Plant Nutrients and Soil Fertility Management

10

Seventeen chemical elements such as C, H, O, N, P, S, K, Ca, Mg, Fe, Mn, Cu, Mo, B, Zn, Cl, and Ni have so far been recognized as essential for plants. Plants cannot complete their life cycles and accomplish normal physiological functions in the absence of these nutrients. Growth and yield of crops are reduced by their deficiencies. There are some other elements, namely, sodium (Na), silicon (Si), vanadium (V), iodine (I), and cobalt (Co), reckoned to be beneficial for growth of certain plants and microorganisms. Plants often suffer from inadequate supply of nutrients by the soil. These inadequacies are met by the application of fertilizers. Fertilizers are any materials added to soils or plant leaves to supply nutrients. There are various natural and synthesized materials used as fertilizers. Composts, farmyard manures, poultry manure, oilcakes, guano, etc. are very good organic fertilizers obtained from natural materials. These substances contain low concentrations of nutrients; so they are needed in huge amounts. Moreover, their composition is not fixed; and estimating their required amounts is difficult. If added in adequate amounts and well ahead of time, they give good results. Industrial fertilizers are soluble, fast acting, and high analysis materials. They contain nutrients in available forms, and therefore, they are very efficient in correcting current deficiencies. Nutrients may be lost from applied fertilizers, especially nitrogenous fertilizers. Some nitrates and phosphates are transported from agricultural lands to surface and groundwater reservoirs. These contaminants have tremendous environmental impacts. Slow-release N fertilizers are being used to minimize loss of nitrogen from crop fields. There are some methods of fertilizer application that might reduce nutrient losses.

10.1 Soil Fertility Is the Capacity of Soils to Supply Plant Nutrients

Soil fertility may be defined as the ability of a soil to supply plant nutrients in available forms, in adequate amounts required for normal growth and reproduction of plants, and the absence of any toxicity. A soil having these qualities is a fertile soil. A soil lacking these qualities is a non-fertile (or poorly fertile) soil. Soil fertility is a state of the soil that is created by the complex interactions of physical, chemical, and biological properties. Sandy soils are poorly fertile; sands hold fewer and leach out more nutrients. Well-structured soils are more fertile; plant roots can extend to, and draw nutrients from, larger volume of soil here. Soils containing high amount of easily weatherable minerals, dominance of 2:1 type of clay minerals, a pH around 6.5, high cation exchange capacity, high base saturation percentage, high organic matter content, and absence of acidity, alkalinity, salinity, sodicity, and pollution are usually fertile. A fertile soil has a high biological activity.

However, nutrient is one of the factors of plant growth. Plants have some other demands on soil (such as water, oxygen, and warmth) as well. If the soil has the capacity to meet all these demands of plants satisfactorily, it is a productive soil. A fertile soil is, therefore, not always productive. Soil fertility is different from soil productivity. Soil productivity is the ability of a soil to produce desired yield of crops under optimum management. Soil fertility is one of the elements of soil productivity.

10.2 A Nutrient Is a Chemical Element Needed for Normal Growth and Reproduction of Plants

A plant nutrient (also known as an essential element or a nutrient element) is a chemical element, without which normal growth and reproduction of plants are not possible. Arnon and Stout (1939) proposed three criteria for an element to be essential for plants:
1. A given plant must not be able to complete its life cycle without the element.
2. The function of the element must not be replaceable by another element.
3. The element must be directly involved in plant metabolism—for example, as a component of an essential plant

constituent such as an enzyme—or it must be required for a distinct metabolic step such as an enzyme reaction. Although plant tissues may contain more than 90 chemical elements, only 17 elements strictly meet these criteria and are established as plant nutrients. These elements are grouped into major elements or macronutrients and minor elements or micronutrients, depending on the relative amounts of requirement. Macronutrients are needed in large amounts (>1,000 mg kg^{-1} shoot dry matter) and micronutrients (<100 mg kg^{-1} shoot dry matter) are needed in relatively small amounts (Marschner 1993). Otherwise, macro- and micronutrients are equally important in plant physiology.
Macronutrients: C, H, O, N, P, S, K, Ca, and Mg
Micronutrients: Fe, Mn, Cu, Mo, B, Zn, CI, and Ni

Besides these, Si, I, V, Co, and Na have been established as micronutrients and beneficial elements for some plants (Marschner 1993; Brady and Weil 2002). Beneficial elements are not actually essential for plants but their presence enhances growth.

10.2.1 Nitrogen Constitutes Chlorophyll, Proteins, Enzymes, Nucleic Acids, and Many Other Compounds in Plant

Plants can take up nitrogen both as NH_4^+ and NO_3^- by roots from soil. Ammonium is readily assimilated into amino acids. Nitrate is mobile; it is translocated via the xylem to the shoots. Whether in root or shoot, it must be reduced to ammonia to be suitable for assimilation. Reduction of nitrate to ammonia by plants occurs in two steps; in the first step, nitrate is reduced to nitrite by the enzyme nitrate reductase, and in the second step, the nitrite is reduced to ammonia by the enzyme nitrite reductase. It is referred to as assimilative nitrate reduction which leads, through amination and transamination, to the formation of organic compounds, including amino acids, proteins, nucleic acids, alkaloids, growth regulators, etc. The key reactions of assimilation include formation of the two amino acids glutamate and aspartate and their amides, glutamine and asparagine.

Some organisms, mostly bacteria and actinomycetes, are capable, either freely or symbiotically with higher plants, of utilizing gaseous nitrogen. N_2 is reduced to NH_3 in cells of the organisms; this NH_3 is eventually transformed into amino acids. Nitrogen, thus fixed, finds its way to the soil after death of the organisms. This is known as biological nitrogen fixation.

Nitrogen is the element needed by plants usually in the largest amount (1 to >3% of plant on dry weight basis) after C, H, and O. It is a constituent of the chlorophyll molecule, which gives plants the green color and an ability to convert solar energy into chemical energy through the process of photosynthesis. Using solar energy, plants fix atmospheric CO_2 and produce the primary food material glucose. Nitrogen is a constituent of other important biomolecules such as amino acids, proteins, nucleic acids (RNA and DNA), nucleoproteins, etc. Nitrogen is a necessary component of several vitamins, for example, biotin, thiamine, niacin, and riboflavin. It is a constituent of all enzymes. Therefore, nitrogen plays a key role in all metabolic activities of plants. Protein is a constituent of protoplasm, and nucleic acids build up the genetic materials. So, nitrogen is linked with both vegetative growth and reproduction of plants. Nitrogen enhances vegetative growth by increasing cell division leading to increased leaf numbers, stem elongation, branching, and flowering. Plants with adequate nitrogen look healthy and deep green.

10.2.1.1 Nitrogen Deficiency
Due to reduced synthesis of chlorophyll, nitrogen deficient plants show chlorosis (yellowing) of the leaves. Nitrogen is very mobile within the plant, and so yellowing starts first on older leaves, with progressively younger leaves yellowing as the deficiency becomes more severe. Nitrogen deficient plants become stunted, produce fewer branches and leaves. N-deficient crops may reach maturity earlier (early flowering and fruiting) than plants with adequate N. N-deficient crops give lower yields.

10.2.1.2 Excess Nitrogen
Excess N may cause plants to grow profusely, but at the same time may delay initiation of flowering or fruiting, which results in lower yields. Excess N can also encourage tender and succulent plant growth that may be more susceptible to certain plant diseases and insects. Plants with excess N may also be more susceptible to lodging and breakage than plants with normal N supply. There may be increased sensitivity of N-deficient plants to low temperature. Therefore, application of nitrogen in excess of normal requirement may decrease yield. Quality of crops is also affected by excess nitrogen. For example, Takano (2003) observed reduction of sugar content in fruits of peach due to excess nitrogen application.

10.2.2 Phosphorus Constitutes Nucleic Acids, Phospholipids, and Phosphoproteins

Phosphorus is required in lower amounts than other macronutrients; it ranges between 0.1 and 0.5% in plant leaf dry weight. It is an essential constituent of several compounds, including nucleic acids (DNA and RNA), phosphoproteins, phospholipids, sugar phosphates, enzymes, and energy-rich phosphate compounds. These substances control photosynthesis, respiration, cell division, and many other plant growth processes. Primarily P is involved in energy transfer through high-energy phosphate compounds ADP and ATP during metabolic reactions. Phosphorus is a vital component of the

building blocks of genes and chromosomes that carry hereditary traits from one generation to the next. Phosphorus is also a component of phytin, a major storage form of P in seeds. About 50% of the total P in legume seeds and 60–70% in cereal grains is stored as phytin or closely related compounds. Phosphorus is critical in the early developmental stages of growth. It stimulates seed germination, young root formation, seedling growth, flowering, fruiting, and seed development. It enhances maturity.

10.2.2.1 Phosphorus Deficiency

Phosphorus deficiency reduces leaf expansion, leaf surface area, and number of leaves. Phosphorus deficiency reduces shoot and root growth. Generally, inadequate P slows the processes of carbohydrate metabolism including photosynthesis and respiration, which results in a buildup of carbohydrates and the development of a dark green leaf color. Other effects of P deficiency on plant growth include delayed maturity; reduced quality of forage, fruit, vegetable, and grain crops; and decreased disease resistance. Phosphorus-deficient tomato leaves develop a purple color. Leaf edges often turn scorched brown in deficiency of phosphorus. An inadequate supply of P can reduce seed size, seed number, and viability.

10.2.2.2 Excess Phosphorus

Excess P may induce K and micronutrient deficiency, particularly of iron and zinc.

10.2.3 Sulfur Constitutes Some Proteins and Activates Many Enzymes

Sulfur ranges from 0.1 to 0.5% of the plant leaf dry weight. It is a component of the amino acids cysteine, cystine, and methionine. They are highly significant in the structure and function of proteins. Sulfur activates some enzyme systems and it is a component of some vitamins. Plants contain a large variety of other organic sulfur compounds, namely, thiols and sulfolipids, and secondary sulfur compounds, namely, allins, glucosinolates, and phytochelatins. These compounds play an important role in physiology and protection against environmental stress and pests. Sulfur promotes nodulation in legumes. It catalyzes chlorophyll production. Sulfur compounds are also of great importance for food quality and for the production of phyto-pharmaceutics. Sulfur is contained in some oil glycosides, which impart characteristic odor and taste in such plants as mustard, onions, and garlic. Sulfur increases oil contents in seeds of soybean and flax. Canola seed contains up to five times the sulfur concentration of cereals. Sulfur can, in some crops, effectively reduce copper toxicity by creating Cu–S complexes.

10.2.3.1 Sulfur Deficiency

The classic symptom of S deficiency is a paleness of the younger foliage. However, often all of the foliage has a pale green color. Leaf yellowing is also caused by nitrogen deficiency, but in nitrogen deficiency, older leaves are yellowed first. In some cases, the leaf veins may be lighter in color than the surrounding tissue. Sulfur deficiency symptoms in canola include poor seed development. Sulfur deficiency delays maturity and produces mature pods on green stems, with poor seed development within the pod.

10.2.3.2 Excess Sulfur

Sulfur toxicity rarely occurs. Excess sulfate-S (SO_4^-) can reduce the uptake of some anions such as nitrate (NO_3^-) and molybdate (MoO_4^-).

10.2.4 Potassium Activates Many Enzymes, Enhances Carbohydrate and Protein Synthesis, and Acts as an Osmoregulator

Potassium is not found in any organic or structural compounds of the plant body; it is still involved in the synthesis of hundreds of organic compounds in plant cell. Potassium acts chiefly in enzyme activation, gas exchange, and osmotic regulation. It is associated with the activation of more than 60 different enzymes related to carbon, nitrogen, and phosphorus metabolism. Potassium enhances carbohydrate and protein synthesis. Potassium ions in vacuoles of plant cells regulate the osmotic potential of the cells and tissues and control the movement of water and solutes. Potassium ions in the guard cells regulate opening and closing of stomata, thereby controlling CO_2, O_2, and H_2O vapor exchange with the atmosphere during photosynthesis, respiration, and transpiration, respectively.

The benefits of proper K nutrition include improved disease resistance, vigorous vegetative growth, increased drought tolerance, improved winter hardiness, and decreased lodging.

Potassium enhances disease resistance in plants by strengthening stalks and stems, contributes to a thicker cuticle in leaf which guards against disease and water loss, controls the turgidity within plants to prevent wilting, and enhances fruit size, flavor, texture, and development.

10.2.4.1 Potassium Deficiency

Some crops exhibit characteristic deficiency symptoms when adequate amounts of K are not available. Potassium deficiency symptoms differ considerably among plants. For example, in cotton, yellowish or bronze mottling of leaves in the beginning and yellowish-green, brown specks at tip around margin and between veins afterward occurs due to K deficiency. As deficiency continues, whole leaf becomes reddish brown, dies, and sheds prematurely.

Plants become short with fewer, smaller bolls or short, weak fibers. In soybean, firing of tips and margins of lower leaves (yellowing, browning, and chlorosis along leaf margins) is a common symptom. Generally, potassium deficiency causes stunted growth with smaller dense leaves. Starting with the older leaves, the leaf tips and edges turn scorched brown and leaf edges roll. In corn, margins of the lower leaves turn brown. In some other plants, white spots and yellowing of edges of lower leaves occur. Leaf tips may be scorched.

Potassium-deficient crops are slow growing and possess poorly developed root systems. Lodging of cereal crops such as corn and small grain is common. Seeds are small and shriveled due to K deficiency. Fruits are often lacking in normal coloration and are low in sugar content.

Symptoms of K deficiency may sometimes be easily confused with deficiency symptoms for sulfur, magnesium, and zinc.

10.2.4.2 Excess Potassium
Excess potassium may cause calcium and magnesium deficiencies.

10.2.5 Calcium Is a Constituent of Cell Wall and Activator of Many Enzymes

Calcium is an intracellular regulator of plants. It regulates plant structure and functions as a constituent of cell wall and cell membrane, as activator of enzymes, and as modulator of plant growth hormones (Hepler 2005). Calcium is a constituent of plant cell wall; as calcium pectate in the middle lamella, it increases cell wall strength and thickness. Calcium produces strong structural rigidity by forming cross-links within the pectin polysaccharide matrix. It controls permeability of cell membranes and regulates movement of ions and metabolites in plants. It helps in translocations of carbohydrates and amino acids. It increases cell division and elongation; it is needed for normal mitosis, and it is involved in chromatin or mitotic spindle organization. It is essential for continued growth of apical meristem. It is an activator of several enzymes, including phospholipase, arginine kinase, adenosine triphosphatase, adenyl kinase, and amylase. It influences activities of plant growth hormones; it retards the activity of auxins and enhances cytokinin. Calcium enhances nitrate uptake.

