a given pH (7.0, 7.5, or 8.0) is mixed with a standard amount of soil. After a standard period of stirring and standing, the pH of the soil and buffer suspension is measured. The depression of pH from that of the buffer solution is equated with the amount of lime needed to increase soil pH to certain levels, as shown in Table 3.4.

The Shoemaker, McLean, and Pratt buffer method (SMP) is recommended for use in the North Central states and is used in about 18 states. The buffer consists of a combination of p-nitrophenol, triethanolamine, potassium chromate, calcium acetate, and calcium chloride. The buffer agent is adjusted to pH 7.5 with NaOH. This method is well suited for soils with appreciable buffer acidity and considerable XA1. In the southeastern

FIGURE 3.10 The effect of liming on soil pH and the effective cation exchange capacity of an Ultisol. (From Sanchez, Villachica, and Bundy, 1983, used by permission of the Soil Science Society of America.)

FIGURE 3.11 Soil pH as a function of added calcium carbonate. The soil on the left is the least buffered and the soil on the right is the most buffered. (Data from Shoemaker, McLean, and Pratt, 1961.)
The particle size of limestone is determined by the fineness of grinding. The dissolution of large particles, larger than those able to pass an 8-mesh screen, is so slow that they have little or no effect on soil pH. This fraction has an effective rating of zero. Particles passing an 8-mesh screen but retained on a 60-mesh screen are rated 50% effective. Particles passing a 60-mesh screen are rated 100% effective. The CCE and the calculated fineness factor are multiplied together to determine the effectiveness of a ground limestone or the effective calcium carbonate (ECC). If an entire sample passes the 8-mesh screen and 50% is retained on the 60-mesh screen, the fineness factor will be 75. For a sample with a CCE of 90, the ECC will be 67.5.

**Limestone as a Liming Material**

Most of the lime used to neutralize soil acidity is ground limestone. Limestone containing all CaCO₃ is calcitic, and limestone containing varying amounts of both CaCO₃ and MgCO₃ is dolomitic limestone. The two most important properties of ground limestone are its neutralizing value and its particle size. The first determines how much calcium can be neutralized by a given amount of limestone, the second how rapidly the limestone will dissolve and neutralize soil acids.

The neutralizing value of liming materials is easily determined by adding a known amount of lime to a known amount of acid and allowing neutralization to go to completion. The excess acid is titrated with a base, and the neutralizing value is equated to the amount of acid neutralized by the sample. The neutralizing value is expressed as the calcium carbonate equivalent (CCE), with pure CaCO₃ rated as 100. If a limestone contained only CaCO₃, and no impurities, the CCE would be 100. The CCE of other pure liming materials is given in Table 3.5. Wood ashes from hardwoods have a CCE of about 80 and are a good liming material for gardens.

**Table 3.5 Neutralizing Value of Liming Materials**

<table>
<thead>
<tr>
<th>Material</th>
<th>Calcium carbonate equivalent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium carbonate</td>
<td>100</td>
</tr>
<tr>
<td>Dolomite</td>
<td>109</td>
</tr>
<tr>
<td>Calcium hydroxide</td>
<td>136</td>
</tr>
<tr>
<td>Calcium oxide</td>
<td>179</td>
</tr>
<tr>
<td>Calcium silicate</td>
<td>86</td>
</tr>
</tbody>
</table>

United States, about four states use the Adams and Evans buffer method. The buffer reagent is a combination of p-nitrophenol, boric acid, potassium chloride, and potassium hydroxide adjusted to a pH of 8.0. The method is well suited to soils that have a low ECEC and little need for lime. The lime chloride, and potassium hydroxide adjusted to a pH of 8.0. The method is similarly determined with buffer solutions; however, liming to no more than pH of 5.2 is recommended because above pH 5.2 the availability of some of the micronutrients is reduced.

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**Use of Lime**

Lime can be applied at any time between the harvest of one crop and the planting of the next. The major considerations are the availability of the lime and the convenience of spreading. Lime is usually broadcast on the soil surface before tillage operations so that the soil and limestone are mixed to increase soil and lime contact. Calcium carbonate is quite insoluble, dissolves slowly, and has very limited downward mobility. Calcitic lime, however, dissolves more rapidly than dolomitic lime. The rate of neutralization is importantly related to fineness, uniformity of distribution in the soil, and the rate of diffusion of Ca from the lime particles to the sites of neutralization. A reasonable diffusion rate for Ca²⁺ is 0.35 cm in 100 days or 0.78 cm in 500 days. If limestone is applied at a rate of 2.7 tons/acre (6 tons/ha) in particles 0.60 mm in diameter (30 mesh), the average distance between particles of lime will be 1.04 cm. This statistic illustrates the importance of fineness and uniform distribution. Subsoils of many Ultisols and Oxisols limit root growth through Al toxicity, deficient Ca, or both. Deep incorporation of lime or downward movement of lime over a long period of time will help to increase yields by increasing the available water supply. The high cost of applying lime to subsoils and the lack of available equipment greatly limit the deep incorporation of lime.

Liming, in a sense, reverses some of the natural processes that make soils acidic. It is only natural to expect that once an acid soil has been limed, leaching and plant growth will eventually lower the pH again. Studies conducted in Ohio showed that the annual loss of Ca by leaching was greater than the Ca removed in harvested crops. When rotations include a
legume crop, liming of acid soils is required every three to five years in Illinois to maintain a satisfactory soil pH. In no-till systems there is limited mixing of soil by tillage operations, and surface applications of N fertilizers will tend to cause rapid acidification of the upper 3 inches of soil. The depth of soil sampling and the application of lime will need to be adjusted accordingly.

**Overliming**

Overliming can be a problem when soils have low CEC and a very small amount of buffer or reserve acidity, which easily allow an increase in pH. Overliming is most likely on soils with low ECEC, such as sandy soils with permanent-charge clays and LAC soils. Plant response to overliming is highly variable and depends on the cultivar. Overliming is expensive, and crops are injured primarily by the reduced availability of certain micronutrients.

**Effect of Flooding on Lime Needs**

Lime requirements for upland rice are determined in the same way as for other crops. Flooded or paddy rice, however, rarely needs lime because the consumption of H⁺ during reduction in anaerobic soil increases soil pH. In fact, most paddy soils when flooded have an equilibrium pH between 6.5 and 7.5. When the O₂ supply of the soil is exhausted, soil microorganisms are forced to use progressively weaker electron acceptors. After O₂, the next strongest electron acceptor available is nitrate, followed by MnO₂, Fe(OH)₃, and sulfate. Two examples of the reaction are

\[2\text{NO}_3^- + 10e^- + 12\text{H}^+ = \text{N}_2 + 6\text{H}_2\text{O}\]  
\[\text{MnO}_4^- + 2e^- + 4\text{H}^+ = \text{Mn}^{2+} + 2\text{H}_2\text{O}\]  (3.21)  (3.22)

**ACID RAIN INPUTS**

Unpolluted rain in equilibrium with the normal CO₂ content of the atmosphere has a pH of 5.6 (5.67 for pure water). A meter of this rain, which is about a year’s supply in humid regions, can dissolve about 320 to 400 pounds/acre of CaCO₃ (400 to 500 kg/ha), which is roughly equal to the amount of lime needed to maintain the pH of agricultural soils in Illinois. The burning of fossil fuel releases oxides of S and N which eventually return in the precipitation; they cause the pH of the precipitation to be less than 5.6 and to become an acid precipitation. In the northeastern United States the precipitation in 1981 contained an acid equivalent, from the effects of acid rain, of 28.8 pounds/acre of CaCO₃ (32.3 kg/ha). At Knoxville, Tennessee the annual figure has been reported to be 83 pounds/acre (93 kg/ha). By comparison, the acid-producing potential of the average N fertilizer application in the United States is 179 pounds/acre (201 kg/ha).

The fixation of N by alfalfa can amount to the equivalence of 500 pounds/acre or more of CaCO₃ (560 kg/ha). Since only part of the total precipitation is due to the acid rain component, it can be seen that acid rain contributes a small amount to the total acid input of soils in the humid region of United States.

**SOIL ACIDIFICATION**

Plants that prefer quite an acidic soil include rhododendron, blueberry, azalea, cassava, and tea (see Figure 3.12). Scab disease of Irish potatoes, caused by an actinomycete, has been controlled by maintaining an acid soil in which the organism is inactive. Large areas of land are not generally acidified in the way that liming is routinely used to increase the pH of large fields. Acidification is most frequently applied in nurseries and horticultural situations.

Sulfur and sulfur compounds are the most popular acidifying compounds. Elemental S is the most economical and is oxidized to sulfuric acid by bacteria, mainly *Thiobacillus*:

\[2\text{S} + 3\text{O}_2 + 2\text{H}_2\text{O} = 2\text{H}_2\text{SO}_4\]  (3.23)

Microbial catalysis promotes the reaction, which is irreversible and occurs slowly. Aluminum (and Fe) sulfate is commonly used in horticultural situations. The reaction is

\[\text{Al}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O} = 2\text{Al(OH)}_3 + 3\text{H}_2\text{SO}_4\]  (3.24)

The Al(OH)₃ precipitates, leaving the acid to acidify the soil. Some of the Al₂(SO₄)₃ may react with the soil to produce additional acidification:

\[\text{Al}_2(\text{SO}_4)_3 + 3\text{CaX} = \text{Al}_2\text{X}_3 + \text{CaSO}_4 + \text{H}_2\text{SO}_4\]  (3.25)

**FIGURE 3.12** Tea is a calcifuge and dislikes soils containing free calcium. Tea grows well on soils that have a pH of 4.5 and a high percentage of exchangeable aluminum saturation.
TABLE 3.6 Finely Ground Sulfur to Lower Plow Layer pH to about 6.5

<table>
<thead>
<tr>
<th>Broadcast, kg/ha*</th>
<th>Band, kg/ha</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Soil pH</strong></td>
<td><strong>Sandy soil</strong></td>
</tr>
<tr>
<td>7.5</td>
<td>400-600</td>
</tr>
<tr>
<td>8.0</td>
<td>1000-1500</td>
</tr>
</tbody>
</table>

*Multiply by 0.892 for pounds per acre.

Source: Jones, 1982, used by permission of Prentice-Hall, Englewood Cliffs, N.J.

Gypsum, CaSO₄, has been found to be effective in increasing sorghum yields on calcareous soils in Kansas. The major benefit appeared to be increased availability of Zn. Calcareous soils are not usually made acid because costs are high. When soils are leached of salts, the requirements for S are reasonable, allowing for economical soil acidification. Sometimes S is applied as a fertilizer to increase acidity in a small fraction of the soil mass. The S is applied in a band where early root growth occurs. Suggested rates of S for soil acidification are given in Table 3.6.

Acid organic materials may be beneficial, but they are not practical where a significant decrease in soil pH is desired. Most N fertilizers increase soil acidity, and their effects on soil acidity are discussed in the next chapter.

REFERENCES


Nitrogen is a part of all living cells. In plants N is a constituent of chlorophyll, all proteins including the enzymes, and many other compounds. Of the nutrients removed from the soil by plants, only H atoms are present in a greater number than N atoms. A lack of N causes leaves to become yellow and stunts growth. Conversely, with an adequate supply of N, vegetative growth is rapid and foliage dark green in color. The large need of plants for N and the limited ability of soils to supply available N cause N to be the most limiting nutrient for crop production on a global basis.

INVENTORY OF THE EARTH'S NITROGEN

About 98% of the world's N exists in the lithosphere (see Table 4.1). Nitrogen is a component of coal and many other rocks and minerals. Ammonium is fixed in the clays of sediments and in mica minerals of rocks in the same voids where K is fixed. The second largest N reservoir is the atmosphere, which contains about 2% of the total. Most of the N in the atmosphere is believed to have originated from the lithosphere, and even today volcanic gases contribute N to the atmosphere. By contrast, the amount of N in soils is very small, being only 1/5 000th of that of the atmosphere. Many productive mineral soils contain about 4 000 kg/ha (or about 4 000 pounds/acre) in the furrow slice. About 90% of the soil N is unavailable in organic matter, and most of the remainder exists as fixed ammonium in clays. At any one instant about 1% or less of the total N in soils is available to plants and microorganisms as nitrate or exchangeable ammonium. The amount of N in the biosphere, like that in the soil, is a very small part of the total, but this N is very mobile and life depends on it.

THE SOIL NITROGEN CYCLE

Although the great bulk of the earth's N is in the rocks and sediments of the lithosphere, the most important reservoir of N for plants and animals is the atmosphere. Pure, dry air is about 78% N by volume, which means that it can supply 77 350 metric tons/ha (34 500 tons/acre) of N. Considering the average biological need for N, the atmosphere contains about a million years' supply. The annual rate of removal of N from the atmosphere by fixation and its addition to soils, is approximately balanced by an equal amount of N returned to the atmosphere by denitrification. Thus, over time, a quasi-equilibrium exists between the amount of N in the atmosphere and the amount of N in soils on a global basis.

The N cycle in soils is a part of the earth's overall N cycle. The net effect of this overall cycle is that N circulates through the soil and eventually returns to the atmosphere through a series of processes: fixation, mineralization, nitrification, immobilization, and denitrification. These processes, as shown in Figure 4.1, can be viewed as a series of irreversible reactions that are mediated by microbial catalysis and that shuttle N back and forth at the discretion of the microorganisms.

Nonbiological Fixation

Some N fixation is nonbiological and is caused by lightning discharges. Other N in the atmosphere originates from the burning of fossil fuels and forests and from the emission of magmatic gases. This N is added to soils as nitrate and ammonium in precipitation. It has been estimated that of the 12.8 kg/ha (11.4 pounds/acre) of N naturally added to soils annually, 72% comes from biological N fixation and 28% from the other sources.
**Biological Nitrogen Fixation**

Considering the large amount of N added to soils by biological fixation and the importance of N in plant growth, biological N fixation can be considered one of the most important processes in nature. In a way, it is similar to photosynthesis. There is a ubiquitous need for N in nature, and in every ecological niche there are microorganisms that fix N. The great diversity of fixation sites and organisms is illustrated by a flooded rice field (paddy), as shown in Figure 4.2.

Biological N fixation systems have been grouped into four categories. These systems, the representative organisms involved, and the amounts of N fixed annually are given in Table 4.2.

**Symbiotic Fixation**

In symbiotic systems the host plant supplies the N-fixing organisms with fixed C, a photosynthate, and the host plants benefit from the N fixed. The N-fixing microorganisms are bacteria, actinomycetes, and blue-green algae.
66  

Soil and Fertilizer Nitrogen

TABLE 4.2 Relative Annual Rates of Nitrogen Fixation

<table>
<thead>
<tr>
<th>Symbiotic systems</th>
<th>N, fixed, kg/ha</th>
</tr>
</thead>
<tbody>
<tr>
<td>Legumes, bacteria</td>
<td></td>
</tr>
<tr>
<td>Alfalfa</td>
<td>128-600</td>
</tr>
<tr>
<td>Lupins</td>
<td>150-169</td>
</tr>
<tr>
<td>Clover</td>
<td>104-160</td>
</tr>
<tr>
<td>Soybeans</td>
<td>57-94</td>
</tr>
<tr>
<td>Cowpeas</td>
<td>84</td>
</tr>
<tr>
<td>Nonlegume-nodulated, actinomycetes</td>
<td></td>
</tr>
<tr>
<td><em>Alnus</em> (alder)</td>
<td>40-300</td>
</tr>
<tr>
<td><em>Ceanothus</em></td>
<td>60</td>
</tr>
<tr>
<td>Plant-algal associations</td>
<td></td>
</tr>
<tr>
<td>Lichens</td>
<td>39-84</td>
</tr>
<tr>
<td>Gunnera</td>
<td>12-21</td>
</tr>
<tr>
<td><em>Azollas</em></td>
<td>313</td>
</tr>
<tr>
<td>Nonsymbiotic systems, free-living organisms</td>
<td></td>
</tr>
<tr>
<td>Blue-green algae</td>
<td>25</td>
</tr>
<tr>
<td><em>Azotobacter</em></td>
<td>0.3</td>
</tr>
<tr>
<td><em>Clostridium pasteurianum</em></td>
<td>0.1-0.5</td>
</tr>
</tbody>
</table>

Source: Data from various sources as given by Evans and Barber, 1977.

(cyanobacteria). All these organisms, which are called diazotrophs, have a very simple cell structure without a nucleus and synthesize the enzyme nitrogenase. Dinitrogen, N₂, is reduced to NH₃ (from valence of 0 to -3). In a chemical plant N is fixed by using high temperature and pressure. The diazotrophs accomplish the same feat at ambient temperature and atmospheric pressure. Biological N fixation is not free because the energy for fixation is derived from a photosynthate. For soybeans it has been estimated that the energy used to fix N is equal to the energy in about 20 bushels/ha of grain or 8 bushels/acre.

Since Greek and Roman times the use of legumes to increase soil fertility has been a common practice. Hermann Hellriegel and H. Wilfarth of Germany in 1888 found that nonleguminous crops, such as barley and oats, grew in sand culture in direct response to the amount of N supplied. For legumes, however, there was no relation between their growth and the addition of fertilizer N. In this way the link between nodules on legume roots and N fixation was discovered. Legumes are dicots that develop a symbiotic N fixation relation with bacteria of the genus *Rhizobium*. It is estimated that over half of the biologically fixed N added to the earth is due to legume symbioses in agricultural production, and this is equal to two times the amount of N added to soils in fertilizers. The importance of legumes in agriculture is shown by their high rates of N fixation (see Table 4.2).

*Rhizobia* tend to be host-specific, although some infect several different hosts, and more than one species may infect a single plant. The bacteria can live in the soil for long periods of time in a nonsymbiotic state. However, to ensure that the proper species is present, farmers usually plant seed inoculated with bacteria that will form an efficient N-fixing system with the legume. Bacteria living near the root of a host plant apparently have a recognition mechanism that triggers a host-bacteria recognition event. The presence of the bacteria adjacent to a root hair causes branching and curling, followed by the invasion of the bacteria. An infection thread is formed and penetrates the root as the bacteria continue to divide and multiply. The plant's response is to form a tumorous nodule containing cells that become packed with *bacteroids*, which are bacteria that have undergone morphological and metabolic change. The bacteroids are supplied with a photosynthetic light energy source, which is used for respiration and N-fixing activities. The N fixed as ammonia is excreted from the bacteroids to the legume cells and is then transported as C·N compounds in the vascular system. The relationship is one of true symbiosis, since there is a direct connection between the host and symbiont for the transfer of photosynthate to the symbiont and for the transfer of fixed N to the host (see Figure 4.3).

*Rhizobia* form associations with many trees. However, the most important symbiotic relationships with dicotyledonous woody shrubs and trees are those with certain actinomycetes of the *Frankia* genus. The infection of roots and nodule formation have similarities to the legume-rhizobia systems. *Alnus* is a pioneer genus of large trees that grow in the Rocky Mountains and on the Pacific slope. They are found on freshly exposed
parent materials and are an important N contributor in the early stages of soil formation. After clear-cutting of Douglas fir forests in the Pacific Northwest of the United States, *Ceanothus-Frankia* symbiosis contributes a significant amount of N for the regeneration of the Douglas fir forests (see Table 4.2). Nodules on the roots of *Ceanothus*, a showy genus of shrubs and woody vines, are shown in Figure 4.4.

One of the best-known symbiotic algal N-fixing associations consists of blue-green algae and the fungi in lichens. The fungi fix N that benefits the fungi, and the algae appear to benefit from the biotin and thiamine produced by the fungi. In wet and tropical environments blue-green algae invade the stems of herbaceous dicots of the *Gunnera* genus. Glands are formed on the stems, similar to nodules on roots, and the algae fix N in the glands. The most important symbiotic algal association for agriculture is the *Azolla-Anabaena* association, which is used for rice production in flooded fields. The azolla is a floating fern with roots that penetrate below the water surface (see Figure 4.2). The anabaenas, which are blue-green algae, live in the fronds of the fern. There is no vascular connection between the two organisms. Up to 60 percent of the fern's N comes from ammonia produced by the anabaenas. The benefits derived from the association by the algae are unknown. The rapid growth of biomass that is possible under favorable conditions allows for the production of large amounts of green manure rich in N (see Table 4.2). In rice paddies the N is released to the rice when the organic matter is mineralized. The floating biomass can also be skimmed off the surface of ponds and used as a high-protein animal feed. Thus, great diversity exists in the symbiotic N-fixing systems that account for the addition of large amounts of N to soils in natural ecosystems as well as in agricultural fields.

**Nonsymbiotic Fixation**

Several kinds of heterotrophic bacteria are N fixers and are of minor importance in agricultural soils. These heterotrophs must compete with other soil organisms for the limited supply of organic substrates that are available for their C and energy. *Azotobacter* and *Beijernickia* are aerobes and occur in temperate and tropical soils, respectively. *Clostridium* is a heterotrophic bacterium that thrives only under anaerobic conditions. *Azospirillum* is a bacterium that has been found to live in the rhizosphere of the roots of tropical grasses and fix some N.

Blue-green algae live near the soil surface and fix N nonsymbiotically. They are photosynthetic and need not compete for the limited supply of organic substrates. However, because of shading by the soil surface and drying at the surface, they are quite inactive in most soils. In rice paddies and other flooded areas, blue-green algae in the water fix large amounts of N and contribute significantly to the N needs of plants.

**Mineralization**

All the mineral N added to soils by fixation or fertilizer is subject to uptake by roots and microorganisms and to conversion into organic soil N. The organic N is reconverted to mineral form by a wide variety of heterotrophic organisms — bacteria, fungi, and actinomycetes — in a process called mineralization. These organisms secrete extracellular enzymes that decompose proteins. In many well-drained mineral soils about 2% of the organic N is mineralized annually. For soils with 0.05% to 0.10% N, this amounts to 25 to 50 kg/ha (22 to 45 pounds/acre) for a 20-cm-thick plow layer.

Since ammonia, NH₃, is the first mineral form produced, the process has also been called ammonification. Ammonia is a gas and can be lost from the soil by volatilization when mineralization occurs on the soil surface. Much of this NH₃ may be absorbed by leaves if there is a plant canopy. Conversely, near cattle feedlots and certain industrial sites, the atmosphere may be enriched with NH₃, and a significant amount of NH₃ may be adsorbed by nearby soils and lakes. The ammonia molecule is polar and readily combines with a proton to form ammonium, NH₄⁺ (see Figure 4.1). Ammonia is stabilized in acid soils, but in alkaline soils few protons are available and volatilization increases as the soil pH increases.

**Factors Affecting Mineralization**

The amount of N mineralized tends to be related to the amount of SOM and environmental conditions. About 1% to 4% of the total N is mineralized per year, unless the soil is too cold or too dry for microbial activity.
The optimum water content for mineralization in well-aerated soils is 50% to 75% of the water-holding capacity. After flooding of aerobic soils, the anaerobic organisms take over and mineralization may be little affected. Soils that tend to mineralize a good amount of N when aerated will tend to mineralize a good amount of N when flooded. Thus, rice farmers commonly apply animal manure before flooding and get a good yield of N from mineralization. Drying the soil below the optimum moisture content reduces mineralization and reduces the amount of N available. The longer the dry period, the stronger the anaerobic organisms take over and mineralization may be little affected.

Soils that tend to mineralize a good amount of N when aerated will tend to mineralize a good amount of N when flooded. Thus, rice farmers commonly apply animal manure before flooding and get a good yield of N from mineralization. Drying the soil below the optimum moisture content reduces mineralization and reduces the amount of N available. The longer the dry period, the stronger the anaerobic organisms take over and mineralization may be little affected. It has been suggested that rapid mineralization in savannah soils after a long dry period produces much NO₃–, and that this substance contributes to the loss of XCa...Na by leaching before plants reestablish and actively absorb the anions formed during the flush period. Freezing followed by thawing also stimulates mineralization.

The optimum temperature for N mineralization is 40 to 60 degrees C. In compost piles the thermophiles take over and may be active at temperatures exceeding 65 degrees. In general, temperatures favorable for root growth are favorable for mineralization. Early-growing crops that are planted in wet and cold soils may be stimulated by early applications of N fertilizer.

Mineralization is affected by enzyme activity. The fact that there is a strong positive correlation between the clay content of soils and SOM content suggests that clays may inactivate the proteolytic enzymes in some way.

**Ammonium Fixation**

The ammonium formed by mineralization appears in the soil solution and establishes an equilibrium with the exchangeable ammonium. The similarity in ionic radius and energy of hydration of NH₄⁺ and K⁺ causes the ions to compete for fixation sites in micaceous minerals. The upper limit of fixation in field soils is about 1 to 2 meq/100 g of soil. About 10 percent of the N in soils may be fixed, and its distribution in the soil profile parallels that of the clay. Just as with K⁺, an equilibrium for NH₄⁺ exists between the ions that are exchangeable and those that are in solution, and between ions that are exchangeable and those that are fixed. Although considerable fixed NH₄⁺ may exist in soils, it is of minor importance in meeting the daily N needs of growing plants.

**Nitrification**

The starting point for nitrification is the NH₄⁺ produced by mineralization. In aerobic soils with a pH of 6.0 or higher, NH₄⁺ is rapidly oxidized by specialized chemoautotrophic bacteria, which are widespread in nature.

The process is nitrification, and it occurs in two steps. Bacteria of the genus *Nitrosomonas* and several other bacteria oxidize the NH₄⁺ to nitrite as follows:

\[
2\text{NH}_4^+ + 3\text{O}_2 \rightarrow 2\text{NO}_2^- + 2\text{H}_2\text{O} + 4\text{H}^+ \quad (4.1)
\]

The valence of N goes from –3 to +3, and the energy released is sufficient to enable bacteria to fix all the C they need from CO₂. Notice that the first step in nitrification produces protons and is a natural soil acidification process. Nitrification may significantly lower soil pH when large amounts of ammonium fertilizers are applied. Little if any nitrite accumulates because the nitrite excreted by *Nitrosomonas* is quickly picked up by bacteria of another genus, *Nitrobacter*, and oxidized to nitrate as follows:

\[
2\text{NO}_2^- + \text{O}_2 \rightarrow 2\text{NO}_3^- \quad (4.2)
\]

The valence of N goes from +3 to +5. Nitrate is stable in the soil solution. However, it remains soluble and is subject to loss from soils by leaching.

**Factors Affecting Nitrification**

Ammonification or N mineralization is quite insensitive to the soil environment, and the production of NH₄⁺ in soils is quite ubiquitous. Nitrification is much more environmentally dependent. Whether the NH₄⁺ accumulates or is nitrified depends largely on acidity and the O₂ supply. The nitrifiers are sensitive to H⁺. Their activity is reduced below pH 6.0 and becomes negligible below 5.0. Some soils with pH 4.0 or less, however, may contain some NO₃–, and it appears that the organisms derived from acid soils are frequently more tolerant of H⁺. Optimum pH is 6.6 to 8.0 or higher.

All nitrifiers need O₂, and nitrification ceases in its absence. For this reason, nitrification is sensitive to soil structure and water content. In aerobic soils, optimum water content is generally 50% to 67% of the water-holding capacity. Oxygen diffuses very slowly through water so that nitrification may be occurring in the outer part of an aggregate at the same time that there is denitrification in the interior. Waterlogging or flooding suppresses nitrification, and the NH₄⁺ produced in rice paddies tends to be absorbed by roots and not be nitrified.

Nitrification is temperature-sensitive and occurs mostly in the range 5 to 40 degrees C with an optimum between 30 and 35 degrees.

In summary, nitrification occurs rapidly in most well-drained and moist agricultural soils with a pH 6.0 or higher. NO₃– is the main form of N absorbed by roots. In acid forest soils nitrification is commonly inhibited by acidity, and it is believed that plants in forests absorb much of the N as NH₄⁺. Under the anaerobic conditions of flooded soils, the lack of O₂ inhibits nitrification, and NH₄⁺ is the predominant form of N absorbed.
After the uptake of $\text{NH}_4^+$ and $\text{NO}_3^-$ by roots and the heterotrophic microorganisms, the conversion of the mineral N into organic N is called immobilization (see Figure 4.1). Mineralization and immobilization are two opposing and interdependent processes that strongly control the supply of available nitrogen in soils. Nitrification can occur between mineralization and immobilization, controlling whether the available form of N will be $\text{NH}_4^+$ or $\text{NO}_3^-$. The available N is absorbed by both the heterotrophs and plant roots; thus, both are benefited. Moreover, root exudates and sloughed-off root cells provide a readily available source of energy and C for the heterotrophs. The heterotrophs are therefore additionally benefited by the plants. Soil conditions favorable for growth of the heterotrophs are favorable for plant growth, which means that there is a strong correlation between mineralization and plant immobilization of N. As a consequence, mineralization and immobilization comprise a subcycle of the soil's N cycle, one that governs the level of available N in unfertilized soils at any given instant. Since mineralization and immobilization occur simultaneously, plants may have an adequate supply of available N, even though soil tests indicate that little N is available at a given instant.

**Carbon-to-Nitrogen Ratios**

Mineralization is carried out by a wide variety of heterotrophic organisms that have a dietary need for both C and N. The $\text{NH}_4^+$ produced by mineralization represents an amount of N in the substrate in excess of microbial needs. The C : N ratio ($%\text{C}/%\text{N}$) of the substrate provides an indication of the adequacy of N for the mineralizers and the amount of N that will appear as excess. The SOM has a C : N ratio typically in the range of 10 to 12 : 1, and when SOM is mineralized it provides an excess of N, which can be used by roots. Residues of legume crops and farm manures, also provide an amount of N in excess of mineralization needs and a surplus that can be used by growing crops. As the C : N ratio of substrates increases, there is relatively less N for the C, and substrates with ratios above 30 are not likely to contain enough N to meet microbial needs. These materials in soils are decomposed through the reuse of any mineralized N by the decomposers or mineralizers, and plant roots may be starved for N. During the decomposition or rotting of substrates, there is a continual loss of C as respiratory CO$_2$, with an accompanying increase in the N percentage and a decrease in the C : N ratio (see Figure 4.5). When the ratio decreases below 30, excess N from mineralization will again appear, and the period of N stress for plants disappears.

Many materials added to soils, such as straw and sawdust, have C : N ratios of about 80 and 400, respectively. Their addition to soils before planting can create a period of N starvation for crops. It requires about 20 pounds of N per ton of straw to supply the mineralization N deficit of the straw and prevent a period of net immobilization of N.

**Denitrification**

Denitrification is the chemical reduction of nitrate and nitrite to gaseous forms: nitric oxide, nitrous oxide, and dinitrogen:

$$\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2 \text{O} \rightarrow \text{N}_2$$

The valence of N decreases from 5 or 3 to 2, 1 or 0. The capacity for true denitrification, the formation of N$_2$, is restricted to certain chemoheterotrophic bacteria. These bacteria are aerobes. Under anaerobic condition, however, they use NO$_3^-$ for their electron acceptor instead of O$_2$. They need a decomposable source of organic matter to supply C and electrons. Thus, the two most important conditions needed for denitrification are an anaerobic environment and a C source.

**Factors Affecting Denitrification**

Because a lack of O$_2$ favors the chemical reduction of nitrate and nitrite to gaseous forms, denitrification is affected by soil structure and water content, but conversely to nitrification. Anaerobic microenvironments are cre-
ated in soils when the \( O_2 \) demand exceeds the supply. A significant amount of denitrification and loss of gaseous N occur in many well-drained soils through denitrification in the interiors of aggregates. Flooding creates conditions very conducive to denitrification, if nitrate is present. Since \( NO_3^- \) is produced in an aerobic environment and denitrification occurs in an anaerobic environment, denitrification is enhanced by the alternate wetting and drying of soils. Paddy rice fields are very vulnerable to denitrification losses in rain-fed systems because fields are likely alternately to dry and resaturate.

