

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/299657222>

# Soil Fertility and Plant Nutrition

Chapter · August 2014

DOI: 10.1016/B978-0-444-52512-3.00249-7

CITATIONS

11

READS

21,269

3 authors, including:



**Joshua Michael McGrath**  
University of Kentucky

42 PUBLICATIONS 587 CITATIONS

[SEE PROFILE](#)



**Chad J Penn**  
United States Department of Agriculture

105 PUBLICATIONS 1,418 CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



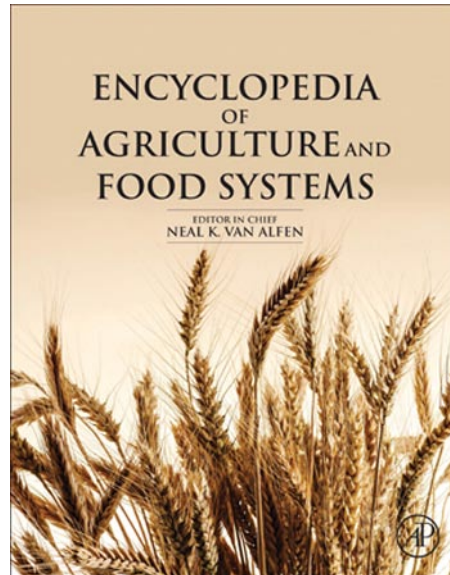
Vegetative Filter Strips [View project](#)



Use of Fly Ash for Phosphorus Trapping in Bioretention Cells [View project](#)

**Provided for non-commercial research and educational use only.  
Not for reproduction, distribution or commercial use.**

This article was originally published in *Encyclopedia of Agriculture and Food Systems* published by Elsevier, and the copy attached is provided by Elsevier for the author's benefit and for the benefit of the author's institution, for non-commercial research and educational use including without limitation use in instruction at your institution, sending it to specific colleagues who you know, and providing a copy to your institution's administrator.



All other uses, reproduction and distribution, including without limitation commercial reprints, selling or licensing copies or access, or posting on open internet sites, your personal or institution's website or repository, are prohibited. For exceptions, permission may be sought for such use through Elsevier's permissions site at:

<http://www.elsevier.com/locate/permissionusematerial>

McGrath J.M., Spargo J., and Penn C.J. Soil Fertility and Plant Nutrition. In: Neal Van Alfen, editor-in-chief. *Encyclopedia of Agriculture and Food Systems*, Vol. 5, San Diego: Elsevier; 2014. pp. 166-184.

© 2014 Elsevier Inc. All rights reserved.

## Soil Fertility and Plant Nutrition

**JM McGrath**, University of Maryland, MD, USA

**J Spargo**, Pennsylvania State University, PA, USA

**CJ Penn**, Oklahoma State University, OK, USA

© 2014 Elsevier Inc. All rights reserved.

### Glossary

**Chlorosis** Yellowing or lighter shade of green.

**Immobile nutrient** The immobile elements cannot translocate within the plant to meet need and therefore their deficiency typically occurs in the younger leaves first.

**Internode** The distance on the stem between leaves.

**Interveinal** Between the leaf veins.

**Meristem** The growing point of a plant.

**Mobile nutrient** A mobile element is able to translocate to areas of the plant with the most need. Typically, mobile elements move from the older or lower leaves to the upper or younger leaves to support new growth.

**Necrosis** Browning or dying of plant tissue.

### Introduction

Soil fertility and plant nutrition encompasses the management of essential elements necessary for plant growth, typically to achieve selected management objectives. Although soil fertility plays a vital role in natural systems, the scope of this article is limited to plant production for human uses (e.g., food, feed, fiber, energy, and landscape esthetics). An element is considered essential if it is required for plant metabolism and for completion of the plant's life cycle (Epstein and Bloom, 2005; Havlin *et al.*, 2005). Typically, 17 elements are considered to meet these criteria and they are divided into macro- and micronutrients (Table 1). This division is based on their relative abundance in plant tissue rather than on their necessity for plant growth. Macronutrients are generally present in plant tissue at concentrations above 0.2%, whereas micronutrients are present below 0.01% (dry weight basis). Carbon (C), hydrogen (H), and oxygen (O) are derived from carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O), which are transformed through photosynthesis to produce carbohydrates and are, therefore, present in the highest concentrations of any element in plant tissue. They are not, however, considered mineral elements and are almost always available in amounts necessary for their direct use in complete plant metabolism.

The essential mineral macronutrients can be divided into primary macronutrients, which include nitrogen (N), potassium (K), and phosphorus (P), and secondary macronutrients, calcium (Ca), magnesium (Mg), and sulfur (S). The eight micronutrients are copper (Cu), manganese (Mn), iron (Fe), boron (B), nickel (Ni), molybdenum (Mo), chlorine (Cl), and zinc (Zn). Other mineral elements may be essential for some plants or benefit crop quality or growth, although not being essential for metabolic processes or completion of the plant's life cycle; often these elements are referred to as 'beneficial elements.' Beneficial elements include cobalt (Co), sodium (Na), silicon (Si), selenium (Se), and vanadium (V). Silicon is present in concentrations on the order of some of the macronutrients in many plant tissues and has beneficial properties but is not generally considered essential to metabolic processes or the life cycle of any plants outside the family Equisetaceae (Epstein, 1994). However, there is an emerging

school within the soil fertility research community that believes it may be more essential than previously thought.

Many other elements are taken up by plants in varying degrees but are not considered essential as defined above. Both essential and nonessential elements may be toxic to plants if accumulated at high enough concentrations to interfere with metabolic functions. Therefore, soil fertility and plant nutrition as a discipline encompasses management of these essential elements in the soil to provide them in adequate or sufficient amounts for plant metabolic processes and reproductive activities to be completed. Optimum soil fertility requires not only adequate quantities of the essential elements but also that they be in a form and location available for plant uptake and therefore optimum plant nutrition.

### Soil Fertility Management

#### History of Soil Fertility and Plant Nutrition

Actively managing soil nutrients to provide optimum plant nutrition has been a core practice of agricultural production throughout human history. For many centuries agricultural production relied on recycling of organic residuals, such as manure and crop residues. Industrialization and population growth of the nineteenth century demanded increased agricultural production and coincided with the development of commercially produced P fertilizers. Providing adequate P fertilization allowed the true potential of N fertilization to be realized, and industrial production of inorganic N fertilizer soon followed with the development of the Haber-Bosch process in 1909. Stewart *et al.* (2005) estimated that N, P, and K fertilizers likely account for 40–60% of yield in the United States and England and much higher in the tropics. Industrially fixed N fertilizer has been estimated to account for 40–48% of the world's protein supply (Erismann *et al.*, 2008).

In a macrosense, the relationship between the development of commercial P and N fertilizers reflects one of the guiding premises of soil fertility explicitly stated as the theory of the minimum developed by Carl Sprengel in 1828 and popularized as 'Liebig's law of the minimum,' which states that

**Table 1** Essential nutrients and beneficial elements, their ionic plant-available forms, and their role in plant growth and development

	<i>Element(s)</i>	<i>Form taken up by plants</i>	<i>Role</i>
Nonmineral macronutrients	Carbon (C)	CO <sub>2</sub>	Directly involved in photosynthesis
	Hydrogen (H)	H <sup>+</sup> , OH <sup>-</sup> , and H <sub>2</sub> O	
	Oxygen (O)	O <sub>2</sub>	
Mineral primary macronutrients	Nitrogen (N)	NH <sub>4</sub> <sup>+</sup> and NO <sub>3</sub> <sup>-</sup>	Found in chlorophyll, nucleic acids, and amino acids. Major component of proteins and enzymes controlling most biological processes
	Phosphorus (P)	HPO <sub>4</sub> <sup>2-</sup> and H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	Component of adenosine di- and triphosphate (ADP and ATP), which is essential for energy storage and transfer. Essential component of deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). Important for most plant development processes and component of plant tissues, particularly concentrated in seeds
	Potassium (K)	K <sup>+</sup>	Not incorporated in cell structure. Found in ionic form. Regulates water usage and provides disease resistance and stem strength. Involved in photosynthesis, drought tolerance, winter hardiness, and protein synthesis
Mineral secondary macronutrients	Calcium (Ca)	Ca <sup>2+</sup>	Essential for cell elongation and division. Required for root and leaf development and function and formation of cell membranes and walls (e.g., Ca pectate). Involved in activation of enzymes
	Magnesium (Mg)	Mg <sup>2+</sup>	Primary component of chlorophyll and important to photosynthesis. Component of ribosomes required for protein synthesis. Involved in phosphate metabolism, respiration, and enzyme activity
	Sulfur (S)	SO <sub>4</sub> <sup>2-</sup>	Required for synthesis of and contained in amino acids, which are essential for protein formation. Promotes nodulation in legumes. Involved in development of enzymes, seed production, and chlorophyll formation
Mineral micronutrients	Copper (Cu)	Cu <sup>2+</sup>	Enzyme catalyst and required for chlorophyll formation
	Manganese (Mn)	Mn <sup>2+</sup> and Mn <sup>4+</sup>	Involved as catalyst and in activation for enzyme systems. Serves as a catalyst in chlorophyll synthesis
	Iron (Fe)	Fe <sup>2+</sup> and Fe <sup>3+</sup>	Catalyst in chlorophyll synthesis. Involved in oxidation and reduction reactions during respiration and photosynthesis
	Boron (B)	H <sub>3</sub> BO <sub>3</sub> , BO <sub>3</sub> <sup>-</sup> , and B <sub>4</sub> O <sub>7</sub> <sup>2-</sup>	Essential for germination of pollen, growth of pollen tubes, seed and cell wall formation, and development and growth of new cells in meristematic tissue. Associated with translocation of sugars, starches, N, and P
	Nickel (Ni)	Ni <sup>2+</sup>	Component of the urease enzyme. Essential for plants supplied with urea and for those in which ureides are important in N metabolism
	Molybdenum (Mo)	MoO <sub>4</sub> <sup>2-</sup>	Required for synthesis and activity of the enzyme system that reduces NO <sub>3</sub> <sup>-</sup> to NH <sub>4</sub> <sup>+</sup> in plants (nitrate reductase). Essential for N fixation by rhizobia
	Chlorine (Cl)	Cl <sup>-</sup>	Involved in plant energy reactions, plant-water relationships, regulation of stomata guard cells, drought and disease resistance, enzyme activation, and cation transport in plants
	Zinc (Zn)	Zn <sup>2+</sup>	Involved in the synthesis of plant growth compounds and the enzyme system. Necessary for the production of chlorophyll, carbohydrates, and growth hormones
Beneficial elements	Cobalt (Co)	Co <sup>2+</sup>	Complexes with N and synthesis of vitamin B <sub>12</sub>
	Sodium (Na)	Na <sup>2+</sup>	Essential for halophytic plants partially replacing K <sup>+</sup>
	Silicon (Si)	H <sub>4</sub> SiO <sub>4</sub>	Possibly photosynthesis regulation enzyme activity
	Selenium (Se)	SeO <sub>3</sub> <sup>2-</sup> and SeO <sub>4</sub> <sup>2-</sup>	Not essential to plants but required by animals
	Vanadium (V)	VO <sub>3</sub> <sup>-</sup>	May be involved in fixation by rhizobia or biological oxidation-reduction reactions

production is limited by the amount of the most limited nutrient relative to the plant's need (Jungk, 2009). In other words, regardless of how much N is added, yield would be limited if P were not available in sufficient quantities. Once adequate P was provided through fertilization, after the development of P fertilizers, only then could additional yield be

attained through N fertilization. Through the rigorous application of the scientific method, Sprengel and his contemporaries launched the discipline of soil fertility and plant nutrition to meet the world's growing demand for food. Perhaps Sprengel's greatest contribution was the understanding that mineral nutrients external to the plant were required for

plant growth. Identifying the essential elements and understanding that they must be provided external to the plant was a fundamental shift in agricultural production. Before Sprengel's work, some nutrients were supplied through recycling of crop residues and manures, and N could be provided through N-fixing crops in rotation; however, the majority of nutrients were lost from the system (due to system inefficiencies) and crop production was limited and agricultural lands were often depleted after a few years of cropping. Daniel Webster understood the importance of conservation of matter to this system when he stated "it is upon this fundamental idea of constant production without exhaustion, that the system of English cultivation, and indeed, of all good cultivation is founded" in his lecture 'On the Agriculture of England' presented 13 January 1840 (Webster and Everett, 1851).

The development of the concepts of soil fertility and plant nutrition and the realization that nutrients had to be supplied externally through fertilization to avoid the 'exhaustion' of the soil in the early nineteenth century by a new breed of soil chemists and agronomists helped to avoid the Malthusian Catastrophe, predicted in 1798 by Thomas Robert Malthus. These principles underpinned the 'Green Revolution' of the twentieth century. Tilman *et al.* (2002) estimated that, between 1960 and 2000, global cereal production doubled while global N use increased sevenfold and P use increased three and one-half fold. However, this increase in production and concomitant increase in fertilizer use has not come without cost. There are questions regarding the environmental sustainability of continuing to fix N and mine P for fertilizer, both due to resource availability (of energy and the mined minerals) and concerns about the impact of N and P losses from agriculture to surface and groundwaters (Cordell *et al.*, 2009; Dawson and Hilton, 2011). As a result, although managing soil nutrients for optimum plant nutrition and yield continues to be a pressing concern in light of global population growth, the management of nutrients in an efficient manner to protect resources is an important component of any discussion of soil fertility and plant nutrition.