Calcium retards senescence of leaf and abscission of flowers and fruits. It promotes cotyledon expansion.

10.2.5.1 Calcium Deficiency
Calcium is not usually a limiting nutrient. However, there are several defects that can be associated with low levels of Ca, including poor root development, leaf necrosis and curling.

In extremely acidic soils, calcium deficiency may occur in some agronomic crops. The new leaves become often chlorotic in corn. Many fruits and vegetables demonstrate dramatic symptoms such as black heart in celery and broccoli, tip-burn in lettuce and cabbage, white heart or hollow heart in cucurbits, blossom end rot in tomatoes. Tree fruit with low calcium will exhibit increased storage problems such as bitter pit in apples, cork spot in apples and pears, and cracking in cherries.

10.2.5.2 Excess Calcium
Calcium has little toxic effects on plants. Most of the problems caused by excess soil Ca are the result of secondary effects of high soil pH. Excess Ca may cause reduced uptake of other nutrients such as P, K, Mg, B, Cu, Fe, and Zn.

10.2.6 Magnesium Is a Constituent of Chlorophyll and Activator of Many Enzymes

Magnesium is the central element of the chlorophyll molecule which is responsible for the fixation of solar energy into chemical energy and the production of food materials such as $C_6H_{12}O_6$ from CO_2 and H_2O. Magnesium is both an enzyme activator and a constituent of many enzymes, including those required in carbohydrate, protein, nucleic acid, and lipid metabolism.

Magnesium is needed for storage and translocation of such important plant constituents as carbohydrates, proteins, and fats. It regulates the energy balance of plants; it facilitates reactions between enzymes and ATP. It is a component of pectin, important for stability of cells, and phytin, an energy-rich phosphate store important for seed germination. It is an integral part of ribosomes and the cell matrix. It aids in stabilization of cell membranes. It is required for cell wall synthesis. It enhances P translocation, nitrogen fixation, and iron utilization. Magnesium increases the concentration of vitamin C in fruits. It increases the nutritional quality of frozen vegetables.

10.2.6.1 Magnesium Deficiency
Interveinal chlorosis of the older leaves is the classic symptom of Mg deficiency in plants. In the beginning, a pale green color appears, becoming more pronounced in the older leaves. In some plants, the leaves will curl upward and may also turn red-brown to purple in color. Chlorotic spots between leaf veins, necrosis (dead spots), and red discoloration of stems occur during prolonged periods of deficiency. Magnesium deficiency may be confused with zinc or chlorine deficiencies, viruses, or natural aging since all have similar symptoms.

10.2.6.2 Excess Magnesium

Magnesium toxicity is not generally seen. Crops grown on heavy montmorillonite clay soils that have been poorly fertilized with potassium may exhibit excesses of magnesium in their tissue. Higher tissue levels of magnesium are usually found in the older leaves. High Mg levels may induce K deficiency.

10.2.7 Iron Acts in Electron Transfer in Plant Body

Some plants need more Fe (>0.1%) than others; it is a macronutrient for these plants. Otherwise plants need <0.1% Fe. Iron is, therefore, generally placed in the middle of the macro- and micronutrients. It has many important physiological functions, the most important of which appears to be the exchange of electrons during biochemical reactions.

Two major groups of proteins—the heme proteins and the Fe–S proteins—contain iron. The heme proteins contain a heme iron–porphyrin complex, which acts as a prosthetic group of the cytochromes. Cytochromes are electron acceptors–donors in respiratory reactions. There are some other heme proteins such as catalase, peroxidase, and leghemoglobin. Catalase catalyzes the conversion of hydrogen peroxide into water and O_2, whereas peroxidases catalyze the conversion of hydrogen peroxide to water during photorespiration reactions, and in the glycolate pathway. Catalase also protects chloroplasts from free radicals produced during the water-splitting reaction of photosynthesis. Leghemoglobin acts in nitrogen fixation by nodule bacteria. Peroxidases catalyze the polymerization of phenols to form lignin.

10.2.7.1 Iron Deficiency

Iron is needed to form chlorophyll in plants; its deficiency causes chlorosis, usually first in younger leaves. Early symptoms include green leaf veins with yellowish or whitish color between veins. At advanced stage, the newest leaves may become nearly white because leaf veins and areas between veins lack any green or yellowish-green color. Brown, necrotic areas may develop along leaf margins and between veins in severe cases. Affected leaves are generally smaller than normal.

Some woody plants, including azalea, birches, blueberry, dogwood, magnolia, oaks, white pine, rhododendron, and sweet gum, are particularly sensitive to iron deficiency. The most severely affected crops suffering from Fe deficiency are sorghum, corn, and potatoes.

10.2.7.2 Excess Iron

Iron is toxic when it accumulates to high levels usually in strongly acid and waterlogged soils. It can act catalytically via the Fenton reaction to generate hydroxyl radicals, which can damage lipids, proteins, and DNA.

10.2.8 Manganese Acts in Nitrate Assimilation, Hill Reaction, and Electron Transfer

Physiological functions of manganese in plants include synthesis of chlorophyll, maintenance of lamellar structure of the chloroplast, assimilation of carbon dioxide during photosynthesis, assimilation of nitrate, electron transport, mobility of iron, and production of riboflavin, ascorbic acid and carotene. It participates in Hill reaction, where water is split during photosynthesis (Amesz 1993). It is an activator of many enzymes, including oxidases, peroxidases, dehydrogenase, kinases, and decarboxylases. As a constituent of enzymes, it helps in respiration and protein synthesis. It catalyzes oxidation and reduction reactions within plant tissue. Manganese accelerates germination and maturity.

10.2.8.1 Manganese Deficiency

Yellowing of leaves between the veins is the characteristic symptom of Mn deficiency in plants. The veins remain dark green; the color persists even when the chlorotic parts die. Most crops deficient in manganese become yellowish to olive green. Sometimes a series of brown-black specks appear. In small grains, grayish areas appear near the base of younger leaves. In cereals and grasses, grayish or brownish spots and streaks occur in the middle or basal parts of younger leaves. Manganese deficiency symptoms in dicotyledons occur as small yellow spots on the younger leaves, which turn brown or black. The abscission of developing leaves commonly occurs and flower formation is reduced. Stem and root become stunted. Their apices may die back. Flowers are often sterile.

10.2.8.2 Excess Manganese

Manganese toxicity is characterized by raised interveinal areas giving a puckered appearance; red, brown, or black spotting of the older leaves; and an uneven distribution of chlorophyll. If the toxicity continues, the plants will wilt and die prematurely. Plants particularly susceptible to manganese toxicity are lucerne, cabbage, cauliflower, cereals, clover, pineapple, potato, and tomato.

10.2.9 Copper Is a Structural Element in Regulatory Proteins and a Cofactor of Many Enzymes

Copper acts as a structural element in regulatory proteins and participates in photosynthetic electron transport, mitochondrial respiration, oxidative stress responses, cell wall metabolism, and hormone signaling (Marschner 1993). Cu ions act as cofactors in many enzymes such as Cu/Zn superoxide dismutase, cytochrome oxidase, amino oxidase, laccase, plastocyanin, and polyphenol oxidase. At the cellular level,

Cu also plays an essential role in signaling of transcription and protein trafficking machinery, oxidative phosphorylation, and iron mobilization (Yruela 2005). Copper mediated enzyme systems are involved in building and converting amino acids to proteins. Copper is important to the formation of lignin in plant cell walls, which contributes to the structural strength of the cells and the plant.

10.2.9.1 Copper Deficiency

Copper deficiency reduces photosystem I (PSI) electron transport due to decreased formation of plastocyanin (Shikanai et al. 2003). Decrease in photosystem II (PSII) activity was also observed in Cu-deficient chloroplasts. Severe Cu deficiency results in changes in the thylakoid membranes, which can influence the conformation and function of the photosystems.

Typical signs of Cu deficiency appear first at the tips of young leaves and then extend downward along the leaf margins. The leaves may also be twisted or malformed and show chlorosis or even necrosis (Marschner 1993). The death of the growing points often leads to excessive tillering in cereal crops and excessive branching in dicots. Excessive wilting, lodging, and reduced disease resistance result from the weak cell walls caused by Cu deficiency. Reduced seed and fruit yield is caused mainly by male sterility.

10.2.9.2 Excess Copper

Redox cycling between Cu^{2+} and Cu^+ can catalyze the production of highly toxic hydroxyl radicals, with subsequent damage to DNA, lipids, proteins, and other biomolecules. Thus, at high concentrations, Cu can become extremely toxic causing symptoms such as chlorosis and necrosis, stunting, leaf discoloration, and inhibition of root growth (Marschner 1993). Toxicity of Cu may result from (1) binding to sulfhydryl groups in proteins, thereby inhibiting enzyme activity or protein function; (2) deficiency of other essential ions; (3) impaired cell transport processes; and (4) oxidative damage.

Typical toxicity symptoms of copper appear in young tissue and include dark green leaves followed by induced Fe chlorosis in which the leaves may appear nearly white and thick, short, or barbed-wire-looking roots which can be mistaken for chemical damage and depressed tillering.

10.2.10 Molybdenum Regulates Nitrogen Metabolism in Plants

Because of its involvement in the processes of N_2 fixation, nitrate reduction, and the transport of nitrogen compounds, molybdenum plays a crucial role in nitrogen metabolism of plants (Srivastava 1997).

Molybdenum is a constituent of the following enzymes: (1) nitrate reductase which catalyzes the key step in inorganic nitrogen assimilation; (2) aldehyde oxidase(s) that have been shown to catalyze the last step in the biosynthesis of the phytohormone abscisic acid; (3) xanthine dehydrogenase, which is involved in purine catabolism and stress reactions; and (4) sulfite oxidase, which is probably involved in detoxifying excess sulfite (Mendel and Hansch 2002). According to Mishra et al. (1999), nearly all nitrogenases contain the same two proteins, both of which are inactivated irreversibly in the presence of oxygen: an Mo–Fe protein (MW 200,000) and an Fe protein (MW 50,000–65,000). The Mo–Fe protein contains two atoms of molybdenum and has oxidation–reduction centers of two distinct types: two iron–molybdenum cofactors called FeMoco and four Fe–S (4Fe–4S) centers. The Fe–Mo cofactor (FeMoco) of nitrogenase constitutes the active site of the molybdenum-containing nitrogenase protein in N_2-fixing organisms.

10.2.10.1 Molybdenum Deficiency

Nitrates accumulate in Mo-deficient plant leaves and the plant cannot use them to produce proteins. As a result, the plant becomes stunted, with signs similar to those of nitrogen deficiency. The edges of the leaves may become scorched by the accumulation of unused nitrates. The main symptoms of molybdenum deficiency in nonlegumes are stunting and failure of leaves to develop a healthy dark green color. The leaves of affected plants show a pale green or yellowish green color between the veins and along the edges. In advanced stages, the leaf tissue at the margins of the leaves dies. The older leaves are the more severely affected.

In cauliflowers, the yellowing of the tissue on the outer leaves is followed by the death of the edges of the small heart leaves. Narrow, distorted leaves develop; the symptom is known as "whiptail of cauliflower."

10.2.10.2 Excess Molybdenum

Molybdenum toxicity in plants seldom occurs under field conditions. However, marginal leaf scorch and abscission may occur due to molybdenum toxicity. Excess Mo causes yellowing or browning of leaves and depressed tillering. Excess Mo levels in plants are more of a concern to animal life. Overconsumption of plant tissue high in molybdenum can lead to a condition called molybdenosis.

10.2.11 Boron Contributes to Cell Wall Development and Cell Division

Boron functions in cell wall development, cell division, fruit and seed development, sugar transport, and hormone development. Boron is involved in the functioning of meristematic tissues in plants or the cells which are rapidly multiplying. Plants can be separated into four groups based on their B requirement for growth and development: (1) Lactifers

(latex-forming species) have by far the highest B requirement, (2) followed by leguminous plants, (3) then the remaining dicots and the lily family of monocots, and (4) finally the graminaceous plants (Bonilla et al. 2009).

Boron forms boron–polysaccharide complex in cell walls indicating boron cross-linking of pectin polymers. Boron is involved in membrane processes. Rapid boron-induced changes in membrane function could be attributed to boron-complexing membrane constituents. Boron may affect metabolic pathways by binding apoplastic proteins to *cis*-hydroxyl groups of cell walls and membranes and by interfering with manganese-dependent enzymatic reactions (Blevins and Lukaszewski 1998). In addition, boron counteracts toxic effects of aluminum on root growth of dicotyledonous plants.

10.2.11.1 Boron Deficiency

Boron deficiency is a widespread problem for field crop production where large losses of yield occur annually both quantitatively as well as qualitatively. In China 40% yield losses are due to boron deficiency (Goldbatch et al. 2007). Significant losses of yield or quality resulting from boron deficiency may occur as well in vegetable crops.

10.2.11.2 Excess Boron

Physiological effects of boron toxicity in plants include reduced root cell division, decreased root and shoot growth, reduced leaf chlorophyll, inhibition of photosynthesis, lower stomatal conductance, deposition of lignin and suberin, reduced proton extrusion from roots, increased membrane leakiness, peroxidation of lipids, and altered activities of antioxidation pathways (Reid 2007).

Boron toxicity is characterized by yellowing of the leaf tips, interveinal chlorosis, and progressive scorching of the leaf margins. In soybeans, the leaves may have a rust-like appearance.

10.2.12 Zinc Is a Constituent of All Six Classes of Enzymes

All six enzyme classes of enzymes (oxidoreductases, transferases, hydrolases, lyases, isomerases, and ligases) contain zinc. There are structural, catalytic, and cocatalytic Zn-binding motifs in plants. Cysteine is the preferred ligand in structural Zn sites. In catalytic sites, Zn forms complexes with histidine and water. Cocatalytic sites have aspartic acid and histidine as preferred ligands. The fourth type of Zn-binding site (protein interface) suggests a role of Zn in the quaternary protein structure (Auld 2001). The enzyme carbonic anhydrase is found in cytosol and chloroplasts; it catalyzes the reversible hydration of CO_2. It can have 2, 4, 6, or 8 units, each with one Zn atom coordinated to histidine residues at the active site.