Acidity affects both the rate of denitrification and the type of gas produced. Denitrifiers are sensitive to \( H^+ \), although denitrification has been reported to be rapid in a soil with a pH of 4.7. Above pH 6.0 the major gas produced is \( N_2 \), and in more acid environments the liberation of NO becomes pronounced. Nitrification is very slow at 2 degrees C and increases to a maximum at 25 degrees or higher. Significant denitrification can occur when it is too cold for crops to be growing. During late fall and very early spring in the temperate regions, there is a substantial loss of N through denitrification.

The growth of plant roots may inhibit denitrification by serving as a sink for \( NO_3^- \) and creating drier soil with a greater \( O_2 \) diffusion rate. On the other hand, root exudates provide a source of carbon and deplete \( O_2 \) near their surfaces to stimulate denitrification. When \( NO_3^- \) moves by leaching below the zone of biological activity, or \( C \) source, it is beyond the sphere where denitrification occurs; it may remain unchanged and move farther downward, and there it pollutes the groundwater. In agriculture, denitrification represents a large loss of nitrogen, and there are few practical things that can be done to prevent it.

**Summary Statement**

Nitrogen is continually added to soils by fixation, precipitation and gaseous adsorption. The N content of the soil, however, does not increase continually but tends to reach an equilibrium or steady state where additions are balanced by losses. The losses or leaks from the cycle are due to volatilization, leaching, and denitrification. As a result of these losses, there is a need for a constant influx of N to maintain a steady N content. Soils do not become so enriched with N (except maybe some Histosols) that they produce high grain yields for decades without N fertilizer.

There is great variation in the partitioning of added fertilizer N as climate, soils, crops, yields, and soil management practices vary. Some estimates of the fate of N fertilizer are 30% to 70% removed in harvested crop, 5% to 10% leaching loss, 10% to 30% gaseous loss, and 10% to 40% incorporated into soil organic matter. As a general rule, 50% of fertilizer N is absorbed by the crop; 25% is lost by denitrification, leaching, and volatilization; and 25% remains in the soil as mineral N or is incorporated into new organic matter.

**Nitrogen Uptake**

Both \( NH_4^+ \) and \( NO_3^- \) are commonly present in soil solutions, and both are readily taken up by roots. The rapid nitrification rates in well-aerated soils with pH 6 to 8 means, however, that plants absorb predominately \( NO_3^- \). Nitrate remains soluble in the soil solution and is readily moved to plant roots by a mass flow of water. It has been estimated that for corn 79%, 20% and 1% of the nitrogen at root surfaces are there through mass flow, diffusion, and root interception, respectively.

In some soils acidity or anoxia has prevented nitrification, and the predominant form of available N is \( NH_4^+ \). In general, calcifuge plants, which naturally grow under acid conditions, prefer \( NH_4^+ \). The calcioles, plants with a wide pH tolerance, prefer \( NO_3^- \). At the extreme are cranberry plants, which are unable to absorb or metabolize \( NO_3^- \). Rice grown on flooded soil, where nitrification tends to be inhibited, is more productive with ammonium than with nitrate fertilizer. It has not been proved, however, that \( NH_4^+ \) is clearly the most efficient form of N for rice.

When plants absorb N mainly as \( NH_4^+ \), there is an excess of cation uptake compared to anion uptake, and \( H^+ \) is excreted, which decreases the pH in the rhizosphere. When uptake is mainly \( NO_3^- \), there is an excess uptake of anions, and \( OH^- \) is excreted, which increases the pH of the rhizosphere. In a respiring rhizosphere the hydroxyl reacts with carbon dioxide to form \( HCO_3^- \). The question whether \( NO_3^- \) or \( NH_4^+ \) is the superior or more efficient form of N for plants is still unanswered.

**Basis of Nitrogen Fertilizer Recommendations**

Most agricultural soils are at or near a steady state in their total N content, which varies slightly from year to year. The variations in mineralization, denitrification, and leaching rates from one soil to another and from one year to another complicate the use of a test for total soil N or N mineralization rate as a basis for making N fertilizer recommendations. Recommendations for N fertilizers are based primarily on yield response data obtained from N fertilizer rate experiments.

**Grain Crops**

Fertilizer rate experiments in Illinois were used to develop Table 4.3, which gives the economically optimum corn yields and optimum N rates per bushel of corn produced. The economically optimum N fertilizer rate for corn is based on a corn:N price ratio—the price of a bushel of corn divided by the price of a pound of fertilizer N. Corn grown at Brownstown had the least ability to absorb N fertilizer and profitably increase yields; the economic optimum yield was 83 bushels/acre with a corn:N ratio of 10. Soils at Urbana were the best for corn production; the economically optimum yield was 171 bushels/acre with a corn:N ratio of 10. Notice in Table
TABLE 4.3 Economic Optimum Yield* and Optimum Nitrogen Rate Experimentally Determined for Continuous Corn at Four Locations in Illinois

<table>
<thead>
<tr>
<th>Location</th>
<th>Yield</th>
<th>Rate</th>
<th>Yield</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brownstown</td>
<td>83</td>
<td>1.30</td>
<td>86</td>
<td>1.47</td>
</tr>
<tr>
<td>Carthage</td>
<td>144</td>
<td>1.22</td>
<td>147</td>
<td>1.29</td>
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<tr>
<td>DeKalb</td>
<td>141</td>
<td>1.28</td>
<td>143</td>
<td>1.31</td>
</tr>
<tr>
<td>Urbana</td>
<td>171</td>
<td>1.17</td>
<td>173</td>
<td>1.24</td>
</tr>
</tbody>
</table>

*Yield in bushels per acre and optimum N rate in pounds of nitrogen per bushel.

Source: Data from Illinois Agronomy Handbook, 1986, Urbana, Ill.

4.3 that it took less N per bushel of yield to produce the optimum yield at Urbana as compared to Brownstown: 1.17 versus 1.3. Based on the optimum N rate—pounds of N per bushel of yield—multiplied by the optimum economic yield, the amount of N fertilizer recommended for Brownstown is 108 (83 X 1.3) pounds per acre of N for a corn : N ratio of 10. For Urbana the N fertilizer recommendation is 200 (171 X 1.17) pounds/acre of N. The basic equation for the N fertilizer recommendation is:

\[ \text{pounds N per acre} = \text{YG} \times \text{optimum N rate} \] (4.3)

where YG is the yield goal (bushels per acre) and the optimum N rate is the pounds of N needed per bushel of yield to produce the economically optimum yield. Some examples of equations for N fertilizer recommendation for corn and sorghum production in Iowa are given in Table 4.4.

The basic N fertilizer recommendation for corn is modified by consideration of the previous crop and the amount of manure to be applied. The equation used in Michigan for corn N recommendations as pounds per acre is:

\[ N = [(\text{YG} \times 1.36) - 27] - [40 + (0.6 \times \% \text{ls})] - (4 \times \text{fm}) \] (4.4)

The ls is for legume stand, which is evaluated as the number of alfalfa or clover plants per unit area. If an alfalfa stand was rated very good, 100%, then 100 pounds \([40 + (0.6 \times 100)]\) would be subtracted to account for the N contribution of the previous alfalfa crop. The fm refers to tons of farm manure applied per acre. A 10 ton/acre application of manure would mean a subtraction of 40 \((4 \times 10)\). For a YG of 150 bushels/acre, when corn follows an excellent stand of alfalfa or clover and 10 tons/acre of manure are applied, the N recommendation is:

\[ \text{pounds N} = 177 - 100 - 40 = 37 \] (4.5)

Sometimes a previous soybean crop is equated to 40 pounds of fertilizer N. This basic method is also used to make N recommendations for small grains and other nonlegume crops. The method can be called the N balance method in that an attempt is made to determine crop N needs and the amount of N expected to be available. The difference between need and availability is the fertilizer recommendation.

Other factors are used to modify the recommendation, depending on the crops and conditions. In areas of limited precipitation and leaching, there is opportunity for NO\(_3^–\) to be carried over. A test to determine the amount of NO\(_3^–\) in the root zone is used in many of the western states. The samples for nitrate should be obtained at a minimum depth of 60 cm (24 inches) and, if possible, at a depth of at least 120 cm (48 inches). Montana recommends an adjustment when straw with a high C : N ratio is plowed down before planting. Twenty pounds/acre (22 kg/ha) of N is recommended to account for the immobilization of N by microorganisms. Arizona makes an adjustment for N in irrigation water. A summary of some N fertilizer evaluation systems used in various regions of the United States is given in Table 4.5.

TABLE 4.4 Nitrogen Recommendation Procedure for Corn and Sorghum Based on Yield Goal and Optimum Nitrogen Rate per Bushel in Iowa

<table>
<thead>
<tr>
<th>Soil association</th>
<th>N equation for pounds of N per acre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moody</td>
<td>(N = \text{YG} \times 0.9)</td>
</tr>
<tr>
<td>Marshall</td>
<td>(N = \text{YG} \times 1.1)</td>
</tr>
<tr>
<td>Clarion - Nicollet - Webster</td>
<td>(N = \text{YG} \times 1.2)</td>
</tr>
<tr>
<td>Tama - Muscatine</td>
<td>(N = [180 + (\text{YG} - 150)] \times 1.3)</td>
</tr>
</tbody>
</table>

Source: Data from General Guide for Fertilizer Recommendations in Iowa, 1982.

Legume Crops

Legume crops vary in their N-fixing efficiency. Alfalfa and clover are not benefited by N fertilizer except, perhaps, to become more rapidly established when the N-fixing system is not fully operative. State agricultural experiment stations are becoming more conservative in recommending N, to avoid possible groundwater contamination, and they are eliminating N recommendations for soybeans. In addition, the application of N fertilizer to efficient N-fixing legumes may reduce N fixation without affecting yields (see Figure 4.6). Some of the least efficient N-fixing legumes, on the other hand, are routinely fertilized with N such as peanuts in Georgia, peas in Washington, and navy beans in Michigan.

Crops Grown on Histosols

Histosols are organic soils, and they contain a greater quantity of total N than mineral soils. As a consequence, the N mineralization potential is very
TABLE 4.5 Summary of Some Factors Used in Current Nitrogen Evaluation Systems in the United States

<table>
<thead>
<tr>
<th>Region</th>
<th>Crop</th>
<th>Average nitrogen factor*</th>
<th>Average nitrogen credits **</th>
</tr>
</thead>
<tbody>
<tr>
<td>Northeast</td>
<td>corn</td>
<td>1.16</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>Soybeans</td>
<td></td>
<td>134</td>
</tr>
<tr>
<td>Mid-Atlantic</td>
<td>corn</td>
<td>1.18</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>16</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>71</td>
</tr>
<tr>
<td>Southeast</td>
<td>corn</td>
<td>1.25</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>27</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>49</td>
</tr>
<tr>
<td>Midwest</td>
<td>corn</td>
<td>1.24</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>29</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>89</td>
</tr>
<tr>
<td>West</td>
<td>corn</td>
<td>1.41</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>32</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>80</td>
</tr>
<tr>
<td>West</td>
<td>wheat</td>
<td>2.10</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>80</td>
</tr>
<tr>
<td>Southwest</td>
<td>wheat</td>
<td>2.15</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NA</td>
</tr>
<tr>
<td>Northwest</td>
<td>wheat</td>
<td>2.40</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NA</td>
</tr>
</tbody>
</table>

* Pounds of nitrogen per bushel of yield goal.

** Pounds per ton or pounds of nitrogen per acre. NA refers to inadequate data or may mean that in the region the material is an infrequent source of N.

Source: Selected data from Meisinger, 1984.

Nitrogen Fertilizers

Manure was the dominant fertilizer for thousands of years in areas where animals were used for power and food. Most of the nutrients in feed appear in the manure, and if the manure is efficiently managed, it can be very effective in the maintenance of soil fertility. Peruvian guano was the first fertilizer imported into the United States in 1824. This organic fertilizer consisted of the excreta and remains of birds whose primary diet consisted of fish. Guano contains about 13% N, which is mostly organic. In 1830 NaNO₃ was imported from Chile. This inorganic material of natural origin contains about 16% N. These materials were used in the southern United States largely on speciality crops, such as cotton and tobacco. In the nineteenth century the byproduct NH₃ produced from the coking of coal used in steel manufacturing was neutralized with H₂SO₄ to produce (NH₄)₂SO₄. Today, 95% or more of the N in fertilizers is produced by direct NH₃ synthesis.

Ammonia Synthesis

Modern NH₃ synthesis had its beginning when Haber and Bosch constructed the first commercial plant in Oppau, Germany, in 1913. The process reacts H and N directly, using high temperature and pressure in the presence of an iron catalyst. The reaction is

\[ 3\text{H}_2 + \text{N}_2 = 2\text{NH}_3 \]  (4.6)

Today over 80 percent of the plants use the steam-reforming method. Natural gas, CH₄, is the feedstock for H, and the N is obtained from the atmosphere. A flowchart of the major steps is given in Figure 4.7. In the first step steam, CH₄, and air are reacted or reformed to produce H₂, N₂, and CO. These gases are cooled and reacted with additional water to produce more H₂ by the shift reaction. The CO₂ produced in the shift reaction is removed by absorption in an alkaline solution. Any carbon-oxygen compounds present must be removed because they poison the catalyst, and this is accomplished in the methanation step. The gases leaving methanation contain about 74% H₂, 0.8% CH₄, and 0.3% argon on a dry basis. Ammonia synthesis occurs when the N and H gases are passed over an iron catalyst, promoted with potassium and alumina, at high temperature and pressure.

The Major Nitrogen Carriers

Economics drives the production of N toward the material or carrier that supplies it at the least cost. This carrier is anhydrous ammonia, NH₃, which contains 82% N. Its cost advantage is due to low costs both in production and in transportation, for NH₃ is transported by pipeline. Two large pipelines transport NH₃ from plants in Louisiana, Texas, and Arkansas to terminals as far west as Aurora, Nebraska, as far north as Garner, Iowa, and...
Soil and Fertilizer Nitrogen

As far east as Huntington, Indiana. In 1965 \(\text{NH}_4\text{NO}_3\) was the second most popular carrier and urea was third. By 1978 there was greater consumption of urea than of \(\text{NH}_4\text{NO}_3\) in the United States. These 3 carriers are the basis for making N solutions, which have increased steadily since 1965. These trends are shown in Figure 4.8.

**Anhydrous Ammonia**

As already mentioned, \(\text{NH}_3\) is manufactured by direct synthesis from H and N gases and is 82% N. At normal pressure \(\text{NH}_3\) is a gas and is transported and handled locally as a liquid under pressure. Specialized equipment is required to handle the liquid under pressure. It is injected into the soil to prevent serious loss through volatilization (see Figure 4.9).

The gaseous \(\text{NH}_3\) protonates to form \(\text{NH}_4^+\) in the soil and becomes \(\text{XNH}_4^+\), which is stable. Gaseous ammonia can be lost, depending on three factors. Studies have shown that volatilization losses at pH 7 are low but increase 10 times when the pH is increased to 8, and 50 times when the pH
Soil and Fertilizer Nitrogen

is increased to 9. Loss increases as soils become drier or wetter than field capacity. The interaction between the moisture content of soil and the depth of injection and their affect on NH₃ loss are shown in Figure 4.10.

Urea

Urea is the second most popular N carrier and the most popular dry carrier. It requires no specialized equipment for storage and handling and is preferred over NH₃ in situations in which the fertilizer is applied by broadcast on lawns or field crops. The CO₂ from ammonia synthesis is used to produce urea:

\[ 2\text{NH}_3 + \text{CO}_2 = \text{NH}_2\text{COONH}_4 \] (carbamate) \hspace{1cm} (4.7)

\[ \text{NH}_2\text{COONH}_4 = \text{NH}_2\text{CONH}_2 \text{ (urea)} + \text{H}_2\text{O} \] \hspace{1cm} (4.8)

Urea is more expensive than NH₃, because there are additional manufacturing steps, and has greater transportation costs, because urea has a lower N content (46%).

A method for making urea prills or granules uses the falling-curtain technique recently developed at TVA. Small seed urea granules are placed on longitudinal shelves in a rotating drum and sprayed with a concentrated urea solution as the drum rotates and the granules fall from one shelf to another. The technique is efficient in producing a wide variety of particle sizes. The dried prills or granules are coated with a conditioner to prevent the hygroscopic urea from taking up water from the air and caking (to a solid mass).

When urea is applied to the soil, the hydrolysis of urea is catalyzed by urease:

\[ \text{CO(NO}_2\text{H})_2 + \text{H}_2\text{O} + \text{urease} = 2\text{NH}_3 + \text{CO}_2 \] \hspace{1cm} (4.9)

In effect, the application of urea is similar to the application of NH₃, and the N in urea is similarly subjected to volatilization loss. Surface applications of urea, in the absence of movement into the soil by water, commonly result in losses of 20% to 30% of the N. On the other hand, urea is widely used to fertilize flooded rice in fields where anaerobic conditions inhibit nitrification and the subsequent loss of N by denitrification. Superlarge urea granules with a diameter of about 2 cm have been developed for hand application deep in the mud of rice paddies in Asia.

Biuret, \( \text{NH}_2\text{-CO-NH-CO-NH}_2 \), is formed during urea synthesis and in the processing of solutions following urea synthesis. The amount of biuret formed depends on temperature and other conditions and is commonly 0.8% to 2.0% of the finished product. For most plants this level of biuret is not toxic when the urea containing it is placed in the soil, for the biuret is readily decomposed and its N becomes available. If urea is placed with or close to seeds, they may be damaged, depending on the biuret content of the urea. Biuret is also toxic to citrus plants and some other crops if urea is used as a foliar spray. Citrus is able to tolerate up to 0.25% biuret in urea used for foliar application. Corn and soybeans can tolerate solutions made with urea containing 1.5% biuret.

Ammonium Nitrate

Ammonium nitrate is produced by oxidizing NH₃ to HNO₃ and neutralizing the nitric acid with more NH₃. Both urea and NH₄NO₃ granules can be made by the falling-curtain technique or by spraying concentrated solutions from the top of a tower and collecting the congealed particles at the bottom. Both processes require that the prills be dried and coated to prevent the adsorption of water from the air and caking. Ammonium nitrate is 33% N, with half of the N in nitrate form and the other half in ammonium form. If NH₄NO₃ is applied on the surface, less NH₃ is lost to volatilization, as compared to urea; and the substance is well suited for top-dressing lawns and so on. After ammonium nitrate moves into the soil, however, the loss of N by NO₃⁻ leaching, and denitrification is more likely.

Ammonium nitrate mixed with 6% fuel oil is used for blasting in mines. Under proper conditions it is explosive but poses no threat in its normal use as a fertilizer. Thin layers of NH₄NO₃ by themselves will not burn unless continuous heat is applied. Large piles in bulk storage or in bags, however, may become sufficiently heated to ignite under conditions of confinement.
and gas pressure; they may, if ignited, transmit fire rapidly through the mass and possibly cause an explosion. Even so, there are international trade restrictions on NH₄NO₃, which have helped make urea the most popular dry N fertilizer worldwide. In some countries the use of ammonia nitrate is prohibited, and it is commonly mixed with lime to produce a material that contains 75% NH₄NO₃ and has a N content of 26%. This substance is called calcium carbonate-nitrate, CAN.

Nitrogen Solutions

Anhydrous ammonia, urea, and ammonia nitrate are soluble in water and are used to make fertilizer solutions. Solutions using NH₄ have vapor pressure and are used primarily as a source of N in the manufacture of compound fertilizers. Solutions containing only NH₄ are called aqua ammonia. Solutions without NH₄ have no vapor pressure and can be used as dry materials are used, except that they are liquid. It is easy to incorporate herbicides at the time of application and to meter the fertilizer solution into irrigation water. Nitrogen solutions are designated to indicate their composition. A solution of 28.0 (0-40-30) contains 28.0% N, 0% NH₄, 40% NH₄NO₃, and 30% urea by weight. The material contains 30% water. The concentration of N is limited by the crystallization or salting-out temperature. The composition and properties of three common N solutions are given in Table 4.6.

Ammonium Phosphates

Ammonium phosphates are produced by the neutralization of phosphoric acid with ammonia and are important P fertilizers, which are considered in Chapter 5.

Controlled-Release Nitrogen Fertilizers

The N fertilizers that have been discussed are water-soluble, and the N may be quickly absorbed by plants or lost from the soil. For the maintenance of turf, this rapid dissipation of the N requires several applications of N fertilizer annually. Thus, there is a need for controlled-release N fertilizers to reduce the cost of application and increase the efficiency of N use, which is seldom greater than 50 percent. Controlled release is achieved by making insoluble materials or coating soluble materials.

Sulfur-coated urea, SCU, has been under development at the Tennessee Valley Authority for about 20 years. Urea is the least expensive major dry N carrier. Sulfur is also relatively inexpensive, and the final product has good handling characteristics. Urea granules are coated with sulfur and then coated with a sealant. The thickness of the S coating affects the rate of N dissolution. A total coating of 20% to 22% results in the dissolution or release of 20% to 25% of the N in the first week. SCU-10 and SCU-40 release 10% and 40% of their N by dissolution in seven days, respectively. SCU costs about 35% to 40% more than urea per pound of N and is too expensive for general agricultural use. It has been found to be effective in reducing N loss for rice production under rain-fed conditions where soils are subject to periodic flooding and drying.

Urea-formaldehyde, ureaform, is the reaction product of urea and formaldehyde in aqueous solution. Ureaform contains 38% N, of which 30% is soluble in water at 25 degrees C. It is desirable to have 50% to 70% of the remaining N soluble in boiling water.

Isobutylidene diurea, IBDU, is produced by the reaction of urea with isobutyraldehyde and contains 32% N. Most IBDU is manufactured in Japan and Germany.

Other controlled-release N fertilizers are being developed and tested in various countries. All these materials are more expensive than urea and are used mainly on lawns, golf courses, horticultural gardens, and for the production of some fruits and vegetables. Controlled-release materials are a component of many lawn and garden fertilizers.

Minor Nitrogen Carriers

Ammonium sulfate was once the leading N fertilizer produced as a by-product of the coking of coal in the manufacture of steel. It is still produced as a by-product and in some instances is manufactured by neutralizing H₂SO₄ with NH₄. The principal disadvantage is its low N content, which is 21%. Its advantages include its sulfur content and good physical condition. The fertilizer is strongly acidic, which can be a disadvantage when used on acid soils or an advantage when used on alkaline soils where the acid effect may be desirable for azaleas, and the like.

Calcium nitrate, 15.5% N, is produced by reacting HNO₃ and CaCO₃. The nitrate is a readily available source of N and used for soil application on winter season vegetables and as a foliar spray on both vegetables and fruits. Potassium nitrate, 13% N, is manufactured by reacting HNO₃ with KCl and is used in the production of fruits and vegetables.

<table>
<thead>
<tr>
<th>TABLE 4.6 Characteristics of Urea–Ammonium Nitrate Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grade, percent N</td>
</tr>
<tr>
<td>Composition by weight, percent</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
</tr>
<tr>
<td>Urea</td>
</tr>
<tr>
<td>Water</td>
</tr>
<tr>
<td>Specific gravity, 60°F</td>
</tr>
<tr>
<td>Salting-out temperature, °F</td>
</tr>
</tbody>
</table>

Organic Nitrogen Fertilizers

Manure, crop residues, and many other organic materials have been added to soils to increase the nutrient supply. The benefits come largely from their N content. Nitrogen in organic form can be stored in the soil; however, the N is available only after mineralization. Historically, nonleguminous crops have been rotated with legumes so that they can take advantage of the N resulting from the decomposition of legume residues. A cover crop that grows in the fall and early spring takes up mineral soil N and converts it into organic matter, thereby reducing leaching and denitrification losses. Plowing under the cover crop allows a gradual release of N by mineralization during the growing season. The advent of cheap N fertilizer has greatly reduced the importance of organic N fertilizers in the world during the twentieth century. Given present concerns about the environment and the interest in sustainable agriculture systems, organic fertilizers may be more sought after in the future.

Nitrogen Carrier Comparisons

Economic considerations play a major role in the selection of N fertilizers and are responsible for the trends shown in Figure 4.8. Nitrification of ammonium in soils tends to cause plants to take up N as nitrate; thus, many short-term experiments conclude that ammonium and nitrate forms are comparable for increasing yields on a per-pound-of-N basis. In flooded soils ammonium N is superior to nitrate in increasing yields because nitrate loses N through denitrification. On the other hand, ammonia and ammonium forms applied on or at the soil surface are more subject to volatilization loss than nitrate. The major practical difference in N fertilizers is their effect on soil pH.

Acidity and Basicity

Nitrification is an important soil-acidifying process; when ammonium fertilizers are used, there is considerable potential to increase soil acidity. The differences in the acidity and basicity of ammonium and nitrate fertilizers are discussed in Chapter 8, Mixed Fertilizers.

References

When scientists began to add nutrients to soils to improve their fertility, phosphorus (P) was soon discovered to be one of the limiting elements. Indeed, P became known as the master key to agriculture because lack of available P in soils limited the growth of both cultivated and uncultivated plants. To correct this deficiency, farmers have added P to soils in the form of manures, minerals, and manufactured fertilizers. Now many soils have a sufficient or high content of P, and the waters that drain from some agricultural lands also have a large amount of P, increasing the growth of algae and other plants in surface waters. In the erosion of high-P soil, sediments with a high content of P are deposited into surface waters. Consequently, in areas of the world where farms are managed to obtain maximum yields, environmental concerns are great. Thus, during the past decade, P has become known as the key to eutrophication—in eutrophication surface water becomes highly productive in algae and aquatic weeds.

Managing our entire resources requires a complete understanding of the forms of P in soils, the changes brought about when soluble P is added to soils, and the interactions between soluble P and soil pH.

INVENTORY OF THE EARTH'S PHOSPHORUS

For convenience, the earth's supply of P can be divided into two groups. The first group consists of the P that is sufficiently concentrated to be mined. The second group consists of the P that exists in the soil and in other geologic material where the P concentration is too low to be mined but the P becomes slowly soluble for plant or other biological growth. Natural soils will contain from 50 to over 1,000 mg of total P per kilogram of soil. Of this quantity, from 30% to 50% may be in organic form in mineral soils.

Deposits of rock phosphate for mining are relatively common throughout the world. The largest deposits and production in the United States are in Florida and North Carolina. Significant deposits are also located in Utah, Wyoming, Idaho, Tennessee, and Montana. Very large deposits of rock phosphate exist in other countries on the several continents: for example, Morocco in Africa, USSR in Europe, Brazil in South America, China in Asia, and in Australia. Lesser quantities exist in many other countries. The deposits are marine in origin, and the rock phosphate mined will be fluoroapatite, chloroapatite, and hydroxyapatite. Substitutions with carbonate are common. Mining of these deposits forms the basis of the phosphate fertilizer industry.

PHOSPHORUS CYCLING IN SOIL DEVELOPMENT

Apatite is the principal mineral supplying P before soil has been extensively weathered. It accounts for more than 95% of the P in igneous rocks. Apatites have a general chemical form of

$$\text{Ca}_{10}(X)(\text{PO}_4)_6$$

where X can be F, Cl, OH, or CO.

Forms in Young and Moderately Weathered Soils

Generally, mineral deposits occur largely as fluoroapatite, although chloroapatites are quite common. Fluoroapatite is the predominate form in soils, but hydroxyapatite is found in many calcareous soils. Before calcareous soils have been extensively weathered, apatite is their only source of P; the lack of P in solution will limit biological growth. Moreover, in the first stages of the evolution of many soils, the small amount of P available is a severe limitation to plant growth. Under these conditions the competition for P among microorganisms and macroorganisms is so strong that the P weathering from apatite will be rapidly incorporated into biological tissue and then slowly accumulate in organic compounds or humus (SOM). The very low concentration of P in solution limits the opportunity for P to move within the soil. This state for P is depicted by the left side of Figure 5.1. There is little soluble P, apatite is the predominate mineral form, and organic P is slowly accumulating.

How limiting the small amount of available P can be in the early stages of soil evolution is seen by applying solubility product principles to the dissolution of apatite. Using, for example, $\text{Ca}_{10}(\text{OH})(\text{PO}_4)_6$, which has a $\text{pK}_s = 114.6$, in equilibrium with $\text{CaF}_2$ with a $\text{pK} = 10.41$, we may calculate that total P is less than 1 part per billion (ppb) in solution, assuming that the soil contains free CaCO$_3$ in equilibrium with the atmosphere at a pH of 8.3. At a pH of 7.0, the level would be about 8 ppb. Thus, at pH between 7.0 and 8.3, apatite has a very low solubility, which together with its crystalline nature accounts for the persistence of apatite in soils that are young or only moderately weathered.
Soil and Fertilizer Phosphorus

The relative distribution of soil phosphate forms as related to time of soil development.

**FIGURE 5.1** The relative distribution of soil phosphate forms as related to time of soil development.

**Forms in Strongly and Intensely Weathered Soils**

Hydrolysis of soil minerals and leaching during soil evolution remove cations, and soil pH is lowered. The greater acidity at lower pH increases the solubility of apatite, giving increased P activity in the soil solution. The lower pH, in turn, increases the solubility of Fe and Al compounds, which will precipitate with the P released to the solution. Thus, as soil ages (see Figure 5.1), there is a decrease in apatite P and a corresponding increase in Fe and Al phosphorus. The increase appears more often in the Fe-P fraction than the Al-P fraction. During this transitional phase, the organic P fraction has been accumulating with humus until it occupies an important portion of the total P in the soil, perhaps as much as 50 percent of the total in surface soils.

Ultimate weathering leads to the situation shown along the right side of Figure 5.1. Soils have become almost totally depleted of Ca, Mg, and other cations, and the soil is very acid. Phosphorus is adsorbed or precipitated by Fe and Al, and soil organic P has become depleted. In many humid tropical areas, soil weathering has reached this stage and has produced LAC soils. It is common to find that more than 50 percent of the ECEC is Al-saturated and that the soil contains a variable charge arising from amorphous Fe and Al oxides and hydroxides. As shown in Table 5.1, total P has decreased drastically by this stage of weathering. The ultimate weathering of soil leaves it acid (For example see Table 5.1, pH 4.8), with the Ca-P fraction totally depleted, with organic P very low, and with the majority of P present as Fe-P.

**PHOSPHORUS IN FERTILIZED AGRICULTURAL SOILS**

Additions of P to soils began long before the manufacture of commercial fertilizers as we know them today. The use of manures, and perhaps rock phosphate and organic sources of P, began as early as recorded time. Thus, the final form of P that exists in soils depends on the state of weathering of the soil and the type and quantity of P that has been added.

Soils will vary from the calcareous, relatively unweathered forms to highly weathered tropical soils such as Oxisols. To understand what form P will take when soils are fertilized, we need to know the possible forms of P in soils. They are shown in Figure 5.2. Each of these forms of P may coexist in a particular soil, and each is converted from one form to another by components passing through the solution phase. These forms coexist because the rates of dissolution of one compound and of precipitation of another are many times kinetically very slow. Thus, the rate of either formation or dissolution of a particular form of P may be extremely important, even though there is no indication of rates in Figure 5.2.