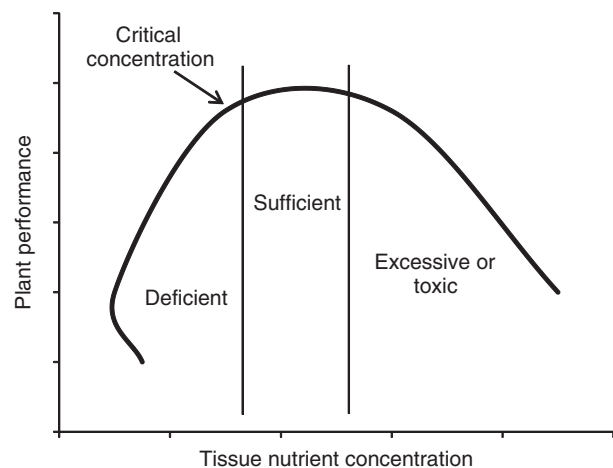
### Soil Fertility Evaluation

Modern soil fertility management integrates the disciplines of soil chemistry, soil biology, soil physics, and plant science to develop practices that provide the essential elements required for plant growth in sufficient quantities to maximize production while providing for environmental protection. In agricultural systems, this may mean optimizing production for economic return, whereas in other systems, such as phytoremediation or landscaping, there may be other goals that should be accounted for when planning a soil fertility strategy (e.g., rapid stand establishment, sufficient ground cover, or species biodiversity). Beyond management of soil nutrients, soil fertility must also address factors contributing to the soil's ability to supply nutrients and the plant's ability to efficiently utilize nutrients present. Optimum soil nutrient status alone will not provide for optimum system performance as numerous other factors influence plant nutritional status. Factors such as soil pH, moisture status, salinity, and physical condition as well as biotic stressors have a profound effect on a

plant's interaction with nutrients. These factors are covered elsewhere in this encyclopedia and should be considered integral to comprehensive soil fertility and plant nutrition management. Most soil fertility management strategies have three key components: soil fertility assessment, nutrient recommendations, and performance evaluation to inform future decisions.

The goal of any soil fertility and plant nutrition program is to holistically address the factors influencing crop nutrient utilization in order to maximize plant performance. Therefore, the ultimate goal is to have each of the essential nutrients present in plant tissue at a sufficient concentration to support metabolic functions of the plant. For each essential element, there is a critical concentration within plant tissue above which added nutrients will not increase plant performance but may increase tissue concentrations of that nutrient. Below the critical concentration, plant performance will likely suffer due to a deficiency of that nutrient. Beyond the sufficiency range, concentrations of certain essential elements in plant tissue may be toxic and decrease plant performance; this range is often referred to as excessive or toxic range. Figure 1 shows an idealized response curve with the critical concentration and the deficient, sufficient, and excessive or toxic ranges identified. The actual concentrations for each nutrient will vary with plant species, plant part, and growth stage.

Soil fertility assessment is a critical component to soil fertility management. The traditional goal of this assessment has been to evaluate the ability of a soil to supply the essential nutrients for optimum crop performance. Performance may be determined by yield, crop quality, or some other metric depending on management goals. Beyond quantifying essential elements present, soil fertility assessment should also evaluate other factors that might influence the soil nutrient supply to the plant, such as pH or compaction. Increasingly, modern soil fertility assessment also accounts for the potential



**Figure 1** Nutrient concentration in plant tissues as it relates to plant performance. Below the critical range plants are considered deficient. The range where nutrient concentration in the tissue increases, but performance does not, is considered the sufficient range. At some point beyond the sufficiency range, excessive nutrient concentrations can limit plant performance and this is considered the excessive or toxic range.

environmental impact of soil nutrients. There is a wide range of techniques used to assess soil fertility. Generally, soil fertility assessment can fall into three broad categories: direct assessment of soil physical or chemical characteristics; quantification of essential elements in plant tissue; or evaluation of plant response to soil nutrient status. A key component of any soil fertility assessment is the interpretation of results to generate fertilizer recommendations. Typically, one analyzes the nutrient content of soil or tissue samples or evaluates the expression of deficiency or sufficiency in plants and then interprets these findings to recommend rates of nutrient to apply to avoid or correct deficiencies.

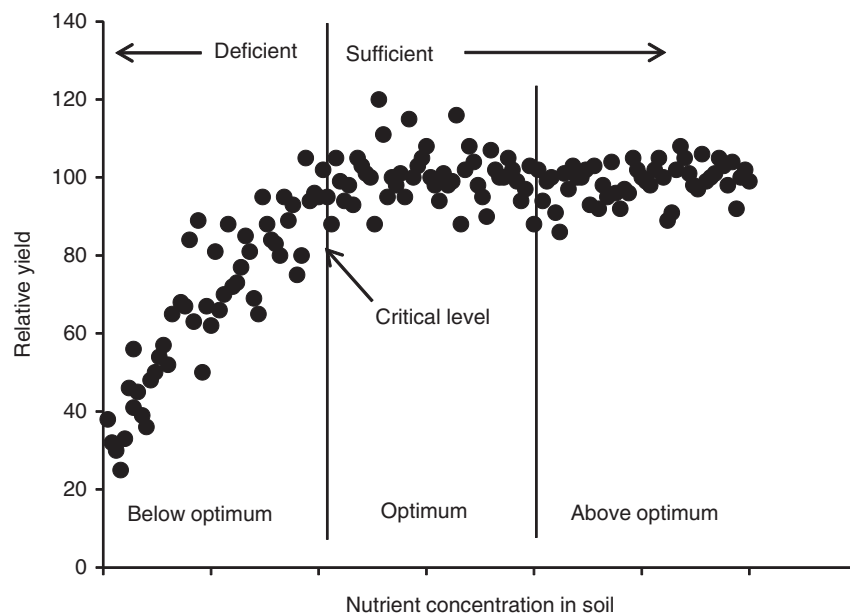
### Soil analysis

The first broad category of soil fertility evaluation is soil testing or the chemical extraction of soil nutrients to estimate their plant availability. Research in soil testing began in the nineteenth century following Sprengel's work, but systematic research into soil testing and plant nutrient status began in earnest in the 1920s. With the development of more advanced analytical capabilities, organized soil testing programs were established in the United States in the 1940s. Peck and Soltanpour (1990) defined soil testing as "...rapid chemical analyses to assess the plant-available nutrient status, salinity, and elemental toxicity of a soil...a program that includes interpretation, evaluation, fertilizer and amendment recommendations based on results of chemical analyses and other considerations." This definition identifies four key components of a soil fertility assessment. The first is an assessment of the soil nutrient status, typically through a chemical extraction of soil or plant tissue. However, the other three components are equally important: the results of the nutrient quantification must be interpreted to provide an index of the relative proportion of the nutrient present that is available for plant use; they must then be evaluated in the context of

potential plant response to fertilizer; and finally they must be translated into a recommendation for the amount, form, placement, and timing of a fertilizer application to provide optimum nutrient status for crop growth.

The soil test typically extracts a portion of the total amount of the element present. The amount extracted is proportional to the amount that is available for plant uptake. A response curve is then defined, typically through empirical laboratory, greenhouse, or field experiments, which predicts the potential for crop response to added fertilizer. Therefore, a soil test provides a relative index of potential responsiveness that forms the basis of a fertilizer or lime amendment. Interpretation of soil test results follows closely the definition provided previously for plant nutrition sufficiency (Figure 1). An idealized soil testing response curve is provided in Figure 2. Generally, no response to added fertilizer is expected above the critical soil test level identified in Figure 2. The relative index of soil nutrient supply capacity varies according to recommendations system, but generally the scale is divided into areas, 'below optimum,' 'optimum,' and 'above optimum' or 'excessive' nutrient concentration. A yield response to added fertilizer is expected when soil test levels are below optimum (i.e., below the critical threshold). Starter or maintenance levels of fertilizer may be recommended in the optimum range. Some nutrients may cause environmental risk or plant toxicity above the optimum range.

Nutrient recommendations are determined by soil test results; however, even when two labs use the same methods and generate equivalent results, their nutrient recommendations may differ. These disparities arise due to differences in soil test interpretation and recommendation philosophies. Over the years, three basic philosophies have emerged. These include the sufficiency approach, the build and maintain approach, and the base cation saturation ratio (BCSR) theory. Both the sufficiency approach and the build and maintain approach



**Figure 2** Empirical relationships are defined between soil nutrient concentrations and yield response. As the soil concentration increases less fertilizer is required to optimize yield.

follow the general concept that there are definable critical levels of nutrients in soil and that below this level crops are likely to respond to additional applied nutrients. When nutrient concentrations are in the optimum range, just above the critical level, there is a low probability of crop response with further addition of that nutrient. With the build and maintain approach, fertilizer recommendations are made with the goal of building the soil's nutrient levels into the optimum range, then maintaining these levels by applying nutrients at rates that approximate crop removal. The sufficiency approach is a more conservative philosophy where nutrient recommendations are intended to only meet crop needs and not build soil fertility. No nutrients are recommended above the critical soil test level. The sufficiency approach is designed to 'feed the crop,' whereas the build and maintain approach is designed more to 'feed the soil.' In theory, the sufficiency approach is a more profitable system because fertilizer is applied only when there is likely to be an economic return. However, in practice the sufficiency approach is also more risky due to the inherent uncertainty associated with soil testing.

The third philosophy, the BCSR theory, promotes the idea that maximum yields can only be achieved by creating a balanced ratio of Ca, Mg, and K in the soil. The concept is rooted in the work conducted by Dr. Firman Bear and his colleagues at the New Jersey Agricultural Experiment Station in the 1940s (Bear and Prince, 1945; Bear and Toth, 1948). Bear's work showed that the luxury consumption of costly fertilizer K by alfalfa could be reduced by applying high rates of relatively low-cost Ca (as ground gypsum or calcitic lime). As an aside, Bear also pointed out that another effective strategy to reduce luxury consumption of K by alfalfa was to use split applications of moderate doses of fertilizer K rather than infrequent high rates (a best management practice still recommended today). Bear and his colleagues suggested that there were ideal ratios of Ca, Mg, and K; however, they provided no data to support these claims, so it is unclear how they were developed.

Around the same time, Dr. William Albrecht and his colleagues at the University of Missouri began to investigate the BCSR theory. This work and its findings are summarized in the Albrecht Papers (Albrecht and Walters, 1996). They conducted a series of experiments on soils and soil minerals amended to achieve a wide range of Ca:Mg:K ratios. Based on this work, Albrecht suggested that a balanced soil should have a cation saturation of 60–75% Ca, 10–20% Mg, and 2–5% K. It is unclear how Albrecht derived these values; in fact, much of the data Albrecht and his colleagues published illustrated that optimum yields occurred over a wide range of Ca, Mg, and K ratios. Further, careful evaluation of the work a number of years later revealed several fundamental flaws in the methods Albrecht and his colleagues used. Over the years, a number of soil scientists have evaluated the BCSR theory (see review by Kopittke and Menzies, 2007). This work has failed to support claims of BCSR theory and has illustrated that using it to manage soil fertility results in inefficient use of both capital and natural resources. Nonetheless, the importance of attaining an ideal BCSR, especially pertaining to the importance of very specific Ca:Mg ratios, continues to be promoted. These claims include the following: improved soil structure, reduced weed pressure, increased resistance to insect and disease, and

reduced leaching of other nutrients. There are no research data that support these claims.

Most of the guidelines developed by US Land Grant Universities and used by both public and private soil test labs follow a combination of the sufficiency and build and maintain approaches, the goal being to provide adequate, but not excessive, levels of essential nutrients to promote healthy plant growth. The nutrient guidelines are intended to help growers optimize crop yield and quality, maximize return on fertilizer investment, and minimize nutrient losses to the environment.

### *Plant tissue analysis*

Soil fertility evaluation does not rely on soil testing alone. Visual diagnosis of plant nutrient deficiencies, in-field measurements of plant nutrient status, laboratory analysis of tissue nutrient concentrations, and remote sensing of plants can all be valuable tools in identifying plant nutrient deficiencies, so that they can be corrected or prevented. Soil testing can be used before planting or in season to guide nutrient applications. Plant tissue analysis can be used in season to identify or confirm visually observed nutrient deficiencies (Table 1). When combined with a soil testing program, plant tissue sampling and testing or analysis can be very useful in determining the cause of visual deficiency symptoms. There are many tools available for in-field plant analysis, including the leaf chlorophyll meter that measures light absorption at specific wavelengths and handheld or equipment-mounted photometers that measure light reflectance. These tools are often used to calculate various vegetative indexes based on the ratio of light reflectance at different wavelengths to estimate sufficiency or predict nutrient need through more advanced algorithms. However, these types of diagnostic tools are beyond the scope of this article, which is limited to traditional visual diagnosis and plant tissue analysis.

It is important to take a holistic approach to soil fertility management and interpret tissue test results in the context of soil test results, field conditions, plant health, and other potential plant stresses. Many factors can influence relative nutrient availability or the ability of a plant to take up available nutrients, causing a nutrient deficiency to be expressed visually or in tissue nutrient concentrations. For example, a grower may visually identify P deficiency in a corn field due to the presence of stunted, purple-colored plants. If only a tissue sample was collected and it showed P deficiency, the grower may then conclude that additional P is required. However, a soil sample may reveal that there was adequate P in the soil, but that the pH was low, limiting P availability, evaluation of the whole plant could reveal that a root disease, such as Pythium root rot, induced the above-ground P deficiency symptoms. In either case P fertilizer was not truly required, even though a tissue test alone would have indicated that it was. There are many examples where soil nutrient concentration is not the culprit of a deficiency identified visually or through tissue analysis, so caution should be applied when interpreting plant tissue concentrations. A valuable application of tissue testing is to confirm nutrient deficiencies within problem areas observed in a field. For example, many nutrient deficiencies result in plants exhibiting interveinal chlorosis. If the symptom is exhibited sporadically across the field, tissue samples can be collected from within the affected regions and

compared with results from samples collected from unaffected regions. This comparison along with soil test results from both areas can be used to narrow which specific nutrient might be causing the symptoms. However, it is important to remember that it is not enough to identify a nutrient deficiency, the cause must also be determined before corrective action can be taken. It does no good to apply a nutrient that is deficient if soil compaction, pH, root disease, or other problems are limiting uptake of that nutrient by the crop.