Zn metalloproteins are regulators of gene expression. A Zn-finger lateral shoot-inducing factor increases lateral shoot growth by altering cytokinin concentrations in petunia, tobacco, and Arabidopsis (Nakagawa et al. 2005). Zinc is needed for growth hormone, seed and grain production, protein synthesis, maturation of seed, and growth of stalks and height of plants.

10.2.12.1 Zinc Deficiency

Plants become stunted and leaves become dusty brown in Zn deficiency. White area develops between the veins. Leaves become characteristically undersized, sharp, small, and pointed in Zn deficiency. Decreased tillering, spike or spikelet sterility and interveinal chlorosis develop on leaves. White bud forms in corn due to Zn deficiency. Loss of leaf luster and death of shoots often occur in dicots.

10.2.12.2 Excess Zinc

Wang et al. (2009) conducted an experiment on the effect of excess Zn on mineral nutrition and antioxidative response in rapeseed (*Brassica napus*) seedlings. They observed significantly lower concentrations of P, Cu, Fe, Mn, and Mg and increased lipid peroxidation in excess supply of Zn. NADH oxidase and peroxidase activity increased, but superoxide dismutase, catalase, and ascorbate peroxidase activities decreased in leaves and roots of plants under high Zn. In their opinion, excess Zn exerts its toxicity partially through disturbing nutrient balance and inducing oxidative stress in plants. Cui and Zhao (2011) also observed similar changes in enzyme activity in corn (maize, *Zea mays*) growing in Zn contaminated soils.

10.2.13 Chlorine Controls Stomatal Opening and Internal Water Balance

Chlorine is essential for the functioning of the stomatal openings, which control internal water balance. It functions in photosynthesis, specifically during the Hill reaction and in maintenance of cation balance and transport within the plant. Chlorine aids in sugar translocation in plants. It controls water use efficiency in plants. It enhances crop maturity. It helps in disease control (Chen et al. 2010). Several enzymes such as ATPase, alpha amylase, and asparagine synthetase require Cl for stimulation or activation (Power and Prasad 1997).

10.2.13.1 Chlorine Deficiency

Chlorine deficiency symptoms include wilting due to restricted and highly branched root system often with stubby tips. Chlorine deficiency is characterized by leaflet wilting, followed progressively by chlorosis, bronzing, and finally, necrosis. Chlorine deficiency in cabbage is marked by an absence of the cabbage odor from the plant.

10.2.13.2 Excess Chlorine

Leaf/leaflet size is reduced and may appear to be thickened. Leaf margins are scorched and abscission is excessive. Overall plant growth is reduced. Chloride accumulation is higher in older tissue than in newly matured leaves.

10.2.14 Nickel Is a Component of a Number of Enzymes

Nickel may stimulate germination and growth of various crop species. Nickel functions in urea metabolism, and it may also be required in low concentrations by legumes dependent on symbiotically fixed nitrogen either for the growth of *Rhizobium* or for the utilization of fixed nitrogen or both.

Ni has been identified as a component of a number of enzymes, including glyoxalases, peptide deformylases, methyl-CoM reductase, and ureases, and a few superoxide dismutases and hydrogenases. Therefore, Ni plays a role in various important metabolic processes, including ureolysis, hydrogen metabolism, methane biogenesis, and acetogenesis (Collard et al. 1994).

10.2.14.1 Nickel Deficiency

Nickel deficiency is becoming increasingly apparent in crops, especially for ureide-transporting woody perennials. In an experiment on pecan (*Carya illinoinensis*), Bai et al. (2006) observed that foliage of Ni-deficient pecan seedlings exhibited disruption of nitrogen metabolism via ureide catabolism, amino acid metabolism, and ornithine cycle intermediates. Disruption of ureide catabolism in Ni-deficient foliage resulted in accumulation of xanthine, allantoic acid, ureidoglycolate, and citrulline, but total ureides, urea concentration, and urease activity were reduced. Disruption of amino acid metabolism in deficient foliage resulted in accumulation of glycine, valine, isoleucine, tyrosine, tryptophan, arginine, and total free amino acids and lower concentrations of histidine and glutamic acid. Ni deficiency also disrupted the citric acid cycle. Disruption of carbon metabolism was also via accumulation of lactic and oxalic acids. It appears that mouse-ear, a key morphological symptom, is likely linked to the toxic accumulation of oxalic and lactic acids in the rapidly growing tips and margins of leaflets.

10.2.14.2 Excess Nickel

Ni-toxicity symptoms include the formation of Ni^{2+}-organic acid and Ni^{2+}-NA complexes, the overproduction of NA, and high levels of free histidine. Other responses include the induction of MTs and thiol glutathione and high concentrations of glutathione, cysteine, and O-acetyl-L-serine. In addition, some enzyme activities may be enhanced such as serine acetyltransferase and glutathione reductase.

At high concentrations, nickel inhibits shoot and root growth for which plants become stunted. Excess Ni has been reported to cause leaf necrosis and chlorosis of plants. Chlorosis and along-vein necrosis appeared in newly developed leaves of water spinach by the application of excess Ni. Some plants accumulate very high concentration of Ni in their shoots without showing any toxicity symptoms. They are Ni-hyperaccumulators.

More than 310 Ni-hyperaccumulator plants have been identified, including members of the families Acanthaceae, Asteraceae, Brassicaceae, Caryophyllaceae, Fabaceae, Flacourtiaceae, Meliaceae, Myristicaceae, Ochnaceae, Poaceae, Rubiaceae, Sapotaceae, and Stackhousiaceae; Brassicaceae contains 60 Ni-hyperaccumulators capable of accumulating as high as 3% nickel (Chen et al. 2009).

10.3 There Are Positive and Negative Interactions of Nutrients in Plant

Two or more nutrients may interact in plants. Nutrient interactions are generally measured in terms of growth response and change in concentration of nutrients. When an increase in crop yields by the addition of two nutrients is more than adding only one, the interaction is positive (synergistic). If adding the two nutrients together produces fewer yields than the individual ones, the interaction is negative (antagonistic). When there is no change, there is no interaction. A nutrient may interact simultaneously with more than one nutrient. This may induce deficiencies, toxicities, modified growth responses, and/or modified nutrient composition. However, most interactions are complex (Fageria 2001). Nutrients interact for many different reasons. Some nutrients follow the same absorption pathway, some may compete for the same nutrient carrier, some nutrients may activate the biochemical reactions of others, and some nutrients may enhance the permeability of membranes that increase the movement of other nutrients. For example, N enhances photosynthesis that increases assimilation of P and S. Interactions of phosphorus with nitrogen, potassium, zinc, and copper frequently occur in crops. In these cases, the addition of one nutrient without the second may not improve growth. There are nonspecific and specific interactions between mineral nutrients in plants. A typical example of a nonspecific interaction is between nitrogen and phosphorus. Two examples of specific interaction are provided by Marschner (1993) as (a) competition between potassium and magnesium at the cellular level, which usually involves the risk of potassium-induced magnesium deficiency and (b) replacement of potassium by sodium in natrophilic species. Interactions vbetween two mineral nutrients are important when the contents of both are near the deficiency range. Increasing the supply of only one

mineral nutrient stimulates growth, which in turn can induce a deficiency of the other by a dilution effect. In principle, these unspecific interactions hold true for any mineral nutrients with contents at or near the critical deficiency contents (Marschner 1993). Optimal ratios between nutrients in plants are therefore often as important as absolute contents. For example, a N/S ratio around 17 is taken to be an index of optimum nutrition of both the nutrients. Critical nutrient ratios have been proposed for some nutrients, particularly N/P, N/K, N/S, Ca/Mg, etc. However, using nutrient ratios has also been criticized because the same nutrient ratio may be obtained when both nutrients are sufficient, when both nutrients are deficient, and when one of them is deficient (Sect. 10.21.2.2).

10.4 Plants Absorb 14 Nutrients from the Soil

Plants get C from CO_2, O from O_2 and H_2O, and H from H_2O. They absorb other nutrients in ionic forms from soil. Plants can absorb nutrients as ions present in soil solution and as exchangeable ions on soil colloids. These absorbable forms are called available nutrients in soil. The available forms of different nutrients are given in Table 10.1.

Of the 14 nutrients absorbed by plants from soil, three (N, P, and K) are commonly deficient because they are removed from soil by crops in greater amounts. Some other nutrients (Mg, S, Zn, B, and Mn) may as well sometimes be deficient. Nutrient deficiencies are more common in regions with highly weathered soils (Oxisols and Ultisols), and in high rainfall areas (humid tropical). Iron, zinc, copper, and manganese deficiencies often occur in calcareous (Calcids, Calcisols) and limed soils. In acidic soils, Ca, Mg, P, and Mo and, in alkaline soils, Fe, Mn, and Zn may be deficient.

Table 10.1 Available forms of plant nutrients

Elements	Available forms
N	NH_4^+, NO_3^-, N_2[a]
P	$H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}
S	SO_4^{2-}
K	K^+
Ca	Ca^{2+}
Mg	Mg^{2+}
Fe	Fe^{2+}, Fe^{3+}
Mn	Mn^{2+}
Cu	Cu^{2+}
Mo	MoO_4^{2-}
B	H_3BO_3, BO_3^-, $B_4O_7^{2-}$
Zn	Zn^{2+}
Cl	Cl^-
Ni	Ni^{2+}

[a]Some microorganisms can utilize N_2 as a nutrient

10.4.1 Soils Should Supply Adequate Nutrients to Plants for Optimum Growth

Soils must supply plants with nutrients adequate for their normal growth and yield. But the concept of "adequate nutrient supply" is itself arbitrary. All plants do not need the same amount of any nutrient; plants widely differ in their requirements of nutrients; and even the same plant needs different amounts of nutrients at different stages of growth. Moreover, two different soils with the same nutrient level would supply different amounts of nutrients to plants if there are differences in physical and chemical conditions of the soils that affect root growth and nutrient uptake. So, a generalization of "adequate nutrient level" is difficult. However, 1.0 mg kg^{-1} extractable Cu, Mn, and Zn and 4.5 mg kg^{-1} Fe in soil were considered adequate by McKenzie (1992). Tamimi et al. (1997) proposed adequate levels of available P, K, Ca, and Mg for soils of Hawaii (Table 10.2).

10.4.2 Nutrients in Soil May Be Available or Unavailable to Plants

A nutrient can be present in soil in the following forms: dissolved in soil solution (soil water with dissolved ions, salts, acids, and bases), exchangeable cations and anions on soil colloidal surfaces, insoluble compounds, soil organic matter, and soil minerals. Sum of all these forms is the total nutrient content. As pointed out earlier, only the soluble and exchangeable forms constitute the available nutrient. Available nutrients in soil are extracted with various extractants; common extractants are dilute solutions of salts, acids, alkalis, or their mixtures. A small proportion of total nutrient is available to plants. For example, total P content in soils may lie between <400 and >1,000 mg kg^{-1}, but available P usually remains below 25 mg kg^{-1} (only 2.5–5% of total). Plants obtain nutrients readily from the soil solution. The concentration of available nutrients in soil solution and the replenishing of the soil solution in the rhizosphere are of tremendous importance to plant nutrition. Wild (1996) gives concentrations of some nutrients in soil solution as 5–200 mg L^{-1} NO$_3$–N, 10–100 mg L^{-1} SO$_4$–S, 0.01–0.60 mg L^{-1} H$_2$PO$_4$–P, 10–200 mg L^{-1} Ca^{2+}, 5–100 mg L^{-1} Mg^{2+} and 1–40 mg L^{-1} K$^+$.

Table 10.2 Adequate levels of available nutrients (mg kg^{-1}) in soils of Hawaii

Nutrient	Heavy soils	Light soils
P	25–35	50–85
K	200–300	200–400
Ca	1,500–2,000	3,000–4,000
Mg	300–400	600–800

10.5   Nitrogen Remains Mainly in the Organic Form in Soil

Sources of nitrogen in soil include air, soil solution, soil organic matter, crop residues, animal manure, and fertilizers.

Although air contains about 78% nitrogen, most plants cannot use this element from air. Precipitation brings some nitrogen (5–10 kg ha^{-1}year^{-1}) to the soil as dissolved nitrate and ammonium in rainwater. Some free living bacteria and cyanobacteria have the ability to assimilate atmospheric N$_2$. They utilize nitrogen for their biochemical needs and add nitrogen to the soil after their death. About 1–5 kg ha^{-1}year^{-1} nitrogen may be added to soils in this way. *Rhizobium* can fix about 100–200 kg N ha^{-1}year^{-1} in association with host legumes (Chap. 9).

The most immediate source of nitrogen for plants is the soil solution. It contains very low concentrations of NO$_3^-$ (5–200 mg L^{-1}) and NH$_4^+$. Ammonium ion may also be held on exchange complexes. NO$_3^-$ is very mobile and may easily be leached to the groundwater. The soil solution is continually replenished with NH$_4^+$ and NO$_3^-$ by the mineralization (coupled with ammonification) of organic matter and nitrification of NH$_3$.

More than 90% nitrogen in soil is in the organic form. Proteins, amino acids, and nucleic acids associated with soil organic matter contain nitrogen. Organic nitrogen is slowly mineralized to supply plants with available nitrogen. Often the total N content of soil is a better index of nitrogen supply than available nitrogen. On an average, total N content of soils may range from <0.1 to >0.5%.

Crop residues and animal manures are important sources of nitrogen in soil. The amount of N in these sources depends on their amounts and concentration of N in the residues. Generally, crop residues and animal manures contain 0.5–1.5% N. Organic nitrogen is continually converted into inorganic nitrogen through mineralization. Inorganic nitrogen is also being converted into organic nitrogen through immobilization. Ammonia gets converted into nitrate by nitrification; nitrate is biologically reduced to nitrogen gas through denitrification. Nitrogen gas is bound as organic compounds by biological nitrogen fixation. These processes with the reactions involved have been discussed in Chap. 9 in connection with nitrogen cycling. Volatilization is a chemical transformation of nitrogen which involves the loss of mainly ammonia in soil to the atmosphere. Volatilization usually occurs in soils with pH above 7.5 and in calcareous, saline, and sodic soils. It may occur substantially in wet soils (Chap. 13). These transformations have profound environmental impacts.