**TABLE 5.1** Change in Phosphorus Forms with Weathering in Venezuelan Soils

<table>
<thead>
<tr>
<th>pH</th>
<th>Total P</th>
<th>Organic P</th>
<th>Ca-P</th>
<th>Al-P</th>
<th>Fe-P</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.9</td>
<td>692</td>
<td>235</td>
<td>70</td>
<td>33</td>
<td>43</td>
</tr>
<tr>
<td>5.9</td>
<td>298</td>
<td>79</td>
<td>88</td>
<td>20</td>
<td>33</td>
</tr>
<tr>
<td>5.0</td>
<td>144</td>
<td>85</td>
<td>3</td>
<td>14</td>
<td>19</td>
</tr>
<tr>
<td>4.8</td>
<td>59</td>
<td>11</td>
<td>0</td>
<td>2</td>
<td>17</td>
</tr>
</tbody>
</table>


**FIGURE 5.2** The soil phosphorus cycle.
Soil Solution Phosphorus

Phosphorus in solution may exist both as orthophosphate or as higher polymers. Phosphorus in the soil solution, however, will be almost exclusively as orthophosphate, \( PO_4^{3-} \). If polyphosphates are added to the soil solution in the form of fertilizers, they will hydrolyze to orthophosphate in a relatively short time. This reaction will be faster if enzyme-activated, but it also proceeds by chemical hydrolysis. It is expected that 50 percent of added polyphosphate will be hydrolyzed to orthophosphate in 9 to 16 days.

The individual species of orthophosphate that will be in solution vary with pH, as shown in Figure 5.3. In most agricultural soils the pH will be between 4.0 and 9.0; hence, the ion species present will be \( H_2PO_4^- \) and \( HPO_4^{2-} \). The ion species present is somewhat relevant to plant uptake of P, since it has been shown that plants prefer the monovalent ion. But the rate at which \( H_2PO_4^- \) is converted to \( HPO_4^{2-} \) in solution is so rapid that plants have little difficulty obtaining the necessary P for growth, even in soils with pH of 8 or higher, when levels of total P in solution are sufficiently high. Other ion pairs—made up of \( CaHPO_4 \), \( MgPO_4 \), and \( CaPO_4 \)—may exist in soil solution if soil pH is above 7.0, but again the dissolution of these ion pairs will be rapid if the soluble \( HPO_4^{2-} \) is removed from solution.

The concentration of P found in soil solution may range from <0.01 to 7 or 8 mg/L, depending on soil pH, recent additions of fertilizer P, and other soil factors. It would be unusual to find soil solution concentrations higher than 8 mg/L since precipitation will limit P to below this value in any soil pH range. The maximum level of P in solution will be in soils with a pH between 6.5 and 8.0.

![Figure 5.3: Mole percentage of each orthophosphate species as a function of pH.](image)

**FIGURE 5.3** Mole percentage of each orthophosphate species as a function of pH.

Adsorbed Phosphorus

The adsorbed fraction of soil P is often considered to be the labile soil P. Adsorbed P is the portion of soil P that is bonded to the surface of other soil compounds when a discrete mineral phase is not formed. For example, soluble P added to a soil solution may be bound to the surface of amorphous Al hydroxide without forming a discrete Al-P mineral. This would be an example of adsorbed P. Labile P is defined as the fraction that is isotopically exchanged with \(^31\)P or that is readily extracted by some chemical extractant or by plants. Thus, labile P may include some or all the adsorbed P in a particular soil. On the other hand, in some soils the labile P may also include some precipitated P, or it may not include all of the adsorbed P. Labile P has been an important working concept for the soil scientist in relating soil P to plant-available P. It is a measurable fraction, even though it may include P from several of the discrete fractions of P held in soils. Soil tests for P generally try to measure all or part of the labile P.

Two approaches to understanding adsorbed P are important in soil fertility. Models to describe the partitioning between liquid and solid phases of soils have been developed from laboratory measurements. These are very important because they describe how P will react in soils when broadcast and thoroughly mixed with them. This knowledge is necessary to predict how much P will be in solution for plant uptake and how much will be in the solution that moves from the soil to runoff waters.

Soils vary greatly in their ability to adsorb P and in the relation between solution P and adsorbed P. Extremes are illustrated in Figure 5.4. Generally, both very sandy soils and soils with a large amount of organic matter hold only small quantities of P in the adsorbed form, and they do not form strong bonds with the adsorbed P. If we assume that 0.2 mg/L of P is a desired quantity for plant growth, 25 mg/kg (50 pounds/acre) of P would be adequate to raise the level from near zero to adequate for Grayling sand. The Brookston loam Ap, which is more typical for agricultural soils, would require 61 mg/kg (122 pounds/acre) of P and the B horizon of the highly weathered Griffin soil would require 735 mg/kg (1470 pounds/acre).

During the past 100 years when modern agriculture and the fertilizer industry was developing, there was little concern about the consequences of high levels of adsorbed P in agricultural soils. Indeed, the greater problem during the early part of this period was how to obtain maximum uptake of P with limited application of P fertilizer. But this situation has changed drastically for heavily fertilized soils (see Table 5.2). With greater amounts of adsorbed P have come greater amounts of P in the water that runs off agricultural lands and percolates through soils. To this point in time, because most subsoils have a great capacity to adsorb P, there has been little increase in the P content of agricultural drainage waters and of groundwaters.

A number of equations have been developed to describe quantitatively the distribution of P between the adsorbed and solution phases. The two most common are based on well-known equations formulated by Henry...
FIGURE 5.4 Partitioning of phosphorus between the solution and the solid phase of four soil horizons varying widely in texture and chemical properties. The texture of Griffin B and Ontonagon A is clay, of Brookston A loam, and of Grayling A sand.

Freundlich and Irving Langmuir for representing the volume of gas absorbed as a function of pressure. According to the adapted Freundlich equation,

$$\frac{P_{\text{ads}}}{m} = k (P_{\text{sol}})^{1/n}$$  \hspace{1cm} (5.1)

TABLE 5.2 Median Phosphorus Soil Test Values of Mineral Soils for Each of Six Geographical Regions in Michigan

<table>
<thead>
<tr>
<th>Region</th>
<th>Median P soil test value, pp2m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Northern lower</td>
<td>42</td>
</tr>
<tr>
<td>West central</td>
<td>83</td>
</tr>
<tr>
<td>Thumb and eastern</td>
<td>41</td>
</tr>
<tr>
<td>South central</td>
<td>44</td>
</tr>
<tr>
<td>Southwest</td>
<td>72</td>
</tr>
<tr>
<td>Upper Peninsula</td>
<td>36</td>
</tr>
</tbody>
</table>

Source: Mients and Warncke, 1983.

Where $P_{\text{ads}}/m = P$ adsorbed per $m$ grams of soil,

$P_{\text{sol}} = P$ concentration (or activity) in the equilibrium solution, and $k$ and $n$ are constants defined experimentally for a given soil.

The use of this equation may be illustrated as follows. If $k$ and $n$ have been experimentally determined as 500 and 3, respectively, for a given soil, the quantity of $P$ that must be adsorbed to give 0.2 ppm $P$ in the soil solution is calculated as follows:

$$\log P_{\text{ads}} = \log 500 + \frac{1}{3} \log 0.2$$  \hspace{1cm} (5.2)

$$\log P_{\text{ads}} = 2.70 + \frac{1}{3} (-0.699) = 2.467$$  \hspace{1cm} (5.3)

$$P_{\text{ads}} = 293 \text{ mg/kg soil}$$  \hspace{1cm} (5.4)

The Langmuir equation is

$$\frac{P_{\text{ads}}}{m} = k (P_{\text{sol}})^b / \left[ 1 + k (P_{\text{sol}})^b \right]$$  \hspace{1cm} (5.5)

where $P_{\text{ads}}/m = P$ adsorbed per $m$ grams of soil,

$P_{\text{sol}} = P$ concentration (or activity) in the equilibrium solution,

$b = $ the maximum $P$ that can be adsorbed,

$k = $ a constant related to bonding energy.

A useful form of this equation is

$$k = \frac{\theta}{P (1 - \theta)}$$

where $\theta$ is the fraction of the adsorption maximum that is occupied by $P.$

Once $b$ and $k$ are experimentally determined, it is easy to calculate the quantity of $P$ that must be adsorbed to raise the level in solution to a desired level.

For the four soils shown in Figure 5.4, it would require 1,470, 150, 122, and 50 pounds per acre of $P$ for Griffin B, Ontonagon A, Brookston Ap, and Grayling A horizons, respectively, to raise the $P$ level in solution from 0 to 0.2 mg $P$/L, a value which is necessary for normal plant growth.

From another point of view, this is the quantity of $P$ that each of the soils would adsorb from applied wastewater before the soil solution level would exceed 0.2 mg $P$/L.

The chemical form of adsorbed $P$ would also be useful information, since this knowledge would help us to determine what minimum amount of $P$ must be applied to increase availability. Components of soils that are important in adsorbing $P$ are clays, Fe and Al oxides and hydroxides, and CaCO$_3$. Iron coatings that are associated with clay minerals may account for much of the clay's ability to adsorb $P.$ Amorphous oxides of Fe and Al are much more effective at adsorbing $P$ than crystalline compounds. As soils weather, they become able to adsorb large quantities of $P$ because they have formed amorphous Fe and Al oxides and hydroxides. But as the weathering process continues, these amorphous compounds crystallize, exposing less surface area and fewer hydroxyls. They therefore adsorb less total $P.$

Calcium carbonate is a principal adsorption site for $P$ in calcareous soils, but it has been shown recently that Fe compounds also function in adsorption in calcareous soils. Phosphate adsorbed onto CaCO$_3$ may later crystallize to precipitated P compounds.
Precipitated Phosphorus

Many insoluble compounds containing P form in soils. The principal compounds that are found or are precipitated when soluble P fertilizers are added to soils depend on soil pH and the other ions that are available for precipitation. We will discuss the precipitates of P in three groups of soils based on their pH.

Calcareous Soils

Unless amounts of soluble P have been added to a calcareous soil, apatite P is expected to be the predominant precipitated form. Since it is a complex molecular form and crystalline in nature, apatites are so slow to dissolve that they do not furnish sufficient soluble P to maintain a soil in a fertile condition. Levels of P in soil solution depend on pH when apatite controls the solubility and are less than 0.01 mg P/L (10 ppb) for soil pH greater than 7.0.

When the solution level of P is increased by adding soluble P, for example, by adding 0-45-0, dicalcium phosphate dihydrate, CaHPO$_4$•2H$_2$O, forms within a few minutes. This compound is not a stable phase in soils, and within three days anhydrous dicalcium phosphate, CaHPO$_4$, forms. It has been shown that octacalcium phosphate, Ca$_8$(HPO$_4$)$_2$•2.5H$_2$O, forms in two to three months. Dicalcium phosphate and octacalcium phosphate are very significant in maintaining soil fertility of calcareous soils, since both maintain much more soluble P than does apatite. Conversion of these phosphates to less soluble forms, such as apatite, requires many months or years. The practical significance of this is that we can fertilize calcareous soils and expect to maintain suitable levels of P for plant growth for several months or even years, even though much of the P precipitates.

Mildly Acid Soils

In the pH range of 5.5 to 7.0, adsorption may be more important than precipitation in controlling the level of P in soil solution. It is assumed that the soluble P materials which precipitate in this pH range will precipitate Fe or Al phosphates. The precipitation products that form will involve many complex species. Potassium and NH$_4$; taranakites, H$_3$(K,NH$_4$)Al$_2$(PO$_4$)$_2$•18H$_2$O, form as well as mixed species including Ca, Mg, Al, and K. Simple compounds such as strengite, FePO$_4$•2H$_2$O, and variscite, AlPO$_4$•2H$_2$O, are likely to form only in very acid soils.

Strongly Acid Soils

Strongly acid soils are found in many areas of the world, including the southeastern United States and the humid tropical areas of South America, Africa, and southeastern Asia. It would be a mistake to assume that all these soils have similar properties. But many do possess sufficient soluble and exchangeable Fe and Al to precipitate P. Although strengite and variscite become good model compounds for precipitated P in the strongly acid soils, much of the P in these soils will be occluded in amorphous Fe and Al oxides and hydroxides. Fractionation schemes, which include an occluded or reductant-soluble fraction, will show the predominant fraction of P to be in this form. Identifying specifically precipitated compounds is extremely difficult, and so is distinguishing between the adsorbed and precipitated phases. Phosphorus will be strongly held in these soils, and the native soil fertility will be very limited because little P is soluble. These acid soils require careful management with respect to P. They can be quite productive if adequate P fertilizer, as well as other fertilizer nutrients, are utilized. Generally, band placement of P fertilizer is useful because plants will take up more P when economical P rates are used and the P is band-placed rather than incorporated. Levels of P may be built up in these soils after repeated applications of fertilizer.

Biologically Incorporated Phosphorus

Plants absorb P directly from the soil solution. The total quantity removed by crops per year is small compared to the N and K removed, ranging from 6.0 to 26 kg/ha (5 to 23 pounds/acre) of P, with meadow hay absorbing small amounts and mangolds large amounts. In most agronomic plants the P content will be between 0.1% and 0.4%. The concentration in plant tissue decreases considerably with age; for example, leaves from corn plants one foot high contained 0.48% P, and the leaves from corn plants at tasseling contained 0.22% P. Excessively high values of P in plant tissue have been reported to be as much as 1%, but these were associated with P accumulation brought about by a deficiency of another nutrient such as Zn.

Modern high-yielding varieties of plants have increased the level of P absorbed by plants. For example, three hybrids—Pioneer 3780, Michigan 5922, and Pioneer 3572—yielding an average of 13.04 Mg/ha (208 bushels/acre) of grain and 8.32 Mg/ha (5.82 tons/acre) of stover, removed an average of 26.3 kg P/ha in grain and 4.7 kg P/ha in the stover. Alfalfa is a great accumulator of P and is expected to remove 59 kg P/ha for a 22-metric-ton annual yield (10 tons/acre).

Since P is accumulated in the reproductive portion of the plant, which is usually harvested, the residue returned to the soil often has a low level of P. The ratio of P in the harvested portion to the residue is usually greater than 2:1. Although the fraction returned in the residue is important, it is normally less than 1% of the total organic soil P. Soil microorganisms will also compete for available P, but little data are available about the quantity of P that may be incorporated into living microorganisms. It is expected that microorganisms function more in turnover of organic P than in retention.

Soil Organic Phosphorus

As shown in Figure 5.2, organic soil P will include both biologically available organic P and resistant organic P. The exact chemical nature of
organic soil P has been difficult to identify precisely. One form, inositol P, has been measured and is the largest identifiable fraction of organic P (see Table 5.3). The structure of one inositol compound is shown in Figure 5.5. There can be from one to six phosphate groups attached to the ring structure shown, which gives a number of slightly different compounds, all referred to as inositol P, and all with similar properties.

The other known organic compounds such as phospholipids, nucleic acids, phosphoproteins, and sugar phosphates may be present, but they usually represent a small percentage of the organic P. The majority of the organic P present is as part of the stable humus material formed in soils. Like the N in humus, it is stable but difficult to identify as a precise organic compound; it is released slowly as the humus decomposes in the soil.

Organic P is important in supplying P for plant growth when fresh organic materials are added to soils. From 6% to 16% of labeled P added in the form of fungal mycelia was taken up by wheat plants in a five-week growing period. Uptake from an inorganic P source under similar growing conditions was above 20% of the P added.

Movement of P to plant roots is generally by diffusion rather than by mass flow. The contribution of mass flow to the movement of P to roots can be easily calculated if three assumptions are made, about the transpiration ratio, the average concentration of P in plant tissue, and the average concentration of P in soil solution. For example, if we assume that 350 grams of water are used to produce 1 gram of dry plant tissue (transpiration ratio of 350 to 1), that the plant tissue concentration is 0.25% P, and that the soil solution contains on the average 0.1 mg P/L, then 350 ml X 0.1 mg P/L equals 0.035 mg P, which will move with the water. One gram of tissue contains 2.5 mg P; therefore, 1.4% of the P would reach roots by mass flow. Since the level of P in solution is generally less than 0.2 mg/L, mass flow will not play an important part in P movement to roots in other than highly fertilized soils.

It has long been known that mycorrhizal fungi will increase the availability of nutrients to many plants. The mycelia of the fungi, their masses of interwoven filaments, will become intimately associated with the plant roots and function in a symbiotic relationship. The mycelia become an extension of the roots. The increased availability of P to the host plant through mycorrhizal fungi is well known. Although better documented with tree species, numerous studies have shown that agronomic crops planted in soil of low fertility but containing the mycelia grow better, take up more nutrients, and have better yields. But evidence has also shown that well-fertilized agronomic crops will outyield unfertilized crops that are grown in low-fertility soil and have mycorrhizal fungi associated with their roots. Agronomic crops grown in less-developed countries where natural P levels are very low are expected to benefit more from the P taken up by the mycelia of mycorrhizal fungi than do highly fertilized crops in developed countries.

**BASIS OF PHOSPHORUS FERTILIZER RECOMMENDATIONS**

Recommendations for P fertilizer are made on the basis of a soil-testing program in which P soil tests have been correlated with field fertility studies. Preliminary evaluations of a particular soil test for P or compari-
sons of different soil tests may involve greenhouse studies. During the past fifty years, many different extractants have been developed in attempts to measure labile P or P in the soil that would correlate with the yield response to P fertilization. Three in widespread use will be discussed here. Others may be equally effective in local situations if properly correlated with field trials, and additional extractants may be developed in the future.

In 1945 Bray and Kurtz developed two extractants for P in soils, one for reserve P and one for available P. The available P test (Bray-Kurtz P1) utilized 0.025 N HCl + 0.03 N NH₄F as the extracting solution. Soil-to-solution ratios have varied from 1 : 7 to 1 : 50, and shaking time has varied from 1 to 30 minutes. Most soil-testing laboratories in the North Central region of the United States are now using a 1:10 soil-to-solution ratio with a five-minute extraction period. A ratio of 1 : 50 with a one-minute extraction period has been shown to be much more effective on soils that are calcareous or have received applications of rock phosphate. But the procedure utilized in soil-testing laboratories has been very satisfactory in distinguishing between soils with small, medium, and large amounts of available P.

Olsen developed the sodium bicarbonate extractable P test for use on calcareous soils. The P is extracted with 0.5 M NaHCO₃ buffered at pH 8.5 with a soil-to-solution ratio of 1 : 2 and a 30-minute shaking or extracting time.

The more acid soils of the Piedmont area of the southeastern United States as well as the acid, highly weathered soils of other regions of the world contain very little P that is extracted with either the Bray-Kurtz P1 or Olsen's test. For these soils, Melich developed a stronger acid extractant utilizing 0.05 N HCl + 0.025 N H₂SO₄, and later an improved extractant using 0.2 N CH₃COOH, 0.2 N NH₄Cl plus 0.015 N NH₄F plus 0.012 N HCl.

Analytical determination for P in solution is generally by the Murphy-Riley method utilizing the blue color of molybdenum and ascorbic acid as the reducing agent. This method is widely adaptable to colorimetric methods including autoanalyzers and flow injection analyzers.

Most extractants utilized in soil tests do not remove the precise fraction of the nutrient in the soil that is absorbed by plants during a growing season. This does not make the soil test less useful or desirable. But the fraction that is extracted must correlate with the amount removed by plants during the growing season. Thus, in interpreting a soil test, the most important factor is that it correlate with uptake of the nutrient and with the yield response to the nutrient. Generally, P soil tests are evaluated as low, medium, high, and very high. Soil that tests low in P will require additions of P fertilizer that supply more than the quantity removed by the crop being grown because the P added to the soil in fertilizer becomes fixed. Soils testing medium in P will require applications of slightly more than that removed by the crop for adequate yield and growth. When a soil tests high in P, no yield response is expected to P fertilizer. Here different approaches to fertilizer management may be followed. First, a starter fertilizer banded at planting time may be used to apply a maintenance amount of P. The intent is to apply the quantity of P that is removed by the growing crops so that the high amount of P found by the test will be maintained. Alternately, no P fertilizer is applied, and the soil is retested at frequent intervals to determine when P must again be applied.

When a soil tests very high in P, the probability of P being lost to surface waters through runoff and erosion is great. To reduce the risk of environmental degradation, farmers should not apply P fertilizer to soils testing very high in P. A possible exception is for potato production, a crop which sometimes gives yield responses to P fertilizer, even though soils test very high. The soil should be retested frequently to determine when P levels have been reduced to the point of requiring the addition of P again.

### Recommendations for Phosphorus Fertilization of Crops

Since fertilizer recommendations are specific to the area and crop, only general guidelines will be given here. They must be modified to fit the soil type, the climate, and the yield goal of the farmer for a particular area. It is important for a farmer to have realistic yield goals when planning a fertilizer program. Fertilizing for 200 bushels of corn per acre is futile and expensive if the soil and climate will support only 120 bushels/acre.

From Table 5.4, it is apparent that soybeans and corn require considerably less P than does wheat. But the major difference comes with potatoes and other vegetable crops. Although it is easy to adjust and fertilize a crop that requires a large amount of P, the danger of excessive residual P in these soils is great, and this causes concern about the environment.

### PHOSPHORUS FERTILIZERS

The beginning mineral for most, if not all, P fertilizers is apatite, or rock phosphate. The mineral deposit is exposed generally by strip mining, which removes the surface material or overburden. Then the mineral deposit is

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**TABLE 5.4 Guidelines for Phosphorus Recommendations for Several Agronomic* Crops**

<table>
<thead>
<tr>
<th>Soil P test, mg/kg</th>
<th>Corn</th>
<th>Wheat</th>
<th>Soybeans</th>
<th>Potatoes</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>30</td>
<td>39</td>
<td>22</td>
<td>76</td>
</tr>
<tr>
<td>30</td>
<td>13</td>
<td>22</td>
<td>0</td>
<td>70</td>
</tr>
<tr>
<td>50</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>61</td>
</tr>
<tr>
<td>80</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>48</td>
</tr>
<tr>
<td>175</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*Yield goals assumed: corn, 140 bushels/acre; wheat, 70 bushels/acre; soybeans, 50 bushels/acre; and potatoes, 400 cwt/acre.
is seldom in a pure form and must be separated from impurities, including inert material, before it is utilized. Once it is separated from impurities, rock phosphate may be finely ground and marketed directly as a fertilizer source of P. This product generally contains from 11.5% to 17.5% total P. None of the P will be water-soluble, but from 5% to 17% of the total P is soluble in citric acid. The term available P is applied to P fertilizers and includes the P soluble in citric acid.

There are two alternative manufacturing processes to make rock phosphates into a more soluble P fertilizer. The first is direct acidification of rock phosphate; in the second the product is phosphoric acid or elemental P, which becomes a basic material for further manufacture.

**Direct Acidification of Rock Phosphate**

If sulfuric acid is mixed with rock phosphate, the P is rendered soluble by the following reaction:

$$\text{Ca}_4\text{F}(\text{PO}_4)_3 + 7\text{H}_2\text{SO}_4 = 3\text{Ca(H}_2\text{PO}_4) + 7\text{CaSO}_4 + 2\text{HF}$$ (5.6)

The product is commonly called superphosphate, 0-20-0, and contains soluble monocalcium phosphate and calcium sulfate. The HF is a toxic gas that escapes during manufacturing and usually is, and certainly should be, recovered as a by-product. Although this product is less common in the United States today because of the expense of shipping a low-analysis fertilizer, it is an excellent source of P and carries both Ca and S in addition to P.

Partially acidifying rock phosphate is a practice that merits consideration in developing countries where sophisticated manufacturing may not be possible. Waste sulfuric acid, which is often available, can be used to react partially with rock phosphate, producing a material which contains considerable soluble P. Although this soluble P is not as effective as 0-20-0, it is much more useful than direct application of rock phosphate.

Acidification of rock phosphate with phosphoric acid produces a high-grade, water-soluble product known as triple superphosphate, 0-45-0, according to the following reaction:

$$\text{Ca}_4\text{F}(\text{PO}_4)_3 + 14\text{H}_2\text{PO}_4 = 10\text{Ca(H}_2\text{PO}_4) + 2\text{HF}$$ (5.7)

Although the manufacturing is similar to that for 0-20-0, this material does not carry gypsum in the final product. It also requires the production of phosphoric acid for manufacture.

**Phosphoric Acid Production**

Phosphoric acid is prepared by the wet-process acid method and by the electric furnace elemental P method. Wet-process acid is prepared by reacting rock phosphate with sulfuric acid, allowing sufficient time for gypsum to crystallize, and filtering the material to obtain the phosphoric acid. Although the reaction is similar to that in equation 5.6 illustrating the manufacture of ordinary superphosphate, the differences are significant. As shown in the following equation,

$$\text{Ca}_4\text{F}(\text{PO}_4)_3 + 10\text{H}_2\text{SO}_4 + 20\text{H}_2\text{O} = 10\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 6\text{H}_3\text{PO}_4 + 2\text{HF}$$ (5.8)

additional sulfuric acid and water are added to the rock phosphate. Usually about eight hours are allowed for digestion of the mixture, after which time the crystals of gypsum, CaSO_4 • 2H_2O, are sufficiently large to be filtered easily. This acid may be directly used for acidification of rock phosphate but requires further purification and concentration before it can be used for the manufacture of polyphosphate fertilizers.

Electric furnace phosphoric acid is prepared by heating rock phosphate along with carbon and silica to temperatures in excess of 1,400 degrees C in a reducing atmosphere. The reaction produces elemental P, which may be oxidized to form P_2O_5, which when hydrated becomes phosphoric acid. This process will produce a high-purity acid and with proper control one with the desired ratio of orthophosphate to polyphosphate for use in liquid fertilizer manufacture. But because the electric furnace manufacturing process is more expensive, most of the phosphoric acid that goes into fertilizer manufacture is prepared by the wet-process method.

**Manufacture of Ammonium Phosphates**

In addition to being used for manufacturing 0-45-0, which was discussed previously, phosphoric acid is utilized for the manufacture of monoammonium phosphate (MAP), diammonium phosphate (DAP) and ammonium polyphosphate (APP). Ammonium orthophosphate can be prepared to yield two products, MAP and DAP, depending on the degree of ammonification. Several methods are used to manufacture the products. Basically, phosphoric acid is treated with ammonia. If the neutralization is carried out to a limited extent, MAP is produced with a typical analysis of 11-48-0, as follows:

$$\text{NH}_4 + \text{H}_3\text{PO}_4 = \text{NH}_4\text{H}_2\text{PO}_4$$ (5.9)

If neutralization is carried out to obtain a higher ratio of ammonia to phosphoric acid, DAP is produced with a typical analysis of 18-48-0, as follows:

$$2\text{NH}_4 + \text{H}_3\text{PO}_4 = (\text{NH}_4)_2\text{HPO}_4$$ (5.10)

Grades between the two mixtures can be obtained with intermediate ammonification.

With the development of superphosphoric acid came the possibility of producing higher-analysis ammonium phosphates, usually called ammonium polyphosphates, APP. The most commonly used superphosphoric acid contains about 50% orthophosphate, with the remainder as higher
polymers of phosphoric acid. The major portion of the higher polymers are present as pyrophosphates, making up 43% of the total P. Ammonium polyphosphates have formed an important part of the liquid fertilizer industry. A rather simple process of carrying out the neutralization reaction in a pipe reactor allows the liquid fertilizer to be prepared on site by neutralizing the superphosphoric acid with ammonia. Typical grades are 11-32-0 and 11-37-0. A typical grade of APP when the fertilizer is in the dry form would be 15-62-0.

USE OF PHOSPHORUS FERTILIZERS

Use of Rock Phosphate

Rock phosphate may be directly applied to soils, usually by broadcasting and incorporating it into the soil with tillage. Years of research work carried out several decades ago showed that this material is not effective when utilized in a soil management scheme in which soils are limed to maintain soil pH above 6.0. As shown earlier in this chapter, the solubility of rock is so limited that it is of little use under slightly acid to neutral conditions.

Rock phosphate may be of considerable value, however, if applied to highly weathered acid soils that have very little available P. Rock phosphate added to these soils may be readily soluble since the pH is low, and very often the Ca concentration (activity) is also low. The importance of Ca activity is shown in Figure 5.6. It is also known that Ca activity may not be closely related to pH (see Table 5.5). For this reason, the consequences of using rock phosphate, even on very acid soils, are sometimes unpredictable. Nevertheless, rock phosphate is the source most often available in many lesser-developed countries. In these countries the price of importing soluble, manufactured P fertilizers will preclude their use. When rock phosphates are locally available, they may be used to advantage. But it must be emphasized that the rock phosphates will be more soluble on acid soils containing little Ca. If the management program for these soils includes some application of lime, the lime should be added after rock phosphate has been applied to the soil and has had sufficient time to react, a period of more than six months. Under these conditions rock phosphate may be a very satisfactory fertilizer.

Use of Superphosphates

Superphosphates are very soluble materials and hence satisfactory for any application that requires a source of soluble P. Generally they are excellent sources when coupled with a management program that utilizes liming to maintain soil pH above 6.0, and this includes calcareous soils. When superphosphates are used on acid soil, the adsorption, and sometimes the precipitation, of P will be considerable and rapid as the soluble P reacts with Fe and Al that is either dissolved or present in the amorphous form in soils.

Often these materials will be band-placed near the seed at planting time to slow down the process of fixation. In this placement technique, the band of fertilizer will become very acid as the fertilizer adsorbs water from the surrounding soil and dissolves. The pH in the band may become much lower than 3.0. Although root growth cannot penetrate such an acid band,

<table>
<thead>
<tr>
<th>Soil</th>
<th>pH</th>
<th>Ca²⁺ activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Warsaw loam</td>
<td>5.38</td>
<td>9.1 X 10⁻⁴</td>
</tr>
<tr>
<td>Munising sandy loam</td>
<td>4.86</td>
<td>8.8 X 10⁻⁴</td>
</tr>
<tr>
<td>Bradson</td>
<td>4.22</td>
<td>1.7 X 10⁻⁴</td>
</tr>
<tr>
<td>Tatum</td>
<td>4.94</td>
<td>3.0 X 10⁻⁴</td>
</tr>
</tbody>
</table>

the P diffusing from this band will be in high concentration and readily available for plant uptake. A residue of dicalcium phosphate, CaHPO₄, has been shown to remain in the band.

When these soluble materials are applied to a calcareous soil, particularly if incorporated, they will react first to form dicalcium phosphate dihydrate, CaHPO₄ • 2H₂O. Then the anhydrous form, CaHPO₄, will appear, followed in a few weeks by a less soluble octacalcium phosphate, Ca₄H₆(PO₄)₂. This form is stable for months or years, but recent evidence suggests that beta-tricalcium phosphate, βCa₃(PO₄)₂, will form given sufficient reaction time. Both forms of dicalcium phosphate and octacalcium phosphate are sufficiently soluble and dissociate with enough rapidity to furnish P for plant uptake. Consequently, this conversion to the less soluble P compounds is not a loss to soil fertility. Further conversion to beta-tricalcium phosphate and to apatite, if this latter conversion indeed occurs, leaves P in forms that are not sufficiently soluble for optimum P availability in calcareous soils.

The Fate of Applied Fertilizer Phosphorus

The desire and goal of every farmer is to have a high percentage of applied fertilizer utilized by the current crop. With P, however, this is far from reality. The uptake of P may be from 5% to 30% of that applied during the current year. The remainder converts to insoluble compounds, adsorbed P, or organic P. These compounds may be available for crops grown in later years.

Initial Reactions of Soluble Fertilizer Phosphorus

Most fertilizers are hygroscopic and attract water once they are added to soils. Water may move to the fertilizer granule either by capillary adjustment or by the movement of vapor, but the result is the formation of a saturated solution of fertilizer material in water. The initial reactions will then depend on the characteristics of the fertilizer. The pH of the soil surrounding the fertilizer particle reflects the pH of a saturated solution of the material. The wide variance that may be obtained is shown in Table 5.6.

When monocalcium phosphate, 0-45-0, is added to a soil, it forms a very acid solution. If the individual fertilizer particles have been broadcast and incorporated into the soil, this acidity is soon neutralized by the soil. But if the fertilizer material has been placed in a band, the soil surrounding the band will become very acid and may have a pH as low as 2.2. Precipitation occurs within the fertilizer band, giving a residue of dicalcium phosphate, CaHPO₄. The saturated solution of P will move slowly into the soil where P may be absorbed by plants or utilized by microorganisms—if the extreme pHs and high ionic strengths are not detrimental to the organisms. The P may also be adsorbed by soil particles or converted to less soluble compounds.