The results of tissue analysis are highly dependent on how and when the sample was collected. Some of the essential elements are considered mobile nutrients within plants because they can be translocated from mature plant parts to the areas of the plant that are actively growing (meristem), so that deficiencies will occur initially in the older parts of the plant. Conversely, immobile nutrients cannot translocate and therefore deficiency symptoms are typically exhibited initially in the youngest part of the plant. **Table 2** provides a list of the essential mineral elements, their relative mobility within the plant, relative and average concentration in plant tissue, and typical deficiency symptoms. The relative concentrations presented in **Table 2** are provided to give perspective on the relative proportion of each nutrient in plants, where the average concentration presented for each nutrient is divided by the average concentration of Mo in plant tissues (Havlin *et al.*,

2005). As the sufficiency range for nutrient concentrations varies greatly between plants, the part of the plant sampled, and the timing of sample collection, it is best to refer to optimum ranges supplied by local soil and plant tissue testing laboratories.

Most laboratories that provide soil and plant tissue testing services provide instructions on which part of the plant should be sampled and the appropriate timing for tissue sampling. For example, when sampling corn seedlings (< 12 in. tall), the entire plant should be sampled by cutting it off approximately 1 in. above the soil surface; for vegetative growth stages the uppermost collared leaf should be sampled, and at tasseling the ear leaf should be sampled. Once the plant enters reproductive stages, some essential nutrients begin to move to the seed or fruit from other parts of the plant and therefore a tissue sample taken after initial flowering may not accurately represent nutrient uptake and availability. Similarly, tissue sampling and tissue test results are often used inappropriately to determine fertilizer need. In corn, for example, during the first two vegetative growth stages (up to V2 or two fully collared leaves) the plant utilizes very little soil N and relies primarily on N provided by the seed. Therefore, tissue samples collected at this time provide very little value in terms of determining additional N need. Once the plant reaches the rapid growth stage ( $\approx$ V4 - tasseling), tissue N concentrations fluctuate

**Table 2** Essential elements, their mobility, relative and average concentration in plants, and common deficiency symptoms

Essential element	Mobility	Concentration in plants <sup>a</sup>		Common deficiency symptoms
		Relative	Average	
Nitrogen	Mobile	1 000 000	1.5%	Stunted chlorotic plants with increased susceptibility to stress. Early maturity
Phosphorus	Mobile	30 000	0.2%	Overall stunted plant and poor root development with purple to reddish color
Potassium	Mobile	400 000	1.0%	Scorching or firing along leaf edge. Deficient plants grow slowly with poor root development. Weak stalks with lodging common and small seed or fruit. Low stress tolerance
Calcium	Immobile	200 000	0.5%	Poor root growth with roots often turning black and rotting. Failure of terminal buds and apical tips of roots to develop
Magnesium	Mobile	100 000	0.2%	Leaves show a yellowish, bronze, or reddish color while leaf veins remain green
Sulfur	Somewhat mobile	30 000	0.2%	Chlorosis of longer leaves or chlorotic stunted plants. Resembles N deficiency; however, upper leaves tend to show deficiency first
Copper	Immobile	100	6 ppm	Reduced leaf size. Uniformly pale yellow leaves. Leaves lack turgor and may develop bluish green color, become chlorotic, and curl. Flower production fails
Manganese	Immobile	1 000	50 ppm	Interveneal chlorosis. Appearance of brownish black specks
Iron	Immobile	2 000	100 ppm	Interveneal chlorosis. In the case of severe deficiency the entire leaf may turn white
Boron	Immobile	2 000	20 ppm	Reduced leaf size and deformation of new leaves. Interveneal chlorosis if deficiency is severe. Possibly distorted stems. May cause flower or fruit abortion, poor grain fill, and stunted growth
Nickel	Mobile	0.1	0.01 ppm	Limited information available on deficiency symptoms
Molybdenum	Immobile	1	0.1 ppm	Interveneal chlorosis, wilting, and marginal necrosis of upper leaves
Chlorine	Mobile	3 000	100 ppm	Chlorosis of upper leaves and overall wilting of plant. Deficiencies may show in upper leaves, even though mobile
Zinc	Immobile	300	20 ppm	Shortened internodes between new leaves, death of meristematic tissue, deformed new leaves, and interveneal chlorosis

<sup>a</sup>Relative nutrient concentrations are expressed on the basis of their concentration relative to molybdenum. Concentrations are expressed on a dry matter mass basis and adapted from Havlin, J.L., Beaton, J.D., Tisdale, S.L., 2005. Soil Fertility and Fertilizers: An Introduction to Nutrient Management. Upper Saddle River, NJ: Pearson Prentice Hall.



wildly due to the rapid growth of the plant and variation in uptake relative to tissue development. Therefore, recommendations based on tissue samples collected at this time may be highly unreliable. Owing to the many factors that influence nutrient concentrations in tissues, great caution should be taken when interpreting tissue sample results and trying to formulate fertility recommendations. Their best utility is in comparing 'good' and 'bad' areas within the same field as they were exposed to the same growing and management conditions.

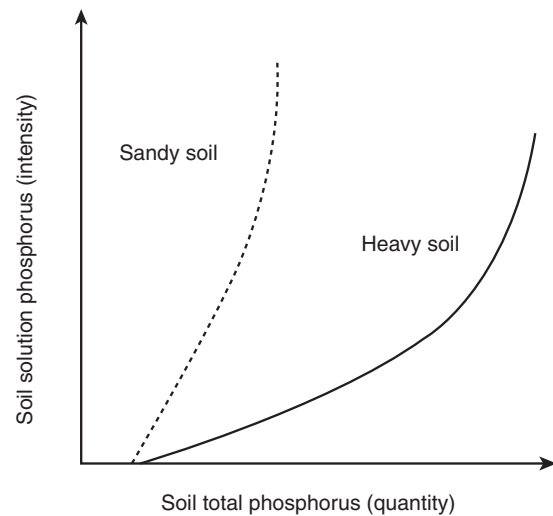
A unique tissue test that has gained popularity recently is the corn stalk nitrate test (CSNT). The CSNT is an end-of-season test that provides a retrospective assessment of the season's nitrogen management. Corn plants show no visual evidence of overfertilization. The CSNT can provide this information, allowing producers to know when a field received more nitrogen than needed for maximum yield. After pollination, nitrogen from the leaves and stalk is mobilized and transported into the developing grain. During this process and after black layer, nitrate uptake from the soil into the plant also continues. If more nitrogen is available to the plant than needed for maximum yield, nitrate accumulates in the stalk, particularly the lower stalk. The CSNT is a robust test that is able to identify when N was available in excess of crop need and along with other information on N management it can be used to fine tune N management in future growing seasons (Binford *et al.*, 1990). However, the range of stalk nitrate concentrations is very narrow in the optimum and below optimum ranges and therefore of limited utility in accurately identifying when very little N is available.

## Soil Characteristics Contributing to Nutrient Supply

### Soil Mineralogy

Soil mineralogy is one of the dominant soil properties controlling the amount of nutrients present in the root zone and the rate at which they are made available to plants. Nutrient supply is simply the quantity of nutrients held onto the soil particle surface, either as a result of natural geologic parent material or anthropogenic activity (i.e., fertilization). A simple but important concept regarding the role of soil mineralogy in soil fertility and plant nutrition is the notion that plants can take up nutrients only from solution. The focus is often on the amount or 'quantity' of nutrients present in the soil, but the ability of a soil to supply nutrients is also determined by the soil's ability to potentially release those nutrients into the soil solution where they are then available to the plants. The concentration of the nutrient that is found in or easily dissolves or desorbs into solution is known as the 'intensity.' The quantity–intensity relationship for a given soil is a measure of the soil's buffering capacity with respect to that nutrient. An example of quantity–intensity relationship is shown in Figure 3.

In general, the quantity is some measure of the total nutrient supply that is not necessarily 100% labile. This could be the nutrient concentration determined by a total digestion under strong acid and heat, or some other type of harsh extraction. However, the intensity is the concentration of that same nutrient that is labile or in solution, often estimated with



**Figure 3** Example of quantity–intensity (Q/I) curves for soil phosphorus for sandy and 'heavy' (high clay content) soils.

ion-exchange membranes or water extraction analysis. The quantity–intensity curve varies depending on the nutrient and chemical characteristics of the soil, particularly the mineralogy and pH. Essentially, the quantity–intensity curve describes the ability of the soil to supply the solution with the nutrient. As it is not feasible to determine the quantity–intensity relationship in every case where a nutrient recommendation is required, it is the goal of agronomic soil testing to provide some of this information using rapid and affordable techniques.

The slope of the quantity–intensity curve is considered to be the buffering capacity for the specific nutrient and soil depicted. In general, as the soil quantity (i.e., supply) of the nutrient increases, the ability of that nutrient to be released into solution increases. However, note that the slope of this curve is not generally constant; this is especially true for certain nutrients that are strongly bound to the soil, such as trace metals or P onto Fe oxide minerals. In such cases, the soil shows a limited capacity to release the nutrient into solution when the quantity is low, but as the quantity becomes larger, a given increase in quantity will result in a greater increase in intensity, or solution concentration, compared with the case where the quantity is lower. In other words, at higher quantity concentrations, further increases in the quantity through fertilization will yield more efficient release of the nutrient into solution. This is why for certain soils it is important to 'build up' P concentrations so that plants can have access to soil P.

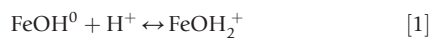
### Permanent-charge versus variable-charge minerals

As previously mentioned, soil mineralogy can have a profound impact on the quantity–intensity relationship. With regard to the mechanism by which soil minerals retain nutrients, minerals can be classified into two different groups: permanent-charge (or variable potential) minerals and variable-charge minerals. Permanent-charge minerals retain a constant negative charge regardless of solution conditions (i.e., pH and ionic strength). Permanent-charge minerals obtain their inner-layer charge from isomorphous substitution occurring in 2:1 clay minerals. In addition to possessing negative charge, for a

mineral to sorb a cation nutrient from solution, the negative charge must be physically accessible to cations in solution. Thus, it is found that some minerals with high levels of permanent negative charge are unable to sorb many cation nutrients from solution, such as illite and biotite, as their inner layer is mostly clamped shut with K ions holding the layers together tightly. Instead, it is mostly vermiculite and montmorillonite that possess a permanent negative charge which is accessible to solution cations. In addition to vermiculite and montmorillonite, there are amorphous 2:1 minerals that possess accessible permanent negative charge; such minerals are most common in recently developed volcanic (Andic) soils. Zeolites (tectosilicates) are a group of soil minerals that possess a large amount of accessible permanent negative charge but are not 2:1 minerals.

Permanent-charge minerals can retain only cation nutrients from solution, such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{K}^+$ ,  $\text{Cu}^{2+}$ , etc. However, variable-charge minerals can become positively charged depending on solution pH, which allows them to sorb anion nutrients, such as  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$ . This variable charge occurs mostly on the terminal hydroxide groups located on the edges of 1:1 minerals (such as kaolinite) and Fe, Al, and Mn oxides or hydroxides (such as goethite and gibbsite). Although not a mineral, soil organic matter contains numerous variable-charged functional groups that behave similarly. Similar to the 2:1 minerals, there exists both crystalline and amorphous 1:1, oxide, and hydroxide minerals. Equations [1 and 2] show generic reactions where charge development occurs due to protonation or deprotonation of hydroxide groups.

Protonation of a metal hydroxide mineral resulting in a positively charged surface site (eqn [1]).



Deprotonation of a metal hydroxide mineral resulting in a negatively charged surface site (eqn [2]).



Note that the degree of each reaction can be quantified by a specific  $k$  value (i.e., reaction constant) for each mineral. Thus, as pH increases, the negative charge on the mineral surface increases, whereas the positive charge decreases, and when pH decreases the negative charge decreases and positive charge increases. For example, if the surface functional groups shown in eqns [1] and [2] were located on goethite, the  $k$  value would equal to  $10^{6.2}$  and  $10^{-11.8}$ , respectively. As you would expect, this change in charge can impact the ability of the surface of variable-charge minerals to retain anion and cation nutrients. Each variable-charge mineral possesses a unique point of zero charge (PZC), which is the pH at which the net charge equals zero. When the pH is greater than the PZC of the mineral, the net charge on the mineral is negative. Note that this does not necessarily mean that there is no longer any positive charge; it simply means that there is more negatively charged sites than positively charged sites.

### ***Ion-exchange reactions (nonspecific sorption)***

Nutrient ions are attracted to sites of opposite charge located on minerals and organic matter, either permanent or variable charge. When ions bind to the mineral sites by weak

electrostatic attraction (i.e., no direct contact with the surface), this is known as ion exchange. Ion exchange is characterized by a weak and reversible bond known as nonspecific sorption. Ions that bind by this mechanism can be easily and rapidly displaced by other ions of the same charge. This reversible nature of ion exchange is extremely important to both agronomic production and environmental quality. Specifically, if bonds retaining nutrient ions are excessively strong then there is less potential for them to be released into solution for subsequent nutrient uptake or transport. Yet the reversible nature of the ion-exchange reaction is still strong enough to prevent all nutrients from simply passing through the soil and directly to groundwater and surface water, being lost from the agroecosystem and having potentially negative implications.