10.5.1   Nitrate Leaching from Soils Causes Groundwater Contamination

Nitrate, whatever its sources in soil may be, undergoes the following changes:

1. It may be taken up by plants.
2. It may become incorporated in the soil organic matter, where it will remain unless it is remobilized by soil organisms.
3. It may be leached out of the soil.
4. It may be denitrified.

There is little difference between nitrate from fertilizers and that produced by microbes from organic matter. Very little nitrate is retained in soil, and much added nitrogen fertilizer is lost through leaching and denitrification in some situation. Nitrate leaching results in groundwater contamination, and it has now become a major environmental problem. Concentrations of nitrate increased in many natural waters to alarming levels around major agricultural areas. Health problems related with water contamination of nitrate include the "blue-baby syndrome" of infants and stomach cancers of human (Ewing and White 1951; Deak 1985). Infants and pregnant women are especially vulnerable to health problems from drinking water with nitrate levels above 10 mg L^{-1}. Nitrate levels of up to 3 mg L^{-1} in well water is generally taken to be naturally occurring and safe for drinking. Therefore, some soil management practices to reduce nitrate leaching are essential. The United States Environmental Protection Agency has set the primary drinking water standard for nitrate at 10 mg L^{-1} (USEPA 2007).

10.5.2   Soil Is a Source of Atmospheric Nitrogen Oxides

The term NOx represents the more reactive nitrogen oxides, including nitric oxide (NO) and nitrogen dioxide (NO$_2$). These oxides play a crucial role in the chemistry of the atmosphere. NO and NO$_2$ react with sunlight and unburned gasoline and contribute to the development of photochemical smog. Atmospheric NOx also reacts to produce nitric acid which is very soluble and, along with sulfuric acid, significantly contributes to acid rain. There is another environmentally important oxide of nitrogen, the nitrous oxide (N$_2$O). An increase in N$_2$O in the atmosphere would result in a decrease in the ozone layer. Because it can absorb infrared radiation, the excess production of N$_2$O can contribute to global warming. Concentrations of N$_2$O in the atmosphere are rising exponentially at 0.3%, driven mostly by microbial activity in nitrogen-rich soils associated with agriculture (Hall et al. 2008).

Soils are a major source of atmospheric NOx (Yienger and Levy [1995]). A major part of the global emission of NOx, N_2O, and NH_3 occurs from the soil. Including emissions from animal waste management, about three-quarters of the global emission of NH_3 and N_2O take place from soil. Soils contribute about one-third to the global emission of NOx (and NH_3) and more than 50% to the global atmospheric N_2O budget. The contribution to the global budgets of agricultural soil and land-use-related emissions is 36% for NOx, 31% for N_2O, and 70% to NH_3. In the IPCC ([1992]) assessment, the global N_2O emissions from natural soils were estimated to be in the range 3.2–7.7 Tg N year^{-1}. IPCC ([1995]) estimated the direct contribution from agricultural soils receiving mineral nitrogen fertilizers, manure, and N_2-fixing legumes at 3.5 (1.8–5.3) Tg N year^{-1}.

NOx and N_2O are emitted from soils by the microbial processes of nitrification and denitrification. Some N_2O is produced in soils by a nonbiological process known as chemodenitrification. These processes depend on biogeochemical and physical properties of the soil, including microbial species, soil texture, soil water, pH, redox potential, and nutrient status (Conrad [1996]). Soil emission fluxes are also tightly linked to land-use-management including application of natural and synthetic fertilizers, tillage, irrigation, compaction, planting, and harvesting (Frolking et al. [1998]).

10.6   Phosphorus Is an Element of Agronomic and Environmental Significance

Sources of phosphorus in soil include soil solution, minerals, organic matter, crop residues, manures, and fertilizers. Many factors influence the content of phosphorus in soil. Among these are (1) the type of parent material from which the soil is derived, (2) the degree of weathering, and (3) the climatic conditions. In addition, soil phosphorus levels are affected by erosion, crop removal, and phosphorus fertilization. There are different pools and fractions of phosphorus in soil. These pools and fractions are discussed in the following sections.

10.6.1   Three Major Phosphorus Pools in Soil Include Solution and Active and Fixed Phosphorus

Among the three pools of phosphorus in soil, the solution P pool is relatively small containing only a fraction of a kilogram of P in a hectare of land. Here it mainly remains in the primary orthophosphate form ($H_2PO_4^-$) if the soil is not alkaline. In weakly alkaline conditions, the HPO_4^{2-} ion is dominant, and in strongly alkaline conditions, the PO_4^{3-} ion predominates. Plants absorb P mainly as the primary orthophosphate ion. A vigorously growing crop may quickly deplete the P in the solution pool if it is not being continuously replenished. The active P pool contains P in the solid phase and remains loosely held on particles so that it may be easily released to the soil solution when solution P pool is impoverished. It includes weakly adsorbed P, some calcium and aluminum phosphate compounds, and organic P that is easily mineralized. Because the solution P pool is very small and because P may be frequently released from the active P pool, the active P pool becomes the main source of available P for crops. The ability of the active P pool to replenish the soil solution P pool in a soil is what makes a soil fertile with respect to phosphate. The fixed P pool contains inorganic phosphate compounds that are very insoluble and organic compounds that are resistant to mineralization. Phosphate may remain fixed in soil for a very long time so that it hardly affects the P availability in soil. The inorganic phosphate compounds in this fixed P pool are more crystalline in their structure and less soluble than those compounds in the active P pool. Some fixed P may be converted to the active P pool. There may be an equilibrium between soluble P and active P and between active P and fixed P $\left(\text{soluble P} \Leftrightarrow \text{active P} \Leftrightarrow \text{fixed P}\right)$.

10.6.2   Inorganic Phosphorus Is One Major Fraction of Soil Phosphorus

Inorganic phosphorus in soil consists of P in solution and as insoluble compounds and minerals. The concentration and ionic forms of phosphorus in soil solution that were mentioned above are governed by two types of reactions: precipitation–dissolution (Sect. 8.4.3) and adsorption–desorption processes (Sect. 8.4.4). Some adsorbed phosphate may become trapped on the surface of soil minerals if any Fe or Al oxide coating is precipitated on the mineral. The trapped phosphate is then termed as occluded phosphate (Solis and Torrent [1989]). Most inorganic phosphorus compounds in soils fall into one of two groups: (1) those containing calcium and (2) those containing iron and aluminum (and less frequently, manganese) (Brady and Weil [2002]). Common iron phosphate compounds are strengite ($FePO_4 \cdot 2H_2O$), vivianite [$Fe_3(PO_4)_2 \cdot 8H_2O$], and tinticite [$Fe_6(PO_4)_4(OH)_6 \cdot 7H_2O$]; aluminum compounds are variscite ($AlPO_4 \cdot 2H_2O$), berlinite ($AlPO_4$), and tarakanite [$H_6K_3Al_5(PO_4)_2 \cdot 8H_2O$]; and calcium compounds are fluorapatite [$3Ca_3(PO_4)_2 \cdot CaF_2$], oxyapatite [$3Ca_3(PO_4)_2 \cdot CaO$], carbonate apatite [$3Ca_3(PO_4)_2 \cdot CaCO_3$], and hydroxyapatite [$3Ca_3(PO_4)_2 \cdot CaCO_3$]. Inorganic P represents the dominant component of the soil P in calcareous soils accounting for about 75–85% of total soil P (Jiang and Gu [1989]). Calcareous soils and those developed from phosphate-containing rocks are particularly rich in apatites—the tricalcium phosphates. Apatites are slowly weathered and it very slowly releases phosphorus in soil solution. In highly

weathered well-developed soils, most apatites have been exhausted due to weathering. Long-term fertilizer P addition increases the inorganic P contents significantly in many agricultural soils. The contents of inorganic P fractions in a calcareous soil of China receiving annual fertilizer P application were in the order of Ca_{10}–P > Ca_8–P > Fe–P > Al–P > occluded P > Ca_2–P (Wang et al. 2010).

10.6.3   Organic Phosphorus Is Another Major Fraction

The organic phosphate fraction may account for 50–80% of the total phosphorus in some soils. This fraction represents only a few individual organic phosphorus compounds; the majority is bound to the complex of humus. During fractionation in alkaline solution, some major organic P fractions are identified. These fractions include sugar phosphates (inositol phosphate), phospholipids, and nucleic acids (Tisdale et al. 1997). Inositol phosphate may comprise more than 50% of total organic P in some soils. Phospholipids may range from 1 to 10%. Phosphoglycerides are probably the dominant fraction, but little is known about the other phospholipids in soils. Orthophosphate monoesters are the major functional class of organic P in most soils, of which the higher inositol phosphates are usually dominant (Turner et al. 2002). Orthophosphate diesters dominate organic P inputs to the soil from plants and microbes, but are rapidly degraded upon release and typically represent only a small proportion of the soil organic P (Anderson 1980). Nucleic acids and their derivatives are also present in soils in similar extents to the phospholipids. Both immobilization of inorganic P and mineralization of organic P can occur concurrently in the soil, making the organic P fraction a dynamic entity.

10.6.4   Availability of Phosphorus in Soil Is Governed by Its Chemical Environment

Phosphorus availability depends on several soil conditions. Some of these are the amount of clay, the type of clay (kaolinite and iron oxides retain more P than 2:1 clays), the pH, the soil P, the soil temperature, the compaction, the aeration, the moisture content, the kind and amount of fertilizer, the time and method of application, the granule size of fertilizer, and placement. Only a small fraction of total P becomes available in soil. For example, Olsen P content may be only 10 mg kg^{-1} in a soil containing 400–1,000 mg kg^{-1} total P.

Availability of phosphorus in soil is indicated by the abundance of orthophosphate ions in soil solution. It is a pH-dependent phenomenon (Hopkins and Ellsworth 2005) as soil pH determines the ionic forms of phosphate and directs the reactions in which these ions participate. At low pH, iron, aluminum, and manganese become highly soluble in soil. They react with soluble phosphate ions to form insoluble phosphates. At high pH in sodic and calcareous soils, soluble calcium reacts with soluble phosphate ions to form insoluble calcium phosphates. Therefore, phosphorus deficiency is likely in acid, alkaline, sodic, and calcareous soils. Liming in acid soils will improve P availability, but over-liming will again induce P deficiency. Soluble $H_2PO_4^-$ ions may further be adsorbed by soil colloids, including clay and hydrated oxides of Fe and Al. Adsorbed phosphate is not readily available to plants. It becomes available when it is again desorbed.

10.6.5   Phosphorus Availability Is Judged from Its Chemical Extractability

There are several methods of determining "available" phosphorus content of soils. These methods employ a variety of extractants, which are dilute solutions of salts, acids, and alkalis with or without buffering agents. These methods actually extract the phosphorus which is "extractable" by the particular extracting solution. To have an idea of the phosphorus-supplying capacity of a soil to a crop, the amount of extracted phosphorus is correlated with the amount of phosphorus taken up. Extractable P is often called "soil test P." The fundamental goal of soil P testing has always been to identify the optimum soil test P concentration required for plant growth. Other objectives of soil P testing include (1) to "index" the P-supplying capacity of soils, thus estimating the time before fertilization would again be required; (2) to group soils, in terms of the likelihood of an economic response to P, based on their physical and chemical properties; and (3) to identify when soils are sufficiently excessive in P to contribute to nonpoint source pollution of surface waters (Sims et al. 1998).

Popular methods of determining available or extractable P include Bray and Kutrz 1 (0.025 M HCl in 0.03 M NH_4F), Bray and Kurtz 2 (0.1 M HCl in 0.03 M NH_4F) (Bray and Kurtz 1945), Mehlich 1 (0.0125 M H_2SO_4 + 0.05 M HCl) (Mehlich 1953), Mehlich 3 (0.2 M CH_3COOH, 0.25 M NH_4NO_3, 0.015 M NH_4F, 0.013 M HNO_3, 0.001 M EDTA) (Mehlich 1984), and Olsen (0.5 M $NaHCO_3$, pH 8.5) (Olsen et al. 1954) methods.

Phosphorus extracted by the Bray and Kurtz 1 method has been shown to be well correlated with crop yield response on most acid and neutral soils. For acid soils, the fluoride in the Bray and Kurtz extractant enhances P release from aluminum phosphates by decreasing Al activity in solution through the formation of various Al–F complexes. A Bray and Kurtz 1 P value of 25–30 mg kg^{-1} is often considered optimum for plant growth. Mehlich 1 method is also known as the dilute double acid method. It is used as a multielement extractant

for P, K, Ca, Mg, Cu, Fe, Mn, and Zn. Mehlich 1 method extracts P from aluminum, iron, and calcium phosphates and is best suited to acid soils (pH < 6.5) with low cation exchange capacities (<10 cmol/kg) and organic matter contents (<5%). Kuo (1996) reported that Mehlich 1 method was unreliable for calcareous or alkaline soils because it extracts large amounts of non-labile P in soils with pH > 6.5, soils that have been recently amended with rock phosphate, and soils with high cation exchange capacity (CEC) or high base saturation. Mehlich 3 method is well suited to a wide range of soils, both acidic and basic in reaction. Mehlich 3 method is similar in principle to the Bray and Kurtz 1 because it is an acidic solution that contains ammonium fluoride. Acetic acid in the extractant also contributes to the release of available P in most soils. It is more effective than Mehlich 1 method for predicting crop response to P on neutral and alkaline soils because the acidity of the extractant is neutralized less by soil carbonates (Tran and Simard 1993). Olsen method was developed to predict crop response to fertilizer P inputs on calcareous soils. The Olsen P method is best suited for soils with >2% calcium carbonate, but has been shown in some research to be reasonably effective for acidic soils (Fixen and Grove 1990).