The exact nature of these reactions is controlled by the soil properties and by the placement of the fertilizer. If the fertilizer is broadcast and mixed with a large volume of soil, it will dissolve quickly, and the P will reach an equilibrium that is governed by the properties of the soil. For calcareous soil this will include adsorption by CaCO₃, or Fe oxides and hydroxides and precipitation as dicalcium phosphate, octacalcium phosphate, and tricalcium phosphate. In acid soils adsorption by Fe and Al oxides and hydroxides and clay minerals are thought to be the most important reactions. Precipitation as Fe and Al phosphate compounds will also occur.

Banding the fertilizer material will delay the time for the fertilizer to reach equilibrium with the soil. This has been particularly advantageous when applying P to soil that has very little available P. Band placement requires less P to reach a satisfactory yield than broadcasting and mixing. Early season growth effects may also be obtained by band placement of fertilizer, even in soils that have considerable available P. The ultimate fate of fertilizer that is band-placed is to reach equilibrium with the soil. When plowing was a standard tillage practice, even the banded fertilizer was well mixed with the soil once a year. But with zero-tillage methods, this may no longer be the case. Residual effects of band-placed fertilizer may persist for relatively long periods of time under reduced-tillage systems.

Residual Soil Phosphorus

A number of important questions come up concerning residual soil P. (1) What is the fate of P that is converted to a residual form in soils? (2) Do common soil test methods accurately assess residual P? (3) Should additional fertilizer P be added for crop growth, even if residual P is high?

Much of the residual P remains in a labile form. It may be as adsorbed P or precipitated P. A portion of this P is measured by most soil-testing procedures. But some soils contain more P in the residual form, which can be removed by repeated cropping or measured by soil testing. For most agronomic crops, when a soil contains sufficient residual P so that the test is high, little benefit is gained from additional fertilizer P, even if band-placed at planting time. Certain crops are an exception to this rule: potatoes, as indicated earlier, usually give a yield response to added P fertilizer even when the soil test levels are very high.

<table>
<thead>
<tr>
<th>TABLE 5.6 Content and pH of Saturated Solutions of Fertilizer</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Compound</strong></td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>Ca(HPO₄)₂ • H₂O</td>
</tr>
<tr>
<td>(NH₄)₂HPO₄</td>
</tr>
<tr>
<td>K₂HPO₄</td>
</tr>
</tbody>
</table>

*Source: Sample, Soper, and Racz, 1980.*
Effect of No-Till on Soil Phosphorus

Two conditions that occur with no-till systems that have an important bearing on soil P. First, P applications must be made to the soil surface or applied in a band close to the surface. And second, organic matter is deposited on the surface of the soil rather than being incorporated into the plow layer.

Surface and band applications of P fertilizer without cultivation lead to nonuniform distribution of P in the soils. This is of little concern if the soil initially has a high level of available P. Since most management systems have just recently converted to no-till systems, at present many soils have high levels of P to a considerable depth in the profile. It is likely that it will take many years of no-till management before P is removed by roots from soil layers below the surface and deposited on the soil surface as organic residues. But ultimately the distribution of P will be less than desirable for crop growth, since root growth is likely to be much more extensive in the surface layer that has a high level of P. If the P content of lower layers of soil becomes so low that root growth is restricted, management practices such as an occasional plowing or deep placement of P fertilizer would need to be used in no-till systems.

Accumulation of organic P in the few surface centimeters of soils under no-till systems has the effect of increasing soluble and labile P in the layer most exposed to runoff, which will increase the P in the runoff water. This may be relatively unimportant, however, in that no-till and conservation tillage systems are very effective in reducing surface runoff so that the total P leaving a field will be greatly reduced.

Environmental Concerns about Soils Containing Large Amounts of Phosphorus

Levels of P in surface waters greater than 10 ppb (10 micrograms P/L) have been associated with increased algal growth in streams and lakes. Continued high levels of P input to surface waters has led to eutrophication. Although agriculture may be a contributor to surface water degradation through inputs of P from heavily fertilized fields, it need not continue to be in the future. Responsible farm managers must be aware of how to control P losses. First, runoff water and soil erosion are the principal means of moving P from agricultural lands to surface waters. Conservation tillage and no-till systems that control erosion and water runoff are effective in reducing P loss, even though they may ultimately increase P concentration in the small quantities of water that are lost.

Second, soil tests should be utilized even when soils contain high levels of P to define when P should not be added. Continued application of fertilizer P when soil tests are high is not a sound practice economically or environmentally.

References


Soil and Fertilizer Phosphorus


CHAPTER 6
Soil and Fertilizer Potassium

Of the elements essential for plants, potassium and calcium are the two most abundant in the earth’s crust. Potassium accounts for 2.6% of the earth’s crust, and calcium for 3.6%. It has been estimated that the average plow layer in the United States contains 0.83% K, which equals 16,600 pounds/acre or 18,600 kg/ha. Most of the soils in the western half of the United States are minimally or moderately weathered and contain 1.7% to 2.5% K. By contrast, many soils of the southeastern Coastal Plains contain only 0.3% K. Therefore, many soils have large amounts of total and plant-available K, and responses to K fertilizers are nonexistent or small. On the other hand, the contents of many soils are low in both total and plant-available K, and yield responses to K fertilizers are large. For this reason over 80% of the K fertilizer applied in the United States is used in the Lake States, the Corn Belt, Appalachia, and the Southeast, areas with udic soil moisture regimes.

Potassium is not complexed or bound up into organic matter to any degree, compared to N; essentially all of it is associated with the mineral fraction. For this reason soil K and soil N can be considered opposites. Soil N exists mainly as organic N, and a minor amount exists as mineral N. By contrast, soil K is mostly mineral, and the daily K needs of plants are little affected, if at all, by organic associated K, except for exchangeable K adsorbed on organic matter. As a result mineralization of organic N is the major source of plant-available N, and the weathering of K minerals is the major process for converting unavailable K into forms that plants can use.

THE POTASSIUM CYCLE

Soil parent material contains K that is mainly in feldspars and micas. These minerals weather, and the K ions released, K+, appear as exchangeable and solution K. From solution the K ions may undergo various changes in the
soil, including fixation and uptake by plants or microorganisms, after which they may return again to the soil solution. In humid regions K is removed by leaching, as shown in Figure 6.1. A potassium ion could, hypothetically, be released from primary minerals by weathering and occur as an exchangeable cation. It could become fixed, released from fixation, and become an exchangeable cation again; desorb into the solution; be absorbed by roots, leached from leaves, and returned to the soil solution again; and then be carried to the groundwater by leaching.

Over time, theoretically, all the K in the primary minerals is released and eventually removed from the soil by leaching. The most-weathered soils have few weatherable minerals in the coarse silt and fine sand and are in general infertile soils with little capacity to supply K (and Ca, Mg, etc.) for plant growth. In the larger K cycle, the K ions leached from the soil appear in the oceans where they encounter and reenter various 2:1 clays, which may then be deeply buried and the clays converted into micas or mica-like minerals. When sediments containing these K minerals are uplifted for another cycle of soil formation, the K begins another weathering cycle through the soil. The amount of K available in unfertilized soils today depends on the amount and kinds of K minerals that were in the parent material and the kinds and degree of changes that took place during soil genesis.

**FORMS OF SOIL POTASSIUM**

The major forms of soil K consist of the unavailable K in primary and secondary minerals and the available K composed of exchangeable K (XK) and solution K.

**Primary Minerals**

The major K primary minerals in soils are feldspars and micas, which have the following chemical formulas.

**Feldspar**

- Microcline: $\text{KAISi}_3\text{O}_8$
- Orthoclase: $\text{KAISi}_3\text{O}_8$

**Mica**

- Muscovite: $\text{K(Si}_3\text{Al)}\text{Al}_2\text{O}_10\text{(OH)}_2$
- Biotite: $\text{K(Si}_3\text{Al)}\text{(Mg,Fe}^{+3}\text{)}\text{Al}_2\text{O}_10\text{(OH)}_2$

The K content decreases from about 13% to 14% for feldspars to about 10% for micas.

Feldspar particles in soils tend to be larger in size than mica particles. In some well-drained Mollisols developed from till in Saskatchewan, Canada, over 50% of the mica was in the clay with only a minor amount in the sand, but over 50% of the feldspar was in the sand and a minor amount in the clay (see Figure 6.2). Finer-sized particles have greater specific surface
and weather more rapidly than coarser particles. In most soils the mica­ceous minerals are more important than feldspars in replenishing the plant-available K.

Many sandy soils whose clay content is low have low fertility because most of the sand and silt particles are quartz. The most infertile soil in Wisconsin is Boone sand, which developed from quartzitic sandstone. If a soil has developed from arkose (feldspathic) sandstone, however, it could be sandy and provide much more available K than a soil like Boone sand. The weathering of feldspar in the sand fraction contributes to the release of large amounts of K in some sandy Ultisols of the Coastal Plains in Delaware.

As a general rule, fine-textured soils have greater K-supplying power than coarse-textured soils. This greater supply of K is related, in part, to the fact that mica is nearly a universal constituent of the clay in soils.

Quartz is composed of Si-O tetrahedral units, and the chemical formula SiO_2 could be written Si_4O_8. Compare this to the feldspar formula, KAlSi_3O_8. In a sense one of every four of the tetrahedrals has Al^3+ substituted for Si^4+, and the charge is balanced out by the inclusion of a K^+ in the feldspar structure. Feldspars are quite resistant to chemical breakdown and weather slowly; the microcline weathers more slowly than the orthoclase. During weathering there is a complete breakdown of the crystal structure and release of the component parts. The K is released into the soil solution; however, some of the Al and Si form a gel that coats the weathering surface and forms a protective barrier which inhibits further dissolution of the feldspar. Although feldspar is an important source of K, its slow dissolution rate results in poor correlations between the amount of feldspar in a soil and the amount of K absorbed by crops.

The K in micas is interlayer K between the 2:1 layers (see Figure 2.1).

During weathering a H_3O^+ is very effective in exchanging for a K^+ along the edges, which is followed with an expansion of the interlayer space in the edges. Internal crystal-bonding differences cause trioctahedral biotite to weather more rapidly than dioctahedral muscovite. This weathering allows K to leave the structure more easily in biotite than in muscovite.

The four primary K minerals were finely ground and used in an experiment to measure their ability to supply K for oats. The removal or uptake of K by the oats paralleled the weathering rate sequence, with biotite being the most easily weathered and supplying the most K; microcline weathering was the slowest and supplied the least K for uptake. Removal of K by carbonated water extraction paralleled the plant removals (see Table 6.1).

The relative weathering rates and release of K from microcline, muscovite, and biotite have been reported to be 1.0, 1.8, and 190, respectively. Many experimenters have found that biotite is a good source of K for growing plants. There is evidence that roots play a role in the removal of K from biotite and that plants differ in their capacity to extract or use biotite K. The rapid weathering rate of biotite accounts for its low content in most soils, whereas the very slow weathering rate of muscovite accounts for its presence in the clay fraction of most soils.

Secondary Minerals

The interlayer K of micas is lost first along particle edges during weathering, as other cations diffuse into the interlayer space and hydrate. These processes cause expansion between layers, and the partially weathered mineral that has lost some K and contains more water than unweathered mica is hydrous mica. Historically, hydrous mica has been called illite, and the two names have been used interchangeably. The weathered hydrous mica edges have sites—voids which have lost K—that strongly readorb K^+ with an accompanying collapse of the expanded layer edges. The low energy of hydration and the ease with which the hydration water is lost facilitate movement of a K into the fixation site. This positioning converts a K into

<table>
<thead>
<tr>
<th>Source of K</th>
<th>K removed by oats (gains over control), grams/pot</th>
<th>K removed by five extractions, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>K_2SO_4</td>
<td>0.253</td>
<td></td>
</tr>
<tr>
<td>Biotite</td>
<td>0.203</td>
<td>217</td>
</tr>
<tr>
<td>Muscovite</td>
<td>0.177</td>
<td>141</td>
</tr>
<tr>
<td>Orthoclase</td>
<td>0.062</td>
<td>78</td>
</tr>
<tr>
<td>Microcline</td>
<td>0.011</td>
<td>51</td>
</tr>
</tbody>
</table>

*30 grams in 200 ml of carbonated water shaken for 96 hours.

Source: Data of Plummer, 1918, and modified from Rich, 1968.
unavailable or fixed K. Figures 2.1 and 2.2 give models of muscovite and hydrous mica, respectively.

When all or nearly all the interlayer K between two layers has been removed, the layers separate and expand, thus transforming hydrous mica into vermiculite. The negative charge that was originally balanced by K appears as CEC. The various crystal forms of K are in equilibrium with each adjacent member in the weathering sequence; in the laboratory solutions with high-K concentrations have been used to reverse the sequence. In field soils the application of K fertilizer produces local pockets of high-K concentration and promotes the reentry of K into the interlayer space. Hydrous mica along particle edges is then converted to mica. The weathering sequence of mica, changes in K content, and equilibrium relationships are illustrated in Figure 6.3.

The mica mineral-weathering sequence, shown in Figure 6.3, becomes a K continuum in terms of the transitional properties of the K minerals and the availability of K in soils. When a mica particle loses K along the edges, the edge section is converted to hydrous mica. Before the weathering front reaches the particle interior or mica core, the outer edges may have lost all their K and may have been converted into vermiculite. It has been theorized that an interlayer wedge-shaped zone is created in the hydrous mica at its juncture with the unweathered mica core. In this wedge-shaped zone the adsorption sites closest to the unweathered mica core have the shortest distance between layers and the greatest affinity for K. There is decreasing affinity for K in the wedge zone toward the particle edge as the interlayer distance increases (note the wedge-shaped zone of the hydrous mica in Figure 6.3). Thus, a K availability continuum, consisting of unavailable mica K, fixed K and XK adsorbed to sites with different energies of adsorption, is created. The unavailable K occurs in the i (interior) positions and the exchangeable K at the p (planar) and e (edge) positions, as shown in Figure 6.4. The e position, near the site of a vacated structural K, has a special affinity for K and holds XK more strongly than on the planar surfaces (p site). Since the various forms of K tend toward equilibrium with one another, they operate as buffers to moderate the rate at which solution K is depleted when K is absorbed by roots.

**Potassium Fixation**

Potassium fixation is associated with mica wedge zones. In field soils the moisture content and other conditions are normally such that expanding clays, vermiculite and smectite, do not fix a significant amount of K. If soil samples are artificially dried, the removal of interlayer water and the subsequent contraction of the layers may cause some K fixation. This fixing of K has some implications for drying soil samples before testing them for available K. Drying tends to bring the soil K relationships to equilibrium. If samples are collected just after harvest and the XK has been depleted by plant uptake, drying will increase XK. If samples are collected shortly after
FIGURE 6.4 The exchangeable potassium is adsorbed at the p or planar position and at the edge or e position. Nonexchangeable potassium is fixed in the interlayer position. Strongly hydrated cations, like calcium, enter the interlayer space and remain exchangeable. Hydroxy-Al islands hold layers apart and may trap ions in the interlayer space. (After Rich, 1968, used by permission of the Soil Science Society of America.)

A large application of K fertilizer, drying will tend to fix K. The 2:1 clays in acid soils may contain some interlayer hydroxy-Al which prevents collapse of layers and K fixation. These clays, however, may contain K trapped between the islands of a hydroxy-Al matrix (see Figure 6.4).

The importance of K fixation depends on the situation. In some agricultural soils K fixation serves to conserve K because it reduces K loss by leaching. On the other hand, some agricultural soils have such large K-fixing capacities that large amounts of K fertilizer have little influence on yields. In Michigan, for example, crop yields were little increased, if at all, by K fertilization in a field that occupied a downslope position in the landscape. It was found that hydroxy-Al-interlayered vermiculite clay had formed on the upper slopes in an acid environment and was moved down-slope by erosion and deposited where soils were much more alkaline. The greater alkalinity removed much of the interlayer hydroxy-Al and restored the clay's K-fixing capacity. The K fertilizer was satisfying the soil's K-fixing capacity and was not available for crop growth. Banding of K fertilizer in soils with high fixing capacity has been found to increase the effectiveness of K fertilizer.

Exchangeable and Solution Forms

When a K+ leaves the interlayer space, it will very likely be adsorbed onto a cation exchange site and become XK. The XK maintains an equilibrium with the K in solution, and together the exchangeable and solution K make up the available K. After removals or additions of K, the time required for equilibration between solution K and XK is usually less than an hour; days or weeks are required for equilibration between exchangeable and fixed K. The solution K is equal to 1% to 3% of the exchangeable K in most soils. Depletion of solution K by plant uptake or leaching causes XK to move quickly into solution to reestablish the equilibrium. Since the XK tends toward an equilibrium with the fixed K, some fixed K will slowly become exchangeable. The reverse is true when the solution K is increased by K fertilizer (see Figure 6.3).

In some extremely weathered tropical soils there is little if any feldspar or mica K, and most of the K is exchangeable. In the kaolinitic and oxidic minerals of severely weathered tropical LAC soils, there is little if any K fixation. This is the situation for the Molokai soils, of suborder Torrox, in Hawaii; these soils developed from basalt, which contains few K minerals. On the other hand, some Oxisols in Africa have developed from granitic basement rocks rich in mica and still contain enough mica (muscovite) to provide sufficient K for low-intensity farming (see Figure 6.5).

Because the mineral component in Histosols is limited, most of the K exists as XK, and the soil has little or no capacity to fix K. Mineral materials tend to occur in Histosols as contaminants, and the amount of mineral material affects the K relationships in Histosols.

Leaching Loss

The loss of K by leaching is related to the concentration of K in the soil solution and the amount of water that leaches through the soil. The typically low concentration of solution K minimizes the losses that occur. As-
Soil and Fertilizer Potassium

Assuming a K concentration of 4 mg/kg of water and the leaching of 25 cm of water, the loss is equal to 10 kg/ha or 9 pounds/acre. These losses are typical of soils containing high-activity clay, HAC, and are small relative to the uptake of high-yielding crops. Leaching losses and the extent of K movement tend to increase as soils become more sandy.

Significant leaching losses are more likely on LAC soils because of their low CEC and limited K fixation. As much as 25% of the K was lost by leaching during the first year when 500 kg/ha of K was applied to Oxisols on the savannah in Brazil. Normally, K application rates and leaching losses are much less. However, losses of K by leaching appear to be more serious on LAC soils than on HAC soils, and K from fertilizer applications moves more deeply. In arid areas where soils are only minimally weathered and leaching does not occur, K fertilizers are usually unnecessary.

**Forms versus Plant Uptake**

The importance of the various forms of K as a K source for plants is illustrated by the results of a greenhouse experiment in which nine consecutive crops of alfalfa were grown on thirteen different soils. The soils contained an average of 1.62% total K, equal on a furrow slice basis to 36 210 kg/ha (32 302 pounds/acre). The amounts of exchangeable, fixed, and residual K (in micas and feldspars) were 1%, 3%, and 96% of the total, respectively (see Table 6.2). The alfalfa crops removed 399 kg/ha (356 pounds/acre) with 44% from a depletion of XK, 39% from fixed K, and 17% from the residual K. The uptake of one unit of K was correlated with 2 units of XK, 7 units of fixed K, and 517 units of residual K. During this period K uptake was significantly correlated with exchangeable and fixed K but not with residual K.

**PLANT AND SOIL POTASSIUM RELATIONSHIPS**

Of the nutrients removed from soils, plant uptake of K is often second to uptake of N. It is not uncommon for annual crops to remove over 224 kg/ha or 200 pounds/acre (see Figure 6.6).

**TABLE 6.2 Amounts of Various Forms of Potassium in Thirteen Iowa Soils and Removal by Thirteen Consecutive Crops of Alfalfa**

<table>
<thead>
<tr>
<th>Form of potassium</th>
<th>Soil potassium</th>
<th>Potassium uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kg/ha</td>
<td>pounds/*</td>
</tr>
<tr>
<td>Exchangeable</td>
<td>358</td>
<td>320</td>
</tr>
<tr>
<td>Fixed</td>
<td>1 084</td>
<td>967</td>
</tr>
<tr>
<td>Residual</td>
<td>34 768</td>
<td>31 015</td>
</tr>
<tr>
<td>Total</td>
<td>36 210</td>
<td>32 302</td>
</tr>
</tbody>
</table>

*Kilograms or pounds based on 2 000 000 of soil.

Source: Data from Pratt, 1951.

**UPTAKE AND ROLE IN PLANTS**

Potassium is absorbed from solution as an ion, K⁺, and plant uptake is closely related to solution concentration. Uptake is active and against a concentration gradient unless the solution concentration K is high. Potassium is associated with many enzymes involved in photosynthesis, organic compound synthesis, and translocation of organic compounds. The relative uptake of K early in the growing season is generally greater than that for N and P. Potassium is not complexed into organic compounds in plants and may be lost from plants late in the season through leaching of foliage and leakage from roots. Thus, the amount of K in plants may be greater some time during the growing season than at harvest (see Figure 1.6).

In cereals the K is concentrated in the vegetative parts so that the harvest of corn for silage removes large quantities of K compared to that removed by the harvest of corn grain. Potassium is mobile in plants. Deficiency symptoms appear on the oldest leaves as a chlorotic marginal firing. In advanced stages the entire leaf turns yellow and is necrotic. Weak stalks and lodging of grain crops are also caused by K deficiency. The deficiency symptoms for many crops is a yellowing and the eventual death of cells near leaf margins.

**POTASSIUM UPTAKE FROM SOILS**

Various studies have shown that the amount of exchangeable K in many soils is about equal to the annual uptake of productive crops, and that the amount in solution at any given instant is equal to 1% to 3% of the...
exchangeable K. Assuming that the solution K is equal to 2% of the exchangeable, the soil solution in effect will have to be depleted and replaced with K about 50 times during the growing season. Assuming that crop needs and exchangeable K in the plow layer are both 200 kg/ha (or about 200 pounds/acre) and that the solution K is equal to 2% of the exchangeable, 4 kg of K will be in solution per hectare. Daily maximum uptake rates of 8 to 10 kg/ha have been reported for corn. Thus, the solution would contain only a 12-hour supply during the period of maximum uptake. Obviously, mass flow will not move enough K to the roots to supply plant needs. Of the K taken up by corn, it has been estimated that 2% comes from root interception, 20% from mass flow, and 78% from diffusion. Most of the diffusion occurs within 4 mm of the root surface. The average K in the saturated extracts of 142 soils of the North Central region of the United States was found to be 4 mg/kg with a range of 1 to 80. For the soil solution to transport enough K to roots by mass flow, the concentration would need to be over 40 mg/kg.

The uptake of K is strongly correlated with the solution concentration of K ions, which depends on the equilibrium relation between the solution and the exchangeable K, and between the exchangeable and the fixed K. Early in the season plants deplete the solution K, which is rapidly replaced from the exchangeable K. As solution K is depleted over time, replacement of solution K slows down, for K ions exchange from sites having greater energy of adsorption. Less K comes from p sites and increasingly more K comes from specific adsorption sites on mica edges or in expanded sections of mica wedges. Over time the solution concentration of K and the amount of exchangeable K decrease. The lowered XK encourages the movement of fixed K to exchange positions. These events create a pattern in which XK is reduced early in the season and fixed K later in the season (see Figure 6.7).

**FIGURE 6.7 Uptake of potassium from one kilogram of loam soil by six corn plants in the greenhouse and loss of potassium from exchangeable and nonexchangeable forms in the soil. (From Black, 1968, used by permission of John Wiley & Sons.)**

**Potassium Buffer Capacity**

Removal of K from the soil solution by plant uptake during the growing season is usually associated with a decrease in XK, which is followed by a decrease in nonexchangeable K, as shown in Figure 6.7. Changes in XK are associated with changes in the concentration of K in solution, that is, with K availability. The ability of the soil to maintain the solution concentration of K during the growing season while XK is being depleted is the potassium buffer capacity, KBC. The KBC can be ascertained from graphs in which are plotted the amount of XK on the ordinate and the solution K concentration on the abscissa. The slope of the line, or the ratio of the change in amount of XK to the change in solution K concentration, is the KBC. A steep line reflects a high KBC, which renders the soil capable of maintaining the solution K while experiencing a large decrease in exchangeable K. Well-buffered soils tend to have high CEC and contain large amounts of XK and mica wedge K.

**Quantity and Intensity Relationships**

The quantity and intensity, or Q/I, relationship concept was introduced in 1964 to express the KBC. Similar graphs are produced, except that on the ordinate is the change in exchangeable K associated with various K activity ratios, AR'.

To obtain the data for the graph in Figure 6.8, fixed quantities of solution with the same $a_{\text{Ca}^2+}$ and $a_{\text{Mg}^{2+}}$ are made with varying $a_{\text{K}^+}$. The solutions are mixed with soil and allowed to stand for a period of time. In effect, this creates soils with differing amounts of XK. Then the solutions and soil are separated and the solutions analyzed for K, Ca, and Mg. The gain or loss of K in the solution represents loss or gain from the soil, respectively. This gain or loss is attributed to a change in the amount of XK and is expressed as change in K, in milliequivalents per 100 grams, and plotted on the ordinate. The final solution concentrations of K, Ca, and Mg are converted into activities and used to calculate the AR' of the final solutions and are plotted on the abscissa. Calculation of the AR' is as follows:

$$\text{AR}' = \frac{a_{\text{K}^+}}{(a_{\text{Ca}^2+} + a_{\text{Mg}^{2+}})^{1/2}}$$

The slope of the line in the graph is a measure of the KBC (see Figure 6.8). The steep slope for soil A represents a soil strongly buffered with K, one that has a large capacity to maintain the AR' by changes in the amount of XK (and fixed K) during the growing season. Where the line crosses the abscissa at zero change in XK, the soil is at its equilibrium AR'. The Q/I relationship expresses both the intensity (/) or instant K availability and the subsequent availability (Q).

Extremely weathered soils with kaolinitic and oxidic mineralogy, and with little or no fixed K and little exchangeable K, are poorly buffered.
Soil and Fertilizer Potassium

FIGURE 6.8 Typical quantity-intensity curves. The steeper curve for soil A indicates that, compared to soil B, it has a smaller change in solution K (I) with a change in the quantity of exchangeable K (Q) and, therefore, a greater potassium buffer capacity (KBC).

Such soils are unable to maintain a satisfactory AR\textsuperscript{+} as K is taken up during the growing season.

Luxury Consumption

Fixation and leaching tend to maintain an AR\textsuperscript{+} low enough to prevent luxury consumption of K in most soils. Large applications of K fertilizer, however, can bring about excessive or luxury consumption of K. The results of an experiment as shown in Table 6.3, illustrate how the uptake of K rises to luxury levels.

A large quantity of field soil was collected and brought to the greenhouse. The soil was divided into three samples. One was untreated; a second was leached with a salt solution, which removed the XK; and the third sample was leached for several hours with HCl, which removed both the XK and the fixed K. These treatments were the first three listed in Table 6.3. Part of the soil from which the XK and fixed K had been removed, by the third treatment, was then given a large application of K fertilizer, which restored the fixed K and the XK. The amount of K applied was equal to 800 pounds/acre; this procedure made up the fourth "treated plus K fertilizer" treatment. Crops were then grown on these parcels of soil. Removal of the XK reduced yields to 62% of the untreated soil yields. Removal of the XK and fixed K reduced yields to only 21% of the untreated soil yields. The addition of K fertilizer to the soil that had had both
the exchangeable and fixed K removed produced a yield that was 149% of the yield of the untreated soil. Decreases in the uptake of K were comparable to the exchangeable and fixed K removed. By contrast, however, the K fertilizer produced such high levels of solution K that uptake was 968% of the untreated soil uptake. Such an uptake constitutes luxury consumption of K. The yield was increased 149%; however, the increase in K uptake was 968%.

**FACTORS AFFECTING UPTAKE OF POTASSIUM**

Potassium uptake at the root level is closely related to the concentration gradient between soil and root, the rate of K diffusion through soil to root surfaces, and the surface area of roots. Plants grown on different kinds of soils with the same exchangeable K may take up different amounts of K during the growing season and yield differently owing to differences in the KBC. The effect of temperature on K uptake is very complex because chemical transformations of K in the soil are temperature-dependent, and root growth and other plant processes are affected by temperature. Several other factors that affect K uptake from soils will be discussed.

**Soil Moisture**

Diffusion of K through soil water to roots is the most limiting step in K uptake during the growing season. As soils dry K diffusion decreases, making the available K, in a sense, less available for uptake. And as soils dry there is also less water in which the K can diffuse, and the diffusion paths are more tortuous.

The effects of dry weather on yields and K uptake are variable. If dry weather causes more deeply penetrating roots to grow and forage through a greater volume of soil, yields and total K uptake may increase. The results are highly dependent on the forms and amounts of subsoil K.

**Cation Exchange Capacity**

As the CEC increases, a given amount of exchangeable K will equilibrate with less K in solution, which is the dilution effect. Fine-textured soils require a higher level of exchangeable K to produce the same AR + and yields that coarse-textured soils do. Many states account for variations in CEC when making K fertilizer recommendations. For example, the desired exchangeable K level for general cropping in Ohio is calculated as follows:

\[
\text{desired soil test level} = 220 + (5 \times \text{CEC})
\]

Soils with higher CEC usually have fine texture and have slower K diffusion rates as compared to coarse-textured soils with the same water content.

**Exchangeable Cation Suite**

An increase in the quantity of any cation increases the solution concentration or activity of that cation when all other factors remain constant. In calcareous soils the opportunity for Ca ++ dissolution is great, and a low AR + may depress K uptake under these conditions. Corn grown on the highly calcareous Harpster soil in Iowa frequently had K deficiency symptoms when corn grown on nearby noncalcareous Webster soils yielded very well. The yield differences were associated with significant differences in plant composition. The normal and calcareous soils produced different-sized plants with nearly identical amounts of K + Ca + Mg in milli-equivalents per 100 grams. In the normal plants, however, K made up 60% of the total cations as compared to only 13% for plants grown on calcareous soil.

**Soil pH Influences**

In acid soils with exchangeable Al, increasing soil pH decreases the amount of exchangeable Al + and allows K to compete more effectively against Ca and Mg for exchange sites. With more K ions adsorbed onto exchange sites, there is more adsorbed K and less K in solution. The removal of the interlayer hydroxy-Al of clays increases the potential for K fixation. A pH increase is accompanied by an increase in pH-dependent CEC, creating more sites for cation adsorption, including adsorption of K. The addition of lime adds Ca ++ and Mg ++ ; it also decreases the AR + . All four of these effects reduce solution K + or Ca ++ and the AR + . By contrast, however, these effects reduce the loss of K from soils by leaching. If liming reduces Al toxicity, plants may grow larger and take up more K. Thus, the relation between soil pH and K availability is complex, and liming has a highly variable affect on K uptake.

**Soil Aeration**

Active accumulation of K by roots depends on metabolic energy. When soils become water-saturated and respiration is reduced for lack of O 2 , nutrient uptake is reduced. Of the nutrients absorbed in the greatest amounts, K has its percentage of composition and uptake reduced considerably more by poor aeration than do some of the other nutrients, as shown in Table 6.4. The data in Table 6.4 also show how the uptake of one ion, in this case K, and plant growth may be reduced with perhaps normal uptake of other ions and an increase in their percentage of composition.

**Plant Differences**

A difference in the K-exploiting ability of grasses and legumes has received much attention. Legumes are inferior to grasses in their ability to extract soil K. When both are grown together in soils with marginal levels of K,
the legumes may encounter K deficiency while the grasses grow well. Using biotite as a K source in greenhouse experiments, researchers found that the legumes may encounter K deficiency while the grasses grow well. Using biotite as a K source in greenhouse experiments, researchers found that wheat can use biotite K and alfalfa cannot. Similar results have been obtained by comparing ryegrass and red clover. Differences in the K uptake from a given soil by different varieties or cultivars have also been found. It appears that genetic improvement of plants can bring more efficient use of soil K with corresponding yield increases.