Other characteristics of ion exchange include charge balance and selectivity. All ion-exchange reactions are charge balanced; for example, one mole of  $\text{Ca}^{2+}$  can exchange with 2 mol of  $\text{K}^+$ . This is why ion exchange and soil charge are typically quantified in units of equivalents, which is the same as a mole of charge (i.e., molecular weight normalized for valence of the ion). The selectivity of ion-exchange reactions has several implications. At equal concentrations, ions with a greater charge density are preferred over ions of lesser charge density. For example,  $\text{Al}^{3+}$  is preferred over  $\text{Ca}^{2+}$ , which is preferred over  $\text{K}^+$ . Similarly,  $\text{K}^+$  is preferred over  $\text{Na}^+$  because  $\text{K}^+$  has a greater charge density; although the two ions possess the same charge,  $\text{K}^+$  is a smaller ion due to a lower degree of hydration. Although ions of greater charge density are selectively sorbed over ions of lesser charge density, this is somewhat concentration dependent due to the fact that ion-exchange reactions are subject to Le Chatelier's principle (the equilibrium law that states if a system at equilibrium undergoes a shift in concentration the system will adjust to try and counteract the shift in equilibrium). For example, consider a soil system where  $\text{K}^+$  ions are sorbed to the clay surfaces and  $\text{Ca}^{2+}$  is added to the soil solution. For each mole of  $\text{Ca}^{2+}$  added to the system, two moles of  $\text{K}^+$  will be replaced and moved to the soil solution.

Although  $\text{Ca}^{2+}$  is selectively sorbed over  $\text{K}^+$  at equal concentrations, if the concentration of  $\text{K}^+$  becomes large enough, it can displace the  $\text{Ca}^{2+}$  at the surface (i.e., reverse reaction). Note that ion-exchange reactions are subject to the laws of thermodynamics and are quantified by the reaction constant  $k$ . As a result, if the concentration on one side of the reaction becomes much greater than the concentrations on the opposite side, the reaction will proceed toward the side with lower concentrations in order to equilibrate the system to maintain the reaction constant (Le Chatelier's principle). Thus, as a plant depletes the soil solution of nutrients, this offsets the balance between ions sorbed onto the surface and ions in solution, and Le Chatelier's principle tells that the ions sorbed onto the surface will desorb into solution in order to maintain equilibrium between the surface and solution. In this way, the soil serves as a 'nutrient warehouse' that acts to supply the solution for plants; one of the challenges of nutrient management is to resupply the warehouse when it becomes depleted.

The sum of all cation charges (equivalents) that are held onto the soil by the ion-exchange mechanism is the cation-exchange capacity (CEC). Likewise, the sum of all anion

**Table 3** General description of the ability of cations and anions to bind by specific sorption, nonspecific sorption, or both

	<i>Specific sorption (ligand exchange or chemisorption)</i>	<i>Nonspecific sorption only (ion exchange)</i>	<i>Both specific and nonspecific sorption</i>
Anion	$\text{OH}^-$ , $\text{PO}_4^{3-}$ , $\text{AsO}_4^{3-}$ , $\text{SeO}_3^{2-}$ , and $\text{F}^-$	$\text{CO}_3^{2-}$ , $\text{Cl}^-$ , $\text{Br}^-$ , $\text{I}^-$ , $\text{NO}_3^-$ , and $\text{B}(\text{OH})_4^-$	$\text{MoO}_4^{2-}$ , $\text{SeO}_4^{2-}$ , $\text{SO}_4^{2-}$ , and $\text{CrO}_4^{2-}$
Cation	$\text{Ni}^{2+}$ , $\text{Co}^{2+}$ , $\text{Cu}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Mn}^{2+}$ , and $\text{Ag}^+$	$\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Li}^+$ , $\text{Na}^+$ , $\text{Ba}^{2+}$ , and $\text{NH}_4^+$	$\text{K}^+$ , $\text{Cd}^{2+}$ , and $\text{Hg}^{2+}$

*Note:* Ions listed under specific sorption can also bind by nonspecific sorption, but those listed under nonspecific sorption never bind by specific sorption. Those listed under 'both' have only a weak ability to bind by specific sorption mechanisms.

charges held onto the soil by the ion-exchange mechanism is the anion-exchange capacity (AEC). In general, the composition of nutrients on the ion-exchange sites is proportional to the solution composition of ions. For example, if the soil CEC contains 20%  $\text{Al}^{3+}$ , 40%  $\text{Ca}^{2+}$ , 10%  $\text{K}^+$ , 10%  $\text{Na}^+$ , 10%  $\text{H}^+$ , and 10%  $\text{Mg}^{2+}$ , then the solution will contain those ions in a similar ratio.

### Ligand-exchange and chemisorption (specific sorption) reactions

Ligand exchange and chemisorption are the names given to the 'specific' sorption reactions for anions and cations, respectively. Specific sorption differs from ion exchange (nonspecific sorption) in that the reaction results in a strong covalent bond, because the ion is bound directly to the surface with no water molecule in between. As a result, nutrients held by specific sorption are bound somewhat irreversibly, that is, a portion of nutrients that are sorbed by this mechanism will not completely desorb (i.e., hysteresis). In addition, specific sorption occurs dominantly on edge terminal hydroxide groups among variable-charge minerals as opposed to permanent-charge minerals, which mostly retain nutrients by weak ion-exchange reactions. Another difference between ion exchange is that specific sorption reactions can occur on positive, negative, or neutral surfaces; this is due to the fact that the bound nutrient actually becomes somewhat part of the surface (known as the Stern layer) of the variable-charge mineral. Thus, there is a general trend that specific sorption of anions can increase the negative charge (i.e., increase CEC) and sorption of cations can increase positive charge (i.e., increase AEC).

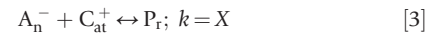
Soil pH has an impact on specific sorption due to the increased competition with  $\text{H}^+$  at low pH and  $\text{OH}^-$  with increasing pH. Particularly, specific sorption of cations (i.e., chemisorption) decreases with a decrease in pH as the cation must compete with protons that have a strong affinity for the surface of variable-charge minerals. Likewise, specific sorption of anions (i.e., ligand exchange) is lessened with increasing pH due to competition with  $\text{OH}^-$ , as  $\text{OH}^-$  is itself a ligand. Cations that can potentially bind strongly via chemisorption are those that easily hydrolyze, which are mostly transition metals, such as the micronutrients  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$ . In general, 'base cation' nutrients, which consist of the alkali and alkali earth metal nutrients ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^+$ ), bind only by ion-exchange reactions, although there are several exceptions discussed later. Anions that can potentially bind by ligand-exchange to variable-charge sites are typically oxyanions, such as phosphate and molybdenate. Anions that can bind strongly by ligand exchange (such as phosphate) will outcompete

anions that can only bind by the weak ion-exchange mechanism (such as nitrate) and anions that can bind by ligand exchange with less strength (such as sulfate). Table 3 shows which ions are capable of binding by specific sorption.

### Precipitation and dissolution

Precipitation and dissolution make up the third category of reaction mechanism that enables soils to both bind and release ions into solution, making them available for plant uptake or mobile for water transport. Precipitation theory states that as the concentration of an ion in solution increases, precipitation of a new solid phase does not occur until the solubility product of that phase has been exceeded.

Generic reaction showing the precipitation of a reaction product from an anion and a cation (eqn [3]).



Equation [3] provides a general reaction where an anion ( $\text{A}_n^-$ ) and cation ( $\text{C}_{\text{at}}^+$ ) react with each other to form a solid precipitant or mineral ( $\text{P}_r$ ). The ions on the left side of the reaction are the reactants, and the solid mineral on the right side is the product. There is equilibrium between the reactants and products that is quantified by the reaction constant  $k$ , which is unique to each mineral. This concept of equilibrium is the same as was described for specific and nonspecific sorption except that the product is a solid mineral. Le Chatelier's principle also applies to precipitation reactions and their reverse reaction, dissolution of the mineral back into the soil solution. Depending on the ion concentrations in solution and the potential presence of a solid mineral, the ions may react with each other to form a solid mineral, thereby leaving the solution where they cannot be taken up by a plant, or conversely the solid may dissolve to resupply the solution with the ions where they can be taken up by a plant.

Many plant nutrients are subject to precipitation and dissolution reactions that can impact nutrient availability. Those most affected ones include P, Ca, Mg, and trace metals. Because most precipitation and dissolution reactions involve  $\text{OH}^-$  or  $\text{H}^+$ , nutrient availability of such ions tend to be highly pH dependent. The impact of pH on nutrient availability is discussed in the Section pH and Soil Fertility.

### Soil Type

Soil type plays a profound role in soil fertility because mineralogy partly dictates soil type and mineralogy controls the capacity and strength in which nutrients are retained. For this

discussion, the term 'soil type' will be relegated to the most broad soil taxonomic category, soil order (based on US Department of Agriculture soil taxonomic classification system).

Because soil orders are classified partly due to their mineralogy, and as mineralogy partly dictates fertility, knowledge of the soil order can provide useful information regarding fertility. As discussed in the Section Permanent-charge versus variable-charge minerals, 2:1 minerals that possess accessible permanent negative charge have the highest CEC among soil minerals and therefore the greatest capacity to retain base cations, such as  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $NH_4^+$ . Typically, these include the soil clay minerals montmorillonite and vermiculite. However, these minerals possess very little AEC as they have little to no variable charge. Because variable-charge minerals have the ability to strongly sorb nutrients by ligand exchange and chemisorption, soils dominated with variable-charge minerals tend to 'fix' ions (i.e., prevent them from entering solution) that are highly susceptible to such reactions (Table 3) and are considered infertile. Another reason variable-charge minerals are typically considered infertile is because they generally have a low CEC. However, soils dominated with variable-charge minerals have the ability to prevent excessive runoff and leaching losses of P and trace metals, thereby preventing a potentially negative environmental impact in cases when excessive nutrients are applied.

As a general rule, 'younger' soils are more fertile than 'older' ones as the former is dominated by permanently charged 2:1 minerals, whereas the latter is dominated with variable-charge 1:1 and metal oxide or hydroxide minerals. In this context, 'younger' and 'older' refers to soil development as impacted by the five soil-forming factors (parent material, climate, organisms, topography, and time). The five soil-forming factors generally transform minerals from primary minerals to high-layer charge 2:1 minerals (i.e., mica and illite), lower-layer charge 2:1 minerals (i.e., montmorillonite and vermiculite), 1:1 minerals, and finally metal hydroxides.

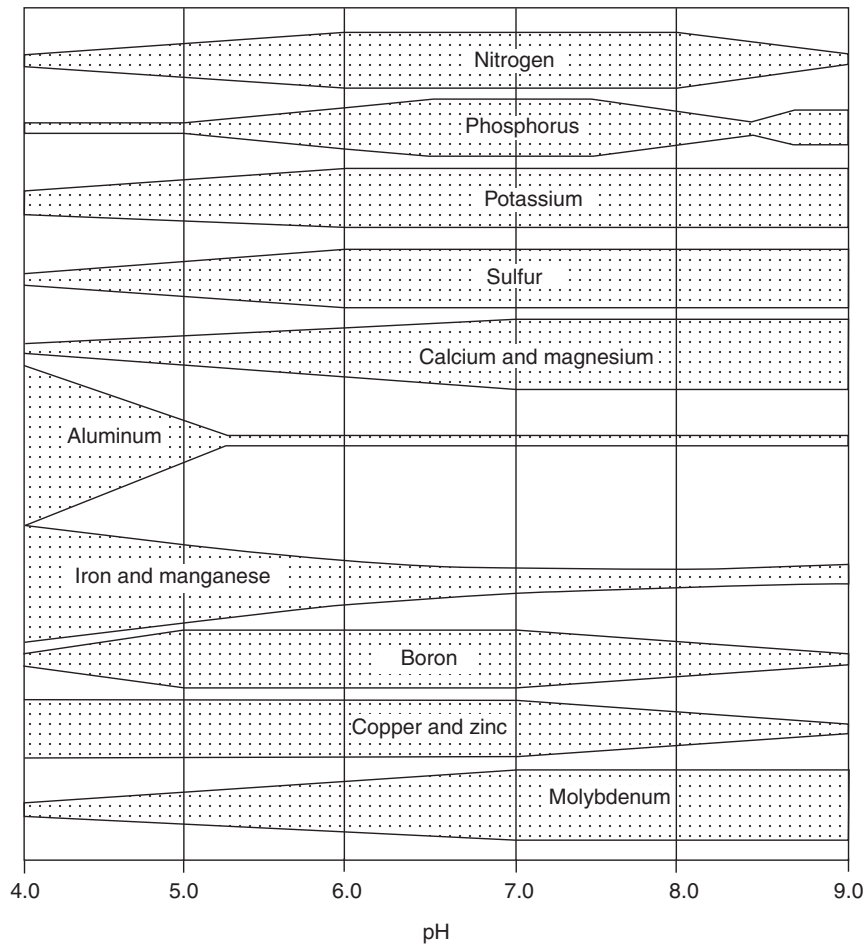
Some of the least developed soil orders, which include Entisols and Inceptisols, do not necessarily fit this general rule because the mineralogy of these soil orders are mostly a function of their parent geologic material. Aridisols are characterized by a high level of primary minerals, mainly sulfates and carbonates. These soils develop in areas of low rainfall and often possess naturally high amounts of K, Ca, Mg, and S but a low CEC and AEC due to the lack of more developed minerals. One of the least developed and most fertile soil orders, Andisols, are derived from relatively recently deposited volcanic materials and are, therefore, rich in amorphous 2:1 minerals with high CEC. Similarly, Vertisols are dominated by montmorillonite and therefore are considered to be highly fertile. As soils weather and 2:1 minerals begin to give way to 1:1 minerals, Mollisols and Alfisols are formed. The former is distinguished by higher levels of organic carbon, making it more fertile than Alfisols, but both soil orders are characterized as having 'high' base cation saturation (>35%). With continued development, Ultisols are formed, which contain less 2:1 minerals and more 1:1 and metal oxides and hydroxides, which results in a lower base cation saturation (<35%) and therefore a decreased CEC. Still, the most developed soil order is the Oxisol, which has very little CEC and is dominated by 1:1 minerals and metal oxides and hydroxides.