10.6.6 Inorganic Phosphorus in Soil Undergoes Precipitation–Dissolution Reactions

Precipitation is the process of formation of discrete and insoluble compounds from soluble substances in solution (Sect. 8.4.2). In soil, soluble inorganic P, phosphate ions, participate frequent precipitation reactions mainly with iron, aluminum, and calcium depending on the pH of the system and on the abundance of both phosphate and cations. In neutral or calcareous soils, Ca^{2+} is the dominant cation. With soluble phosphate ions (fertilizers or products of mineralization) it initially forms dicalcium phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$), which slowly reverts to other Ca phosphates such as octacalcium phosphate ($Ca_8H(PO_4)_6 \cdot 5H_2O$), and ultimately apatite ($Ca_5(PO_4)_3OH$). In acidic soils, Al^{3+} and Fe^{3+} are the major soluble cations. They precipitate the phosphate ions of the soil solution. Iron and aluminum phosphates are the dominant precipitates in acid soils.

$$Ca(H_2PO_4)_2 + CaCO_3 + H_2O = 2CaHPO_4 \cdot 2H_2O + CO_2$$
very soluble   less soluble

$$6CaHPO_4 \cdot 2H_2O + 3CaCO_3 = 3Ca_3(PO_4)_2 + 3CO_2 + 5H_2O$$
less soluble

$$3Ca_3(PO_4)_2 + CaCO_3 = 3Ca_3(PO_4)_2 \cdot CaCO_3$$
very insoluble   insoluble

$$Al^{3+} + H_2PO_4^- + 2H_2O \Leftrightarrow 2H^+ + Al(OH)_2H_2PO_4$$
(soluble)   (insoluble)

The presence of amorphous or partially crystalline Fe and Al oxides that can occlude P as they crystallize in acid soils makes identification of specific Fe–P and Al–P minerals difficult (Pierzynski et al. 2005). In soils that have not been extensively weathered, P mineralogy is dominated by sparingly soluble apatites and other more soluble calcium phosphates—octacalcium phosphate, monetite ($CaHPO_4$), brushite ($CaHPO_4 \cdot 2H_2O$), etc. As soils weather, apatites dissolve, Ca^{2+} ions are released in solution and taken up by plants, and precipitated or sorbed or are lost by leaching. Iron and aluminum phosphates may release phosphate ions in soil solution upon dissolution. In general, the solubility of P-bearing minerals and the availability of P to plants is the greatest under slightly acidic conditions in the pH range of 6.0–6.5 (Cowan et al. 1991).

$$\text{Hydroxyapatite}: Ca_5(PO_4)_3OH + 7H^+ \Leftrightarrow 5Ca^{2+} + 3H_2PO_4^- + H_2O$$
$$\text{Variscite}: AlPO_4 \cdot 2H_2O + 2H^+ \Leftrightarrow Al^+ + H_2PO_4^- + 2H_2O$$
$$\text{Strengite}: FePO_4 \cdot 2H_2O + 2H^+ \Leftrightarrow Fe^{3+} + H_2PO_4^- + 2H_2O$$

10.6.7 Phosphate Sorption–Desorption Regulates Phosphorus Availability in Soil

Sorption is the general term used to describe several processes collectively (surface precipitation, partitioning, polymerization, adsorption, and formation of secondary solid phases). McBride (2000) defined sorption as the transfer of ions and molecules from the solution phase to the solid phase. Sorption in soils results in the retention of a substance (sorbate) by organic and inorganic solid phases (sorbent). Sorption can occur due to physical processes involving van der Waals forces or electrostatic outer sphere complexes, for example, anion exchange, which is referred to as nonspecific adsorption, to chemical processes such as inner-sphere complexes, ligand exchange, and chemisorption, many of which are referred to as specific adsorption (Pierzynski et al. 2005). In addition, chemical precipitation may participate in the removal of ions from water and sometimes is treated as a part of sorption (McBride 2000).

Insolubilization of phosphates by precipitation with Fe, Al, Mn, and Ca and adsorption of phosphates by colloids are together known as phosphate sorption in soil. A large proportion of fertilizer P is made currently unavailable by P sorption. Retention of P by interaction with hydroxides and oxyhydroxides of Fe and Al in dilute solutions of P involves replacement of OH^- by PO_4^{3-}. Since the soil solution is acidic, the surface of these minerals has a net positive charge,

although both (+) and (-) sites exist. The predominance of (+) charges readily attracts $H_2PO_4^-$ and other anions. When the orthophosphate ion is bonded through one Al–O–P bond, the $H_2PO_4^-$ is considered labile and the adsorption is reversible (Hingston et al. 1974). This orthophosphate ion can be readily desorbed from the mineral surface to soil solution. When two Al–O bonds with $H_2PO_4^-$ occur, a stable six-member ring is formed and the adsorption becomes irreversible. Very little desorption of P takes place from this complex (Tisdale et al. 1997). In acid soils, P retention also readily occurs on the broken edges of kaolinite clay minerals. Exposed OH^- groups on these edges can exchange for $H_2PO_4^-$ similarly to exchange with OH^- on the surface of Fe/Al oxides. Phosphorus interactions with calcite involve two reactions: The first reaction at low P concentrations consists of adsorption of P by calcite surface, while the second process is a nucleation process of calcium phosphate crystals (Griffin and Jurinak 1974). Phosphate is less strongly bound to $CaCO_3$ than to the hydrous oxides of Fe and Al and hence is more available to crop plants. The general consensus is that in soils where Al oxide and Fe oxide are available, carbonates may play only a secondary role in P sorption. There are a number of P sorption models, including Freundlich (1926), Langmuir (1918), and Temkin models (Tempkin and Pyzhev 1940). Freudlich and Langmuir isotherms for general adsorption processes have been discussed in Sect. 8.4.4.

Desorption is the release of P from a solid phase into the soil solution by processes other than mineral dissolution. Desorption occurs when plant uptake, runoff, or leaching depletes soil solution P concentrations to very low levels or in aquatic systems when sediment-bound P interacts with low P waters. Only a small fraction of sorbed P in most soils is readily desorbable. Most P added to soils in fertilizers or manures is rapidly sorbed but not easily desorbed.

10.6.8 Soil Phosphorus May Affect Water Quality

Phosphorus is an essential element for all organisms, and it is not toxic itself. Still, phosphorus may exert detrimental effects, even in low concentration, on water quality of lakes and other surface water reservoirs. Excess soluble phosphorus in soil contributes to eutrophication of water, a process characterized by increased growth of undesirable algae and aquatic weeds, followed by oxygen shortages as the biomass decomposes. Eutrophication restricts water use for fisheries, recreation, industry, and human consumption.

Phosphorus in soils is almost entirely associated with soil particles. During erosion and runoff, soil particles with bound P are carried to water bodies. Although most soils have a large capacity to retain P, a large addition of fertilizer P may stimulate leaching and transporting P to lakes and streams. In this way,

water bodies such as lakes, estuaries, or slow-moving streams become enriched with nutrients, particularly phosphate (and nitrate). Consumption of dissolved water due to enhanced algal growth and decomposition leads to a hypoxic condition. At this point, the color of water becomes bluish in the initial and brownish in the latter stages, and odor becomes obnoxious.

10.7 Sulfur in Soils Come from Mineral and Organic Matter

The SO_4^{2-} ion is the available form of sulfur to plants. It remains in soil solution and as an adsorbed anion on colloidal surface. The concentration of SO_4^{2-} in soil solution is very low—10 to 100 mg L^{-1}. The main sources of sulfate in the soil are sulfur-containing minerals and organic matter. Gypsum ($CaSO_4 \cdot 2H_2O$) is a very common secondary mineral source of sulfur in soils developed from sedimentary parent materials. It is also abundant in soils of the arid and semiarid regions. Pyrite (FeS_2) is another important sulfur-containing mineral associated with shale and coal and in hydromorphic soils of the coastal regions receiving ample sulfate with sea salts and plenty of partially decomposed organic matter for reduction of sulfate. These are acid sulfate or potentially acid sulfate soils. In waterlogged soils, sulfate is reduced to elemental sulfur (S), H_2S, or FeS_2. Upon drainage of the soil, these compounds are again oxidized to sulfuric acids and sulfate salts. Sulfur compounds, thus, participate in redox reactions in soil.

$$2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4$$
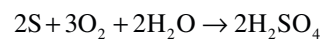
Most sulfur, 60–90%, in soils comes from organic matter, which upon mineralization releases available sulfate slowly. Sulfur is, therefore, concentrated in the topsoil or plow layer. Sulfate mineralization is rapid in warm and well-drained soils. Sulfate can be leached, but the rate of leaching is slower than nitrate. Some sulfate is held by clay colloids.

Atmospheric deposition supplies a considerable amount of plant-available sulfur in soils of industrial countries. The amount of deposition may vary from 8 to 15 kg ha^{-1} $year^{-1}$. Some sulfate is added to soils with other fertilizers such as superphosphates as contaminants. If needed, gypsum and some other salts may be added as sulfur fertilizers.

10.8 Potassium in Soil Remains in Soluble, Exchangeable, Fixed, and Mineral-Bound Forms

Plants absorb K^+ ions from soil solution and exchange complexes. Soils contain soluble K^+, exchangeable K^+, fixed K^+, and K minerals. Soil solution contains only 1–40 mg L^{-1} K^+. There is about ten times higher exchangeable K^+ than solution

K$^+$; so there is a readily available reservoir of potassium to replace solution K$^+$. The amount of exchangeable potassium in a soil depends on the CEC of the soil and on the levels of other cations. Soluble K$^+$ and exchangeable K$^+$ tend to remain in an equilibrium, and when solution K$^+$ is removed by plant uptake or by leaching, some K$^+$ is released into soil solution from exchange complexes. K$^+$ ions in soil are vulnerable to loss by leaching. This is a problem in soils that do not have a large K$^+$ fixing capacity and in soils that have a low CEC. Leaching of potassium is common in sandy and silty soils.

Hydrous micas and illite clays contain potassium as part of their structure. These clays have layered structures, and K$^+$ ions are sandwiched between the layers. This is known as fixed potassium. As the clays weather, the layers peel apart, and the potassium ions are released.

Minerals are the principal sources of potassium in soil. Feldspars (orthoclase, microcline) and micas (muscovite, biotite) are the main K-containing mineral groups found in soil. These minerals release potassium as they weather.

$$KAlSi_3O_8 + H_2O \xrightarrow{\text{Hydrolysis}} HAlSi_3O_8 + KOH$$

$$(\text{Orthoclase}) \qquad\qquad (\text{Hydrogen aluminum silica}$$
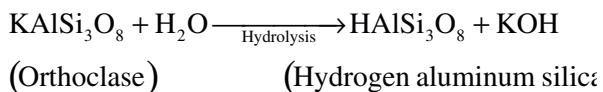
Weathering of feldspar is a very slow process, requiring a long time to release useable K$^+$. So, mineral potassium is unavailable to plants in the short term, but it is an important reservoir of K$^+$ in the long term.

10.9   Calcium in Soil Is Both a Nutrient and a Soil Conditioner

Calcium is both a plant nutrient and a soil conditioner. As a soil conditioner, calcium plays an important role in determining physical and chemical characteristics, that is, structure and pH of soil. Divalent Ca^{2+} ions produce effective soil aggregation, forming crumbs or peds. Soils dominated by calcium are friable and well structured, have good internal drainage, and have good tilth. Calcium carbonate or lime may reduce soil acidity and increase soil pH.

Calcium is absorbed by plants as the divalent cation (Ca^{2+}) present in soil solution and as exchangeable Ca^{2+} on soil colloids. Soil solution contains low concentration of Ca^{2+} (10–200 mg L^{-1}). Calcium is held on soil clay and humus particles more tightly than Mg^{2+}, K$^+$ and other exchangeable cations. Parent materials from which soils are formed also usually contain more calcium than magnesium or potassium. Soil Ca^{2+} does not leach to any appreciable extent because it is strongly attracted to the surface of clay. Soils generally have large amounts of exchangeable calcium (300–5,000 mg kg^{-1}). Normally, Ca^{2+} occupies 70–90% of cation exchange sites above pH 6.0.

Calcium is a part of the structure of several minerals, including apatite [Ca$_3$(PO$_4$)$_2$], calcite (CaCO$_3$), dolomite (CaCO$_3$·MgCO$_3$), feldspars [anorthite Ca$_2$Al$_2$Si$_2$O$_8$], pyroxene [(Na,Ca,Mg,Fe,Al)$_2$·Si$_2$O$_6$], hornblende [Ca$_2$,Na(Mg, Fe^{2+})$_4$(Al,Fe,Ti), (Al,Si)$_8$O$_{22}$(O, –OH)$_2$], and gypsum (CaSO$_4$· 2H$_2$O). Total Ca content of soils can range from 0.1% in highly weathered tropical soils to 30% in calcareous soils.

10.10   Magnesium Behaves Similarly to Calcium in Soil

Magnesium is the eighth most abundant element of the earth's crust. It has also some soil conditioning effect. Actually, Mg^{2+} behaves like Ca^{2+} in soil. Both are divalent cations and they stay in soil solution and exchange complexes. Magnesium also improves soil structure and increases soil pH. Availability of both Ca^{2+} and Mg^{2+} is low in low pH and high in high pH of soil. The primary minerals pyroxene [(Ca,Na)(Mg,Fe^{2+},Fe^{3+},Al)(Si,Al)$_2$O$_6$], amphibole [Ca$_2$,Na(Mg,Fe^{2+})$_4$ (Al,Fe,Ti) (Al,Si)$_8$O$_{22}$(O,-OH)$_2$], biotite [K(Mg,Fe)$_3$(AlSi$_3$O$_{10}$). (OH)$_2$], and olivine [(Mg, Fe)SiO$_4$] and the secondary mineral dolomite (CaCO$_3$·MgCO$_3$) supply most magnesium in soil. The clay minerals montmorillonite [(Na,Ca)$_{0.3}$(Al,Mg)$_2$·Si$_4$O$_{10}$(OH)$_2$·nH$_2$O)], vermiculite [(MgFe,Al)$_3$ (Al,Si)$_4$O$_{10}$(OH)$_2$·4H$_2$O], and serpentine [(Mg,Fe)$_3$Si$_2$O$_5$(OH)$_4$] also contain magnesium.

In coastal regions, small droplets of water containing salts of sea are carried to the atmosphere by coastal winds. The phenomenon is called salt spray. These salts including magnesium are deposited on land as dust (dryfall) or with rain (wetfall). Near the coast, around 10 kg Mg ha^{-1} year^{-1} can be deposited this way.