**Topsoil versus Subsoil Potassium**

The importance of subsoil K depends on the level of available subsoil K relative to the topsoil, on root density, and on the residence time of roots for K uptake. Root development occurs first in the topsoil, and root density is typically much greater in the topsoil than in the subsoil. By the time roots have become abundant in the subsoil, the stage of plant development may play a role in uptake. Subsoil K tests are usually lower than topsoil tests, and all these factors tend to account for more effective use of topsoil K.

Considerable work on roots and nutrient uptake has been conducted at Purdue University by Barber and his colleagues. They found that for corn (maize) 55% of the roots were in the subsoil and accounted for only 10% of the total K uptake. A regional field experiment in the North Central region of the United States found that including subsoil K tests with topsoil tests did little to improve the correlation between soil tests and K uptake.

The opposite situation holds for some Ultisols of the Coastal Plains that have very sandy surface soils overlying much finer-textured subsoils; these subsoils retain large amounts of plant-available K. The yields of corn and soybeans are significantly affected by subsoil K. In Delaware subsurface sampling of such soils is routinely recommended in assessing K fertilizer needs.

### Table 6.4 Effects of Aerating a Saturated Soil on the Percentage of Composition and Uptake of Nutrients by Corn

<table>
<thead>
<tr>
<th>Treatment</th>
<th>N</th>
<th>P</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerated</td>
<td>3.33</td>
<td>0.24</td>
<td>1.50</td>
<td>0.63</td>
<td>0.67</td>
</tr>
<tr>
<td>Saturated</td>
<td>3.86</td>
<td>0.55</td>
<td>0.65</td>
<td>0.96</td>
<td>0.96</td>
</tr>
<tr>
<td>A/S</td>
<td>0.86</td>
<td>0.44</td>
<td>2.31</td>
<td>0.66</td>
<td>0.70</td>
</tr>
</tbody>
</table>

- **Aerated**
  - N: 3.33, P: 0.24, K: 1.50, Ca: 0.63, Mg: 0.67
- **Saturated**
  - N: 3.86, P: 0.55, K: 0.65, Ca: 0.96, Mg: 0.96
- **A/S**
  - N: 0.86, P: 0.44, K: 2.31, Ca: 0.66, Mg: 0.70

**Source:** Data from Lawton, 1945.

**Basis of Potassium Fertilizer Recommendations**

The soil solution K concentration and the I value have been used as a measure of K availability. The XK and Q are related to the ability of the soil to supply K in solution. When experiments are conducted to correlate K uptake and crop yield with I and Q, the best correlations are with Q. This is to be expected when crops remove large amounts of K relative to the amount in solution. Many experiments have shown high correlations between XK and uptake. To measure K availability most soil-testing labs use an extracting solution of 1 M NH₄OH adjusted to pH 7.0. This test is a measure of XK. The amount of K extracted is generally equated to pounds of XK in a 2 000 000-pounds/acre furrow slice in the United States. Experiments are conducted to determine the K fertilizer rate and to develop curves that relate yield to fertilizer rate for soils with varying soil test levels. These data are organized into tables and equations for making K fertilizer recommendations for a particular yield goal.

In highly weathered Oxisols and Ultisols there may be essentially no fixed K to provide for the replacement of XK. Complimentary ions like Ca and Mg may have an impact toward lowering the AR. Thus, it is sometimes recommended that the minimum amount of K be at least 2% to 3% of the sum XCa..Na, in milliequivalents per 100 grams.

**Potassium Fertilizers**

Wood ashes that contained K₂CO₃ were an early source of K for industrial and agricultural use. The first commercial-scale production of K fertilizers began in Germany in 1861, only about fifteen years after Liebig discovered that K was an essential element for plants. Until then salts had been mined in Germany for NaCl, and the accompanying K salts were discarded (Salzburg means salt city). Because K fertilizers were needed, production developed rapidly in Germany and dominated world trade until after World War I.

**Potassium Ore Deposits**

Most of the K ore is now obtained by mining evaporite deposits that were created by the evaporation of ancient seas under arid conditions. Today these deposits exist under overburdens of varying thickness. More than half of the world’s known reserves occur in Canada and the USSR. Other major deposits exist in the United States, Europe, the Middle East, Thailand, Zaire (the Congo), and South America.

The major mining operations in the United States are in southern New Mexico near Carlsbad. Here evaporite deposits occur in the Permian basin. Many ore layers are present with the most productive zone being 1.5 to 3 meters thick at 250 to 610 meters below the surface. The ore is shaft-
mined. Other important operations include solution mining of evaporite deposits in Utah and recovery of brine deposits in Utah and California. Canada has the largest K reserves in extensive deposits in Saskatchewan. The evaporite ore is 660 to 3 050 meters below the surface. In places the ore is too deep for shaft mining, and solution mining is then used. These deposits extend southward in North Dakota, where they are deeper and not mined. About 95% of all the K mined is used for fertilizer manufacture.

**Ore Composition and Fertilizer Manufacture**

Many different salts are found in evaporite deposits. At Carlsbad the ore is composed largely of sylvite, a physical mixture of KCl and NaCl crystals. Present to a lesser degree is langbeinite composed of sulfates of K and Mg. Nearly all the K used for fertilizers comes from the processing of sylvite and basically requires a separation of KCl and NaCl. Over 95% of K fertilizer is KCl and has a K content of at least 49.8%. Three methods for the production of KCl using sylvite ore are flotation, heavy-media separation, and fractional crystallization.

**Fractional Crystallization Method**

Fractional crystallization is a historic method developed in Germany. The separation of KCl from NaCl is based on the different solubilities and temperature characteristics of the two salts. The solubility of NaCl remains quite constant with temperature, whereas the solubility of KCl is greatly increased by an increase in temperature. Saturated solutions of both salts at ambient temperature are heated to boiling. Then enough crushed ore is added to saturate the solution with respect to KCl. The dissolution of KCl depletes the ore of KCl, but the NaCl content of the ore is little affected. The hot brine is cooled to ambient temperature to crystallize out the KCl that dissolved from the ore. The recrystallized KCl is separated from the brine, dried, and sent to storage.

**Froth Flotation Method**

The froth flotation method is the most popular and economical. Other advantages include ease of control and flexibility. Figure 6.9 is a diagram of the flotation process.

The ore is crushed fine enough that relatively pure grains of NaCl and KCl are produced. These are added to a saturated brine of KCl and NaCl which produces a pulp containing 50% to 75% solids. Desliming separates out foreign substances such as clays and other insoluble materials. The ore is then treated with hydrogenated tallow amine, a hydrochloride soap which preferentially adheres to the KCl grains. Air is bubbled through the pulp in shallow, agitated tanks or flotation cells. The KCl particles float to the top and are continuously skimmed off. The NaCl and other salts from the ore remain on the bottom of the cells and are continuously removed. The KCl particles are filtered from the brine, dried, and sent to storage.

**Heavy-Media Separation**

The heavy-media separation method uses large or coarse crystal grains, which are found in the Saskatchewan ore deposits. Less grinding is re-
quired, and the KCl is separated from NaCl based on difference in specific gravity. The ore is coarse-crushed, and particles in the size range 1.6 to 6.5 mm are removed and used while the smaller particles are processed by the froth flotation method.

The heavy-media process uses a saturated brine to which magnetite, Fe₃O₄, with a specific gravity of 5.17, is added. Enough magnetite is added to produce a specific gravity of the saturated brine between 1.98 and 2.13, the specific gravities of KCl and NaCl, respectively. Sized particles in the range of 1.6 to 6.5 mm in diameter are mixed with the specific-gravity-adjusted brine. Centrifugal separation methods are used to remove the KCl, which is debrined, dried, crushed, and sent to storage.

Sizing and Granulation
Elaborate screening and granulation facilities are used to produce particles in sizes appropriate for various uses. Bulk blenders require a particle size that matches the sizes of other materials used in the blend; the particles should have diameters in the range 0.84 to 3.36 mm. Suspension fertilizer manufacturers need particles of KCl with diameters in the range 0.11 to 0.42 mm. Drum granulation to produce complete or mixed fertilizers uses particles in the 0.2- to 1.2-mm size range. Some particle size needs are met by passing KCl from the primary refinery operation through high-pressure compactor rollers. The dense KCl flakes produced are crushed and screened to provide the desired particle size (granulation). Undersized particles are recycled.

Other Processes and Materials
Most commercial K fertilizer plants produce K₂SO₄, by reacting KCl with H₂SO₄. Langbeinite, K₂SO₄ • 2MgSO₄, is used as a source of K, Mg, and S. Reacting langbeinite with KCl produces K₂SO₄ and MgCl₂. Reacting KCl with HNO₃ produces KNO₃. Small amounts of K are produced from natural brines at Searles Lake in California, Great Salt Lake in Utah, and the Dead Sea in Israel. At Great Salt Lake and the Dead Sea brine is taken from the area where water has been retained the longest and brine concentration is the greatest. The brine is pumped into solar evaporation ponds where water evaporates and salt crystallizes.

REFERENCES
Sulfur and the micronutrients can be differentiated from N, P, and K in that they are much less frequently the limiting factor in soil fertility. Moreover, the amounts of S and micronutrients added to soils in fertilizers are relatively small. This chapter considers S and the micronutrients as well as some elements that may produce toxicity in plants and animals.

**SULFUR**

Even though plants use a considerable amount of S, only small quantities must be added to soils to improve their fertility at the present time. This is a paradox, since plants require as much S as P, but P has been considered one of the major fertilizer elements for years. We must consider two factors to understand why only small amounts of S are needed in fertilizers. First, S has been added to soils indirectly for more than 200 years. Gypsum, CaSO₄ • 2H₂O, was applied to soils as early as 1768. Superphosphate, developed as a P source and applied to soils after 1850, contained 12 percent S. One of the first commercial N fertilizers, ammonium sulfate, also contained S. Thus, S was commonly added to the soil along with N and P. A second major factor is that S is added to soils through precipitation; rain furnishes all or part of the S required for growing crops. Industrial development has put more S into the atmosphere, and hence greater quantities of S are added through rainfall.

Modern technology has developed higher-analysis N and P fertilizers that do not contain S. Current clean-air standards are reducing industrial emissions of S. These technical advancements would suggest that S levels in soils may be reduced in the future.

**Sulfur Content of Crops and Atmospheric Deposition**

The S content of crops varies from 45 kg/ha (40 pounds/acre) for alfalfa to 6 kg/ha (5.4 pounds/acre) for rice (see Table 7.1). Some generalizations in Table 7.1 are worthy of note. First, grains remove relatively little S compared to a forage crop. Alfalfa, for example, removes five times as much S as wheat and 7.5 times as much as rice. Second, the stover or straw portion of a crop, which is often returned to the soil, contains a significant amount of S. Finally, the particular crop rotation will have a major effect on the soil fertility level of S. Atmospheric deposition of S is quite variable but usually in the range of 3 to 12 kg/ha (2.7 to 10.7 pounds/acre) in the United States. Thus, a crop rotation that includes a high percentage of alfalfa and forages will receive much more S from the soil each year than is deposited from the atmosphere. On the other hand, a rotation with a high percentage in small grains may more nearly balance removal with atmospheric deposition. Near some industrial sites enough S has been deposited to kill all vegetation.

**Sulfur Cycles**

A simplified S cycle is shown in Figure 7.1. The forms of S added to the atmosphere include SO₂, SO₄²⁻, H₂S, S°, dimethyl sulfide (DMS), and other organic sulfides. The sources of the S released to the atmosphere include natural and manufactured materials. Volcanic activity releases significant amounts of S as SO₂, H₂S, and SO₄²⁻. Soils contribute about one-third of the S. Recently, it was reported that the wetlands release large quantities of DMS to the atmosphere. Oceans are also a source of considerable amounts of S (24% of total) released to the atmosphere, for the most part as DMS.

Emissions brought about through the activities of human beings are...
Sulfur and Micronutrients in Soils and Fertilizers

FIGURE 7.1 A generalized diagram of the sulfur cycle.

Sulfur and Micronutrients in Soils and Fertilizers

FIGURE 7.1 A generalized diagram of the sulfur cycle.

largely associated with power plant operation and automobiles, although other industrial inputs contribute some S. Most of the inputs are as SO\(_4^{2-}\), H\(_2\)S, and SO\(_2\). Once in the atmosphere, all forms can be expected to be oxidized to SO\(_4^{2-}\) by reaction with OH\(^-\), O\(_2\), O\(_3\), and other oxidants. But the length of time necessary for this oxidation can be quite variable. The major S forms are oxidized in less than one week, but COS (carbonyl sulfide) is stable in the atmosphere for many years.

Sulfur from the atmosphere enters the soil portion of the S cycle either through dry deposition or through wet deposition. Sulfate is a source of acidity during wet deposition since it commonly associates with H\(^+\) during this deposition.

Soluble sulfate, SO\(_4^{2-}\), is the principal inorganic ion in well-aerated soil solutions. If the soil solution contains sulfate S equal to 3 to 5 mg/L, it is considered adequate for plant growth. Plants will utilize sulfate, which reaches the roots by mass flow, diffusion, or both. Generally, mass flow will be the major mechanism if there is more than 5 mg/L of S in the solution.

Sulfate in solution is also in rapid equilibrium with adsorbed SO\(_4^{2-}\) in soils. Hydrous oxides of Al and Fe, as well as exposed Al from edges of clay minerals, are the principal sites of adsorption of sulfate. The adsorption is strongly pH-dependent, with the greatest adsorption being found in the very acid soils. Adsorption for a given soil decreases rapidly as pH is increased from 4 to 7. Quantities of adsorbed SO\(_4^{2-}\) are usually greater in the subsoil than in the surface soil because of the greater content of clay minerals and Fe and Al hydrous oxides in the subsoil. The possibility of adsorbing SO\(_4^{2-}\) onto Fe and Al bound to organic matter certainly exists.

More than 90% of the total S in the A horizons of soils exits in the organic form. The N:S ratio in surface soils is relatively constant, with a ratio of about 10:1.3. The nature of this organic S is quite complex. To characterize it, researchers have fractionated organic S into HI-reducible S, which is S not directly bonded to C. It is usually believed to be ester sulfates (-C-O-S) or related compounds. Most soils will have between 30% and 70% of the organic S as the HI-reducible S fraction, but soils have been reported that fall considerably out of this range. The more stable organic S fraction is the carbon-bonded S fraction. Usually 10% to 20% of the organic S in A horizons is in this fraction. The remaining fraction is nonreducible S sometimes referred to as inert or residual organic S.

When soils become poorly aerated (anaerobic), SO\(_4^{2-}\) can be reduced to H\(_2\)S and other reduced S compounds. This reduction would normally be expected to occur only after other electron acceptors such as Mn\(^{4+}\), NO\(_3^-\), and Fe\(^{3+}\) have been used. The H\(_2\)S may escape to the atmosphere or form very insoluble precipitates with Fe, Zn, Cu, and other elements. In addition, DMS is one of the major reduced S forms produced in anaerobic soils, and its release to the atmosphere has already been noted.

Plant Responses to Sulfur

The probability of obtaining a response to S fertilization generally increases from the eastern to western United States. Few cases of a response to S have been reported in the northeastern or midwestern states where atmospheric deposition is significant. Sulfur responses, however, are common in the western United States where many soils have developed from volcanic parent materials and there is little atmospheric deposition. Irrigation water may often furnish S, so deficiencies are less often found on irrigated lands. Sandy-textured soils are more likely to be deficient than fine-textured soils. Crop responses vary with species, but legumes tend to be more responsive than cereals.

Diagnosing Sulfur Deficiencies

As with other nutrients, S deficiencies have been detected through soil testing and plant analysis. The literature would indicate that plant testing is the more reliable guide, although soil testing does identify potentially S-deficient soils.
A number of extracting solutions have been used to extract soils, all of which aim to remove soluble and adsorbed SO\(_4\). A partial, but certainly not complete, list would include CaCl\(_2\), (0.01 to 0.1 M), Ca(H\(_2\)PO\(_4\)), 0.25 M H\(_2\)OAc plus 0.15 M NH\(_3\).F, and 2 N acetic acid containing 500 ppm of P. Although variable with location and crop, the critical level of S is expected to be from 3 to 8 mg/kg. Even when a soil test shows the amount of S to be below the critical level, crops may not respond to applications of S fertilizer because (1) they obtain S from greater depths than were sampled, (2) organic S is mineralized during the growing season, (3) S additions from the atmosphere or water are not accounted for by the soil test, and (4) factors other than S limit yields. In summary, the soil test for sulfate is useful as a guide but will often fail to indicate which soils will respond to applications of S.

Critical values for the total S content of plant tissue have been developed. Data compiled for local areas should be consulted for exact critical values, but a few guidelines will be given here. A total S content of plant tissue that exceeds 0.26% may be considered optimum for ryegrass, alfalfa, and clovers. Values that exceed 0.17% may be considered optimum for small grains, and the content of an ear leaf of corn should be more than 0.12% S to be optimum.

Correcting Sulfur Deficiencies

A number of materials may be used to correct S deficiency, including ammonium sulfate (21-0-0), superphosphate (0-20-0), potassium sulfate, magnesium sulfate, calcium sulfate (gypsum), and elemental S. The recommended amount of S will usually be between 20 and 40 pounds/acre.

MICRONUTRIENTS

A number of elements that are required by plants in very small quantities are known as micronutrients or trace elements. This term usually applies to elements that are contained in plant tissues in amounts less than 100 mg/kg. Although trace elements have been known to affect plant growth for many years, they have been studied intensively since 1950. Two factors have accounted for this. First, when the other growth factors kept yields at relatively low levels, seldom did micronutrients limit growth and yield. But with the advent of modern fertilizer technology, irrigation, and new varieties came very high yield potentials. Micronutrient supplies in soils that were adequate for 40, 50, or even 100 bushels of corn per acre were not adequate for yields of 200 bushels or more. Thus, the need to study soil fertility from the micronutrient standpoint became more pressing.

Our ability to study micronutrients has always been closely tied to our analytical capabilities. Although colorimetric methods have existed for many of the micronutrients, they were laborious and often subject to a variety of interferences. When atomic absorption spectrophotometry became common in the early 1960s, it lent itself well to determinations of the trace metals Zn, Cu, Mn, and Fe as well as other trace metals, such as cadmium and nickel which are potentially toxic. Inductively coupled plasma emission spectrophotographs gave us the ability to analyze for many elements at the same time, thus greatly reducing the cost of analysis.

Classification of Micronutrients and Trace Elements

The micronutrients that are essential for plant growth are zinc, copper, iron, manganese, boron, molybdenum, and chlorine. Others such as vanadium, sodium, nickel, cobalt, and silicon may have some function in plant growth. It is obviously very difficult to purify all growth media to the point of proving essentiality for a trace element. Consequently, others may be added to this list at a later date. The term trace element may be more applicable in the discussion of certain metals that are essential for animal growth or in fact toxic to either plants or animals.

Certain trace elements are essential for animal growth and are generally furnished the animals (including human beings) by the plant material consumed. Included in this list would be cobalt, chromium, selenium, iodine, and perhaps tin and nickel. Other elements are known to be toxic to plants, animals, or both. These include mercury, lead, and cadmium. For many others, the levels will determine the toxic or beneficial nature of the element. For example, Cr, which is required in very low levels for animal growth, may enhance plant growth under some conditions. But Cr can be quite toxic to both plants and animals if present in very high levels.

A complete discussion of all trace elements is beyond the scope of this book. We will focus here on the identification of soils and cropping systems that are likely to be infertile because of micronutrient deficiencies. We will also discuss how to identify and correct the deficiencies. The micronutrients covered will be Zn, Cu, Fe, Mn, B, and Mo.

ESSENTIAL MICRONUTRIENTS

Of the six essential micronutrients that will be considered, four—Cu, Zn, Mn, and Fe—exist as cations in soils, and two—B and Mo—exist as anions or as uncharged molecular species. The discussion will reflect these differences. A general diagram reflecting the different pathways that micronutrients may take in soils is given in Figure 7.2.

The importance of a particular pathway will depend on the micronutrient and the particular soil. Each may be added to the soil's pool of soluble micronutrients by weathering of minerals, by mineralization of organic matter, or by addition as a soluble salt. Once in the soil as a soluble nutrient,

the micronutrient may undergo a number of reactions. Many of the micronutrients will readily precipitate in soils. A given micronutrient may be absorbed by a plant or microorganism. Crop harvest obviously removes micronutrients from the system. Micronutrients are also incorporated into humus, which is formed as plant residues are digested by microorganisms. This process immobilizes micronutrients just as it does other nutrients.

Adsorption of micronutrients, either by soil organic matter or by clay-size inorganic soil components, is an important mechanism of removing micronutrients from the soil solution. Finally, micronutrients may leach from soils. But generally, leaching is a minor component of the mechanisms by which micronutrients are removed from the soil solution.

Copper and Zinc

Both Cu and Zn occur in the earth's crust primarily as sulfide minerals. Igneous rocks contain larger amounts of Cu and Zn than do sedimentary rocks, and both elements concentrate more in basalt than in granite. The earth's crust contains on the average 55 ppm Cu and 70 ppm Zn. Soils commonly vary in total elemental content from 2 to 100 ppm Cu and from 10 to 300 ppm Zn.

Copper

Except for copper's occurrence in certain primary minerals, it is bound strongly by adsorption, principally by organic matter, as shown by reaction 8 in Figure 7.2, rather than by precipitation. Thus, profile distributions of Cu tend to follow the organic matter distribution, with higher concentrations in the surface horizons. These distributions reflect increases in Cu in horizons that have accumulated organic matter (as in spodic horizons). It has been shown that carboxyl and phenol groups are important as the functional groups binding Cu to soil organic matter. Copper is more strongly bonded by organic matter than other metals, with the exception of Fe and Al.

The role of organic matter in Cu chemistry is also indicated by analysis of the soil solution. More than 99% of the Cu in the soil solution is complexed by organic matter. This complexing is of great importance in maintaining adequate Cu in solution for plant use. Of the inorganic forms of Cu, Cu$^{2+}$ is the major ion species for pHs less than 6.9, and the ion pair Cu(OH)$_2$ is the major species for pHs above 6.8. Although CuOH does form, it is never significant relative to the other two species.

Deficiencies of Cu are not commonly found in mineral soils. Organic soils (Histosols) containing little ash are more likely to be deficient. When organic soils are deficient, any one of a number of Cu carriers are satisfactory. Some of the common carriers are listed in Table 7.2. The initial application of Cu should usually be banded at the rate of 6 pounds/acre. Because Cu accumulates in soils, no additional amount need be added for crops that respond little to Cu after a total of 20 pounds/acre has been applied over a period of years. This amount needs to be doubled for highly responsive crops.

If a Cu deficiency is found during the growing season, foliar sprays can be used at one-half to one pound of Cu per acre, dissolved in 30 gallons of water. Common carriers for this purpose are CuSO$_4$ and CuO. Chelated forms of Cu are well adapted to foliar application. The Cu chelates used as sprays should be applied at the rate of about 35 g Cu/acre dissolved in 30 gallons of water.

Zinc

Many data have accumulated indicating a decrease in the solubility of Zn with increasing pH. But precise identification of a solid phase that controls the solubility is difficult. The most important factors affecting Zn solubility appear to be pH and Eh. The Eh of soils is not usually measured, but it is known that Eh of soils is typically in the range of 100 to 200 mV. The most important factor affecting Zn solubility is pH.

Zinc is also taken up by plants in the form of metallic Zn. The principal process by which Zn is adsorbed by soils is by the formation of a phyllosilicate surface complex. This surface complex is formed by the reaction of Zn with the surface hydroxyls of the clay minerals. In this way, Zn is adsorbed on the clay surface without being dissolved in the soil solution.

<table>
<thead>
<tr>
<th>Carrier</th>
<th>Formula</th>
<th>Cu, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basic copper sulfate</td>
<td>CuSO$_4$·Cu(OH)$_2$</td>
<td>13-53</td>
</tr>
<tr>
<td>Copper sulfate</td>
<td>CuSO$_4$·5H$_2$O</td>
<td>35</td>
</tr>
<tr>
<td>Cupric ammonium phosphate</td>
<td>Cu$_2$PO$_4$·10H$_2$O</td>
<td>32</td>
</tr>
<tr>
<td>Copper EDTA chelate</td>
<td>Cu(NH$_4$)$_2$EDTA·H$_2$O</td>
<td>13</td>
</tr>
<tr>
<td>Copper HEDTA chelate</td>
<td>NaCu(HEDTA)</td>
<td>9</td>
</tr>
<tr>
<td>Copper frit</td>
<td>Frit</td>
<td>40-50</td>
</tr>
<tr>
<td>Cupric oxide</td>
<td>CuO</td>
<td>75</td>
</tr>
<tr>
<td>Cuprous oxide</td>
<td>Cu$_2$O</td>
<td>89</td>
</tr>
<tr>
<td>Copper chloride</td>
<td>CuCl$_2$</td>
<td>17</td>
</tr>
</tbody>
</table>

Zn solubility has been difficult. However, Zn uptake by plants declines rapidly as pH increases (see Figure 7.3).

Of the inorganic Zn species in the soil solution, Zn$^{2+}$ is the predominant one for pHs less than 7.7, and ZnOH$^+$ is the predominant species for pHs between 7.7 and 9.1. The ion pair Zn(OH)$_2$ is important only for pHs above 9. Organic matter does complex Zn in soil solution, but the percentage of Zn that is complexed varies over a considerable range, from 28 to 99 with a mean of 60 for 20 soils according to one study.

The importance of organic matter in maintaining available Zn is often illustrated by Zn deficiency, which appears in areas where the surface soil has been removed, either through leveling to prepare for irrigation or during the installation of drainage lines. Here the effect may also be due to increased pH, since removal of the surface layer very often exposes calcareous B and C horizons.

High levels of P in soils has been known to intensify Zn deficiency in a number of crops. It was particularly noticeable in rotations of navy beans, a crop susceptible to Zn deficiency, followed by sugar beets, a crop responding to high levels of P fertilization. Data illustrating this interaction are given in Table 7.3.

The exact cause of the Zn-P antagonism has been difficult to determine. Several factors, however, are important from a soil fertility standpoint. The Zn-P antagonism occurs on calcareous soils and may be related to Fe availability. Moreover, this relationship may not be a soil relationship but one within the plant itself. Applications of Zn will readily overcome the P-induced Zn deficiency. The Zn applications show a considerable residual effect, indicating that the total Zn available in the soil is very important in preventing Zn deficiency (see Table 7.4). The experiment was initiated in 1965, but severe drought in the summer of 1965 eliminated yields that year. Residual Zn was very effective in increasing yield, not only through the two years recorded here but for several additional years. The lower yield for the 3 pounds/acre of Zn banded yearly for this site shows that this rate for applying Zn was not adequate for a soil with this degree of Zn deficiency. Other data have shown that banding Zn is a satisfactory method of supplying it if sufficient quantity is used.

Carriers for Zn are given in Table 7.5. Inorganic carriers have been satisfactory for correction of Zn deficiency. If the less soluble forms of Zn, such as ZnO are used, they should be finely ground. There is considerable evidence that the less soluble carriers should be broadcast and incorporated into the soil, whereas the soluble carriers such as ZnSO$_4$ and Zn chelates should be banded with starter fertilizer at planting time. Rates of 3 to 4 pounds/acre of Zn as inorganic carriers band-applied with a starter fertilizer each year are satisfactory. Chelated material may be applied at one-fifth the rate of the inorganic carriers. A single broadcast application of 25 pounds Zn/acre appears to be adequate for many years.

Considerable success has been obtained by incorporating Zn in starter fertilizers. For example, ZnO incorporated into ammonium polyphosphate becomes soluble and available to plants. Although trace elements such as Zn have been found to be beneficial in stabilizing APP liquid fertilizers, we must question the use of a high-P starter fertilizer as a carrier of Zn in field situations in which the Zn deficiency is induced by high-P soil levels.

### Table 7.3 Interaction of Phosphorus and Zinc with Navy Bean Yield

<table>
<thead>
<tr>
<th>Zinc, pounds/acre</th>
<th>Carrier</th>
<th>No Extra P</th>
<th>174 Extra P*</th>
<th>696 Extra P*</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>-</td>
<td>30.8</td>
<td>20.0</td>
<td>8.8</td>
</tr>
<tr>
<td>4.0</td>
<td>Zinc sulfate</td>
<td>39.1</td>
<td>39.8</td>
<td>34.6</td>
</tr>
<tr>
<td>4.0</td>
<td>Residual (1 year)</td>
<td>29.7</td>
<td>24.3</td>
<td>12.1</td>
</tr>
</tbody>
</table>

*Source: Judy et al., 1964.*

*Pounds P/acre.

### Table 7.4 Effect of Residual Zinc on Yield of Pea Beans

<table>
<thead>
<tr>
<th>Zinc, pounds/acre</th>
<th>Carrier</th>
<th>Time of application</th>
<th>Crop yield, bushel/acre</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>-</td>
<td></td>
<td>4.2</td>
</tr>
<tr>
<td>3.0</td>
<td>ZnSO$_4$</td>
<td>Yearly</td>
<td>17.1</td>
</tr>
<tr>
<td>25</td>
<td>ZnSO$_4$</td>
<td>1965</td>
<td>19.9</td>
</tr>
<tr>
<td>122</td>
<td>Clinker</td>
<td>1965</td>
<td>17.7</td>
</tr>
</tbody>
</table>

*Source: Brinkerhoff et al., 1967; and Vinande et al., 1968.*
Manganese and Iron

To a certain extent, manganese and Fe have similar chemistries in soils. Both will exist in more than one oxidation state: Fe$^{2+}$, Fe$^{3+}$, Mn$^{2+}$, Mn$^{3+}$, Mn$^{4+}$; consequently, both are affected by drainage conditions of the soils. Both are precipitated as oxides and hydroxides, but Fe forms far less soluble compounds. Manganese and Fe have similar chemistries in soils.

Manganese

In well-aerated, high-pH soils, Mn is expected to precipitate as MnO$_2$, and is removed from solution as shown by reaction 2 of Figure 7.2. But as pH decreases, MnCO$_3$ becomes the more stable phase. Here a paradox develops, since high CO$_2$ levels develop in soils when drainage is poor, which decreases the solubility of Mn that comes from the precipitation of MnCO$_3$. On the other hand, poor aeration favors the reduction of Mn oxides.

Soluble Mn is thought to be in the form of Mn$^{2+}$, but it has been shown that 80% to 90% of the Mn in the soil solution is complexed with organic matter. Steam sterilization reportedly makes Mn soluble because it reduces and hydrates Mn compounds. It is true that steam sterilization releases Mn, but the reason appears to be that steam alters the functional groups of soil organic matter. We do not know whether altering the functional groups releases more colloidal organic matter to soil solution, which is capable of chelating Mn, or whether it reduces the soil’s ability to adsorb Mn (see Table 7.6).

The availability of Mn in the field has always been difficult to predict. A number of reasons may account for this. Since Mn solubility is related to oxidation-reduction reactions in the soil, the availability of Mn is closely related to weather. Cool temperatures may slow down the mineralization of organic Mn. On the other hand, cool temperatures associated with high levels of rainfall in early spring may keep more Mn available through reduction of Mn oxides.