## pH and Soil Fertility

Soil pH is considered the 'master variable' in soil fertility for several reasons. Soil pH often has a large impact on (1) precipitation and dissolution of primary minerals, (2) the degree of CEC and AEC on variable-charge minerals, (3) the degree of ion-exchange, ligand-exchange, and chemisorption reactions, (4) microbial activity that impacts nutrient cycling, and (5) the solubility of Al. The general change in nutrient availability with changes in pH is shown in Figure 4. One of the most important aspects of the impact of pH on soil fertility is percent base cation saturation of the CEC. Percent base saturation is quantified as the amount of exchangeable base cations divided by the soil CEC and multiplied by 100%. Soils with low percent base saturation are considered infertile, whereas those with high saturation are fertile. Soils with low-base saturation are dominated by  $H^+$  and  $Al^{3+}$ , contributing to acidity and  $Al^{3+}$  toxicity in plants. Indeed, it is the increased solution concentrations of  $Al^{3+}$  and  $Mn^{4+}$  that are often most detrimental to plant growth under acidic pH conditions. The influence of soil pH on nutrient availability to plants varies with nutrient and soil mineralogy. Details on the interaction between soil pH and nutrient availability is covered in more detail in the following Section Nutrient Cycling and Plant Nutritional Roles of Essential Elements.

## pH management

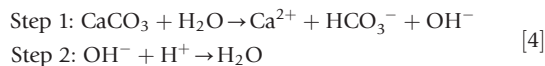
Most weathered soils in humid regions act as weak acid systems where the total acidity is much greater than the active acidity and therefore the potential acidity is great. Soil systems become more acidic as  $H^+$  ions are released into solution through the dissociation or ionization of acids. Many soil processes can contribute to soil acidity, including the dissolution of  $CO_2$  gas (originating from organic matter decomposition or soil microbial respiration) into water to form carbonic acid ( $H_2CO_3$ ), clay structure mutations, hydrolysis of Al, acid rain, leaching or weathering of soils, plant uptake of base cations, and oxidation of S. One of the principle farming practices that contributes to soil acidity is the use of ammoniacal fertilizers, such as ammonium nitrate, which produces acidity as ammonium is oxidized during the nitrification process. As a result of the various natural processes and anthropogenic activities that contribute to soil acidity, many soils require the addition of acid-neutralizing materials, generally called 'liming materials,' to increase the pH and optimize plant performance. Liming materials contain an anion that removes  $H^+$  from solution and precipitates  $Al^{3+}$  into a solid mineral, thereby reducing acidity. Most liming materials are oxides, hydroxides, carbonates, or silicates of Ca or Mg, or both. The standard liming material is Ca carbonate ( $CaCO_3$ ), found as the mineral calcite, or some mixture of Ca and Mg carbonate ( $CaMg(CO_3)_2$ ; dolomite). Other common materials include burned lime ( $CaO$  and  $MgO$ ), hydrated lime ( $Ca(OH)_2$  and  $Mg(OH)_2$ ), and certain byproducts of manufacturing processes. Many manures or biosolids contain appreciable amounts of carbonates and can raise soil pH. The neutralizing power of a potential liming material is expressed by its Ca carbonate equivalent (CCE), which is a normalization of neutralizing power relative to pure calcium carbonate. The higher the CCE, the more potent the liming material is on a



**Figure 4** The relative availability of the essential plant nutrients varies with pH. In this classic figure, the width of the bar indicates relative nutrient availability; as bar width increases, the nutrient availability increases as well. Adapted from Truog, E., 1947. Soil reaction influence on availability of plant nutrients. *Soil Science Society of American Journal* 11, 305–308.

mass basis. Equation [4] presents the generalized lime reaction for calcium carbonate as a two-step process.

Generalized lime reaction using calcium carbonate as the liming material (eqn [4]).



Lime requirement is defined as the quantity of limestone or other basic material required to raise the pH of the soil to the desired value that is needed on the basis of the intended use of the soil. The amount of liming material applied must be sufficient to not only neutralize the  $\text{H}^+$  and  $\text{Al}^{3+}$  in solution (active acidity) but also neutralize much of the exchangeable and nonexchangeable acidity (or potential acidity). The exchangeable and nonexchangeable acidity is the  $\text{H}^+$  and  $\text{Al}^{3+}$  associated with the solid phase, and the two are distinguished from each other through an operational definition: exchangeable acidity is extractable with a 1 M KCl solution. It is this solid phase  $\text{H}^+$  and  $\text{Al}^{3+}$  bound to soil organic matter and clay minerals that buffers the soil solution. Thus, as the solution acidity is neutralized, the exchangeable acidity pool resupplies the solution with  $\text{H}^+$  and  $\text{Al}^{3+}$ , and then the

nonexchangeable pool resupplies the exchangeable pool. Soils that can retain more  $\text{H}^+$  and  $\text{Al}^{3+}$  are more buffered and typically have higher amounts of clay and organic matter. These well-buffered soils require a greater amount of liming material to neutralize acidity, but the soils also remain near neutral for a greater period of time. Conversely, sandy soils with low organic matter require little liming material to neutralize soil acidity but require more frequent liming. Overall, factors that affect lime requirement include initial soil pH, desired soil pH, and soil buffer capacity. Although there are many methods of estimating lime requirement, most soil testing labs utilize some type of calibrated buffer solution, such as the Adams–Evans, Shoemaker–McLean–Pratt (SMP), or Mehlich buffers.

There are some soils that have excessively basic soil pH, and in some instances it is economically feasible to acidify them. This is especially true of high-pH soils that display micronutrient deficiencies; a decrease in pH often alleviates the deficiency. Basic soils are usually treated with elemental sulfur, Fe or Al sulfate, ammonium-containing fertilizers, or sulfuric acid. Although elemental sulfur is often the most economical treatment, it requires microbial activity to be reduced to sulfate, and therefore time, before the pH is decreased. Fe or Al

sulfates or  $\text{NH}_4\text{SO}_4$  do not decrease pH due to the sulfate, but through the hydrolysis of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  that is released from these highly soluble minerals or nitrification of  $\text{NH}_4$ . Sulfuric acid can be injected into irrigation systems and works very rapidly but requires special handling due to its caustic nature. A general acid-producing reaction from application of Al sulfate is shown in eqn [5], which results in the precipitation of an amorphous Al hydroxide mineral.

Acidifying reaction resulting from the application of aluminum sulfate (eqn [5]).



## Nutrient Cycling and Plant Nutritional Roles of Essential Elements

As described in the Section Soil Characteristics Contributing to Nutrient Supply, the macro- and micronutrients are present in varying degrees in soil and their availability is dependent on soil mineralogy and soil chemical and physical characteristics. Understanding how the essential elements cycle in the soil and are utilized by plants is critical to understanding how to manage them to optimize plant performance. Table 2 provides a brief overview of each of the essential elements and their functions in plants. The following sections briefly describe management of each of the essential elements in regard to their plant–soil cycle. In essence, applied soil fertility and plant nutrition revolves around the management of the plant–soil nutrient cycle to provide these nutrients in adequate amounts for optimum plant performance.

### Primary Macronutrients

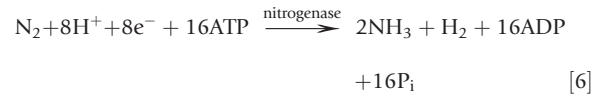
#### Nitrogen

Nitrogen is present in plant tissue at the highest relative abundance of the essential mineral nutrients that comprise from 1% to 5% of plant dry matter. Plants use N to form amino acids, which are subsequently incorporated into proteins and nucleic acids (DNA and RNA). Nitrogen is also an integral component of chlorophyll, the light-absorbing pigment needed for photosynthesis. Because of the high N requirement of most crops and its mobility in the environment, it is also commonly the most limiting nutrient in both managed and natural ecosystems. As a result, N is typically the nutrient that receives the most attention.

Nitrogen behavior is arguably more dynamic than any of the other essential mineral elements (Figure 5). The ultimate source of most plant-available N is  $\text{N}_2$ , which comprises 78% of the earth's atmosphere. However, most plants can only utilize  $\text{NO}_3^-$  or  $\text{NH}_4^+$  from the soil solution, referred to as plant-available forms. Conversion of  $\text{N}_2$  to plant-available N is called fixation and is a very energy-intensive process as it requires breaking the strong triple bonds of the thermodynamically stable  $\text{N}_2$  molecule. Legumes have symbiotic relationships with rhizobia bacteria that can fix  $\text{N}_2$  from the soil atmosphere. Biological  $\text{N}_2$  fixation (BNF) is catalyzed in the presence of the nitrogenase enzyme produced by these bacteria (eqn [6]). For nonleguminous plants, N sources include N fixed from atmospheric  $\text{N}_2$  introduced to the soil system by

nonsymbiotic soil microorganisms capable of BNF, atmospheric deposition of N oxides formed either through electrical discharges or through high temperature combustion, and the application of industrially fixed N fertilizers. Natural processes (e.g., lightning and volcanic activity) as well as human activities (e.g., operation of internal combustion engines and industrial fixation of N to make inorganic fertilizer) convert  $\text{N}_2$  to  $\text{NH}_3$  through thermal fixation, as described in eqn [7].

BNF (eqn [6]).

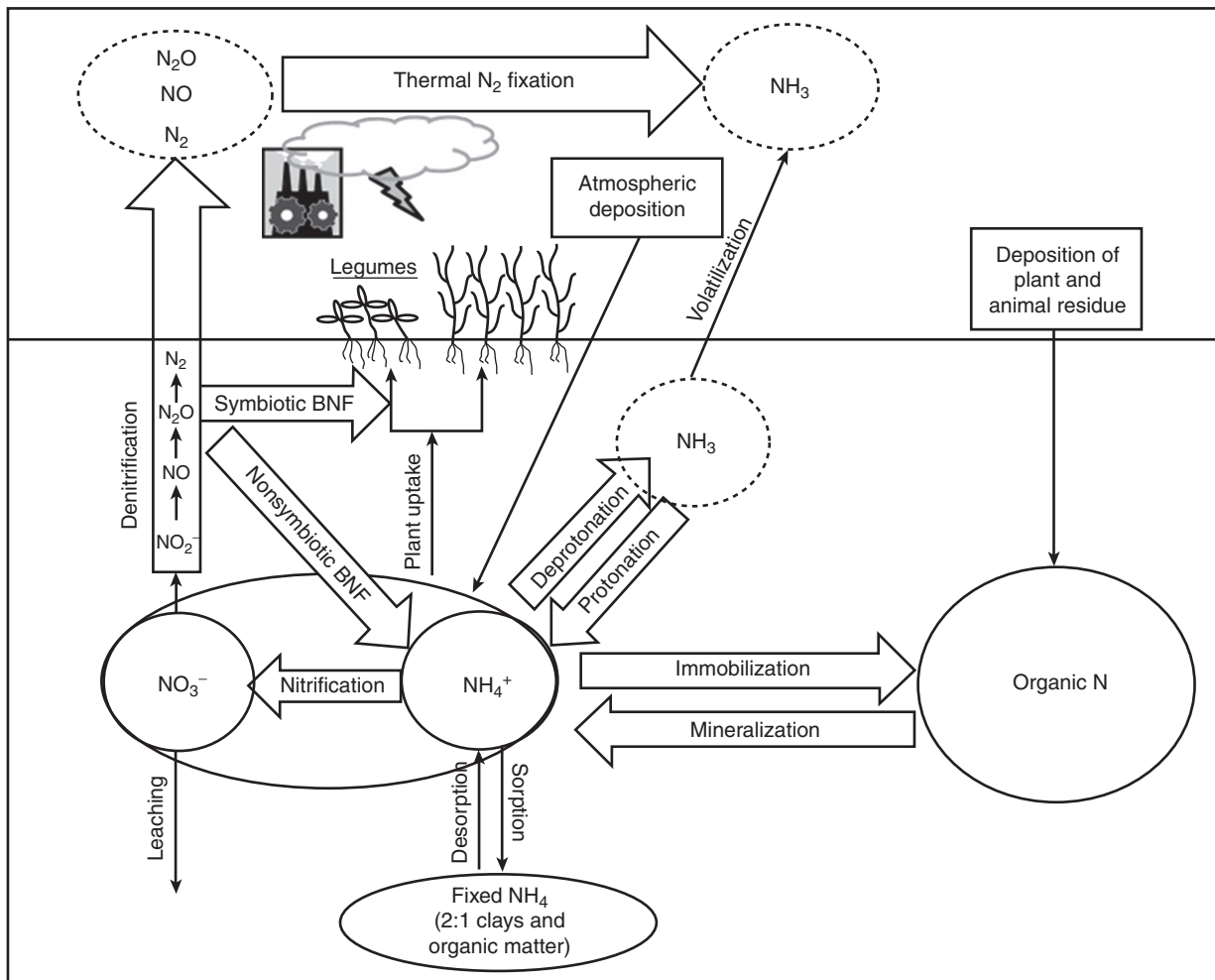


Thermal nitrogen fixation (eqn [7]).