The availability of Mg^{2+} depends on total Mg content in soil, soil pH, CEC, and other cations. High available Mn can directly reduce Mg uptake. High levels of K or Ca provide less Mg to the crop. Whenever the soil K level is higher or when the soil K–Mg ratio is above 1.5:1, plant Mg levels are reduced.

10.11   Iron Is a Micronutrient and a Marker of Soil Genesis

Iron in soils comes from the weathering of many iron-containing minerals of the parent material. The most common iron-containing minerals are biotite [K(Mg,Fe)$_3$(AlSi$_3$O$_{10}$) (OH)$_2$], chlorite, and hornblende [Ca$_2$,Na(Mg,Fe^{2+})$_4$ (Al,Fe,Ti)(Al,Si)$_8$ O$_{22}$(O, –OH)$_2$].

The iron in those minerals is largely in the ferrous state. When they are weathered during soil formation, most of the iron is changed to the ferric state and forms different iron compounds. The kind of parent material and the conditions

under which it is weathered influence the distribution and kinds of iron compounds formed in the soil.

In humid temperate regions where rainfall is high and temperature is low and an organic layer has accumulated, a large part of the bases (sodium, potassium, calcium, and magnesium) of the parent material is dissolved and leached away and a more acid residue is left in the top horizons of the soil. Most iron is reduced, dissolved, and transported to the lower, less acid horizon, where it is precipitated forming new iron compounds such as iron hydrates, oxides, and some organic iron complexes. On the other hand, in tropical regions where rain is abundant and temperature is high, active base elements are also removed by weathering and leaching, iron is oxidized, and an acid soil is formed. The iron is converted largely to hydrated oxides. Some of the hydrated iron subsequently becomes dehydrated to Fe_2O_3. Because the soils of the arid and semiarid regions are less weathered and leached than those formed under heavier rainfall, many of them are calcareous and alkaline in reaction. The iron is less altered and is more uniformly distributed in their soil profiles.

Sizable amounts of the iron compounds form coatings on clay, silt, and sand particles in many soils. The coating may give them their color. The colors of most soils are due to the presence of the iron compounds.

Iron can exist in two valence states: Fe^{2+} and Fe^{3+}. The reversible oxidation/reduction of iron plays an important role in its translocation and transformation in soils and at the same time influence the redox condition of the soil. Even at low concentration, iron oxides within soils have a high pigmenting power and the color of pigments depends on the oxidation states and the predominance of the oxides. Thus color, and distribution of iron oxides within a profile, is helpful in explaining soil genesis and is used widely in soil classification. Iron oxides may affect soil structure and fabric. Different classes of iron oxides include magnetite (Fe_3O_4), hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), goethite (α-FeOOH), lepidocrocite (γ-FeOOH), akaganeite (β-FeOOH), feroxyhite (δ-FeOOH), and ferrihydrite ($Fe_2O_3 \cdot 2FeOOH \cdot 2.6H_2O$).

10.12 Manganese Is an Active Redox Reactant in Soil

Manganese is more abundant than other micronutrients in soil. Common manganese minerals in soil include pyrolusite (MnO_2), manganite (MnOOH), and hausmannite (Mn_3O_4). Total Mn content in soil ranges from 0.02 to 1%, with an average of 0.25%. Volcanic soils are particularly high in Mn; it may be as high as 10% there. Manganese may occur in several ionic forms such as Mn^+, Mn^{2+}, and Mn^{4+}. Only Mn^{2+} is available to plants. Manganese is a fairly mobile element in soil and can be leached, particularly on acid soils. Manganese availability depends on soil pH, organic matter,

and waterlogging. Mn is more available in low soil pH; even it may become toxic at pH below 5.5. On the other hand, it may be deficient in alkaline soils. Mn can be "tied up" by the organic matter. So, soils with high organic matter content can be Mn deficient. Under waterlogging, Mn^{2+} can initially be reduced to Mn^+, which is unavailable to plants. Under long-term reducing condition, however, available Mn can be increased. As soil dries, unavailable Mn^+ is oxidized to available Mn^{2+}; even some available Mn^{2+} can be oxidized to unavailable Mn^{4+}. High levels of Fe, Zn, Cu, and Mo in soil can reduce Mn uptake by plants. High NO_3^- and SO_4^{2-} can enhance Mn uptake.

10.13 Weathered, Leached, and Acid Soils Have Relatively Low Copper Levels

Copper is found in many different compounds in soil—sulfates, sulfides, sulfosalts, and carbonates. The most abundant Cu mineral is the chalcopyrite (the fool's gold—$CuFeS_2$). Total copper in soil ranges from 2 to 250 mg kg^{-1}, with an average of 30 mg kg^{-1}.

Copper in soil is inherited from the parent material. Soils developed from sandstones or acid igneous rocks contain lower Cu than those developed from shales and basic igneous rocks. Highly weathered, leached, and acid soils have relatively low Cu levels than other soils. Copper is strongly fixed by soil organic matter, clay, and oxide minerals. It is one of the least mobile trace elements in soils.

Copper concentrations in the soil solution of mineral soils are controlled primarily by soil pH and the amount of Cu^{2+} adsorbed on clay and soil organic matter. Copper is highly available at low pH (below 5). The lowest concentrations of Cu are associated with the organic or peat soils.

10.14 Fine-Textured Soils Generally Contain More Zinc Than Sandy Soils

The various forms of Zn in soil include minerals, organic matter, adsorbed Zn on the surfaces of organic matter and clay, and dissolved Zn in the soil solution. Total Zn in soil ranges from 10 to 300 mg kg^{-1}. Available Zn (DTPA extractable) has been positively correlated with total Zn, organic matter, clay content, and cation exchange capacity and inversely correlated with free $CaCO_3$, soil pH, and base saturation. Soil pH affects Zn availability; as soil pH increases, Zn availability decreases. Zinc availability to plants is lower in organic soils and in mineral soils with significant amounts of organic matter.

Clay fraction of the soil exerts a strong attractive force for zinc ions possibly due to similarity in size and charge between magnesium and zinc ions. Zinc ion reacts with the clay mineral

lattice, where it may substitute or exchange for magnesium, thus making it relatively unavailable. High soil phosphorus levels have been known to induce zinc deficiency.

10.15 Molybdenum Availability Increases with Increasing Soil pH

Molybdenum is found in soil in minerals and as exchangeable Mo on the surfaces of Fe/Al oxides and clays and soil organic matter. In soil solution, molybdenum may exist in several forms depending on the pH. At pH >5.0, molybdenum exists primarily as MoO_4^{2-}, which is the available form for plants, but at lower pH the $HMoO_4^-$ and H_2MoO_4 forms dominate.

Molybdenum content in soils varies with parent material, degree of weathering, and organic matter content. Total Mo ranges from <3 to 15 mg kg^{-1}, but most soils contain 0.25 to 5.0 mg kg^{-1}. Unlike most other micronutrients, Mo availability increases with increasing soil pH. Molybdenum may be deficient under very acidic soil conditions. Molybdenum deficiency may be corrected by liming, but over-liming may form insoluble $CaMoO_4$. Unnecessary Mo application may create Mo toxicity to the crops and elevated Mo concentration in cereals and vegetables. Soils higher in organic matter generally have higher molybdenum levels. Soil P and S levels may influence Mo availability. Phosphorus increases Mo availability, whereas S decreases it.

10.16 Tourmaline Is the Main Mineral Source of Boron in Soil

There are four main forms of B in soils: water soluble, adsorbed, organically bound, and fixed in clay and mineral lattices. Much of the total boron in soil is present as a component of the mineral group tourmaline [(Ca,K,Na,I) $(Al,Fe,Li,Mg,Mn)_3(Al,Cr,Fe,V)_6(BO_3)_3(Si,Al,B)_6O_{18}(OH,F)_4$]. Most of the remainder is in secondary, moderately insoluble minerals. As soluble salts, B occurs as calcium and sodium borates. Parent rocks differ in boron contents. For example, sedimentary rocks generally have higher levels of B than igneous rocks. Parent materials and their degree of weathering determine the amount of boron in soil. The average concentration of B in the earth's crust is about 10 mg kg^{-1}; in soil it ranges from 2 to 100 mg kg^{-1}. There are low B contents in soils derived from acid igneous rocks, fresh water sedimentary deposits, and in coarse-textured soils low in organic matter. Boron is highly mobile and subject to leaching losses in coarse-textured soils low in clay and organic matter. Boron availability in soil may also be influenced by soil pH. In general, B becomes more available to plants with decreasing pH.

10.17 Chloride Is the Most Mobile Anion in Soils

Chlorine is found in soil as chloride (Cl^-) ion, which is soluble and is contained in negligible amounts in the mineral, adsorbed and organic soil fractions. Chloride has a high mobility in soils, and it is subject to leaching when rainfall or irrigation exceeds evapotranspiration. Chloride inputs to soil come from rainfall, fertilizers, manures, irrigation water, and with seawater flooding. Atmospheric deposition from rainfall averages around 20 kg Cl ha^{-1} $year^{-1}$ with higher levels in coastal regions. Large quantities of chloride can be added where irrigation water contains high levels of chloride. The anions nitrate, sulfate, borate, and molybdate may be antagonistic to chloride.

10.18 Soils Around Industries Contain the Highest Nickel

Nickel is the 22nd most abundant element of the earth's crust (Sunderman and Oskarsson 1991). It is found primarily as oxides or sulfides in soil.

Nickel can exist in soils in several forms such as inorganic crystalline minerals or precipitates, and complexes and adsorbed on organic or inorganic exchange surfaces, water soluble, and free ion or chelated metal complexes in soil solution. Soil generally contains about 4–80 mg Ni kg^{-1}. Nickel is generally uniformly distributed throughout the soil profile. Soils around industrial complexes and mining areas may contain nickel concentrations that may be toxic to plants. Nickel is also released into the environment from anthropogenic activities such as metal mining, smelting, fossil fuel burning, vehicle emissions, disposal of household, municipal and industrial wastes, fertilizer application, and organic manures.

10.19 Nutrients Interact in Soils

Nutrients undergo complex reactions that lead to changes in their availability in soil. At the same time, available nutrients have also complex interactions. These interactions may be positive; increase in availability of one element may increase the uptake of another. It is stimulation. An example of stimulation is the increased demand of magnesium by increased level of nitrogen. Likewise, if more potassium is used, more manganese is required. There may be negative interactions as well; it is called antagonism. High levels of a particular nutrient in the soil can interfere with the availability and uptake of other nutrients by the plant. Those nutrients which interfere with one another are said to be
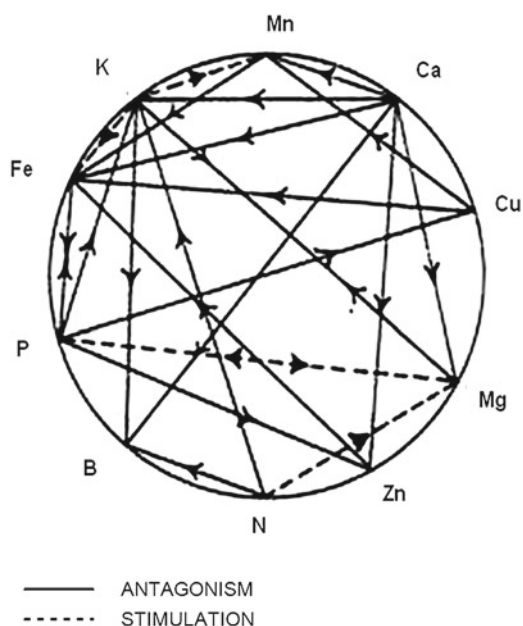
Mulder's chart of nutrient interactions in soil (http://www.montmorillonite.org/Mulders%20chart.htm)

antagonistic. For example, high nitrogen levels can reduce the availability of boron, potassium, and copper; high phosphate levels can influence the uptake of iron, calcium, potassium, copper, and zinc; high potassium levels can reduce the availability of magnesium. Mulder (1953) published a nutrient interaction chart, which is shown in Fig. 10.1. These interactions need to be considered in planning a fertilizer program for crops.

10.20   Any Material That Provides Crops with a Nutrient Is a Fertilizer

When the soil has adequate available nutrient reserves, plants do not need any nutrient supplement. But soils often become deficient in major nutrients, particularly N, P, and K, and sometimes S, Zn, and other micronutrients. Then they need fertilizers. Fertilizers are inorganic or organic, natural or synthesized materials that are added to soil to supply plant nutrients. Fertilizers are added to increase soil fertility and plant growth and yield. Many other materials, including water, lime, pesticide, growth hormones, and soil conditioners, are used to increase plant growth and yield. They do not supply or they are not intended to supply plant nutrients; they are not fertilizers.

Industrially manufactured chemical compounds (mostly inorganic and some organic) with high nutrient contents are popularly used as fertilizers. They are called "commercial fertilizers," "inorganic fertilizers," "chemical fertilizers," and "industrial fertilizers." On the other hand, many natural materials such as composts, manures, oil cakes, fish meal,

and guano are used as fertilizers from ancient times. They are called organic fertilizers.

Industrial fertilizers have specific nutrient concentrations; for example, urea contains 46% nitrogen. Industrial fertilizers are required in relatively small quantity. They are easy to store, easy to distribute in market, easy to apply in field, easy to mix with irrigation water, and easy to handle compared to organic fertilizers. To supply 100–150 kg N ha^{-1} to an annual crop, one would need about 217–326 kg urea per hectare. To supply the same amount of nitrogen from organic fertilizers, one would need 15–20 t ha^{-1} compost or farmyard manure because they contain very little nitrogen (the composition of composts and manures is also variable). It is difficult to collect such a huge quantity of organic residues. Processing, storing, marketing, and applying in field are also difficult. For these reasons, farmers usually depend more on commercial fertilizers. Otherwise, organic fertilizers could prove superior because organic fertilizers act as soil conditioners as well. They also contain some micronutrients. However, if applied on equal nutrient quantity basis, both organic and inorganic fertilizers may prove to be equally effective. Modern farmers usually apply organic fertilizers as part of the total requirement. The other part is supplemented with inorganic fertilizers.