There is an interaction between Mn and Fe. High levels of available Fe in organic soils or high levels of organic matter in sands may lead to a Mn deficiency because a high ratio of Fe to Mn is created within the plant. This ratio is particularly important since certain chelated Mn carriers will actually make the situation worse rather than correcting the Mn deficiency. Data in Table 7.7 show that the application of as little as one pound per acre of Mn as MnEDTA actually reduced the yield of soybeans by about 50%. Similar data were observed for onions. The reason is that the soil had high levels of available Fe and low levels of available Mn. The Mn added as the chelate readily dissociated and was apparently rendered unavailable, leaving the chelate to complex more Fe and thereby increase the available Fe. A number of Mn carriers may be used to correct Mn deficiency, as shown in Table 7.7. Manganese sulfate has been the most satisfactory material for most situations. The inorganic carriers MnO and Mn frit are not water-soluble and must be finely ground to be satisfactory; finer than 100 mesh is essential and finer than 300 mesh is desirable. MnEDTA is not very effective because it contains the Mn$^{2+}$ ion.
TABLE 7.8 Examples of Manganese Carriers

<table>
<thead>
<tr>
<th>Carrier</th>
<th>Formula</th>
<th>Mn, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manganese sulfate</td>
<td>MnSO₄·3H₂O</td>
<td>26-28</td>
</tr>
<tr>
<td>Manganous oxide</td>
<td>MnO</td>
<td>41-68</td>
</tr>
<tr>
<td>Manganese frit</td>
<td>Frit</td>
<td>35</td>
</tr>
<tr>
<td>Manganese EDTA chelate</td>
<td>MnEDTA</td>
<td>12</td>
</tr>
<tr>
<td>Various other organic-manganese complexes</td>
<td>Mn-Organic</td>
<td>5-12</td>
</tr>
</tbody>
</table>


satisfactory for organic soils and sands with high levels of organic matter that may contain a high ratio of available Fe to Mn.

The recommended rate of Mn application when Mn deficiency is suspected varies with soil pH and mineral content. Generally, if soil pH is above 6.5, from 4 to 8 pounds/acre of Mn is recommended for mineral soils. If soil pH is from 6.0 to 6.5, from 4 to 6 pounds of Mn is adequate. In all cases the Mn should be band-placed at planting time for best results. For organic soils, if soil pH is above 6.4, an application of from 4 to 16 pounds/acre of Mn is recommended, depending on the severity of the deficiency. If the pH is from 5.8 to 6.4, then 4 to 12 pounds of Mn is recommended. Foliar sprays with Mn may also be used if they are compatible with other spraying programs or if the Mn deficiency appears after the crop is planted. Foliar sprays may be particularly useful for agronomic crops that do not receive starter fertilizer.

Iron

Few if any soils are deficient in total Fe since the total soil Fe content varies from 1 000 to 10 000 ppm. But the solubility of Fe in soils may be limited by the low solubility of Fe hydroxides and oxides in the pH range in which crops are grown.

Soil conditions that lead to Fe deficiency in plants include pHs above 7.0, low soil moisture content, and low organic matter content. These conditions are encountered in the more arid western states of the United States. When Fe deficiency is seen in other areas, for example in the North Central region of the United States, it is normally associated with removal of the surface soil and exposure of calcareous subsoil. In these areas Fe-in-efficient species, pin oaks, for example, may exhibit severe Fe deficiency.

Because of the very limited quantity of Fe⁺ ions in the soil solutions of calcareous soils, it is obvious that organic matter must play a significant role in keeping Fe in soil solution by forming very strong Fe-organic matter complexes. Plants then obtain Fe from these complexes by reducing the Fe⁺ to Fe²⁺ at the root surface, as shown in reaction 5 of Figure 7.2, and thereby freeing the Fe from the organic complex.

The rate of reduction of ferric to ferrous iron has been found to be greatly increased when a plant is under Fe stress. Staining techniques have been developed to reveal the location of active Fe-reducing sites (Bell, Chaney, and Apple, 1988). Figure 7.4 shows that the active sites in tomato plants are on the younger root hairs located either on laterals or near the tip of the primary root. As is evident, the plants that are grown without Fe and with P added show much more of the staining. A high magnification of lateral root hairs confirms that the site of the reduction is on the root hair and not on the epidermal cells between the root hairs (see Figure 7.5). The dark staining indicates intense activity on these root hairs of an Fe-stressed plant. The plant's ability to respond to Fe-deficient conditions by becoming able to reduce Fe⁺ at the root surface is remarkable and undoubtedly accounts for the rather low number of soils that produce plants with an Fe deficiency in the field, even under calcareous conditions.

Correcting an Fe deficiency is very difficult because it is caused by chemical conditions within the soil and not by low total Fe content. If soluble Fe is added to the soil, it is very quickly precipitated and is then not available to plants. Consequently, treatment of the deficiency must be limited to acidification of the soil, thereby solubilizing some of the Fe present. It is also possible to add Fe as a chelate that is sufficiently stable not to dissociate in the soil. Spraying plants with a soluble Fe source is another possible treatment. The chelates FeEDDHA and FeHEDTA are satisfactory under many soil conditions. Soluble carriers are useful for spraying Fe-deficient plants. Some information about these carriers is given in Table 7.9.

![Figure 7.4](http://example.com/figure7_4.png)
Boron and Molybdenum

Boron and molybdenum are unique micronutrients because they exist in the soil as either anions or uncharged molecules. Because they take these two forms, their chemistry in the soil and the factors that affect their availability are quite different from those of the other micronutrients. Both B and Mo, however, are much more strongly adsorbed by soils than other anions, such as Cl\(^{-}\) and NO\(_3^{-}\).

Boron

Boron exists as undissociated H\(_3\)BO\(_3\) or as the anion B(OH)\(_4^{-}\) in soils and in the soil solution. Either form should be mobile in the soil solution. But both forms are adsorbed strongly by Fe or Al hydroxides. Freshly precipitated Fe or Al hydroxides are known to adsorb much more B than the hydroxides that have aged and crystallized. The bonding is through the hydroxyls at the surface of the precipitated Fe and Al hydroxides. Hence, the more crystalline the hydroxides, the fewer the number of exposed hydroxyls per unit weight of hydroxide. Micaceous clay minerals also adsorb B. Magnesium hydroxides and coatings of other minerals that contain Fe, Al, or Mg hydroxides will adsorb B.

Boron is associated with SOM, and soils with high levels of organic matter usually contain adequate B for high soil fertility. Although the exact way in which organic matter holds B is not clear, it is probable that B is adsorbed by the organic matter. Replacement by other anions or mineralization of the organic matter will release the B.

Boron deficiency is often accentuated when soil contains little moisture. Consequently, symptoms of B deficiency will very often be observed during dry periods, but after the soils are brought back to field capacity by rain, the new growth may not show B deficiency.

In addition to deficiencies of B, toxicities must also be considered. Boron may be added in irrigation waters or in sludges and wastewaters. Toxicities are very crop-dependent; thus, beans may show severe toxicity, whereas sugar beets, under the same conditions, will not show toxicity. A number of B carriers are shown in Table 7.10.

Molybdenum

Concentrations of Mo in soils are very low. Its availability is generally limited by adsorption of MoO\(_4^{2-}\) rather than by precipitation. Hydrous Fe oxides and hydroxides are known to adsorb Mo strongly, which undoubtedly explains why Mo deficiencies are most often observed on very acid soils. In fact, liming alone will generally correct Mo deficiency. But in certain areas of the world where lime is not available, a few ounces per acre of Mo will be a substitute for many tons of lime.

Carriers for Mo are listed in Table 7.11. Usually about 1/8 to 1/4 pound/acre of Mo are adequate to correct Mo deficiency. But in certain areas of the world where lime is not available, a few ounces per acre of Mo will be a substitute for many tons of lime.

Carriers for Mo are listed in Table 7.11. Usually about 1/8 to 1/4 pound/acre of Mo are adequate to correct Mo deficiency. But in certain areas of the world where lime is not available, a few ounces per acre of Mo will be a substitute for many tons of lime.

Table 7.9: Examples of Iron Carriers

<table>
<thead>
<tr>
<th>Carrier</th>
<th>Formula</th>
<th>Fe, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrous ammonium phosphate</td>
<td>Fe(NH(_4))PO(_4) \cdot H(_2)O</td>
<td>29</td>
</tr>
<tr>
<td>Ferrous sulfate</td>
<td>FeSO(_4) \cdot 4H(_2)O</td>
<td>9-12</td>
</tr>
<tr>
<td>Iron chelates</td>
<td>FeHEDTA</td>
<td>5-9</td>
</tr>
<tr>
<td></td>
<td>FeEDDHA</td>
<td>6</td>
</tr>
</tbody>
</table>


Table 7.10: Examples of Boron Carriers

<table>
<thead>
<tr>
<th>Carrier</th>
<th>Formula</th>
<th>B, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Borax</td>
<td>Na(_2)B(_2)O(_5) \cdot 10H(_2)O</td>
<td>11</td>
</tr>
<tr>
<td>Boric acid</td>
<td>H(_3)BO(_3)</td>
<td>17</td>
</tr>
<tr>
<td>Sodium pentaborate</td>
<td>Na(_2)B(_2)O(_5) \cdot 10H(_2)O</td>
<td>18</td>
</tr>
<tr>
<td>Sodium tetraborate</td>
<td>Na(_2)B(_3)O(_7)</td>
<td>20</td>
</tr>
<tr>
<td>Sodium tetraborate pentahydrate</td>
<td>Na(_2)B(_3)O(_7) \cdot 5H(_2)O</td>
<td>14</td>
</tr>
<tr>
<td>Boron frits</td>
<td>Na(_2)B(_2)O(_5) \cdot 5H(_2)O</td>
<td>10-17</td>
</tr>
</tbody>
</table>

Source: Robertson, Lucas, and Christenson, 1981.
TABLE 7.11 Examples of Molybdenum Carriers

<table>
<thead>
<tr>
<th>Carrier</th>
<th>Formula</th>
<th>Mo, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium molybdate</td>
<td>(NH$_4$)$_6$MO$<em>7$O$</em>{24}$•2H$_2$O</td>
<td>54</td>
</tr>
<tr>
<td>Sodium molybdate</td>
<td>Na$_2$MoO$_4$•2H$_2$O</td>
<td>39</td>
</tr>
<tr>
<td>Molybdenum trioxide</td>
<td>MoO$_3$</td>
<td>66</td>
</tr>
</tbody>
</table>


TRACE ELEMENTS THAT MAY BE TOXIC

A number of micronutrients and other trace elements may be toxic to plants, to animals, or to both. There are soils that naturally have large quantities of what is usually a trace element, for example, Se. These soils may pose a threat because of this naturally high level of a particular trace element. The number of acres affected is usually rather few, but in the case of Se, many soils in the western United States naturally contain large quantities.

Manufacturing processes have left waste materials that have high levels of many elements, including Zn, Cu, Cd, Ni, Hg, Pb, and others. A few of these will be discussed to illustrate problems and questions that come up when sludge is utilized as part of a soil fertility program.

Both municipal sludge and sludge generated as a waste product of industry may be available for disposal on land or for recycling on agricultural land to obtain benefit from one or more components of the waste material. The question is whether we can safely use the waste material and obtain a benefit from it? Several rules should be followed before using a waste product. It must be analyzed to determine its exact composition. Normally N in the sludges will be similar to N in manure in availability and may be used to advantage. Phosphorus and other nutrients, if needed by the soil, may also be beneficial. Occasionally micronutrients such as Zn may be needed, and sludges can supply these needs.

Sludges or waste material will often contain other trace metals that are not needed by crops and are potentially toxic. Here the question is how much can be applied to soils before they become a problem. Guides for soil loading based on soil CEC are given in Table 7.12. There may be state and local regulations that also apply.

Certain metals such as Zn are not particularly toxic to plants or animals. Consequently, the soil can tolerate a considerable loading with little problem. A heavy loading of these metals should be accompanied by pH control to maintain a pH above 6.5, which will minimize the solubility of the metal.

Other metals, Cd in particular, must be restricted because they are potentially toxic. Cadmium is a known carcinogen. Furthermore, it readily moves from the soil to the plant root and is easily absorbed by plants. Thus, even relatively low levels in soils become a threat to people consuming the food grown on that soil. Very careful control of applications of Cd is essential. Lead and Hg, although very toxic if consumed by animals, including human beings, are strongly held by soils and do not solubilize and move readily to plant roots. This means that Pb and Hg may be applied to soils in larger quantities than Cd is.

Chromium presents an interesting case. The form used in industry is generally Cr$^{3+}$. In this form the Cr combines with oxygen and exists as Cr(OH)$_2^-$, which is toxic to both plants and animals. Since it is an anion, it is mobile in the soil. If Cr(OH)$_2^-$ is applied to the soil, it can move out of the root zone and to the groundwater. But soils have the ability to reduce Cr$^{3+}$ to Cr$^{2+}$. This reduction is favored by a high content of organic matter in soils and low pH. Once reduced, the Cr is held as an exchangeable ion and also precipitates as the very insoluble Cr$_2$O$_3$. In this form it is not available to plants.

SOIL TESTING FOR MICRONUTRIENTS

Deficiencies of micronutrients are related to plant species, climate, and soil properties, such as pH and organic matter content, in ways that have made it very difficult to develop a single soil extractant for all micronutrients. Perhaps the most universally used extractant for micronutrients and other nonessential trace metals is the DTPA test developed by Lindsay and Norvell (1978). The extract consists of 0.005 M DTPA (diethylenetriaminepentaacetic acid), 0.1 M triethanolamine, and 0.01 M CaCl$_2$ with a pH of 7.3. The DPTA is a strong complexing agent for heavy metals, particularly Zn$^{2+}$ and Cu$^{2+}$. Although this test has been widely shown to correlate well with available Zn in soils, it has been less successful in measuring other available micronutrients.

Some extractants that have been used successfully for micronutrients are listed in Table 7.13. For the best evaluation and recommendations, they must be coupled with soil pH, soil type, and local yield correlation studies.
TABLE 7.13 Extractants for Micronutrients in Soil testing

<table>
<thead>
<tr>
<th>Trace element</th>
<th>Soil extractant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>DTPA</td>
</tr>
<tr>
<td></td>
<td>0.1 N HCl</td>
</tr>
<tr>
<td>Mo</td>
<td>Calcium phosphate</td>
</tr>
<tr>
<td>Cu</td>
<td>0.1 N HCl</td>
</tr>
<tr>
<td>B</td>
<td>Hot water</td>
</tr>
<tr>
<td>Mn</td>
<td>Phosphoric acid</td>
</tr>
<tr>
<td>Fe</td>
<td>DTPA</td>
</tr>
</tbody>
</table>

TISSUE TESTING FOR MICRONUTRIENTS

Micronutrient deficiencies may be diagnosed by analyzing the plant tissue. The methods will vary widely with the particular crop and growing conditions. Generally, a certain plant portion is selected (e.g., ear leaf for corn) and a certain stage of plant growth is used. The tissue is collected and analyzed, and the values obtained are compared with values obtained from high-yielding plants. Some data are given in Table 7.14 as general guidelines for the micronutrients.

MICRONUTRIENTS DEFICIENCY SYMPTOMS

Deficiency symptoms have been used for a long time to identify deficiencies in the field. This has been particularly true for trace element deficiencies. But a number of factors make this practice difficult and at times less than desirable. It must be recognized that when nutrient deficiency symptoms appear on a plant, there has already been a loss in yield for that year's crop. Correcting the deficiency may be important for that year's crop, even though a yield reduction is expected, and it is important to identify what deficiency to expect in subsequent years. Trace element deficiencies are often related to climatic growing conditions, and these may change from year to year. If growing conditions are not taken into consideration, conclusions about apparent yield responses to applied trace elements can become erratic.

Deficiencies in plants are most often manifested as growth irregularities, so that distinguishing between two or more deficiencies may be difficult. In addition, other factors that affect growth, such as weather, chemical damage, and pest damage to crops, may also give similar symptoms. For these reasons it is important to obtain all possible information from the grower before attempting to diagnose a deficiency by plant symptoms. Once a tentative identification is made, it should be verified by treatment with the element in which the plant is assumed to be deficient.

Data in Table 7.15 are given to summarize which factors may help to identify a particular deficiency symptom. Since many deficiency symptoms are similar, identifying where the deficiency occurs may be very important. Some trace elements, such as Mo, are relatively mobile in plants. When the element becomes deficient in the soil, the Mo in the plant is translocated from the old to the new tissue, and the symptoms appear first on the old tissue. On the other hand, if the element, Fe for example, is not mobile in the plant, the deficiency appears first on the new plant growth.

TABLE 7.14 General Guidelines for Evaluating Micronutrient Content in Mature Leaves

<table>
<thead>
<tr>
<th>Micronutrient</th>
<th>Concentration in leaves, mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Deficient</td>
</tr>
<tr>
<td>B</td>
<td>&lt;15</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt;4</td>
</tr>
<tr>
<td>Zn</td>
<td>&lt;20</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt;50</td>
</tr>
<tr>
<td>Mn</td>
<td>&lt;20</td>
</tr>
<tr>
<td>Mo</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

Source: Jones, 1972.
Zinc deficiency is perhaps one of the easiest to recognize under field conditions. It most often occurs on calcareous soils and soils that have high levels of phosphate, either as residual or as a current P application. In general, the Zn deficiency appears early in the growing season and is caused either by cool weather or by the restricted rooting zone of the plants. Zinc deficiency is also commonly associated with particular crops and in fact with particular varieties. For example, when grown on the same soil and in the same rotation, navy beans may show a severe Zn deficiency when sugar beets show no deficiency and do not give a yield response to Zn. Sanilac beans may show a severe deficiency of Zn when Saginaw beans grown side by side give relatively little response to Zn. The same observation can be made about toxicity. Sanilac beans are much more susceptible to Zn toxicity than Saginaw beans if Zn levels are excessive in soils. It is common to find this differential susceptibility to Zn deficiency in different varieties of navy beans, corn, and probably some other crops.

The outward symptom of Zn deficiency is light interveinal tissue. For dicot crops such as navy beans, this disorder appears first in the older leaves and to a lesser degree in younger leaves. The light interveinal tissue takes on the appearance of striping in corn and does not usually affect older leaves but rather appears first on leaves of intermediate age. In corn and sorghum the plants will have shortened internodes (see Figure 7.6) and darkened nodal tissue, indicating an accumulation of Fe at the nodes. As zinc deficiency develops, the shapes of leaves often become abnormal, particularly in crops such as beans and fruit trees (see Figure 7.7). This symptom is very useful in separating Zn deficiency from Mn deficiency since Mn deficiency does not cause abnormally shaped leaves. Delayed maturity is also characteristic of Zn deficiency. The field results of growing navy beans in Michigan revealed a Zn deficiency so severe that there was essentially no yield.

Molybdenum

The deficiency of Mo may affect legume and nonlegume plants quite differently. Molybdenum is required by rhizobia for N fixation. Consequently, a Mo deficiency in a legume plant may be manifested as a N deficiency. It then appears as light color and stunting in plants. Field symptoms of Mo deficiency in the United States have most often been observed on vegetable crops. The youngest leaves are the most often affected. They become mottled and their leaf margins are narrow. The leaves will elongate abnormally and in cauliflower they are often twisted, which is the basis for the common term whiptail applied to the deficiency symptom. Sometimes the leaves may take on a cupping appearance.

Manganese

Manganese deficiency often appears as interveinal chlorosis. Unlike what happens with Zn deficiency, the leaves appear normal except for color and show no abnormal shape. If a Mn deficiency develops when the plant is very young, it may be very uniform in both young and older leaves. If the
deficiency develops after the plant is much larger, however, it will be much more prevalent on the younger leaves. This distribution is uneven because Mn is only slightly mobile in the plant. In Mn-deficient bean plants the tissue between the veins becomes increasingly lighter in color. But the veins remain dark, making this Mn deficiency easy to distinguish from N deficiency (see Figure 7.8)

Small grains quite often show Mn deficiency. Generally, a gray oval-shaped spot develops on the edge of a new leaf. The gray spot will enlarge until it covers much of the leaf and takes on a yellow appearance. The tip of the leaf will remain green during this process. Manganese deficiency in corn and grain sorghum appears as interveinal chlorosis, usually on the youngest leaves. It may be similar to Fe deficiency, but Mn deficiency usually appears on soils with high organic matter content, whereas Fe deficiency seldom occurs on these soils.

On certain vegetable crops such as broccoli, Mn deficiency causes the leaf surface to lose its waxy coating. This loss is quite apparent when comparing deficient plants with plants sufficient in Mn.

**Figure 7.8** Manganese-deficient bean plant grown in a greenhouse.

**Figure 7.9** Iron-deficient bean plants showing severe chlorosis on the new growth.

**Copper**

Because Cu is not translocated in the plant, the deficiency symptoms appear on the new growth. In small grains and corn the leaves appear olive or yellowish green in color, and often the leaves fail to unroll as they emerge. Often the leaf tips will appear as though the plants have been frost-damaged, and there will be some flags. A flag is a wilted or dead leaf or a branch with such leaves on an otherwise healthy-appearing plant.

**Boron**

Boron deficiency symptoms are seldom observed except for sensitive crops such as legumes, sugar beets, and some vegetable crops. In alfalfa the deficiency is shown by yellowing of the leaves and by restriction of the terminal growth. This restriction gives very short internodes and offers a method of separating B deficiency from insect damage, which may give similar visual symptoms but with normal node lengths. Boron-deficient sugar beets develop cross-checked petioles and misshapen leaves. The leaf blades grow uneven on two sides of the plant and more in the horizontal direction than in the vertical direction. When the deficiency is severe, the terminal growth or apical meristem tissue dies, and the roots may develop heart rot.

**Iron**

Iron is the least mobile of the micronutrients in plants. When the deficiency appears, it is on the new growth and may be very severe. The plant leaves will first appear yellow interveinally with green veins. But when the deficiency is severe, the entire area may appear white (see Figure 7.9). It can be
demonstrated that Fe is very immobile by placing a local spot of Fe solution on the surface of a deficient leaf and observing that the leaf will develop a green color in this area only.

REFERENCES


Mixed Fertilizers

The fertilizer industry developed in stages with phosphate materials in the 1840s, potassium materials in the 1870s and the nitrogen materials about 1900. More recently, micronutrient fertilizers have been developed. During the early years of fertilizer manufacturing, dry materials were mixed together. These fertilizers were dusty, and the materials would segregate during transport and application. Then the addition of anhydrous ammonia to dry mixes and their subsequent granulation constituted a major advance. The granular fertilizers are dust-free, and each granule has similar composition and particle size. These free-flowing fertilizers were needed for the new fertilizer application equipment that was being developed. More recently, fluid fertilizers have become very popular.

Overall soil fertility in the United States has been increasing, and in many instances the application of only one nutrient is desirable. Improvements and greater use of soil tests have helped identify these situations. As a result, the use of carriers for direct application of nutrients to the soil, relative to the use of mixtures, has been increasing. Actually, the application of both kinds of fertilizers has been increasing, but, in 1976 the direct application of single-carrier fertilizers surpassed the use of mixtures. In 1982 it was estimated that 21 million tons of mixed fertilizers were produced in the United States and that this represented 44 percent of the total fertilizer production. Of the mixtures, bulk blends of dry granulated materials were the most popular. Dry granular homogeneous mixtures were the second most popular followed by fluid fertilizers. This chapter examines the properties of mixed or compound fertilizers and their manufacture by combining two or more fertilizer carriers or intermediates.

GRADE AND RATIO

The fertilizer grade is the minimum guaranteed amount of plant nutrients expressed in weight percentages of total N, available P₂O₅, water- and citrate-soluble, and water-soluble K₂O in that order. The grade 6-24-24 has a 1-4-4 ratio. Fertilizers are produced with various ratios to correspond to the different needs of various crop and soil situations. Lawn and turf commonly require a large amount of N relative to P and K. For lawns 4-1-1 or 4-1-0 fertilizers are popular. Frequently, a small amount of N and all or part of the P and K are applied near or at planting time in a mixed fertilizer. Later, when the crop’s need of N is maximum, much more N may be applied using a N carrier such as anhydrous ammonia. Thus, many soil management programs make use of both mixed and single-carrier fertilizers.

MAJOR FERTILIZER SYSTEMS

There are two overlapping organizations in the production and marketing of fertilizers in the United States. As discussed in earlier chapters, the major N material, NH₃, is produced near natural gas wellheads or pipelines. The major P source materials for fertilizers—superphosphates, ammonium phosphates, and phosphoric acid—are produced near the rock phosphate mines in Florida, North Carolina, and some western states. Until the 1960s, when mines were opened in Saskatchewan, most of the KCl was produced near Carlsbad, New Mexico. Now 70 percent or more of the K in fertilizers in the United States comes from the Canadian mines. These materials or carriers are frequently applied directly to soils, but they are called intermediates to indicate their role in the manufacture of mixed fertilizers. These fairly concentrated intermediates are transported to regional and local plants near markets, and there they are combined into mixed fertilizers. The production pattern for finished mixed (NPK) fertilizers in the United States has evolved into three main systems: granulation, bulk blending, and fluid fertilizers. The relative importance of these three systems is shown in Table 8.1.

Granulation

The process of granulating dry fertilizers was developed to provide a more uniform product for use in labor-saving mechanical applicators and to reduce the costs of manufacturing and transport. At first dry mixed fertilizers were moistened with water and subjected to mechanical action in a mixer to form more or less uniform-sized particles. After the batch was granulated in the mixer, the particles were dried, screened, and cooled. Oversized and undersized particles were recycled. A coating material was added to minimize lumping and caking during storage. This method of granulation is suitable for small plants and is still important in developing countries.
Mixed Fertilizers

**TABLE 8.1 Consumption of Granulated, Bulk-Blended, and Fluid Fertilizers**

<table>
<thead>
<tr>
<th>Type</th>
<th>Total fertilizers, percent</th>
<th>Total mixed fertilizers, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Granular NPK</td>
<td>16.6</td>
<td>28.6</td>
</tr>
<tr>
<td>Bulk-blended</td>
<td>31.5</td>
<td>54.3</td>
</tr>
<tr>
<td>Fluid</td>
<td>9.9</td>
<td>17.1</td>
</tr>
</tbody>
</table>


In time, the continuous drum or tube granulator, as opposed to the batch mixer, became popular. The granulator is a rotating drum about 1 to 2.5 meters in diameter and 3 to 10 meters long. Incoming materials are screened to remove lumps, which are crushed. The materials are weighed and continuously fed into the granulator at a controlled rate. Steam is discharged under the bed of material and water is sprayed on top. Granulation is controlled by the amount of water added. Discharged particles are dried, cooled, and screened and oversized and undersized granules recycled. A flow diagram of a typical granulation plant is shown in Figure 8.1, and some typical formulations for grades are given in Table 8.2.

In efforts to increase the N content of granular fertilizers, an ammonia-tor was added to the process and, more recently, phosphoric and sulfuric acids were added. Now many chemical reactions occur in the granulator, and both dry materials and slurries are granulated.

**Melt Granulation**

The melt granulation process developed in the 1960s was first used to produce granular ammonium phosphates. Wet-process superphosphoric acid and ammonia are reacted in a confined pipe in which heat is released, evaporating some of the water that is present and producing a melt. The melt is the liquid phase of the solid fertilizer. The reactor developed by TVA is called the pipe-cross reactor (PCR). Phosphoric and sulfuric acid are reacted simultaneously with NH$_3$, with the release of much heat and the formation of a melt. The melt is sprayed into the granulator drum, and with the addition of KC$_1$, a complete mixed fertilizer can be produced (see Figure 8.2). Some advantages of the PCR and melt granulation are

1. Reduced costs for drying, since granules produced from the melt of the PCR have only 1% to 4% water compared to 10% to 15% for regular granulation.
2. Easier compliance with environmental regulations because fewer ammonium chloride fumes are produced.
3. Easier and more precise control of ingredients.
4. Lower plant construction costs.
The progressive development of better manufacturing methods has resulted in a progressive increase in the nutrient concentration of mixed fertilizers from 15% (N + P₂O₅ + K₂O) in 1910 to 44% in 1981. These methods have also achieved a lower cost per pound of plant nutrient.

Caking and Dustiness

Between manufacture and application to the soil, dry fertilizers must be stored in bulk or in bags. It is essential that the fertilizers maintain their free-flowing character and not cake or form lumps in storage. Fertilizer cakes when crystal bonds grow between particles. These crystals may develop during storage through continuing chemical reactions, or thermal effects may produce small crystals from minute amounts of solutions in the fertilizer. Intergrowth of crystals between particles causes cementation or caking. In some instances cohesive forces between particles have produced caking. Large granules reduce the number of contact points between particles; granular materials have less of a tendency to cake than do pulverized materials. Soft granules under pressure in storage piles may deform, which causes relatively large areas of contact between granules and promotes caking.

A frequent misconception holds that moisture absorbed during storage causes caking, but excessive moisture left in the product during manufacture is the true agent. The N materials have the greatest tendency to cause caking if they are not properly dried. In general, they should contain 0.5% or less of free water (nonhydrate water).

Solid conditioning or anticaking dusts in common use include diatomaceous earth (kieselguhr), kaolin clay, talc, and chalk. Usually 1% to 4% of these powdered conditioners is applied. Clays have good adherence to particles, but diatomaceous earths have greater absorbency. Adherence of conditioners can be improved by spraying the fertilizer with a small amount of oil either before or after the conditioner is applied.

Dustiness is a very undesirable property, especially with our increasing concern about the healthfulness of the work environment. Granulation does much to reduce the dustiness of dry fertilizers, but dustiness may still exist. The dustiness of granular fertilizers is caused by poor sizing, which leaves too many fine, soft granules, which in turn break apart; the poor adherence of conditioners; and the formation of surface crystals, which may abrade to form dust. The adherence oil just mentioned is the major way in which dustiness is currently controlled.

Bulk Blending

Granulation is used to produce single-nutrient carriers as well as complete NPK fertilizers. Bulk blending is the physical mixing of two or more granular materials. The practice was first started in Illinois in 1947. Blended fertilizers can be bagged or distributed in bulk. Only 23 percent of the blenders in the United States have bagging facilities.

A major advantage of bulk blending is the ease with which many different grades and ratios can be formulated. Prescription mixes guided by soil analysis are popular. The major intermediates used are granular urea, ammonium nitrate, diammonium phosphate, triple superphosphate, and potassium chloride. These materials are shipped to a plant located in the area where the fertilizer will be used. The materials are mixed and commonly loaded directly into a truck and immediately spread in the field (see Figure 8.3). The entire cycle of weighing, mixing, and discharging may be automated. Low cost is a major reason for the popularity of bulk blending which now accounts for 54 percent of all mixed fertilizers in the United States.
Chemical Incompatibility of Intermediates

The chemical incompatibility of intermediates may cause the mixture to heat up, water to form, gas to evolve, and caking. Only a few materials are troublesome (see Figure 8.4). Mixing of urea with ammonium nitrate must be avoided, for it causes a high degree of wetting and is related to the critical relative humidity (CRH). The CRH is the relative humidity above which the material spontaneously absorbs moisture from the air. Relatively pure urea does not absorb water at 70% relative humidity, but it takes up water continuously at 75% relative humidity at 30 degrees C (86 degrees F). This CRH is typical for most fertilizer materials; however, mixtures of salts usually have a lower CRH than either constituent. When urea and NH₄NO₃, with CRHs of 72.5 and 59.4, respectively, are mixed together, the CRH of the mixture is only 18.1%. Thus, either alone may store well, but when mixed together they are very hygroscopic and take up moisture from the air at low relative humidity.

Urea reacts with monocalcium phosphate monohydrate in superphosphate to release water of hydration and produce severe stickiness:

\[
\text{Ca(H}_2\text{PO}_4\text{). H}_2\text{O + 4CO(NH}_2\text{). = Ca(H}_2\text{PO}_4\text{). CO(NH}_2\text{). + H}_2\text{O (8.1)}
\]

Mixing diammonium phosphate with superphosphates may cause caking during long-term storage.