The soil N cycle is very complex because it varies greatly, both in space and time, due to the influence of biotic and abiotic transformations. The total N content of the surface 20 cm of mineral soils is generally within the range of 0.05 to 0.5%. Soil N can be generally classified as organic or inorganic. Soil N resides in soil solution, soil organic matter, clay mineral surfaces (typically residing in the interlayer of 2:1 clays), or in the soil atmosphere (although this is typically transitive in nature). Forms of inorganic N include exchangeable  $\text{NH}_4^+$ , fixed or nonexchangeable  $\text{NH}_4^+$ ,  $\text{NH}_3$ ,  $\text{NO}_3^-$ ,  $\text{N}_2$ ,  $\text{N}_2\text{O}$ , and N oxides. Inorganic N generally represents less than 5% of the total soil N. Organic N forms include amino acids or proteins, amino sugars, and a large pool of unidentified compounds. Organic N is a component of soil organic matter, including microbial biomass and organic residues from plants and animals. The major N transformations that dominate the soil N cycle include  $\text{N}_2$  fixation, nitrification, mineralization, biological immobilization, chemical immobilization, deprotonation of  $\text{NH}_4$  to  $\text{NH}_3$ , and denitrification.

The interrelationship and transformation of N between the inorganic and organic pools is the most central aspect of the N cycle and dominates the management of N for crop production. Nitrogen mineralization is the conversion of organic N into inorganic forms, both  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , whereas N immobilization refers to the transformation of inorganic N into organic forms. Typically, N immobilization is used to refer to biological processes, such as assimilation by microorganisms; however,  $\text{NH}_4^+$  can also be immobilized by direct adsorption and incorporation into soil organic matter. Furthermore, some microorganisms can directly assimilate  $\text{NO}_3^-$ ; however, this is typically explicitly referred to as  $\text{NO}_3^-$  assimilation. Mineralization typically involves three steps and results in the production of both  $\text{NH}_4$  and  $\text{NO}_3^-$ . In the first step, aminization, heterotrophic soil organisms decompose complex proteins into simple amines and amino acids ( $\text{R-NH}_2$ ). During the second step, ammonification, the amines and amino acids are further decomposed by other heterotrophs, releasing  $\text{NH}_4$  (eqn [8]). Finally, ammonium can be converted to nitrate through nitrification (eqns [9] and [10]). Nitrification itself is a two-step process where obligate autotrophic *Nitrosomonas* bacteria first oxidize  $\text{NH}_4^+$  to  $\text{NO}_2^-$  (eqn [9]) then the obligate autotrophic *Nitrobacter* oxidize  $\text{NO}_2^-$  to  $\text{NO}_3^-$  (eqn [10]).

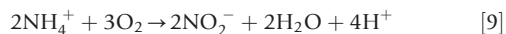


**Figure 5** The soil nitrogen cycle, with major transformations (block arrows), pools (ovals), and movement into, out of, and through the soil system identified.

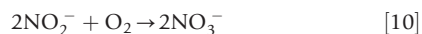
Ammonification (eqn [8]).



Oxidation of ammonium by *Nitrosomonas* (eqn [9]).



Oxidation of nitrite by *Nitrobacter* (eqn [10]).



Nitrogen transport and transformation processes are inextricably linked within the soil system because the form of N present is influenced by both, and they determine storage or loss patterns. The loss of N from the soil system has significant implications for both crop production and environmental quality. The vast majority of industrially fixed N applied as fertilizer is as NH<sub>4</sub><sup>+</sup> or forms that release NH<sub>4</sub><sup>+</sup> when applied, such as urea (CO(NH<sub>2</sub>)<sub>2</sub>). Once in the soil, NH<sub>4</sub><sup>+</sup> can be rapidly deprotonated to form NH<sub>3</sub>, particularly in neutral or alkaline soils, and lost to the atmosphere through

volatilization (eqn [11]). Urea accounts for approximately half of the ammoniacal fertilizer applied. Urea is rapidly converted to NH<sub>4</sub><sup>+</sup> through urea hydrolysis, an enzymatic reaction where urea and water react in the presence of urease to form NH<sub>4</sub><sup>+</sup> and HCO<sub>3</sub><sup>-</sup>. When urea fertilizers are surface applied or incorporated into low CEC soils (particularly if incorporated to shallow depths), this reaction often continues to form NH<sub>3</sub> and CO<sub>2</sub>. The two ammoniacal forms, NH<sub>4</sub><sup>+</sup> and NH<sub>3</sub>, are in equilibrium in the soil and the partitioning between the two is highly dependent on pH.

The deprotonation of ammonium produces ammonia gas that can volatilize to the atmosphere (eqn [11]).



Retention of N in the soil as NH<sub>4</sub><sup>+</sup> is important to crop production as this form provides favorable energy balance to crops in regard to N utilization and because NH<sub>4</sub><sup>+</sup> is held by the soil CEC, it is less susceptible to loss. Nitrification is an important process in the soil N cycle because it is assumed that in most systems the majority of N is lost through NO<sub>3</sub><sup>-</sup>

leaching. Nitrate is a poorly held anion, easily transported out of the soil system through leaching or runoff.

Biological denitrification is the reduction of nitrogen oxides under anaerobic conditions. It can be a major N loss pathway from agricultural soils, particularly when they are periodically inundated with water. It is important to the global N cycle because it is the principle pathway by which inorganic N in soil or surface water returns to the atmospheric N pool as N<sub>2</sub>, N<sub>2</sub>O, or NO, the latter two contributing to greenhouse gases and ozone depletion, respectively.

Nitrogen fertilizer efficiency or N use efficiency are terms generally used to quantify how much of the applied N fertilizer makes it into the target plant or the harvested portion of the crop. There are many ways to calculate N use efficiency (see Section Relevant Websites – Oklahoma State University's NUE website). Nitrogen's mobility in the environment, and specifically the plant–soil system, contributes to low global N use efficiency. For example, [Raun and Johnson \(1999\)](#) estimated N use efficiency in global cereal production at approximately 33% in 1996. One of the most critical steps to increase N use efficiency is determining the correct amount of N required to optimize crop performance. Nitrogen's mobility makes predicting the correct amount of N needed for optimum plant performance very difficult. Most recommendation systems rely on a mass balance approach, as detailed by [Stanford \(1973\)](#). Fundamentally, the mass balance approach accounts for the N requirement of the crop, the amount of N supplied by the soil through mineralization of organic N or residual mineral N present in soil, externally supplied N (e.g., through precipitation), and N lost through various pathways. The difference between N supplied and N required is then determined to be the amount needed through fertilization. Through repeated plot trials, agronomists have developed region-specific, empirical relationships between applied N rate and yield based on Stanford's equation. Some recommendation systems also included economic factors and may be grouped by soil type, rather than relying on estimated yield alone; however, these recommendations are still based on empirical results from N rate response trials ([Sawyer et al., 2006](#)). Regardless of how recommendations are generated, the objective is to maximize return on N fertilizer investment by optimize plant performance and minimizing residual reactive N that can be lost to the environment. Beyond determining the optimum rate, increasing N fertilizer use efficiency is also highly dependent on timing of N fertilizer application. Because N is so mobile in the environment, applied N that is not immediately taken up by plants is at constant risk for transport out of the soil system. One way to mitigate this is to time N applications to match the temporal plant uptake patterns as closely as possible. This can be accomplished by splitting the total amount of N fertilizer thought to be required among multiple applications in an attempt to match the timing of plant uptake. Another method to increase N fertilizer efficiency is the use of 'slow-release' fertilizers designed to release N slowly over time, in the hope that plants then take up the N as it is released, minimizing the time that mobile forms of N are in the soil system and at risk for loss to the environment. Similarly, certain formulations of N or chemical treatments of N fertilizers attempt to disrupt N transformations to limit its mobility in the environment.

Nitrification and urease inhibitors fall into this category. Finally, N fertilizer efficiency can be manipulated by where the fertilizer is placed. For example, as described above, urea fertilizer can rapidly hydrolyze to form NH<sub>4</sub>, which can deprotonate and then volatilize, being lost to the atmosphere as NH<sub>3</sub>. However, simply incorporating urea fertilizer below the soil surface can significantly reduce NH<sub>3</sub> gaseous losses. Overall, soil fertility managers must focus on rate, timing, form, and placement of N fertilizer in order to maximize the efficiency of applied fertilizers.

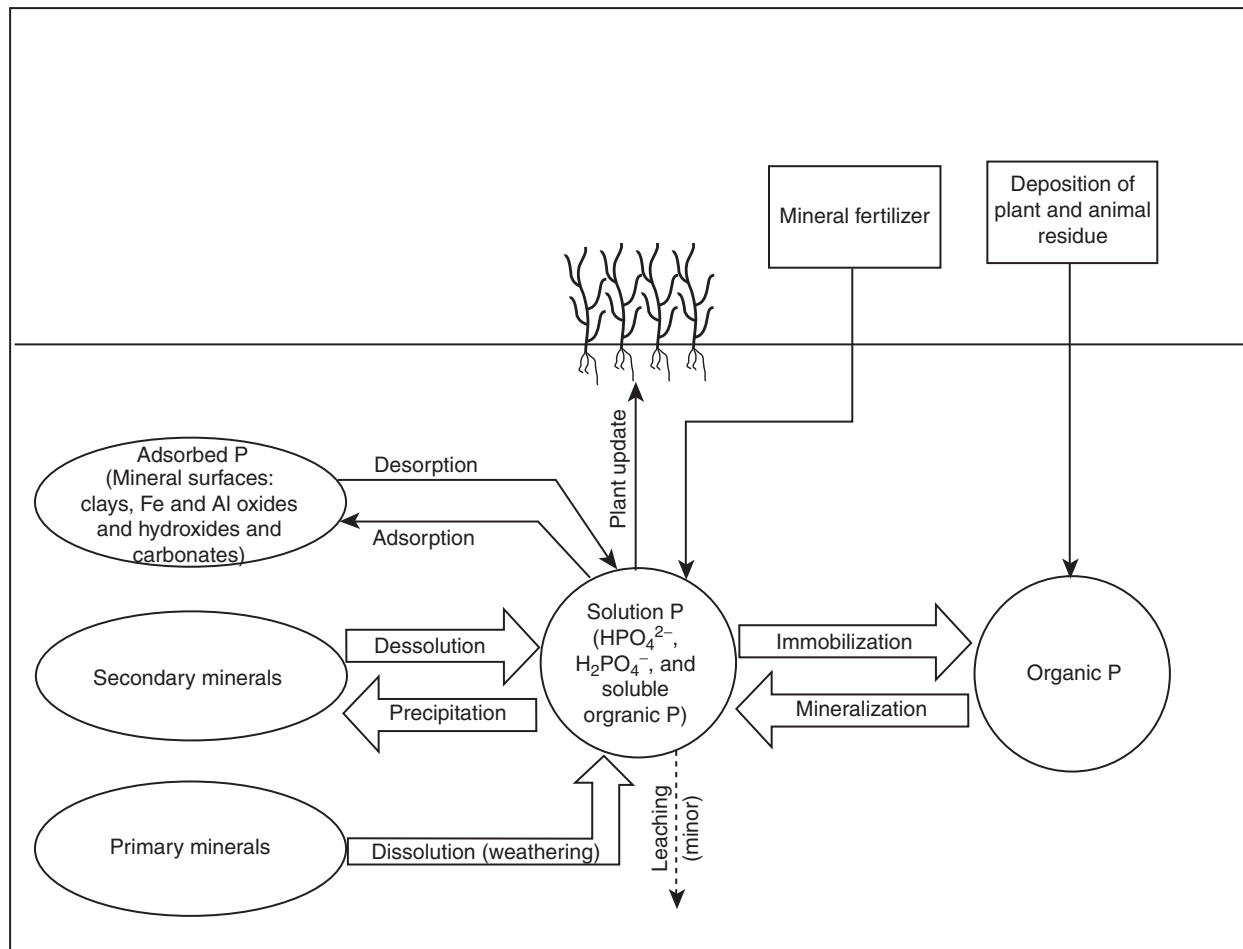
### Phosphorus

Phosphorus is essential for all forms of life on the earth. It is typically less abundant in the soil than N or K, with total P concentrations in soil ranging from 50 to 1500 mg kg<sup>-1</sup>. Likewise, typical total P concentrations in plant tissue are approximately an order of magnitude less than N or K concentrations, averaging 0.2% (dry weight basis; [Table 2](#)). Phosphorus is involved in almost every metabolic and reproductive process in plants and is most often associated with vigorous growth, development of reproductive parts, and energy transfer. Phosphorus is important in the storage and transfer of energy in plants, as a basic building block of ADP and ATP. Sugar phosphates are an essential structural component of DNA and RNA, which contain the genetic coding responsible for plant growth, development, and metabolism. Phospholipids and phosphoproteins are important structural components of membrane chemistry.