10.20.1   Industrial Fertilizers Are Synthetic Products

10.20.1.1   Nitrogen Fertilizers

Ammonia is the basic substance for the production of industrial nitrogen compounds, including fertilizers. Nitrogen from atmosphere and hydrogen from natural gas are used for the production of ammonia in industries. This is called chemical fixation of atmospheric nitrogen which is based on Haber–Bosch process (Tempkin and Pyzhev 1940). The general process may be outlined as

$$N_2 + 3H_2 \xrightarrow[1,200\,^{\circ}C,\,500\,atm]{Catalyst} 2NH_3$$

The overall reaction is

$$7CH_4 + 10H_2O + 8N_2 + 2O_2 = 16NH_3 + 7CO_2$$
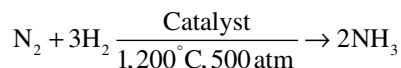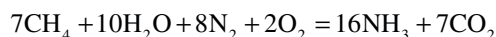
The ammonia thus produced can be utilized directly as a fertilizer (anhydrous NH_3). Other nitrogenous compounds are prepared from ammonia. Such as:

1. $NH_3 + O_2 + NH_3 \rightarrow$ Ammonium nitrate

2. $NH_3 + CO_2 \rightarrow$ Urea

3. $NH_3 + H_2SO_4 \rightarrow$ Ammonium sulfate

Table 10.3 Nitrogen fertilizers

Fertilizer	Formula	% N
Anhydrous ammonia	NH_3	82
Ammonia solution	NH_4OH	20
Urea	$NH_2–CO–NH_2$	46
Ammonium nitrate	NH_4NO_3	33
Ammonium sulfate	$(NH_4)_2SO_4$	21
Monoammonium phosphate (MAP)	$(NH_4)H_2PO_4$	10
Diammonium phosphate (DAP)	$(NH_4)_2HPO_4$	18
Ammonium chloride	NH_4Cl	25
Potassium nitrate	KNO_3	13
Sodium nitrate	$NaNO_3$	16

4. $NH_3 + H_3PO_4 \rightarrow$ Ammonium phosphate

5. $NH_3 + H_2O + NH_4NO_3 \rightarrow$ Nitrogen solution

Several chemical compounds are used as nitrogen fertilizers. Some of them with their percentage nitrogen contents are given in Table 10.3. Fertilizer materials in the table look like pure chemical compounds. Actually commercial fertilizers contain several impurities and contaminants.

10.20.1.2 Choice of Nitrogen Fertilizers

Some of the factors that determine the choice of a fertilizer are price, amount of fertilizer needed, availability in the market, ease of handling and application, ease of storage, loss of fertilizer from field, fertilizer efficiency, etc. Among chemical nitrogen fertilizers, ammonia is the cheapest and the most concentrated material. It is generally a gas but supplied under low pressure as a liquid. Small amount of ammonia may supply the full requirement of N of a crop. But application of ammonia is difficult. It is also corrosive in concentrated form. It may be injected in soil or applied with irrigation water in sprinkler or drip systems. When applied to soil, ammonia is converted to NH_4^+. Ultimately, there remains little difference between effects of ammonia and urea when applied on equal amount basis. Urea is also converted to ammonium. Farmers usually use urea because it contains higher nitrogen, it is cheap, and it is easy to handle.

$$NH_2 - CO - NH_2 + 2H_2O \rightarrow (NH_4)_2CO_3$$
$$(NH_4)_2CO_3 + 2H^+ \rightarrow 2NH_4^+ + CO_2 + H_2O$$
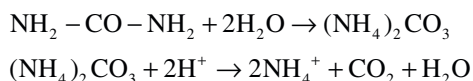
In a well-drained soil, ammonium is rapidly converted to nitrate by the process of nitrification. So, there is also little difference between nitrate and ammonium fertilizers in terms of their effects on crops. MAP and DAP have limited use. They are applied when both nitrogen and phosphorus are needed. Ammonium sulfate (21% N) and ammonium nitrate (33% N) were widely used in the past. These materials are now used in preparing mixed fertilizers.
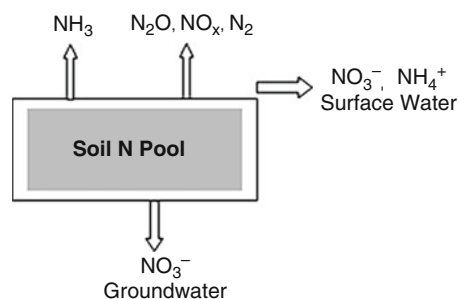
Fig. 10.2 Transfer of soil N to different pools

10.20.1.3 Fate of Applied Nitrogen

Whichever substance is used as nitrogen fertilizers, some of nitrogen is inevitably lost from the applied fertilizers. The chief processes of nitrogen loss are erosion, volatilization, leaching, and denitrification. The pathways of nitrogen loss from soil are shown above (Fig. 10.2).

Leaching loss following nitrification was mentioned in Sect. 10.6.1. Materials containing ammonium such as ammonium sulfate, ammonium nitrate, ammonium phosphate, or substances that produce ammonium after application to soil such as urea behave similarly in this regard. If the pH of soil is high (>7.0), if the soil is calcareous or sodic, and if the soil is saturated with water, considerable nitrogen may be lost by volatilization. Application of ammonia at shallow depths in dry soil can result in considerable loss of ammonia by direct escape from the soil as a gas. Ammonium ions are relatively less mobile than nitrates. Some ammonium may be held by colloids. But NH_4^+ is readily converted to NO_3^- by the nitrification process. Nitrate is highly mobile and easily lost by leaching particularly in coarse-textured soils. When soil does not have sufficient air, some microorganisms use the oxygen from NO_3^- in place of O_2 in soil air and rapidly convert NO_3^- to nitrogen oxide and nitrogen gas (N_2). These gases escape to the atmosphere and are not available to plants. This transformation can occur within 2 or 3 days of water saturation and can result in substantial losses of nitrogen fertilizers. The processes of nitrogen volatilization, nitrification, and denitrification have been described in Sect. 9.4.2.

10.20.1.4 Preventing Nitrogen Losses

The following techniques have been successfully employed to prevent losses of nitrogen from added fertilizers:

1. Granule size of N fertilizer is increased to reduce contact with the soil. Large urea balls are placed at the center of four rice hills to reduce denitrification loss in rice-growing areas of Bangladesh.
2. In many rice-growing areas, urea–mud–neem cake balls are prepared and applied between rows of rice. Neem (*Azadirachta indica*) cake prevents nitrification and denitrification.

Table 10.4 Slow-release and controlled-release nitrogen fertilizers

Fertilizer	Composition	% N content
SRF		
Ureaform	Urea formaldehyde	40
IBDU	Isobutylidene diurea	32
CRF		
SCU	Sulfur-coated urea	31–38
PCSCU	Polymer-coated SCU	30

3. Nitrogen is applied in split dozes. Generally, three splits are done; one-third fertilizer is applied during soil preparation, one-third is applied during most vigorous vegetative growth stage, and the remaining one-third during flower initiation.
4. Fertilizers are applied in narrow bands except being broadcasted. It reduces leaching, volatilization, and denitrification.
5. Nitrification inhibitors such as "nitrapyrin" have been used with variable success.
6. Slow-release (SRF) and controlled-release (CRF) nitrogen fertilizers are used.

10.20.1.5 Slow-Release and Controlled-Release N Fertilizers

There are some slow-release fertilizers (SRF) and controlled-release fertilizers (CRF) (Table 10.4). These materials have low solubility. Some compounds such as sulfur-coated urea prevent nitrification. Nitrogen is released at a slow pace and corresponds to the rate of absorption by roots. These materials are relatively costly and have not yet gained popular use.

10.20.1.6 Residual Effects of N Fertilizers

When part of fertilizers added to the current crop becomes available to the next crop, the fertilizer has a residual effect, we say. Residual effects depend on the rate of N applied, the crop, the amount of leaching, and the soil type. Residual effects of N fertilizers have been observed when deep-rooting cereals such as winter wheat and follow crops such as potatoes to which heavy N dressings have been applied. A significant proportion of the N fertilizer is converted into labile organic N which is readily mineralized during the succeeding crop. However, the proportion of actual fertilizer N remaining in mineral form in the soil by harvest time is very small (Powlson 1997). There will be little residual N from a fertilizer application of 150 kg N/ha to a preceding crop because much of the excess nitrate has been leached out when rainfall is enough.

10.20.1.7 Phosphorus Fertilizers

The natural source of phosphorus is the rock phosphate or phosphate rock that may be primary or secondary but contains the mineral fluorapatite [$Ca_{10}(PO_4)_6(F,OH)_2$]. Phosphate rock is mined and ground to a powder, which can be used directly as a phosphate fertilizer, or is processed for the manufacture of other phosphate fertilizers. Ground rock

Table 10.5 Phosphorus fertilizers

Fertilizer	Formula	% P
Rock phosphate	$Ca_{10}(PO_4)_6(F,OH)_2$	11–15
Phosphoric acid	H_3PO_4	23
Ordinary superphosphate (OSP)	$Ca(H_2PO_4)_2 \cdot CaSO_4$	9
Triple superphosphate (TSP)	$Ca(H_2PO_4)_2$	20
Monoammonium phosphate (MAP)	$(NH_4)H_2PO_4$	21
Diammonium phosphate (DAP)	$(NH_4)_2HPO_4$	20
Ammonium polyphosphate	$(NH_4)_4P_2O_7$	15
Potassium dihydrogen phosphate	KH_2PO_4	23

phosphate is insoluble in soil and is solubilized over time to phosphate ions and absorbed by plants. The acidulation of rock phosphate with sulfuric acid produces ordinary superphosphate (OSP), which is a mixture of monocalcium phosphate and calcium sulfate.

$$Ca_{10}(PO_4)_6F_2 + 7H_2SO_4 = 3Ca(H_2PO_4)_2 + 7CaSO_4 + 2HF$$
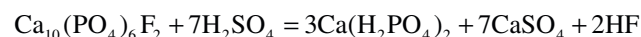
The OSP so produced consists of about one-half monocalcium phosphate and one-half calcium sulfate. It contains 9% phosphorus. The phosphorus in monocalcium phosphate is water soluble. OSP is rarely used today because other phosphorus fertilizers are less expensive on an equivalent phosphorus basis. Treatment of phosphate rock with phosphoric acid produces triple superphosphate (TSP), which is monocalcium phosphate with a higher content of phosphorus. The reaction is

$$Ca_{10}(PO_4)_6F_2 + 14H_3PO_4 = 10Ca(H_2PO_4)_2 + HF$$

TSP contains 20% P and is widely used as a phosphate fertilizer. Ammonium phosphates and polyphosphates may also be used, particularly where both N and P are needed. Table 10.5 shows different phosphorus fertilizers with their percentage concentration.

Industrial phosphate fertilizers are water soluble. When they are applied to soils they can undergo reactions with other soil constituents which may render them insoluble. This is known as phosphate sorption. The nature and degree of phosphate sorption depend on physicochemical properties of soil, particularly pH, clay content, type of clay, organic matter, oxides, and hydroxides of Fe, Al, Mn, etc. The result is the reduction in currently available phosphorus. At both low and high soil pH, phosphorus solubility is reduced. Adjustment of soil pH near neutrality may correct phosphate deficiency in many soils. Typically, only 10–20% of fertilizer P is absorbed by plants during the first year; the remainder is nearly all retained as fertilizer reaction products, which become less soluble with time.

10.20.1.8 Potassium Fertilizers

Huge natural potassium deposits are found in places where ancient seas have evaporated leaving the salts as evaporite

---

This extra material is known as "filler material." Wood ash or lime can be used as filler materials for mixed fertilizers.

10.20.1.11 Liquid Fertilizers

The term liquid fertilizer refers to anhydrous ammonia, aqueous ammonia, N solutions, and liquid-mixed fertilizers. They are true solutions. There are also suspensions or slurry-type mixtures of N, P, and K. They are called fluid fertilizers. Urea, urea–ammonium nitrate solution, ammonium polyphosphate solution, and finely ground KCl are used for making fertilizer solutions or suspensions. Micronutrients and pesticides are readily incorporated into liquid or fluid fertilizers. Fluid fertilizers can be applied to irrigation water in drip and sprinkler or underground injection systems and can be used for direct application to plant foliage. Application of nutrients with irrigation water is called fertigation. It requires sophisticated control systems to regulate water and nutrients. The system needs careful monitoring so that the chemicals used do not get precipitated (Sect. 10.22).

Suspensions contain more material added to the water than can dissolve, so it becomes a thin slurry. One to two percent clay (attapulgite, an alumino–Mg–silicate clay) is added to help hold particles in suspension. This allows for preparation of higher grades, as compared with liquid fertilizers. Similar effects may be obtained from both liquid and dry fertilizers if similar amount is applied in the same manner. The solution fertilizers are quite popular and can be applied with herbicides mixed into the solution.

10.20.2 Organic Fertilizers Are Natural Materials

Many natural organic materials have been used as fertilizers from ancient times. Farmyard manures and composts are very familiar organic fertilizers. Other organic fertilizers include poultry manure, blood meal, bone meal, fish meal, oil cakes, worm castings, peat, seaweed, humic acid, and guano.

Organic fertilizers have low nutrient concentrations. Their composition is also variable, and the calculation of the requisite amount of nutrient is difficult. Huge quantities of materials are needed to supply adequate nutrients for crop growth. Nevertheless, there are many advantages of using organic fertilizers. Organic fertilizers contain nitrogen in the organic form that is slowly mineralized in soil, and available nitrogen is released at a pace favorable to plants. Hence, they act as slow-release fertilizers, and leaching and denitrification losses are minimized. Organic fertilizers act like compound fertilizers containing several nutrients at a time, including micronutrients. For example, farmyard manures contain about 0.5% N, 0.25% P, 0.4% K,

Table 10.8 Nutrient concentration in different animal manures

Farmyard manure	% N	% P	% K
Cow manure	2.0–3.0	0.5–1.0	1.0–2.0
Horse manure	1.0–2.0	0.5–1.0	1.0–2.0
Pig manure	2.0–3.0	0.5–1.0	1.0–2.0
Sheep manure	3.0–4.0	0.5–1.0	2.0–3.0
Poultry manure	3.0–4.0	1.0–2.0	1.0–2.0

Source: http://extension.usu.edu/files/publications/factsheet/HG-510.pdf

0.08% Ca, 0.02% S, 0.4% Fe, 0.003% Cu, 0.004% Zn, and 0.007% Mn. Organic fertilizers improve physical conditions of the soil; they enhance root growth that utilizes nutrients better. Residual effects of organic fertilizers are positive and long-lasting. However, collection, storage, marketing, distribution, and application of huge quantity of organic fertilizers are difficult and cost and labor consuming. Otherwise, organic fertilizers are very effective in increasing growth and yield of crops. They keep the soil biologically active and healthy. Organic fertilizers add multiple nutrients, improve soil structure, increase water-holding capacity, and improve aeration.