Segregation

Bulk handling may induce particles of a fertilizer to segregate, whereupon its composition becomes nonuniform throughout. Segregation of particles is undesirable because the consequent nonuniformity can make it impossible to obtain proper samples of fertilizer to meet analytical guarantees.
Mixed Fertilizers

Agronomic responses may be affected and are a particular problem if a micronutrient intermediate is separated from the bulk of the fertilizer.

Segregation occurs because individual particles in a fertilizer respond differently to mechanical disturbances during handling. Particles of similar physical properties tend to congregate thus destroying homogeneity. Numerous tests have shown that the physical property bringing about the most segregation is particle size. Neither the density or shape of particles within the ranges found in fertilizers causes segregation to an important degree.

During the flow of a bulk-blended fertilizer into a storage bin or truck, particles of the various intermediates may segregate. The finer particles tend to remain where they fall, the larger particles roll down the pile toward the perimeter. This process is called coning. Most of the bulk-blended fertilizer is loaded directly into applicators with large flotation tires equipped with a spinner (fan-type) spreader and immediately spread onto fields.

Vibration in the plant after mixing and during transport and spreading may cause particles to segregate. Smaller particles sift downward into the void spaces between larger particles and collect at the bottom. Granules are segregated as they are propelled through the air by fan-type spreaders. Large particles travel farther than the small particles, causing uneven application of nutrients. Thus, particle size is an important consideration in granulation (see Figure 8.5). It is recommended that 100% of the materials be within the mesh range of –6 to +16, with at least 25% and not more than 45% of +8-mesh size.

Particle hardness becomes a factor during application because soft granules break up into smaller particles. Prilled urea particles tend to be porous and have the lowest crushing strength of the common materials used for bulk blending. New granulation methods for urea produce harder granules, compared to prills, and have significantly decreased caking of urea. Particles that remain intact when pressed by the forefinger against a hard surface are considered to have satisfactory hardness.

Fluid Fertilizers

Fluid fertilizers are of two types; solutions and suspensions. The important advantages of producing and marketing fluids are the simplicity of the mixing facilities and ease of handling. The fluids themselves are dustless, and their other advantages include homogeneity, uniformity of application, the ease with which micronutrients or pesticides are added, the ease with which fluids are applied with irrigation water, and their use as foliar sprays. Disadvantages include lower-analysis products, increased shipping costs, and the possibility of salting out at low temperature (see Figure 8.6).

Liquid Fertilizers

A liquid fertilizer is a clear solution containing plant nutrients. The principal intermediates used for making liquid NPK fertilizers are urea, UAN (urea-ammonium nitrate) solution, ammonium and orthophosphate or polyphosphate solutions, and finely ground soluble KCl. The liquid fertilizers usually have a brown or green color derived from the wet-process phosphoric acid used in their preparation.

The most important source of P is ammonium polyphosphate, APP. Ammonia and low-cost, wet-process superphosphoric acid are neutralized in a pipe reactor. The heat produced drives off most of the water, and the high temperature forms polyphosphates in the APP melt. The APP melt is processed into 10-34-0 or 11-37-0 solutions in which 50% to 75% of the P is polyphosphate. The polyphosphate has higher P content and sequesters (holds in solution) both impurities of the acid and any micronutrients that

FIGURE 8.5 The poor granule-size match on the right caused diammonium phosphate to segregate from the larger, coarse potassium chloride particles. (Photographs courtesy International Fertilizer Development Center, TVA.)

FIGURE 8.6 Simplicity of manufacture and ease of handling are the primary reasons for the popularity of fluid fertilizers produced at rural fertilizer plants such as this one.
are added. It is a simple mixing process to make liquid NPK fertilizer with APP solution by adding some UAN solution to increase the N content and by adding finely ground KCl to supply K.

The major limitation of liquid fertilizers is their generally lower analysis compared to dry fertilizers. For NP fertilizers, higher concentrations of N and P are produced using UAN solution than using urea. For NPK liquid fertilizers, higher grades are produced using urea rather than UAN solution. Urea produces higher grades because NH$_4$NO$_3$ reacts with KCl in solution to produce NH$_4$Cl and KNO$_3$. Potassium nitrate has low solubility at low temperature, and crystals form and settle, or the fertilizer salts out. This is more of a problem in the northern states than in the southern. Most of the popular liquid fertilizers have salting-out temperatures of 0 degrees C or lower.

**Suspension Fertilizers**

The generally low analysis of liquid fertilizers is overcome by the manufacture of suspensions. Suspension fertilizers contain solids held in suspension. The suspended particles may be water-soluble in a saturated solution, insoluble or both. Higher analysis, lower-production cost, and resistance to salting out are advantages of suspensions compared to liquids. Suspension fertilizers are particularly desirable in regions where high rates of fertilizer K are common. A disadvantage is the need for specialized applicators; most suspension fertilizers must be applied by custom applicators.

Manufacture of suspensions is highly varied, but the process has many parallels to liquid manufacture. Similar materials are used, but they may be lower in quality and cost less. The most common suspension agent is attapulgite clay. The usual suspension contains 1% to 2% clay, which forms a gel on vigorous agitation. Particles that settle during storage are easily resuspended when agitated. Suspensions may be stored weeks or months, but if they are stored too long, large crystals that cannot flow properly through the applicators will grow.

**Addition and Incorporation of Micronutrients**

Recommended amounts of micronutrients are usually less than 10 kg/ha (about 9 pounds/acre), which makes it difficult to apply them separately and uniformly in the field. For this reason micronutrients are usually applied in mixed fertilizers rather than separately. Compatibility and uniform distribution are the major objectives of the successful addition of micronutrients to mixed fertilizers.

**Addition to Granular Fertilizers**

The addition of micronutrients during the manufacture of a granular NPK fertilizer or as one of the intermediates during bulk blending provides great flexibility, and the cost is low. The micronutrient granule size must match that of the other materials in bulk blends to prevent segregation during mixing, transport, and application. The relative number of micronutrient granules compared to the total number of granules in the fertilizer is very small, which means that the micronutrient granules are widely spaced after application. For example, the use of 8-mesh granules at a rate of 1 kg/ha would provide about one granule per 1,000 cm$^2$ of the field surface. Some granules would be too far away to help some plants and perhaps, depending on the material, release too much of the micronutrient to other plants. Even so, bulk blending of micronutrient intermediates with mixed fertilizers is popular.

Adding micronutrients as a spray or powder during the manufacturing process prior to ammoniation and granulation, gives them presence in every granule. The problems of segregation and uniformity of distribution are solved, but the micronutrient intermediate may react unfavorably with other intermediates. Extra precautions are needed to maintain good physical properties of the finished product and keep the micronutrient available. When a chelated micronutrient, ZnEDTA for example, is mixed with superphosphate before ammoniation, acid decomposition of the chelate molecule decreases the availability of the Zn. When the process is changed by adding the ZnEDTA with the ammoniating solution, the Zn becomes more available.

The major disadvantage of incorporating micronutrients during manufacture is that there is little flexibility, and it is costly to store many grades with a variety of micronutrients. If there is a regional deficiency of a nutrient, this method may be the most economical.

Micronutrients are coated to granular products to achieve a uniform distribution of them throughout the fertilizer. A finely ground micronutrient, less than 100 mesh in size is dry-mixed with fertilizer granules, then sprayed with a liquid binder and given additional mixing. Mechanical adhesion or the formation of reaction products on the surface of the fertilizer granules makes the micronutrient coating adhere to the granules. Binders include water, oils, waxes, ammonium polyphosphate, and UAN solutions. Water may be used if it presents no caking hazard. Oil should not be added to NH$_4$N.O, because the substances together might explode. No more than 1% oil should be used because the oil may seep through fertilizer bags.

Incorporated and coated micronutrients appear to be similar in agronomic effectiveness. The coatings do not affect the availability of the micronutrients, and they provide more flexibility compared to incorporation during manufacture. A disadvantage of coating, compared to incorporation, is higher cost. Micronutrients are not widely coated in the United States.

**Addition to Fluid Fertilizers**

The addition of micronutrients to fluid fertilizers has become very popular because the micronutrients can be added just before the fertilizer is applied in the field. The fact that these fertilizers are used immediately allows for
Mixed Fertilizers

great flexibility in manufacture; a wide variety of fertilizers with minimal storage requirements can be produced. The addition of micronutrients to liquid fertilizers, however, is greatly limited by the solubility of the intermediates. Only sodium borate and sodium molybdate have sufficient solubility to be effective when the P source is orthophosphate. Metallic sources of micronutrient are more soluble in polyphosphate than in orthophosphate in clear fertilizer solutions. Even so, the solubility of salts of Cu, Fe, Mn, and Zn are generally too low to correct severe deficiencies at usual fertilizer application rates. Sequestering agents that react with the micronutrients have been used to prevent their precipitation by phosphate. Ammonium polyphosphate effectively sequesters all the metallic micronutrients except Mn. It is easy to custom-mix liquid fertilizers containing a variety of kinds and amounts of micronutrients. A disadvantage of some is that rates of fertilizer application may not allow sufficient amounts of the micronutrient to be applied to correct certain deficiencies.

Micronutrient intermediates are easily added to suspension fertilizers with minimal reaction with other components or other undesirable results. Sulfates of Cu, Fe, Mn, and S in fritted form have been used. Suspensions should be applied soon after preparation to avoid settling difficulties and crystal growth.

SALT INDEX

Fertilizers are composed for the most part of soluble salts that increase the ion concentration of the soil solution. This higher ion concentration increases the osmotic pressure of the soil solution and at the same time decreases the water potential. Decreases in water potential are associated with decreases in the rate at which roots and seeds absorb water. Placement of fertilizer close to seeds and roots may reduce germination and growth (see Figure 8.7).

The salt index is a measure of the extent to which various fertilizers or intermediates increase the osmotic pressure of the soil solution. Briefly, the salt index is determined by adding fertilizer to soil and incubating for five days. Then the osmotic pressure of the displaced soil solution is determined. The salt index is a relative value compared to NaNO₃ as 100, and the values of the most widely used materials are given in Table 8.3. Nitrogen and K salts have much higher salt indexes than P salts. The cultivar, placement of the fertilizer, time of application, and soil properties, and the water content in particular will have some bearing on what effect a fertilizer with a given salt index has. The salt index has its greatest value when growers are selecting fertilizers that will be placed with or near seeds.

ACIDITY AND BASICITY

Acids are important intermediates in fertilizer manufacture and raise the possibility that fertilizers can alter soil pH. When urea is hydrolyzed to NH₄⁺, the pH in the immediate vicinity of application may increase to 9.

Later, the NH₄⁺ may be absorbed by roots or nitrified with the production of protons. Whether N is taken up by roots as nitrate or ammonium affects the amount of H⁺ or OH⁻ excreted by roots. Leaching of the nitrate resulting from fertilizer use depletes XCa...Na. The effects of fertilizers on soil pH are complex because the outcome is influenced by plant growth, soil, and leaching. William Pierre did much of the early work and from greenhouse studies drew his conclusions about the effect of fertilizers on soil pH. His work forms the primary basis of the method adopted by the...
Association of Official Agricultural Chemists to determine the acidity or basicity of fertilizers.

The acidity or basicity of a fertilizer is expressed as units of CaCO₃, equivalent to the acidity or basicity produced by the fertilizer. It is assumed (1) that Cl, S, and one-third of the N contribute to soil acidification, (2) that the Ca, Mg, K, and Na cations contribute to soil basicity; and (3) that half of the N is absorbed by plants as nitric acid and half is absorbed as a salt, such as KNO₃. Thus, KNO₃ and Ca(NO₃)₂ are basic and KCl is neutral. The N carriers with an acidic anion are quite acid-forming. In general, it is the N carriers with their acidity potential that affect soil pH (see Table 8.4).

A single application of a NPK fertilizer is unlikely to have any detectable effect on soil pH. Long-time use of NH₃ in a continuous corn program, however, may severely lower pH of acid soils (see Chapter 10). A major limitation of the acidity values is that, because losses by leaching, denitrification, and volatilization vary, there are great variations in the fate of fertilizer N. Some acid-forming fertilizers may produce beneficial effects when used on alkaline or calcareous soils by increasing the solubility of some micronutrients.

A quantitative measurement of acidity and basicity enables fertilizer manufacturers to add some limestone to the fertilizer as a filler to counteract acidity. It is generally more economical to add limestone to soils, as compared to producing neutral fertilizers, if soil acidity becomes a problem when the fertilizer is used.

**Fertilizer and Pesticide Combinations**

The application of pesticides with fertilizers has obvious economic advantages. Fewer trips reduce traffic and may reduce soil compaction. The major considerations of combining pesticides with fertilizers are:

1. The appropriateness of the timing and placement of the combination.
2. Chemical and physical compatibility.
3. Whether the interaction of pesticide and fertilizer alters their effectiveness.
4. Metal corrosion and deterioration of hoses and other equipment.

**Herbicide and Fertilizer Combination**

Since the early 1970s the popularity of herbicide and fertilizer combinations has fostered the *weed and feed* concept. One of the most important considerations is choosing the time that the herbicide-fertilizer combination should be applied for the greatest effectiveness of each. For many crops it is customary to split the N application, which often means that the time of application for both N and herbicide is at preplanting, planting, or post-emergence. The most popular combinations are N solutions, UAN, and herbicides such as fluorometuron for cotton and atrazine or simazine for corn. Nitrogen solution plus 2,4-D is used to control weeds in small grains, sorghum, and pastures. The N readily moves into the soil with water, and the surface application of the herbicide is effective. The larger quantity of fluid may provide more uniform application and render the herbicide more effective. An application of 140 to 190 L/ha of UAN used as a carrier supplies N at 50 to 68 kg/ha (45-61 pounds/acre).

Postemergence application causes leaf burn unless drop nozzles are used to direct the solution below the leaves. Burn injury increases with the rate of application and is greater for advanced stages of plant growth. Growers may express concern about leaf burn. If the leaf burn occurs early in the season, yield may not decrease significantly. It has been reported that as much as 134 kg/ha (120 pounds/acre) of N has been applied via UAN on four-leaf corn without reducing corn yields. Application after the six-leaf stage, however, should be regarded as a salvage operation.

Problems of incorporating herbicides with fluid fertilizers include precipitation of salts, formation of thixotropic gels, and an increase in the salting-out temperature of liquids. The herbicide should be mixed just before application to minimize problems. It should also be continuously agitated. A simple field test can be conducted to obtain some visible evidence of compatibility.

1. Place a liter or pint of the fluid fertilizer in a jar.
2. Add an amount of the herbicide to equal the proportion of the formulation.
3. Shake the jar and immediately observe separation or gelling. Repeat the observation in 30 minutes.

If an emulsifier is to be used, the test can determine the effectiveness of adding the emulsifier.

Some changes are not visible and may appear only when the effectiveness of the herbicide is measured. Many herbicides are complex organic compounds, and they may interact with the fertilizer. 

**Table 8.4 Equivalent Acidity (A) or Basicity (B) of Selected Fertilizers**

<table>
<thead>
<tr>
<th>Fertilizer</th>
<th>Grade</th>
<th>A or B</th>
<th>Equivalent CaCO₃ per unit of N*</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH₄)₂SO₄</td>
<td>20.5-0-0</td>
<td>A</td>
<td>107</td>
</tr>
<tr>
<td>NH₄NO₃</td>
<td>33.5-0-0</td>
<td>A</td>
<td>36</td>
</tr>
<tr>
<td>NH₃</td>
<td>82-0-0</td>
<td>A</td>
<td>36</td>
</tr>
<tr>
<td>Urea</td>
<td>46-0-0</td>
<td>A</td>
<td>36</td>
</tr>
<tr>
<td>N solution</td>
<td>32-0-0</td>
<td>A</td>
<td>36</td>
</tr>
<tr>
<td>Ca(NO₃)₂</td>
<td>16-0-0</td>
<td>B</td>
<td>22</td>
</tr>
<tr>
<td>KNO₃</td>
<td>13-0-44</td>
<td>B</td>
<td>40</td>
</tr>
<tr>
<td>NH₄H₂PO₄</td>
<td>11-48-0</td>
<td>A</td>
<td>36</td>
</tr>
<tr>
<td>(NH₄)₂HPO₄</td>
<td>18-46-0</td>
<td>A</td>
<td>36</td>
</tr>
<tr>
<td>Superphosphate</td>
<td>neutral</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>KCl</td>
<td>0-0-60</td>
<td>neutral</td>
<td>0</td>
</tr>
</tbody>
</table>

*Per 20 pounds or 9 kg of N.

Source: Data from Terman, 1982.
Mixed Fertilizers

Molecules that have many reaction sites for adsorption and reaction with fertilizer salts. Herbicidal action may be increased or decreased. Attapulgite clay in suspension adsorbs paraquat and renders it ineffective.

Herbicides are also incorporated into dry fertilizers. The herbicides, dinitroanilines and carbamates, are sprayed on or impregnated into the fertilizer just before application. These combinations are spread on the soil and incorporated by subsequent tillage. Adding dry granular herbicides to granular fertilizers creates some of the same segregation and reaction problems encountered in adding granular micronutrients to granular fertilizers. In addition, the effectiveness of the herbicide is likely to be reduced in prolonged storage of granular combinations.

Insecticide and Fertilizer Combination

The combination of fluid fertilizers with herbicides has been much more successful than their combination with insecticides. Generally, insecticides are applied to the foliage and fertilizers are applied to the soil. One application, although not very popular, is the use of a liquid starter fertilizer—insecticide combination to control corn rootworm. Some problems encountered include incompatibility of materials, phytotoxicity, and poor insecticide performance.

REFERENCES


CHAPTER 9

Soil Fertility Evaluation

An evaluation of soil fertility is based on observations and tests of both soils and plants. Two primary purposes of the tests are to make fertilizer recommendations and to measure the effectiveness of fertilizer practices. Soil tests can be carried out before crops are planted and are the basis of fertilizer recommendations for most annual field and vegetable crops. Plant analysis is a popular way to make recommendations for perennial crops, for samples of tissue are collected after crops are established, and there is a long time after testing for nutrient accumulation and growth. In addition, the roots of perennials, tree crops for example, are permanent residents throughout a very large volume of soil, which makes soil sampling difficult. Both kinds of tests and plant deficiency symptoms are used for diagnostic purposes.

Plant Deficiency Symptoms

Plants, like animals, exhibit unique symptoms to various nutrient deficiencies. Light green or yellow-colored leaves and slow growth are common nitrogen deficiency symptoms of lawns. Nitrogen, P, K, and S are mobile in plants and are readily moved from the older and lower leaves to the upper or newly formed parts of plants when a deficiency occurs (see Figure 9.1). In fact, it is normal for mobile nutrients to accumulate in the vegetative parts and be moved to the fruit before harvest time. As N is removed from the leaves of corn for grain development late in the season, yellowing and death of the lower leaves is normal. Deficiency symptoms of mobile nutrients appear first on the lower leaves or oldest tissues. By contrast, B, Ca, Cu, Fe, and Mn are quite immobile in plants, and deficiency symptoms appear first on the most recently formed leaves or tissues.

Deficiency symptoms are useful in diagnosing plant growth problems and in selecting sites for soil fertility experiments. If detected early enough
Soil Fertility Evaluation

FIGURE 9.1 Nitrogen deficiency symptom of corn (maize) is a yellow midrib of the lower leaves. Eventually, the entire leaf may turn yellow and die.

in the season, deficiency symptoms can be considered when deciding whether an additional amount of fertilizer should be applied. Sometimes deficiency symptoms appear early in the season and then disappear, with no apparent reduction in yield. On the other hand, certain deficiency symptoms may appear in midseason or later and be associated with yield reductions as large as 50 percent.

SOIL TESTS

The tests for soil pH and lime requirements and the recommendations for liming are considered in Chapter 3. Here the emphasis is on the use of tests and procedures designed to make fertilizer recommendations.

The primary objective of using a fertilizer is to make a profit. The economical use of fertilizer depends on knowledge that can relate the use of fertilizer to a predicted increase in yield. Soil can be sampled and tested and fertilizer recommendations developed before the growing season begins. This is of particular importance to crops that have only about 100 days to grow and accumulate nutrients. Since yields are also a function of climate and management, the effects of climate and management must also be integrated into fertilizer recommendations. A soil-testing program designed to make fertilizer recommendations typically has four parts: (1) sample collection, (2) chemical analysis, (3) interpretation of the chemical tests, and (4) recommendations based on the tests for the crops to be grown.

Soil Sampling

Most soil tests use only 0.1 to 5 grams of soil, yet the volume of soil represented will likely exceed 10,000 tons. The ability to obtain a truly representative sample still remains one of the weakest links in evaluating soil fertility. Instructions for sampling should be obtained from the soil-testing laboratory. The laboratory will supply the farmer with field information sheets and soil sample containers as well as the proper instructions. Four things are needed for sampling: sampling tools—soil sampling tube, auger, or shovel; a clean pail—plastic will reduce the likelihood of micronutrient contamination; a field information sheet; and soil sample containers.

Before obtaining a sample, evaluate the field for uniformity of soil characteristics and past management practices. A sampling unit or area should be quite uniform in the characteristics that affect yields. The size of the sampling unit may vary but should generally be field size or sufficiently large that it can be fertilized differently from other areas. Avoid sampling small areas of unusual drainage, areas that have undergone unusual management in the past, or sites where manure or lime piles have been located. The sampling area should be sketched on the field information sheet and a label put on the containers that will identify the samples and associate them with the field. Unusual areas may be sampled separately if the farmer so desires. The sample should represent the plow layer where conventional tillage is used. From the sampling area obtain 20 to 30 cores that are uniform in size and represent the same soil depth. Obtain the cores at random as shown in Figure 9.2.

Fertilizer carryover and buildup of fertility mean that samples contaminated with soil from below plow layer will tend to be biased to test lower for P and K. As shown in Chapter 5, the P levels of the plow layers of many fields is now so high that P fertilizers are not recommended. No-till systems have created greater P soil test gradients in the upper 15 cm of soils, as compared to conventional tillage, because surface-applied P has limited mobility. Acidity produced by N fertilizer use has similarly created pH gradients in the upper few centimeters of soil. As a consequence, some laboratories recommend a sampling depth of 0 to 7.5 cm for no-till and disk-tilled fields. In Georgia a 10-cm sampling depth is recommended for no-till fields, pastures, lawns, and turf. Additional research is needed to develop better sampling techniques and fertilizer and lime recommendations for no-till fields.
Nitrate and sulfate sulfur tend to be quite mobile in soils, and deeper sampling is required in order to test them. Several Great Plains states recommend sampling at 60 to 120 cm in testing for available N (nitrate). Sampling to 60 cm is encouraged in the Canadian Prairie Provinces for testing of nitrate, sulfate, and soil salinity.

Place the cores in a clean pail and thoroughly mix. Fill the soil sample container; then send the sample and the field information sheet to the soil-testing laboratory. If a nitrate test is requested, moist soil samples should be quickly dried without the use of artificial heat before the samples are shipped. This drying will minimize any change in nitrates through further microbiological activity. Allowing samples to air-dry slowly is generally acceptable because most laboratories dry and pulverize the samples before testing. In any case, it is important to follow the instructions of the testing lab because their interpretation of soil test results is based on a prescribed handling of samples.

Seasonal trends in soil test results have been reported. The seasonal trend has been the most consistent for K. Soil samples taken during the growing season will often test lower than samples taken in the winter or early spring. Illinois adjusts its K soil test results on samples taken between September 30 and May 1. For most soils the seasonal trends are small, and for routine soil tests sampling is encouraged whenever it can be done. Most soil test laboratories recommend that sampling and testing be done every two to four years.

Types of Tests

The kinds of tests available depend on local soil and crop conditions. A standard test usually includes available P, exchangeable K, Ca, and Mg. It also includes their saturation percentages, the CEC, pH, and lime requirement. Greenhouse tests usually include, in addition, salinity and nitrate nitrogen. Some laboratories test for organic matter content, salinity, sulfate, and certain micronutrients and heavy metals. Some labs also offer tests for water quality.

Soil Test Correlation

A good soil test for a nutrient will effectively measure a quantity that will closely correlate with the amount of the nutrient that plants will take up; thus, it will also correlate well with yields. This soil fraction of the nutrient is typically referred to as the available fraction. Greenhouse experiments can be used to do much of the preliminary work in selecting the most efficient soil test method. The development of a soil test correlation program requires field experiments that accomplish four things. First, experimental treatments must be replicated. Second, treatments must include rates of application for a given nutrient element to determine the quantity of fertilizer required for maximum yield at a given soil test level. Third, other growth factors should be managed to obtain high yields, including an adequate supply of other nutrients. Fourth, the trials must be repeated at sufficient locations and number of years to estimate variability caused by climate and location (soil variability). The data from the experiments are used to construct figures, such as Figure 9.3, which relate soil tests to yields. The use of relative yields rather than actual yields enables all trials to be shown as one figure.

The data in Figure 9.3 show that cotton requires a higher K soil test for a given relative yield than does corn, whereas soybeans tend to require an intermediate amount. Similar statements are commonly made for P. For instance, small grains, alfalfa, and clover require higher soil tests than soybeans or corn for the same relative yield. Moreover, because of soil differences, including mineralogy, a K test of 20 for soils in group 1 is as effective as a test of 40 for soils in group 3. The soil groupings in this example are based on CEC, groups 1, 2, and 3 having CECs of 10, 20, and 30 meq/100 g, respectively. These results from Alabama parallel findings in other states, namely, that finer-textured soils must have a higher K test to produce the same crop yield as compared to sandy soils. In Ohio the desired or optimum K test in pounds per acre is 220 plus five times the CEC. This
formula works out to 270, 320, and 370 for soils with CECs of 10, 20, and 30 meq/100 g. In Georgia soils are grouped into three categories for making K recommendations: (1) Coastal Plains soils, (2) Piedmont, mountain, and limestone valley soils, and (3) soils from landscaping, golf greens, greenhouses, and flower beds. Similar studies are conducted to correlate soil P tests with yields.

Soil test correlation data are converted into descriptive terms and into useful interpretations, as shown in Table 9.1. Many different soil test levels are differentiated, depending on need and situation. In Table 9.1 a soil test value associated with a relative yield of less than 50% of the maximum is considered very low. Crops grown on soils with a very low soil test are predicted to yield in the range of 0 to 50% of the maximum yield for the soil and crop conditions. Such soils may be treated with large amounts of fertilizer to build up soil fertility. Soil tests of low and medium ratings represent soils that are predicted to yield 50% to 75% and 75% to 100% of maximum yield. Soils that test high are expected to produce the maximum yield without fertilizer. Very high and extremely high levels indicate that soils contain more of the nutrient in available form than is needed to produce the maximum yield. Such levels are not uncommon for garden samples. Extremely high soil tests may be associated with nutrient toxicities, nutrient imbalances, or environmental contamination. Thus, soil test correlation experiments provide the information to correlate tests of various soils with the relative yield expected for various crops. The next step in making a specific fertilizer recommendation is to calibrate soil tests with yields produced by varying amounts of fertilizer.

<table>
<thead>
<tr>
<th>Rating</th>
<th>Relative yield, percent</th>
<th>Recommendations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very low</td>
<td>&lt;50</td>
<td>Large applications for soil building</td>
</tr>
<tr>
<td>Low</td>
<td>50-75</td>
<td>Annual applications to produce maximum yield and increase soil fertility</td>
</tr>
<tr>
<td>Medium</td>
<td>75-100</td>
<td>Normal applications to produce maximum yields</td>
</tr>
<tr>
<td>High</td>
<td>100</td>
<td>Small applications to maintain soil fertility</td>
</tr>
<tr>
<td>Very high</td>
<td>100</td>
<td>None until soil tests drop to high range</td>
</tr>
<tr>
<td>Extremely high</td>
<td>100?</td>
<td>P may be excessive, contaminate the environment, and cause Fe or Zn deficiency</td>
</tr>
</tbody>
</table>

Source: Adapted from Cope and Rouse, 1973.

Calibration of Soil Tests with Yield Responses

Soil test calibration experiments measure the crop response to varying rates of a fertilizer nutrient applied to plots with various soil test levels. These experiments provide the data needed to construct graphs like the one given in Figure 9.4. The lower the soil test, the greater the amount of fertilizer needed to produce a particular yield or the maximum yield. Knowing the cost of fertilizer and the price of the crop permits a calculation and prediction of the amount of fertilizer that will produce the yield that will in turn earn the maximum profit.

In practice, farmers are asked to record their yield goals on the field information sheet. This value is based in part on weather expectations, previous and current management practices, and soil conditions. Then soil calibration data are used to recommend the amount of fertilizer that is predicted to produce the yield goal. Theoretically, maximum profit is earned with yields that are less than the maximum, usually at 90% to 95% of the maximum range.
Soil Fertility Evaluation

The curves in Figure 9.5 represent four different fertilizer situations. Curve A is an adverse situation in which yields without fertilizer are low, and little potential exists for increasing the yield with fertilizer. The fertilizer optimum rate is less than two units. Curves B, C, and D represent situations with increasing yield potential; differences in yield potentials could reflect differences in soil characteristics, management, or weather. For curve C the maximum profit or optimum yield is obtained with the use of 3.6 units of fertilizer. There is a tendency to recommend a fertilizer rate that will produce a yield near the maximum because with underfertilization loss of profit is greater than with overfertilization as shown in Table 9.2.

Subsoil Testing

It is generally accepted that subsoil water and nutrients are important for plant growth. Even so, very few quantitative studies of the importance of subsoil fertility have been made. These studies suggest that from 0% to 80% of the total nutrient uptake occurred in the subsoil. In the United States it is routine in areas with an ustic soil moisture regime to test for subsoil nitrate and use the test results for making N fertilizer recommendations.

The importance of subsoil fertility is related to the rooting habit of plants, the level of subsoil fertility, and the moisture conditions of the subsoil. If the entire soil profile is kept moist and at a uniform level of fertility, root growth and nutrient uptake will be much greater in the upper soil layers than in the deeper soil layers. When the surface soil dries, nutrient uptake tends to shift to lower soil layers. It has been reported that in Nebraska the first cutting of alfalfa absorbed only 5% of the P from deep in the subsoil. The third cutting, produced after the surface soil had become dry, absorbed 62% of the P from deep subsoil layers. A recent experiment in Kansas was designed to measure P uptake by sorghum grown in plastic cylinders. As the level of available P in the topsoil decreased, more P was taken up from the subsoil. In fact, when the level of P in the surface soil was low and that in the subsoil high, most of the P was absorbed from the subsoil. The experimenters found a close relationship between P uptake and the level of available P and root density. It has been observed that the P fertilizer needs of alfalfa decrease when roots become established in soils with high levels of P in the subsoil.

At present little subsoil testing is done, although it can be an important diagnostic tool. Perhaps, in the future, more effort will be directed toward greater utilization of subsoil fertility, by altering plants genetically so that they tap the subsoil. Then subsoil testing will become more important.

Plant Analysis

The nutrient concentration of a plant is an integrated value that reflects all the factors that have influenced nutrient concentration up to the time of sampling. The nutrient concentration is related to growth and changes over time, as shown in Figure 9.6. When a nutrient is deficient for maximum growth under most conditions encountered in the field, an increase in the supply increases both growth or yield and the nutrient's percentage of composition in the plant. Additional uptake of a nutrient beyond the point of maximum yield continues to increase the nutrient concentration, into the zone of luxury consumption, with no yield increase. Eventually, the concentration in the plant may become toxic and cause yields to decline.