Phosphorus occurs in many forms in the soil. It resides in and moves between three major pools: organic P, inorganic P, and soil solution P as part of the soil P cycle ([Figure 6](#)). Plants can absorb phosphate from the soil solution as either dihydrogen phosphate (H<sub>2</sub>PO<sub>4</sub><sup>-</sup>) or hydrogen phosphate (HPO<sub>4</sub><sup>2-</sup>), depending on soil pH. To a more limited extent, plants can also absorb low molecular weight, soluble organic compounds, such as phytin and nucleic acid, from the soil solution; however, these dissolved organic P compounds are considered a negligible source of P for higher order plants. Inorganic P can be found in forms that are readily available, slowly available, or very stable. The degradation of organic compounds to release phosphate or soluble organic P to solution is referred to as mineralization. Solution P can be fixed through adsorption to clay and mineral surfaces or precipitation of secondary minerals. Phosphate can be released to the soil solution from secondary minerals and primary minerals through dissolution and from clay and mineral surfaces through desorption. Easily mineralized organic P, readily desorbable inorganic P, and soluble P are all forms of P readily available for plant uptake and are often referred to as labile P. Generally, organic P that is more recalcitrant and primary or secondary mineral P are considered nonlabile. The quantity–intensity relationship described in the Soil Mineralogy Section and [Figure 3](#) depicts the relationship between labile P and solution P. As plants remove phosphate from soil solution, labile P replenishes the solution pool. This relationship is highly dependent on soil mineralogy and pH.

Soil P differs from N and K in that it can bind somewhat irreversibly to variable-charge minerals by ligand-exchange (specific sorption) mechanisms. For example, as pH decreases below 6 ([Figure 4](#)), phosphate has less competition with OH<sup>-</sup>





**Figure 6** The soil phosphorus cycle, with major transformations (block arrows), pools (ovals), and movement into, out of, and through the soil system identified.

and the mineral surfaces become more positively charged, which together results in a strong ligand-exchange reaction on the surface. The problem is that the phosphate is often held so strongly that it cannot desorb back into solution until the pH appreciably increases. This is most common in Ultisols and Oxisols because they are rich in Fe and Al oxides and hydroxides. Another way in which P availability differs from N and K is that P is extremely susceptible to precipitation reactions with Al, Fe, Mg, and Ca. At pH below 6, P begins to precipitate as a solid Al or Fe phosphate mineral, which is also a common problem in Ultisols and Oxisols. In addition, as pH increases above 7, P begins to precipitate as a solid Mg and Ca phosphate until the pH reaches approximately 8.2 (Figure 4). Because of the impact of pH on ligand-exchange and precipitation reactions, optimum P availability is assumed to be approximately pH 6.5.

Organic P accounts for less than 50% of P found in surface soils. Plant material and organic wastes supply organic P to soils. These organic materials are typically deposited on the surface, and as P is not easily transported downward through soil, the largest portion of the organic P pool is contained in the topsoil. Most of the soil organic P occurs as stable, organic compounds not readily available for plant uptake. Nonetheless,

mineralization of organic P through microbial activity can provide labile organic P for crop use, albeit at a very slow rate.

Inorganic P in acidic soils not taken up by plants can be fixed or sorbed by iron (Fe) and aluminum (Al) oxides, organic matter, and clay minerals or precipitate as Fe and Al minerals. In alkaline soils, calcium (Ca) phosphates rather than Fe or Al phosphates are the dominant minerals controlling P fixation (Lookman *et al.*, 1996; Van der Zee and van Riemsdijk, 1988). Most inorganic forms of P in the soil are sparingly soluble. Desorption of P from metal oxides, clays, and organic matter or dissolution of Ca, Fe, and Al minerals replenishes soluble P removed by plant uptake or runoff.

Mineralization of organic P and dissolution (or weathering) of stable P minerals are natural processes that provide labile P to crops. However, in soils that have low to medium soil test P values, these processes typically proceed too slowly to supply sufficient available P for plant growth. Therefore, it is often necessary to provide P to crops through fertilization. Organic and inorganic fertilizers are most commonly used to build soil P fertility to the optimum concentrations that can replenish soil solution P for production of crops.

Organic fertilizers, such as manures and biosolids, provide essential nutrients, such as P and N, and add organic matter,

which can improve soil fertility. Best management practices, such as immediate incorporation of manure after application, can reduce the potential for environmental impacts resulting from manure use. When properly managed, manures and other organic P sources can provide nutrients with no more environmental consequences than well-managed commercial fertilizers. However, use of manures as fertilizers can complicate nutrient management because of the unpredictability of organic nutrient mineralization and the fact that many constituents are present in inorganic fertilizers at varying and often unknown concentrations.

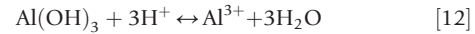
Inorganic fertilizers can be easier to manage than organic fertilizers. The primary advantages of inorganic fertilizer over organic fertilizer, from an environmental standpoint, are: (1) that the application of a specific nutrient is independent of other nutrients; (2) the P content of inorganic fertilizers is known and uniform, permitting the user to apply the desired amount of P accurately; (3) inorganic fertilizers are homogeneous in composition, produced in granular, pelletized, or liquid forms, allowing more even distribution; and (4) dissolution of inorganic fertilizers is more predictable than organic fertilizers, so that timing and rate of application can be accurately determined. Good management practices, such as band application and fertilizer incorporation, can further enhance fertilizer efficiency. Band application of fertilizer increases the concentration of nutrients near the root zone, improving the plant's ability to utilize the nutrients. Furthermore, incorporating or injecting fertilizers reduces fertilizer loss in runoff and erosion (Baker and Lafen, 1982).

### Potassium

Potassium is adsorbed by plants more and is present in plant tissue at higher concentrations than any other essential nutrient except for N (Table 2). It is responsible for water relations and charge balance in plant cells and is highly mobile within the plant. The primary nutrients, N, P, and K, are typically lacking in the soil due to the natural geologic material. However, soils rich in micas (biotite and muscovite), illite, or vermiculite tend to contain naturally adequate levels of K. As the K is bound up as part of the minerals, it requires the influence of the five soil-forming factors to weather the mineral and release  $K^+$  to solution for plants. Older or highly weathered soils or soils in areas with high rainfall are more prone to exhibiting K deficiency due to leaching of  $K^+$ . Potassium is one of the base cation nutrients (along with  $Ca^{2+}$  and  $Mg^{2+}$ ) that typically only bind by ion exchange reactions discussed in the Section Ion-exchange reactions (nonspecific sorption). When  $K^+$  is not bound tightly by the aforementioned minerals or located in solution, it can bind to the soil CEC through nonspecific sorption where it can be easily displaced into solution by another cation. Thus, it is found that  $K^+$  availability decreases when the soil pH decreases below 6 because the soil CEC resulting from variable-charge minerals decreases. Another reason for the decrease in  $K^+$  availability in acid soils is because of increased competition from  $Al^{3+}$  and  $H^+$  ions. Specifically,  $Al^{3+}$  concentrations or, more specifically activity, increase in acidic soils due to the dissolution of Al hydroxide minerals (eqn [12]).

Al hydroxide minerals can dissolve, releasing  $Al^{3+}$  to solution, decreasing  $K^+$  activity, which allows  $K^+$  to leach out of

the root zone (eqn [12]).



This reaction occurs for a variety of Al oxide and hydroxide minerals, and the net result is that soil Al tends to buffer the pH at approximately 5.5. The increased concentration of  $Al^{3+}$  causes the activity of  $Al^{3+}$  to increase and the activity of  $K^+$  to decrease. Thus, the soil CEC and solution becomes dominated with  $Al^{3+}$  and  $K^+$  is then able to leach out of the soil along with other base cations.

Soil K resides in five primary pools: organic matter, primary minerals (feldspars and micas), nonexchangeable  $K^+$  (retained in the inner layer of 2:1 minerals), exchangeable  $K^+$  (sorbed on the surface of 2:1 minerals), and soil solution  $K^+$  that is available for plant uptake. Potassium in soil organic matter comes from the deposition of plant and animal materials, which can be quite high in K content. Unlike other nutrients, K is not a structural component of plant tissue; rather it exists as an ion in solution or bound to charges on tissue surfaces. Therefore, decomposition of organic matter can rapidly and directly contribute  $K^+$  to the soil solution pool. The soil solution pool can also be replenished rapidly through desorption of  $K^+$  from 2:1 clay mineral surfaces. Because exchangeable  $K^+$  is in equilibrium with the solution pool, it can be replenished through adsorption from the solution pool. By contrast, nonexchangeable K held tightly in the inner layer of 2:1 minerals equilibrates very slowly, releasing  $K^+$  to the exchangeable and solution pools over long periods of time and at not a fast enough rate to supply crop needs. The nonexchangeable pool primarily originates from the weathering of soil minerals or the fixation of exchangeable  $K^+$ . Potassium can be lost from the soil system through leaching or plant uptake, adsorbed as  $K^+$ .

### Secondary Macronutrients

#### Calcium and magnesium

Calcium and Mg are often found in soil minerals originating from geologic parent material, and therefore their plant availability is usually a function of the solubility of those minerals. Plants require approximately the same amount of Mg as they do P, with Ca requirement approximately double of that (Table 2). Soils rich in Ca- and Mg-containing minerals are often found in arid and semiarid areas or are younger soils formed from recently deposited parent material. The source of Ca and Mg are typically carbonate minerals that dissolve with decreases in pH that occur with normal agricultural activities and rainfall. As a result, it is typically not required to fertilize for Ca and Mg in these soils. However, assuming that Ca and Mg are present in the soil, Figure 4 shows that their availability decreases as the pH drops below 6. This is because Ca and Mg are base cations that are held onto the CEC by ion exchange reactions if they are not precipitated as a solid mineral. Therefore, acid pH allows  $Al^{3+}$  to dominate the CEC and solution, thereby decreasing Ca and Mg activity and allowing them to potentially leach. Course-textured soils in humid areas are generally very low in Ca; however, the application of agricultural lime to manage soil acidity in these soils typically provides sufficient Ca and Mg for optimum

plant growth. As soil pH increases above pH 8, Ca and Mg availability decreases as a result of precipitation with carbonates.

The soil cycles for Ca and Mg are very similar to the soil K cycle. Plants adsorb  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from the soil solution, which is in equilibrium with mineral forms of the two elements and exchangeable forms sorbed to clay mineral surfaces. The processes of desorption and adsorption maintain the equilibrium between the soil solution and exchangeable  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Both  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in solution can precipitate to form secondary minerals, which can dissolve to replace solution Ca or Mg that has leached out or been removed by plant uptake. Organic residues also contain Mg and Ca that can feed the soil solution pool, but the soil cycle is by far dominated by inorganic cycling.

Plants obtain  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from the soil solution through mass flow and root interception. Calcium is a principle component of cell wall structures and important to cell wall permeability. Because of its importance to cell structure,  $\text{Ca}^{2+}$  is essential for development of terminal buds and shoots and the apical tips of roots and is also involved in the translocation of nutrients and carbohydrates produced through photosynthesis (Tables 1 and 2). As a result, inhibition of new leaf development, root growth, or storage components are common symptoms of Ca deficiency. Even though  $\text{Ca}^{2+}$  is essential for translocation of elements in the plants, it moves through the xylem and not the phloem; therefore, Ca is considered an immobile nutrient with deficiency appearing in new growth first. Magnesium is a principal component of chlorophyll, a structural component of ribosomes, and is required for phosphate transfer from ATP. Although  $\text{Mg}^{2+}$  moves through the soil and into the plant in much the same way as  $\text{Ca}^{2+}$ , it behaves quite differently in the plant. Deficiency symptoms associated with  $\text{Mg}^{2+}$  appear in older leaves first, as it is mobile within the plant (Table 2). Because of its role in chlorophyll and protein synthesis,  $\text{Mg}^{2+}$  deficiency appears similar to N deficiency resulting in chlorotic plants, although this symptom typically first appears as interveinal chlorosis and only causing complete chlorosis in cases of extreme deficiency.

### Sulfur

Similar to Ca and Mg, S is often found in large quantities in soil depending primarily on parent material and climate. However, S differs from Ca and Mg in that it can exist as an anion ( $\text{SO}_4^{2-}$ ). Sulfate retention on the soil is, therefore, impacted by the abundance of variable-charge minerals that increase the soil's AEC as pH decreases. Sulfur is similar to N in that organic matter is an important pool in most soils. More than 90% of the S present in noncalcareous soils resides in the organic pool. Therefore, cycling of organic S is a key component of the soil S cycle. Like N, the cycling of S by microorganisms is reduced under acidic conditions. Plant-available S is present as adsorbed and solution  $\text{SO}_4^{2-}$ . Historically, sulfur deficiency has been considered rare due to high sulfur deposition rates from the burning of fossil fuels. The decline in S deposition due to reduced S emissions has increased the incidence of S deficiency, particularly in high-yielding crops grown on deep sandy soils with low organic matter contents or on soils that developed from parent materials low in S. Plants

primarily absorb  $\text{SO}_4^{2-}$  from the soil solution; however, they can also absorb thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ ) from the soil solution or absorb very small quantities of sulfur dioxide ( $\text{SO}_2$ ) through their leaves. Sulfur is contained in and required for synthesis of amino acids, which are essential in protein formation. Sulfur is also required for the formation of chlorophyll. In legumes S promotes nodulation. Because of its role in chlorophyll and amino acid formation, S deficiency closely resembles N deficiency; however, S is not as mobile as N in the plant and therefore symptoms should be exhibited in younger tissue first.