The relation between plant composition and yield or growth is the basic information that is gained through plant analysis and used to make fertilizer recommendations, as shown in Figure 9.7. The nutrient concentration at the maximum yield is the critical nutrient concentration (CNC); there is a transition zone in which the nutrient concentration changes rather abruptly from deficient to adequate or sufficient. Much research has been done to establish the CNC and transition zones for many plants, and plant analysis is commonly used to predict the potential for applying fertilizer to increase the yield relative to the maximum yield. Some values representative of deficiency and sufficiency for a few crops commonly grown in the western part of the United States are given in Table 9.3.
Fruit and forest trees grow over a long period of time, and CNC values can be of great use in diagnosing problems and formulating management practices. In Michigan, plant analysis was used to document the fact that there were virtually no micronutrient shortages, that in fruit orchards there had been widespread use of complete fertilizers, which were 90 percent unnecessary. Measuring changes in plant composition is a standard method of evaluating the effectiveness of fertilization practices. When tissue analysis is used to measure a forest's response to fertilization, it may take several years before measurable differences appear in foliar dimensions, tree height and diameter, and wood volume.
In general, a nutrient's percentage of composition in a plant decreases as the plant ages, and there is great variation between different parts of the plant. Research data for most economic crops have been summarized and placed in tables, showing when and which part of the plant to sample. For example, the CNC values for corn have been given as 3% for N, 0.03% for P, and 2% for K in the leaf opposite and below the uppermost ear (ear leaf) at silking time.

Crop Logging

Crop logging, which consist of periodically measuring the plant composition, has been widely used for high-value crops including sugar cane, pineapples, and sugar beets. For crops that grow over a long period of time, unusually heavy rainfall or reducing conditions may greatly alter the available supply of some nutrients. Maintaining an adequate supply of N for plants over a long growing season without potential contamination of water supplies is a frequent problem. Periodic plant analysis or crop logging was used in California to determine N fertilization practices that would maximize sugar production and minimize water pollution. For maximum sugar production by sugar beets, it is desirable to have a limited or small amount of N available early in the season to encourage high sugar content in the roots. Later in the season it is desirable to have abundant N to increase the quantity of roots. In an experiment 90 kg N/ha were applied at thinning time, and petiole N remained above the sufficient level until the later part of July, when an additional application was made (see Figure 9.8). This method produced more sugar than if all the N had been applied at planting time and minimized the potential for water pollution.

FIGURE 9.8 Nitrate content in petioles of sugar beets during the growing season in response to two applications of nitrogen fertilizer and no nitrogen application. (Modified from Ulrich and Hills, 1967.)

Rapid Plant Tissue Tests

Analytical plant analysis is an indispensable research tool, one which is useful in soil management, but the tests are expensive and time-consuming. Inexpensive test kits for N, P, and K are available and have been widely used to diagnose plant growth problems in the field. They are particularly useful to verify a particular deficiency symptom. They are of two types. Selected tissue is cut up into small pieces and placed in a vial with distilled water, or plant sap is squeezed onto a prepared paper. Chemicals are used to assay the nutrient content, which in essence is a measure of the nutrients in plant sap. Particular plant parts are sampled at various stages of growth, the same as in analytical tests.

Diagnosis and Recommendation Integrated System

An alternate method of evaluating the status of crop nutrients through the use of tissue analysis, called the diagnosis and recommendation integrated system (DRIS), was developed by Beaufils (1973). This system incorporates tissue analysis with other yield parameters in making recommendations.

The DRIS system emphasizes the importance of nutrient balance within plant tissue and states that maximum yield may never be obtained unless the proper balance or ratio of nutrients is maintained in plant tissue. Having this proper ratio of all plant nutrients does not in fact guarantee a maximum yield because the crop could be destroyed by hail, flooding, or other causes. If the plant nutrient ratio is incorrect, the yields will be lower.

The DRIS system has an advantage over trying to determine critical values in that nutrient ratios in plant tissue tend to be rather constant throughout the growing season. Thus, by applying this system, the farmer avoids having to sample the crop at a precise growth stage and estimate the change that will occur during the rest of the period.

For successful use, the DRIS system must have known norms or indexes for the maximum yields of each crop. And the method of calculating the norms must be readily carried out. Norms have been developed for corn, soybeans, wheat, sugar cane, potatoes, and sorghum; they are referenced by Sumner and his colleagues (1983). Letzsch and Sumner (1983) have developed a computer program for calculation of the norms and offer copies of it for a nominal cost.

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CHAPTER 10
Application and Use of Fertilizers

In general, about 50% of the N, 20% of the P, and 35% of the K, or less, in fertilizers is absorbed by crops during the year of application. Achieving the maximum biological efficiency in using fertilizers depends on the time of application and their placement. Factors that influence decisions about when to apply a fertilizer and where to place it include nutrient mobility and fixation in the soil; plant needs and the location of roots; losses by volatilization and leaching; the amount of soil moisture and the temperature of soils; and salt effects on germination. In general, matching the time of application to plant nutrient demands decreases the opportunity for fixation and loss and increases the opportunity for absorption and a yield response to the nutrient applied. Rates of application and use are also affected by economic and environmental considerations and convenience.

FERTILIZER APPLICATION PRACTICES

Fertilizers are placed either on or in the soil. The major methods of surface placement are broadcasting dry materials, spraying liquids, and apply fertilizer in irrigation water. Methods of placing fertilizer in the soil include band placement, plow down, injection, and application in irrigation water. Only a very minor amount of fertilizer is applied to leaves as a foliar spray.

Fertilizer placement and the time of application are importantly affected by the practices used to establish and manage a crop and the properties of soils and fertilizers. In general, dry and liquid forms are of equal value if they are similarly placed in the soil and applied at the same period of time. The major factor is the amount of nutrient applied. Nutrients in both dry and liquid forms must appear in the soil solution as ions before they can be taken up. As the level of soil fertility increases, placement of fertilizer becomes less important.
The major concern in applying fertilizers is that the nutrients be used efficiently without any detrimental effects on plants or the environment. The major consideration in the placement and time of applying N fertilizers is to prevent the loss of N through volatilization, leaching, and denitrification. Fixation of P, the immobility of P, and the limited mobility of K in soils are the major considerations in the placement and timing of applications of P and K fertilizers. In some soils K fixation becomes an important consideration. There is an interaction between placement and time of application, and it is desirable to discuss them together.

Injection of Anhydrous Ammonia

The method of applying NH₃, related to its gaseous nature. Anhydrous ammonia, 82-0-0, has a vapor pressure at 0 degrees C of 47 pounds per square inch of gauge pressure, and at 38 degrees C of 197. Because it is a volatile liquid, it must be placed 15 to 25 cm deep in the soil to minimize loss by volatilization. As shown in Figure 4.10, the amount lost is related to soil type, moisture content, and depth of application. For row crops the farmer usually chooses an applicator knife or injector to apply the fertilizer between alternate pairs of rows, and pesticides may be applied at the same time. For forages and small grains the injectors need to be about 30 to 40 cm apart to obtain fairly uniform distribution of the N for the roots. Application of part of the N during the growing season ensures more efficient use than if all the N is applied before or at planting time. Now for row crop production it is popular to combine the application of NH₃ with cultivation or with application of a herbicide.

It has become popular to apply anhydrous ammonia with other tillage operations, especially prior to planting. On the other hand, in the Great Plains, where loss of N by leaching is minimal, delivery lines place anhydrous ammonia at the bottom of the tilled layer of undercutting sweeps. This practice after grain harvest effectively controls weeds and leaves crop residues on the surface to reduce soil erosion. In humid regions where nitrate leaching losses are likely, the application should be delayed until soil temperature is below 18 degrees C (50°F) in the fall. The use of nitrification inhibitors to inhibit nitrification of fall-applied ammonium N is unreliable. Frequently, the fall is a time of low labor demand. In some situations soils are dry and firm and the price of the N may be discounted. Fall application of N in humid regions, however, is losing favor because of concern about nitrate pollution of groundwater.

In the United States the first injection of anhydrous ammonia into the soil occurred in the Mississippi Delta region in the early 1940s. The advantages of placing P and K fertilizer within the soil may encourage future farmers to combine the injection of NH₃ with the injection of P and K.

Band Application

During the early days of using fertilizer, agricultural soils were more infertile than today, fertilizers were relatively more expensive, and low rates of application were common. To obtain maximum effectiveness, farmers applied the fertilizers in bands along with the seed. Fertilizers became more concentrated over time, and the salt index and rates of application increased. The salt affected germination, and applicators that separated seed and fertilizer were introduced. The standard recommendation for row crops is a band 2 inches to the side and 2 to 6 inches below the seeds to make sure seed and fertilizer are separated enough to avoid salt injury. In this location the fertilizer is usually in moist soil where early root growth can provide the plant with quick access to the fertilizer. Band placement reduces P fixation and puts a readily available source of nutrients close to roots, allowing the crops to get off to a fast and vigorous start. There is less contact between the P fertilizer and soil, when banded as compared to broadcast, creating zones or small areas of higher P availability. Root growth in a fertilized soil band or zone has commonly been observed to be greater than root growth in the surrounding unfertilized soil (see Figure 10.1). This effect is due mainly to the P.

Band placement of N is not effective. Nitrate is not fixed or adsorbed by the soil and remains very mobile. Surface application is as good as placement in the soil if there is rain or irrigation to move the N into the soil. Ammonium in fertilizer is usually rapidly nitrified to NO₃ and becomes very mobile. Now fertility levels for P and K are frequently so high that band placement of P or K does not increase the yield more than does broadcast application. However, plant analysis may show slightly greater uptake of fertilizer P and K early in the growing season when it is band-placed.

As indicated, there is less and less benefit from banding fertilizer as soil fertility levels increase. There are, however, some important situations in
which band placement is effective. Yield increases with band application of P on Oxisols with high P-fixing capacity are common. Band application of K is also effective on soils with unusually high K-fixing capacity. Band application helps to increase the uptake of micronutrients from fertilizers that are subject to rapid soil fixation in all soils. Low spring temperatures in soil appear to be the reason for the response of spring wheat to banded P on the northern Great Plains.

Broadcast Application

Broadcast application is the spreading of the fertilizer uniformly over the entire soil surface. It is the only practical way to fertilize lawns, forage and pasture fields, and forests on mountain slopes. As already indicated, anhydrous ammonia is not suitable for broadcast application on the soil surface. If the fertilizer contains only N, subsequent rains will move the fertilizer into the soil, and broadcast application may be as effective as any other placement. Urea is rapidly hydrolyzed to NH$_4^+$ under warm and moist conditions. When urea is broadcast under alkaline conditions, however, the NH$_4^+$ reacts with OH$^-$ to form NH$_3$ and water with great potential for loss of N by volatilization. It is not uncommon to lose over 30 percent of the N from surface application of urea. As a consequence, the effectiveness of a broadcast application will be increased if the urea is leached into the soil or incorporated by subsequent tillage.

Phosphorus is readily fixed in most soils and thus moves very little from the point of application. Broadcast applied P is therefore less effective because few roots are active in the immediate surface soil, especially when the surface soil dries. In many forage fields, however, the surface of the soil may remain moist under dense foliage for a considerable part of the growing season, and the uptake of P is effective. For insoluble phosphates, in the form of rock phosphate, broadcast application, and subsequent incorporation into the soil, is more effective than band placement because it provides more soil contacts and opportunities for dissolution. Gypsum and elemental S are common carriers for sulfur and are commonly broadcast because SO$_4^{2-}$ is mobile and readily moves into the soil with water.

All airplane and helicopter applications are by broadcasting. In the United States aerial seeding and fertilization of flooded rice fields is routine. Rough terrain and the inaccessibility of many forests makes aerial application popular. In these instances urea is commonly applied, in a large prill size that drifts little and can be uniformly distributed.

Combining Broadcast Application with Tillage Operations

Fertilizer use in the past has greatly increased soil test levels for P, and the overall fertility level has increased for many soils. Thus, to some extent the negative effects of P fixation from broadcast applications have been diminished. The lower cost of fertilizer relative to labor and other application costs has encouraged higher rates of fertilizer use as well as less attention to effective placement and proper timing. In the fall and winter more labor is available, and, perhaps, soils are firmer for application with bulk spreaders. The price of fertilizer is also more attractive in the off-season. The broadcasting of bulk fertilizer and plowing under the fertilizer is therefore popular. Plowing and subsequent tillage operations mix the fertilizer throughout the plow layer and contribute to effective use of the nutrients.

Application in No-Till Systems

In humid regions reduced tillage to lessen soil erosion and lower the costs of production has proved popular for row crops, especially for corn in the southern Corn Belt. In no-till planting systems there is no conventional plowing. Crop residues and organic matter accumulate at the soil surface. Weeds and competing vegetation are controlled by chemical herbicides. Only a strip of soil 2.5 to 7.5 cm wide is disturbed for each planted row. Fertilizer applications are mainly by broadcast on the surface. The system builds up a concentration of organic crop residues and carryover nutrients in the upper few centimeters of soil. There is greater microbial and root activity in this upper soil zone and greater opportunity for immobilization and mineralization of N. The possibility exists for immobilization of N to decompose crop residues in the upper soil layer. The acidic effects both of acid-forming N fertilizers and of organic matter mineralization are, similarly, concentrated in the few centimeters of surface soil. These effects would appear to have an influence on crop yields; however, yields from no-till have generally not been significantly different from yields of conventional tillage systems. Perhaps the sameness of yield is related to other effects of no-till planting.

In no-till planting there is more water available for crops because infiltration is greater and surface evaporation less. The accumulated organic matter at the surface acts as a mulch and causes lower soil temperatures in the spring. The effect of lower soil temperature, especially in the northern states, has been to stimulate a response to some starter K fertilizer when soil K tests were less than optimum. In addition, the compaction of no-till soil and its blocking effect on aeration has apparently reduced K availability in some experiments. These findings confirm the complexity of the soil-plant-climate system; perhaps additional research will give a clearer picture of the effects of no-till on soil properties and the response of crops to fertilizers. In the future the development of better planters with which to place fertilizer in the soil, together with an occasional plowing, will likely overcome any negative aspects of nutrient and pH stratification.

Fertigation

The application of fertilizers to irrigation water is called fertigation. Anhydrous ammonia was first directly applied as a fertilizer in the 1930s in California when anhydrous ammonia was added to irrigation water. The
two major problems of fertigation have been the inability to distribute nutrients uniformly, because water distribution is not uniform, and fixation of P in the surface soil where root activity is low. There has been much progress in solving both of these problems so that, today, applying fertilizers in the irrigation water is often the most convenient and inexpensive method of application. Fertigation may also offer more flexibility in timing and in rates of application and better control of leaching so that fewer mobile nutrients are lost from sandy soils. Disadvantages include loss of nutrients in runoff water; volatilization loss of N from sprinkler-applied NH₃ and aqua ammonia, especially on calcareous soils; the precipitation of incompatible fertilizer materials; and the clogging of nozzles and emitters.

The major management decisions for fertigation relate to the nature of the fertilizer materials and method of water distribution. Water distribution is by open or gravity systems, such as furrow or flood, or by closed systems, which include sprinklers and drip or trickle. Aqua ammonia and NH₃ are subject to serious volatilization loss from both water and soil surface in both closed and open systems. Losses from sprinkler application in excess of 50 percent have been reported. The loss is enhanced by alkalinity of water and soil, by air turbulence, and by increases in temperature, rate of application, and length of exposure. Ammonia added to irrigation water increases the pH of the water and, in the presence of Ca⁺⁺ and Mg⁺⁺, and HCO₃⁻, causes Ca and Mg salts to precipitate, which can clog closed-system equipment. Urea-ammonium nitrate (UAN) solutions are popular because the N is less volatile and there is more efficient use of N. If dry N carriers are dissolved in water and used in closed systems, they must be free of any coating materials that will plug or clog nozzles and emitters.

Little P is applied by fertigation because the P tends to accumulate at the soil surface where root activity is minimal. In alkaline water the P may precipitate Ca and Mg, again causing a clogging problem. Acids can be added to water to retard precipitation of salts; however, the acids are corrosive and require special handling. Research is being conducted to evaluate the effectiveness of acids for reducing ammonia loss and the precipitation of salts in the application equipment. The K carriers, KCl and K₂SO₄, can be added to irrigation water with no apparent precipitation problems. Soluble sulfate carriers are used to add S. Some soluble chelated forms of micronutrients are also used.

A major limitation of fertigation is the nonuniform distribution of water and the therefore nonuniform distribution of nutrients in open systems. The major advantage of fertigation is the increased opportunity to add fertilizer. Since N is the major nutrient applied, this means better timing of N in relation to plant needs during the growing season. In addition, on sandy soils with pivot sprinkler systems, there is greater control over nitrate N loss by leaching and over groundwater contamination.

**Foliar Application**

Foliar application can be used for the quick correction of a nutrient deficiency in plants. The amount of fertilizer nutrients that can be applied to the foliage is limited by the solubility of the materials, the salt tolerance of the foliage, and the amount of liquid that adheres to the leaves. Most of the interest in foliar fertilization is for the application of micronutrients. Some of these, Mn and Fe for example, are rapidly fixed or converted into insoluble form in alkaline soils, and plants have a very small requirement. Often there must be repeated sprayings, which limits the use for the more valuable crops, such as tree fruits. If the crop is irrigated with overhead sprinklers, the micronutrient can be applied in the irrigation water. Pineapples in Hawaii are regularly sprayed with ferrous sulfate to supply iron. Urea is readily absorbed by the leaves, and pineapples have a high tolerance for foliar salts. As much as 75 percent of the total N needs of pineapples have been supplied from foliar application of urea. The high plant requirements for N, P, and K generally make foliar application of limited use for the application of fertilizers containing these nutrients.

During the seed-filling stage of grains, there is considerable movement of N, P, and K to the seeds. These nutrients are quite mobile in plants; however, leaves are depleted of these nutrients. Some nutrients like Ca, Mg, and Mn are not effectively translocated from leaves to seeds. Thus, it would seem that the addition of certain nutrients by foliar application during seed-filling time might have a significant effect on grain yield. Recent research on the application of foliar nutrients during the seed-filling time of grains has at times shown a significant increase in yield. Some general conclusions from this work are as follows.

1. Urea is the most effective form of N for foliar application. The urea should not be applied when the sun is shining brightly, and biuret in the urea may cause leaf burn and reduce yield. The maximum rate of urea that can be applied at one time without causing serious leaf burn is N at the rate of 22 kg/ha (20 pounds/acre).
2. Where foliar fertilization has increased grain yields, the four nutrients, N, P, K, and S, were applied. A ratio of 10N-1P-3K-0.5S was the most effective for soybeans.
3. Including micronutrients or the less phloem-mobile nutrients (Zn, Cu, Mn, B, Ca, Mg) did not increase soybean yields.

**Deep Soil Placement**

If surface soils are dry and subsoils are moist, the greater water potential in the subsoil encourages greater root growth there and subsequently greater use of the nutrients placed in the subsoil. Root penetration is inhibited into soil layers devoid of Ca. In some very acid and highly weathered soils, deep placement of Ca is necessary in order to promote deep rooting and the use of subsoil water. Deep placement as used here generally means placement in the subsoil; it is expensive and used only occasionally (see Figure 10.2). It is to be expected that a plant's use of nutrients placed deep in the soil is less efficient, because maximum root activity is usually in the plow layer.
FERTILIZER RECOMMENDATION PHILOSOPHIES

Fertilizer recommendations based on soil tests are of three types. First, now that many soils test high for P and K, a maintenance philosophy is employed. Second, soil tests are used as a measure of nutrient sufficiency and are the basis for determining the amount of fertilizer needed. Finally, fertilizer recommendations are based on a consideration of cation balance.

Maintenance Fertilizer Recommendations

One of the most striking effects of human occupancy and the agricultural use of land is the soil's increased content of phosphorus. Ancient campsites and kitchen middens have been located in the United States and Europe by a systematic sampling of soils and a determination of their P content. Thick, dark-colored A horizons with properties similar to mollic horizons, except that they contain 250 ppm or more of P₂O₅ soluble in 1% citric acid, qualify as anthropic horizons. Anthropic horizons are formations greatly affected by human activity. In villages and campsites P is discarded as bones and other refuse, and the P is subsequently fixed and accumulates in the soil. Agricultural land accumulates P from longtime manuring and fertilization. In Michigan the median soil test for P increased from 23 to 105 pounds/acre between 1962 and 1986. Large increases in soil P over a relatively short time for a variety of major crops are given in Table 10.1.

The extent of P carryover depends on soil fixation and crop removal. In Illinois the addition of 9 pounds of P₂O₅ (4 pounds of P) increases soil tests by about 1 pound/acre. Thus, for many soil and cropping situations the P soil test may become high in a few years, for a high test is frequently only 30 to 60 pounds/acre. It is very common for gardens to test very high in P. Some state soil-testing laboratories now report that 50 percent or more of the soil samples test high or very high. Potassium carryover is also very common and related to soil fixation and crop removal. Several states report that about 4 pounds of fertilizer K₂O (3.3 pounds of K) will increase the K soil test 1 pound/acre. Nitrogen carryover is strongly related to leaching and denitrification losses. There may be significant carryover of nitrate N from one year to the next in soils with aridic and ustic soil moisture regimes. Soils in general, however, do not show continuing increases of available N to very high levels as they do for P and K.

Because soil tests are frequently high for P and K, it is becoming popular to make maintenance recommendations for these nutrients. The amount recommended is based on an estimation of about 1.5 times the amount removed in the harvested crops. Soil tests every two to five years are recommended to determine whether recommendations need to be adjusted.

Nutrient Sufficiency Recommendations

Sufficiency recommendations are based on the soil test correlation and calibration procedures discussed in Chapter 9. The soil test value is used to predict or estimate the amount of fertilizer needed to achieve the desired yield goal.

Basic Cation Saturation Ratio

The basic cation saturation ratio (BCSR) or cation balance method attempts to adjust the distribution of the exchangeable Ca, Mg, and K to about 65%, 10%, and 5% saturation, respectively. The percentage of saturation ratio of Ca : Mg, Ca : K, and Mg : K would be 6.5, 13, and 2, respectively. The ratios for the plow layers of fields on which world record corn yields were pro-
duced in 1973 and 1977 were 4, 23, and 6 in 1973 and 3, 18, and 5 in 1977. Research on soils which have a significant amount of CEC and in which the amounts of XCa and XMg are large relative to annual crop needs (Alfisols and Mollisols) has failed to show a significant relation between crop yields and the percentage of saturation of Ca, Mg, and K. Very wide differences in the ratios of these exchangeable cations with one another have been observed with no negative effect on yields. Recommendations based on these ratios tend to result in overfertilization and increase the cost of production.

In some situations the ratios are important. The excessively high XMg relative to the other exchangeable cations is associated with infertility in serpentine soils. High K fertilization can bring on a Mg deficiency for some crops growing on soils with a marginal content of XMg. Oxisols have very little CEC and small absolute amounts of XCa..Na. Crops growing on Oxisols are more sensitive to small soil fertility differences as compared to crops growing on Alfisols and Mollisols. One example of a recommendation for cropping on Oxisols is an absolute minimum amount of K equal to 0.1 meq/100 g of soil and a relative minimum amount of K equal to 2% to 3% of the XCa..Na.

Summary Statement

An eight-year study was conducted on four different soils and locations for corn production in Nebraska. Soil samples from each location were routinely sent to five different soil-testing laboratories for fertilizer recommendations. All three philosophies were represented, and all the corn yields were similar. There were, however, large differences in the kinds and amounts of fertilizer recommended. Consequently, there were large differences in the fertilizer costs. The results generally supported the nutrient sufficiency philosophy as being agronomically and economically sound.

Fertilizer and Plant-Water Relations

Evapotranspiration (ET) is a physical process controlled by the meteorological conditions or the amount of heat available for evaporating water from the soil and vegetation. When water is nonlimiting, the ET or water consumed by a crop is a function of meteorological conditions and not of the rate of plant growth. Under these conditions any management practice that increases yield will increase the efficiency of water use. When water is limiting and soils become dry, soil nutrients are not as available and water use is less efficient.

Water Use Efficiency

The water consumed for each unit of yield is a measure of the efficiency with which water is used. In comparisons of fertilized and nonfertilized fields or experimental plots, the heat available for evaporation of water can be considered a constant. As a consequence, the ET would be expected to be the same on both control plots and fertilized plots. One agronomic modifier of the actual ET is the extent of vegetative cover. Once an adequate vegetative cover is established, however, additional plant growth or cover has no effect or very little effect on ET. Larger plants can intercept more advective or horizontally transferred heat, but this effect is small. Thus, any yield increase brought about by using fertilizer invariably increases the efficiency of water use. Reports of a 50 percent or greater increase in crop yield per inch of water used are common when the response to fertilizer is large. Increased water use efficiency is also verified by the casual observation that doubling the average yields of a crop in a state does not double the use of water or double the water deficit. As water for irrigation becomes more expensive and less available, it becomes more important to maximize production from the limited supply of available water.

Effect of Water on Nutrient Availability

Plants can obtain their nutrients and water from a very small soil volume if both nutrients and water are highly available. When soils dry, however, the matric water potential and hydraulic conductivity decrease. Decreased hydraulic conductivity reduces the movement of water through soil to roots, thereby reducing the rate of water uptake and the rate at which nutrients move to roots by mass flow and diffusion. Plants under water and nutrient stress photosynthesize less. Both top and root growth may be restricted. Droughty conditions, therefore, may restrict root growth and decrease the potential supply of nutrients (and water) positionally available for uptake. Increased soil fertility, on the other hand, may increase the growth rate and the extent of the root system, thereby increasing the amount of nutrients and water that are positionally available for uptake (see Figure 10.3).

The Cisne soil referred to in Figure 10.3 is a claypan soil, Albaqualf, with smectitic clays in the claypan. Research in Missouri on similar soils showed that breaking up the claypan with deep tillage during the dry season produced only temporary results. Fertilization, however, proved to be the most effective means of increasing deep root growth and yields.

As soils dry, there is a decrease in the movement of nutrients to the roots by mass flow and diffusion. In dry soils, compared to moist soils, fewer nutrient ions move to roots by mass flow because there is less water moving. The diffusion path for nutrients (and water) becomes more tortuous as the soil dries, so that fewer ions move to roots by diffusion. And the amount of nutrients released when organic matter mineralizes decreases when soils dry, affecting the supply of N in particular and sometimes decreasing B to the point of deficiency. There is an interaction between soil fertility and soil water so that it may be difficult to determine in times of drought whether yields are reduced more by a lack of water or by a lack of nutrients.
EFFECT OF FERTILIZERS ON SOIL REACTION

Fertilizers as soluble salts are acid, neutral, or alkaline. Most of the net or long-term effects of fertilizer on soil pH are caused by transformations that occur in the soil. The addition of NH₃ produces an immediate alkaline affect owing to hydrolysis; however, subsequent nitrification produces a long-term acidic effect. Ammonium sulfate and NH₄Cl in particular are acid-forming because of the accompanying acidic anion; they are sometimes selected as the N fertilizer when an increase in soil acidity is needed. Nitrate accompanied by Ca, Mg, K, or Na is basic. Potassium chloride and K₂SO₄ have a neutral effect. Of the P materials, only those containing ammonium are acid-forming owing to the nitrification of the ammonium.

In general, the P and K carriers in fertilizers do not significantly affect soil pH. The concern in agriculture centers on the N fertilizers because the most popular N materials are NH₃, NH₄NO₃, and urea, which are acid-forming. The effects of the acid-forming fertilizers depend on the rates of application and the pH and buffering capacity of the soil. Their application on alkaline and calcareous soils may be beneficial. On acid sandy soils, however, changes may be rapid and the effects quite negative.

The negative effects shown in Figure 10.4 are extreme because the buffering capacity of the soil was small and the rate of N application high. In the experiment the development of a pH of about 4 produced Mn toxicity and Mg deficiency. These results show that when acid sandy soils are not limed to increase soil pH and the cropping system excludes legumes, the continued high rates of applying N fertilizer may greatly increase the lime requirement and negatively affect yields.

ECONOMICS OF FERTILIZER USE

Two major decisions relevant to the economics of fertilizer use are the price of fertilizer relative to the price of crops and the price of fertilizer relative to the price of other factors of production. In recent decades the price of labor, machinery, and land have increased much more rapidly than the cost of fertilizers. As a consequence, farmers have tended to substitute fertilizer for other factors of production, and this has accounted in large part for the rapid increase in fertilizer use since World War II. In the past few years, however, the effect of increasing soil test values and the adverse economic situation have moderated the trend.

Profit Maximization from Fertilizer Use

The entire plant growth curve is sigmoidal. In the range where decisions about fertilizer use are made, the addition of fertilizer causes increasing growth at a decreasing rate. Returns are diminishing. The first units of fertilizer produce a greater yield response than later units. Profits from the use of a fertilizer are at the maximum when the last or marginal unit of fertilizer produces a yield increase whose price is equal to the cost of the
unit of fertilizer. The ratio of the price of the crop to that of the fertilizer is 1.0, and the point of maximum profit occurs at a rate less than that needed to produce the maximum yield, as shown in Figure 10.5.

There are several other factors that affect the actual decision regarding fertilizer rate. Since the marginal return from additional units of fertilizer becomes less and less profitable, having an alternative, more profitable investment in which to put their money would influence farmers to apply fertilizer at less than the point of maximum profit. Sometimes a lack of capital and risk are important factors. In many developing countries there is little or no opportunity to make a profit from the use of a fertilizer because its cost is too high relative to the price of the crop.

ENVIRONMENTAL CONCERNS

There are two important environmental concerns regarding fertilizer use. The first is the effect of N and P on the eutrophication of surface waters, and the second is the accumulation of nitrate in both surface water and groundwater.

Nitrogen

The rate and time of application are the two major issues in the use of N fertilizers. Generally, the rates recommended by soil-testing laboratories are acceptable if the soil profile is low in nitrate. In soils with ustic and aridic soil moisture regimes, the nitrate levels in the soil should be measured. The quantity in the profile should be subtracted from the normal recommendation.

Timeliness of application is an important concern in humid regions. To be environmentally acceptable, N should be applied so that it will be retained in the root zone during the growing season. The potential for nitrate leaching is created when more NO\(_3^-\) exists in the soil than plants can use. The extra NO\(_3^-\) becomes leachable, as shown in Figure 10.6. Thus, if N fertilizer rates are just sufficient to meet yield goals, little potential for nitrate leaching is created. Many farmers, however, set optimistically high yield goals and tend to use more N fertilizer than is needed.

Excessive nitrate in drinking water can produce various disorders in livestock and methemoglobinemia, lack of oxygen in blood, in infants. Methemoglobin is a blood pigment that differs from hemoglobin. The United States Public health standard for domestic use is 10 ppm (10 milligrams/liter) N as nitrate in water.

In the early 1970s it was discovered that N\(_2\)O released into the atmosphere causes reactions that decrease the amount of ozone (O\(_3\)). Loss of ozone reduces the atmosphere's ability to screen out ultraviolet radiation. The production of N\(_2\)O is a natural event that occurs by denitrification in the N cycle. Anything that increases N fixation, including N fixed by legumes, increases the formation of N\(_2\)O. At the present time loss of ozone appears to be a valid concern, and the magnitude of the problem is not
known. But any fertilizer practice that contributes to more efficient use of N will minimize N₂O problems.

**Phosphorus**

Generally, the P concentration of the soil solution is very low and P remains quite immobile in the soil. In recent years the carryover of P, however, has greatly increased the level of P in soil tests. The relation between the P revealed by a soil test and the concentration of P in solution for two soils is shown in Figure 10.7. The Hoytville soil is fine-textured and the Hillsdale is a sandy soil. A given amount of P in the sandy soil made the concentration of P in solution higher. Thus, high soil tests on some soils cause concern for eutrophication from P in runoff. Recent research has shown significant downward movement of P in sandy soils with very high soil test levels.

The practice of no-till cropping has introduced an additional way in which P can be lost to the environment. Continuous no-till cropping builds up greater amounts of P in the immediate soil surface and the potential for greater movement of P by erosion. On the other hand, runoff and erosion are generally much less than from soils on which conventional tillage practices are used because more crop residues remain on the soil surface.

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