Concentrations of  $\text{SO}_4\text{-S}$  in the soil solution of most temperate zone soils ranged from 5 to 20 mg  $\text{SO}_4\text{-S}$  per liter, higher than the 3–5 mg  $\text{SO}_4\text{-S}$  per liter required for the optimum growth of most plants. However, recent S deficiencies have been reported globally due to a combination of factors, the primary factor being a marked decrease in S deposition due to air pollution-control measures. Sulfate deposition has clearly decreased over the past 20 years as indicated by the National Atmospheric Deposition Program. For example, the average total wet deposition of sulfate at the Huntington Wildlife Station in Essex County, NY, USA was 22 kg ha<sup>-1</sup> for the period of 1979–83 and decreased by 43% to 14 kg ha<sup>-1</sup> for the period of 2003–07 (NADP, 2008). This decrease in atmospheric deposition combined with increased crop yields and decreased agronomic S inputs is expected to contribute to increasing S deficiencies in crops (McGrath and Zhao, 1995). These predictions have been supported by recent studies showing increased yield responses to S fertilization in previously nonresponsive soils (Chen *et al.*, 2008).

### Micronutrients

The eight essential micronutrient elements are just as important to plant nutrition as the macronutrients; they simply are required in very small, or trace, amounts by plants. The role of each of the essential micronutrient elements in plant nutrition is summarized in Table 1. A deficiency of any of the essential micronutrients results in similar reductions in plant health and vigor as a deficiency of any of the macronutrient elements. Unlike the macronutrients, the range between deficient and toxic levels for many of the micronutrients is generally narrow. Toxic levels of available nutrients may result from over application of fertilizer materials (e.g., B and Mo), or waste residuals such as biosolids (e.g., Cu and Zn). Toxic levels of some micronutrients may also result from soil conditions, such as low pH (e.g., Mn and Fe) or water-logged conditions (e.g., Mn).

Like the macronutrients, micronutrient elements may occur in soil as constituents of primary and secondary minerals or organic matter, adsorbed on mineral and organic matter surfaces, and in soil solution. The importance of any of these solid phases to the supply or buffering of plant-available ionic forms in soil solution depends on the micronutrient and the soil's condition. The ionic form of each of the essential micronutrient elements taken up by plants, summarized in Table 1, provides important information about their behavior in soil. The available forms of Cu, Mn, Fe, Ni, and Zn are metallic cations, whereas B, Mo, and Cl are anions.

As the micronutrients are needed by plants in such small amounts, most soils contain sufficient quantities to satisfy plant needs; however, the amount of available micronutrients in soil solution can be significantly affected by several factors, most notably soil pH (Figure 4). For example, Fe comprises approximately 4% of the earth's crust and is, on average, the fourth most abundant element in soil. It is a constituent of numerous common primary and secondary soil minerals, including olivine, siderite, hematite, goethite, and ferrihydrite. However, the solubility of these common Fe minerals is exceedingly low, resulting in very low concentrations of plant-available  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in soil solution, and deficiencies commonly occur in soils with abundant levels of total Fe, especially where soil pH exceeds 6.5.

Similar to Fe, the other transition metal micronutrients Cu, Mn, Ni, and Zn are extremely sensitive to pH. At high pH all of these metals precipitate as insoluble carbonates and hydroxides. In addition, Cu and Zn are known to bind strongly to variable-charge minerals via chemisorption (specific sorption). For these reasons, Cu, Fe, Mn, Ni, and Zn availability decreases with increasing pH and are commonly deficient above pH 8. However, very acidic soils can have excessive availability to the point of plant toxicity. Molybdenum is the only trace metal micronutrient that becomes more available with an increase in pH above 6 (Figure 4).

There are several other factors or soil properties that govern processes of micronutrient sorption and desorption. These include soil organic matter content, soil texture, CEC, and soil aeration. The influence of soil organic matter, soil texture, and CEC on micronutrient behavior was discussed in the Section Soil Characteristics Contributing to Nutrient Supply. Soil aeration influences metallic micronutrient availability by favoring specific oxidation states of these elements. For example, in water-logged soils the concentration of dissolved oxygen in soil solution is depleted by microbial oxidation of soil organic matter. Under these conditions, the lower valence state, or reduced form, of the metallic micronutrients is favored. In general, the reduced form of the metallic micronutrients is more soluble and available, including Fe, Mn, and Cu.

Another important mechanism responsible for maintaining adequate levels of the metallic micronutrient elements to support plant growth in soil solution is called 'chelation.' Numerous organic molecules in soil can form organometallic complexes with these micronutrients. Chelation protects metallic ions from precipitation and specific sorption and increases micronutrient availability. The chelation of Fe, Cu, Zn, Mn, and Ni increases their concentration in soil solution and movement to plant roots by mass flow or diffusion. There are a number of naturally occurring chelating agents in soil formed from root and microbial exudates, including oxalic and citric acids. A number of synthetic chelates have also been used to enhance micronutrient availability, including ethylenediaminetetraacetic acid (EDTA), ethylenediamine bis (2-hydroxyphenyl)acetic acid (EDDHA), and hydroxy-2-ethylenediaminetriacetic acid (HEEDTA).

Molybdenum is the only trace metal micronutrient that becomes less available with a decrease in pH below 6 (Figure 4). The explanation for this is that Mo exists as an anion in solution (molybdate) that is somewhat susceptible to strong ligand-exchange reactions similar to P. For this reason, it is

observed that Mo availability decreases with decreasing pH due to ligand-exchange reactions onto variable-charge minerals.

Like all micronutrients, B is found in geologic materials and organic matter and is typically slowly released via dissolution, desorption, and mineralization. As B often exists as an anion, it is usually bound to the soil AEC of variable-charge minerals. As a result, increases in pH that precipitate Al hydroxide minerals provide a surface for B to sorb onto, thereby decreasing B availability. The range between sufficient and toxic levels of available B is quite narrow, and certain crops are especially sensitive to excessive B, whereas others are more sensitive to B deficiencies. For example, most cereal crops, cotton, and soybean have low tolerance to high levels of available B, whereas most of the Brassicaceae family crops, alfalfa, and apples tend to be more sensitive to B deficiencies.

Among micronutrients, Cl is unique in that it exists primarily in soil solution, with only small quantities in mineral and organic soil fractions. Adsorption of  $\text{Cl}^-$  to mineral surfaces is negligible; therefore, it is extremely mobile in soils. The principle source of soil Cl is salts in the soil parent material and atmospheric deposition from volcanic emissions or marine aerosols in coastal areas. Chloride is also a principle component of the most common K fertilizer KCl.

#### **Micronutrient fertilizer sources and practices**

In most arable soils, adequate levels of available micronutrients can be achieved by managing the soil conditions that influence their supply to plants, such as soil acidity, aeration, and soil organic matter. However, in very coarse textured or highly weathered soils where large quantities of plant biomass are harvested and the supply of micronutrients is low, the soil supply may need to be supplemented through the use of fertilizers in order to optimize crop yield and plant health. As micronutrients are needed in such small quantities and due to their potential toxicity at high levels, very low (e.g., 0.5–5 kg ha<sup>-1</sup>) and uniform applications are required. Micronutrient fertilizers are commonly applied to soil by blending with macronutrient fertilizers to improve handling and increase uniformity of application. Micronutrient fertilizers are commonly soluble salts or, in the case of the metallic micronutrients, synthetic chelates. In some cases, foliar applications may be used effectively to apply micronutrients to address a deficiency where soil applications are not convenient or possible (i.e., in-season application to annual crops or perennial fruit crops) or where soil conditions (e.g., high pH) may render soil-applied nutrients unavailable.

#### **Summary**

As a discipline, soil fertility and plant nutrition encompasses management of the soil environment to provide the essential nutrients in the required amounts to plants for optimum performance. Essential nutrients are those elements that play a vital role in plant growth, development, reproduction, or metabolic functions. Each nutrient is required at a specific concentration in plant tissue, below which normal plant functions are restricted. Carl Sprengel's theory of the minimum is a foundational principle in soil fertility, stating that if any of the essential nutrients are present below their critical

concentration then that nutrient is limiting, regardless of the amount of other nutrients present. Therefore, soil fertility evaluation to quantify the amount of available essential nutrients present is the basis for any soil fertility and plant nutrition management program. Multiple factors beyond just nutrient concentration in the soil influence the ability of the soil to supply nutrients to the plant and also the ability of the plant to take up and utilize those nutrients. The chemical, biological, and physical soil properties and processes influence plant nutrient utilization as well as other environmental factors such as pest pressure, climate, and crop management practices. Therefore, soil fertility and plant nutrition is an applied science that integrates all of the soil and crop management disciplines to provide optimum nutrient supply to plants for a specific goal (e.g., plant production for food, fiber, energy, or landscape esthetics) while protecting natural resources and environmental quality.

*See also:* Air: Greenhouse Gases from Agriculture. Edaphic Soil Science, Introduction to. Mineral Nutrition and Suppression of Plant Disease. Precision Agriculture: Irrigation. Soil: Nutrient Cycling. Water: Water Quality and Challenges from Agriculture

## References

- Albrecht, W.A., Walters, C., 1996. *The Albrecht Papers: Vol I, Foundation Concepts*. Kansas City: Acres U.S.A., Incorporated.
- Baker, J.L., Laffen, M., 1982. Effects of corn residue and fertilizer management on soluble nutrient runoff losses. *Transactions of the American Society of Agricultural Engineers* 25, 311–348.
- Bear, F.E., Prince, A.L., 1945. Cation-equivalent constancy in alfalfa 1. *Agronomy Journal* 37, 217–222.
- Bear, F.E., Toth, S.J., 1948. Influence of calcium on availability of other soil cations. *Soil Science* 65, 67–74.
- Binford, G.D., Blackmer, A.M., El-Hout, N.M., 1990. Tissue test for excess nitrogen during corn production. *Agronomy Journal* 82, 124–129.
- Chen, L., Kost, D., Dick, W.A., 2008. Flue gas desulfurization products as sulfur sources for corn. *Soil Science Society of America Journal* 72, 1464–1470.
- Cordell, D., Drangert, J.-O., White, S., 2009. The story of phosphorus: Global food security and food for thought. *Global Environmental Change* 19, 292–305.
- Dawson, C.J., Hilton, J., 2011. Fertiliser availability in a resource-limited world: Production and recycling of nitrogen and phosphorus. *Food Policy* 36, S14–S22.
- Epstein, E., 1994. The anomaly of silicon in plant biology. *Proceedings of the National Academy of Sciences of the United States of America* 91, 11–17.
- Epstein, E., Bloom, A.J., 2005. *Mineral Nutrition of Plants: Principles and Perspectives*. Sunderland, MA: Sinauer Associates.
- Erismann, J.W., Sutton, M.A., Galloway, J., Klimont, Z., Winiwarter, W., 2008. How a century of ammonia synthesis changed the world. *Nature Geoscience* 1, 636–639.
- Havlin, J.L., Beaton, J.D., Tisdale, S.L., 2005. *Soil Fertility and Fertilizers: An Introduction to Nutrient Management*. Upper Saddle River, NJ: Pearson Prentice Hall.
- Jungk, A., 2009. Carl Sprengel – The founder of agricultural chemistry: A reappraisal commemorating the 150th anniversary of his death. *Journal of Plant Nutrition and Soil Science* 172, 633–636.
- Kopittke, P.M., Menzies, N.W., 2007. A review of the use of the basic cation saturation ratio and the "ideal" soil. *Soil Science Society of America Journal* 71, 259–265.
- Lookman, R., Jansen, K., Merckx, R., Vlassak, K., 1996. Relationship between soil properties and phosphate saturation parameters a transect study in northern Belgium. *Geoderma* 69, 265–274.
- McGrath, S.P., Zhao, F.J., 1995. A risk assessment of sulphur deficiency in cereals using soil and atmospheric deposition data. *Soil Use and Management* 11, 110–114.
- NADP, 2008. *National Atmospheric Deposition Program 2007 Annual Summary. NADP Data Report 2008–01*. Champaign, IL: Illinois State Water Survey, University of Illinois at Urbana-Champaign.
- Peck, T.R., Soltanpour, P.N., 1990. *The principles of soil testing. Soil Testing and Plant Analysis*. Madison, WI: Soil Science Society of America.
- Raun, W.R., Johnson, G.V., 1999. Review & interpretation. *Agronomy Journal* 91, 357–363.
- Sawyer, J., Nafziger, E., Randall, G., et al., 2006. *Concepts and Rationale for Regional Nitrogen Rate Guidelines for Corn*. Ames, IA: Iowa State University, University Extension.
- Stanford, G., 1973. Rationale for optimum nitrogen fertilization in corn production. *Journal of Environmental Quality* 2, 159–166.
- Stewart, W.M., Dobb, D.W., Johnston, A.E., Smyth, T.J., 2005. The contribution of commercial fertilizer nutrients to food production. *Agronomy Journal* 97, 1–6.
- Tilman, D., Cassman, K.G., Matson, P.A., Naylor, R., Polasky, S., 2002. Agricultural sustainability and intensive production practices. *Nature* 418, 671–677.
- Van der Zee, S.E.A.T.M., van Riemsdijk, W.H., 1988. Model for long-term phosphate reaction kinetics in soil. *Journal of Environmental Quality* 17, 35–41.
- Webster, D., Everett, E., 1851. *The Works of Daniel Webster Biographical memoir [by Edward Everett] and speeches on various occasions*. Boston: C.C. Little and J. Brown.

## Relevant Websites

- <http://www.ipni.net/>  
International Plant Nutrition Institute.
- <http://nue.okstate.edu>  
Oklahoma State University.
- <http://www.nrcs.usda.gov/wps/portal/nrcs/main/national/landuse/crops/npm/>  
USDA-NRCS.