10.20.2.1 Farmyard Manure

The term farmyard manure was originally applied to well-trodden farm materials including vegetable feed wastes, feces, and urine of yarded animals in a farm along with straw to bind up feces. At present, farmyard manures are obtained by decomposing dung, urine, and feed wastes of farm animals. Generally, excreta and waste materials are gradually gathered and dumped in a pit in a shed at a cool dry place near the cattle shed. Care is taken so that the materials are not completely dried in the sun or wetted by rainwater. It needs 5–6 months for the completion of the decomposition process. By this time, the foul odor is gone and the materials have a crumbly appearance. The quality of material depends on the kind of farm animals, their feed, and the conditions of decomposition. Farmyard manures contain several nutrients. Concentrations of N, P, and K in different farmyard manures are given in Table 10.8.

10.20.2.2 Composts

Farms have many kinds of organic residues, including straw, food wastes, tree leaves, weeds, grass clippings, or other plant and garbage wastes, the disposal of which is a problem. These materials are alternatively composted and used as a fertilizer. For composting, organic residues, mostly plant materials with some animal dung and bedding, are gathered in a pile in a dry shaded place providing favorable water and aeration. As the organic matter decomposes, the bulk of the materials is reduced with the production of carbon dioxide and water. Nutrients are continuously reused and recycled by the microbes and conserved within the composting pile.

Table 10.9 Effect of NPK, poultry manure, and kitchen manure on growth of corn

Treatment	Height of 60-day old-plants, cm	Number of leaves plant^{-1}	Yield of grains, g plot^{-1*}
Control	65	5	503[d]
NPK	105	10	1,785[c]
Kitchen compost	100	10	2,117[b]
Poultry manure	135	14	3,000[a]

*Figures followed by different letters in the column vary significantly by Duncan's multiple range test

Table 10.10 Miscellaneous organic fertilizers

Materials	% N	% P	% K
Alfalfa meal	2.0–3.0	0.5–1.0	1.0–2.0
Blood meal	12.0	1.0–2.0	0–1.0
Bone meal	1.0–6.0	11.0–30.0	0
Cottonseed meal	6.0	3.0	1.0
Fish meal	6.0–12.0	3.0–7.0	2.0–5.0
Hoof meal	12.0–14.0	1.5–2.0	0
Kelp	1.0–1.5	0.5–1.0	5.0–10.0
Legumes	2.0–4.0	0–0.5	2.0–3.0
Sawdust	0–1.0	0–0.5	0–1.0
Sewage sludge	2.0–6.0	1.0–4.0	0–1.0

Source: http://extension.usu.edu/files/publications/factsheet/HG-510.pdf

Thus, with a loss of carbon, oxygen, and hydrogen, other nutrient elements are concentrated during the process of decomposition. The finished product is rich, dark, crumbly, and sweet smelling.

The compost pile is occasionally, preferably at 15-day intervals, turned up and down to aerate the debris of the compost pile. It hastens decomposition. The low nitrogen content of many composting materials may retard their decomposition. For this reason, some nitrogen fertilizer is sometimes added to the compost pile for rapid decomposition. Since composts are low in N, P, and K contents, sometimes they are enriched by adding NPK fertilizers.

In the crop field of the Soil Science Department of Chittagong University, we prepared composts from kitchen wastes of eight student hostels. The wastes included vegetable scraps, fish scraps and bones, and chicken scraps. Collected materials were piled up in a concrete bin layer by layer. Each 15-cm layer was separated by a 2.5-cm-thick layer of top soil. Wastes were collected for 2 months and decomposed with occasional turning up for 8 months. An experiment was conducted by applying 20 t ha^{-1} each of this compost and poultry manure, and NPK (120, 60, 100 kg ha^{-1}, respectively) separately on corn (*Zea mays*). The height and number of leaves per plant data show that the prepared compost was as good as inorganic fertilizers (Table 10.9).

10.20.2.3 Green Manuring

Green manuring is a technique of plowing under a crop, usually a legume, when it is at a suitable stage of growth. The green manuring plants should have the ability to grow fast, to grow satisfactorily in poorly fertile soils, and to produce enough succulent biomass that adds organic matter after incorporation into the soil and decomposes at a moderate rate. The crop is grown in a period of fallow between two crops. Legume seeds are sown densely in the field after harvest of a crop, and the seedlings are allowed to grow until flowering. The crop utilizes little native soil nitrogen. About 80–90% of the nitrogen need of the crop is met by atmospheric nitrogen fixation. At the flowering stage, when the plant tissue is still tender and the biomass accretion is at maximum, the crop is plowed under or incorporated into the soil, keeping the soil

moisture level near field capacity to enhance decomposition. The next crop is planted at least after 15–20 days of incorporation. Green manuring adds 2–7 t ha^{-1} organic matter and 100–300 kg ha^{-1} nitrogen depending on the legume species, the type of soil, and environment of decomposition. Thirty to fifty percent of this nitrogen is utilized by the next crop. That is, green manuring can reduce almost 30–50% of the nitrogen fertilizer need of the next crop. The remainder nitrogen is made available in succeeding years. Besides adding nitrogen, green manuring has other functions. Green manure increases soil organic matter, enhances activity of soil microorganisms, and improves soil structure. Deep-rooted green manure crops bring nutrients to the surface soil. Green manuring helps combat weeds. Important green manure crops are alfalfa (*Medicago sativa*), cowpea (*Vigna catjang*), lablab (*Dolichos lablab*), lentil (*Lens esculenta*), pigeon pea (*Cajanus cajan*), sesbania (*Sesbania aculeata*), soybean (*Glycine max*), sun hemp (*Crotalaria juncea*), sweet clover (*Melilotus officinalis*), etc. These crops produce 3–7 Mg ha^{-1} organic matter and contribute 120–300 kg ha^{-1} nitrogen to soil.

10.20.2.4 Miscellaneous Organic Fertilizers

Many plant and animal products and by-products are used as organic fertilizers. These materials are very popular in organic farms, where farmers use all natural materials, organic and inorganic, as fertilizers, soil conditioners and pesticides. Oil cakes, bone meals, fish meals are used as pot mixes in greenhouses and nurseries. Table 10.10 shows nutrient concentrations of some miscellaneous organic fertilizers obtained from different sources.

10.21 Determining the Kind and Dose of Fertilizer Is Called Fertility Evaluation

There are several methods of determining the kind and amount of fertilizers needed for a crop in a soil. The major techniques include visual diagnosis, analysis of plant tissues

Table 10.11 Plant parts and time of sampling for plant analysis

Crop	Sampling time	Plant part to be sampled
Corn (*Zea mays*)	Initial silk	Ear leaf
Wheat (*Triticum aestivum*)	Prior to heading	Top two leaves
Soybean (*Glycine max*)	Prior to pod set	Most recent leaf
Cucumber (*Cucumis sativus*)	Flower to fruit set	Fifth leaf from growing tip
Tomato (*Lycopersicon esculentum*)	Mid-bloom	Leaf adjacent to top flower cluster
Alfalfa (*Medicago sativa*)	Prior to flowering	Top 15 cm
Pea (*Pisum sativum*)	Prior to flowering	Newest fully developed leaf
Cabbage (*Brassica oleracea*)	Mid-season	Upper mature leaves
Potato (*Solanum tuberosum*)	Prior to flowering	Newest mature leaf
Sorghum (*Sorghum bicolor*)	Prior to heading	Second fully developed leaf

and soils, pot culture experiments, and field trials. However, any of the methods individually may not give satisfactory results. For example, plant test values often need to be correlated with soil test values. Soil tests are most useful before planting to predict fertilizer needs; plant tissue tests are best used during the growing season to monitor plant nutrient uptake. Soil samples supplement tissue samples by providing information on soil fertility, pH, and soluble salts. Comparison of the two samples can help reveal whether nutrition or other factors—such as pests, disease, or environmental stress—are involved.

10.21.1 Visual Symptoms May Indicate Nutrient Deficiency and Toxicity

Ideally deficiency of any one nutrient element in a plant should produce characteristic deficiency symptoms that may be corrected by the application of that element only. However, identification of deficiency and need of a particular nutrient element on the basis of visual symptoms is often difficult and confusing. Deficiencies of multiple elements together make deficiency symptoms more complicated. Often deficiencies of two elements produce closely similar symptoms such as nitrogen and magnesium. Besides this, by the time plant nutrient deficiency symptoms become obvious, it may be too late to correct the deficiency by fertilizers. Significant damage has already been done, and it would be difficult for the crop to recover. However, symptoms are useful in determining which nutrients are deficient in perennial crops, where fertilizers are applied in different seasons. Lawns commonly turn light green or yellow when nitrogen is deficient, and this indication of nitrogen deficiency can be very useful for lawn owners. Many trees, shrubs, and flowers develop iron deficiency symptoms when growing on alkaline soils and these symptoms are very important to many gardeners. Nutrient deficiency symptoms may be confirmed by short-duration pot culture, sand culture, and solution culture experiments.

10.21.2 Tissue Test Indicates Nutrient Status in Plants

There are rapid tissue tests and total plant analysis. Rapid tissue tests are generally carried out on sap from leaf and petiole samples with plant tissue test kits, and to get information about nitrate-N, sulfate-S, or phosphate-P. The use of diphenylamine as an indicator of the concentration of nitrate in the sap of corn leaf has satisfactorily been used to judge sufficiency or deficiency of nitrogen in corn. Simplicity of use and immediate results obtained from tissue tests are beneficial to plant nutritionists who diagnose plant growth problems in the field. On the other hand, plant analysis is the total nutrient analysis of plant samples, preferably leaves. Plant tissue analysis should not be confused with tissue tests. Plant tissue analysis is performed on dried plant tissue that has been processed in a laboratory and analyzed for any one or all of total N, P, K, S, Ca, Mg, Zn, Cl, Cu, Fe, B, Mn, Mo, and Co.

Plant tissue analysis measures concentrations of most essential plant nutrients in leaf tissue. Healthy plants contain predictable concentrations of nutrients that vary with plant type and growth stage. Tissue analysis results are an indicator of plant nutritional health and could be an excellent basis for diagnosing whether existing problems are nutritional in nature. However, plant analytical results differ with plant species, plant parts of the same species, growth stage, age of the leaf, position of leaf in plant, etc. Table 10.11 shows suitable parts and time of sampling for some crop plants.

Plant tissue tests are frequently used for fertilizer recommendations for long duration crops like tea, coffee, grapes, sugarcane, pineapple, and fruit trees. Plant analysis has also been employed for corn, wheat, barley, tomato, tobacco, and soybean. In perennial plants, the nutritional status of the plant can be assessed, and the appropriate fertilizer can be applied long before harvest, which allows plenty of time for the plants to benefit from the fertilization.

Chemical tests of plant tissue are used to determine the degree of deficiency or sufficiency of nutrients in plants. Research data have been used to relate nutrient composition
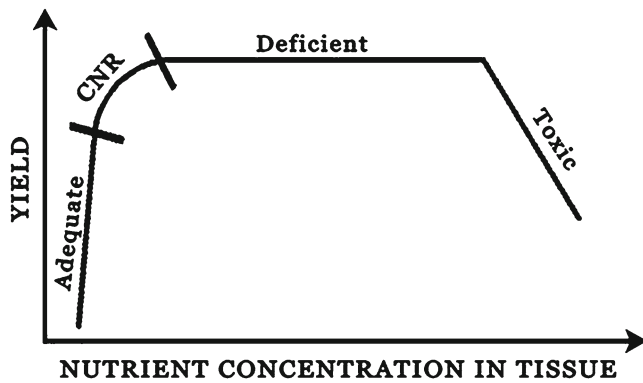
Fig. 10.3 Relationship between nutrient concentration in plant and crop yield

Table 10.12 Critical nutrient ranges and sufficiency ranges for cereals

Nutrients	Critical nutrient ranges	Sufficiency ranges
(%)		
N	1.25–1.75	1.75–3.0
P	0.15–0.25	0.26–0.5
S	0.1–0.15	0.15–0.40
K	1.0–1.5	1.5–3.0
Ca	0.10–0.2	0.2–1.0
Mg	0.1–0.15	0.15–0.50
(mg kg^{-1})		
Fe	15–20	20–250
Zn	10–15	15–70
Cu	2.3–3.7	3.7–25
Mn	10–15	15–100
B	3–5	5–25
Mo	0.01–0.02	0.03–5

Source: Manitoba Provincial Soil Testing Laboratory (1987)

of particular plants to growth or yield. For example, corn plants have sufficient nitrogen for maximum yield when the nitrogen content of the leaf opposite and below the uppermost ear is 3%. Red pine needles with less than 0.35% potassium are deficient in K; maximum growth was obtained when needle K was about 0.5%.

10.21.2.1 Critical Nutrient Ranges in Plants

There are three important threshold markers of nutrient concentrations in plants: (a) The deficiency level, which reflects the nutrient concentration below which deficiency symptoms become visible; (b) the critical nutrient range (CNR), which stands for the nutrient concentration above which the plant is sufficiently supplied with nutrients for achieving the maximum potential yield, and below which growth or yield is considerably reduced and a response to added nutrient occurs; and (c) the toxicological value, which indicates the nutrient concentration above which toxicity symptoms can be observed. Critical nutrient ranges vary among plants and nutrients, but occur somewhere in the transition between nutrient deficiency and sufficiency. The sufficiency range is the nutrient level at which the plant has enough nutrients to function and develop properly, but not so much that it becomes toxic (Fig. 10.3).

For a general understanding, critical nutrient ranges (CNRs) and sufficiency ranges (SRs) of the nutrients for cereals are given in Table 10.12. However, the readers should be aware that a single value or a range may not be applicable to all plants. Critical nutrient ranges for many different crops have been proposed; but establishing well-defined standard critical nutrient ranges or sufficient ranges of all the nutrients for all the crops under widely varied growing conditions is difficult.

10.21.2.2 Diagnosis and Recommendation Integrated System

The critical nutrient concept has many limitations. Critical ranges differ with growth stage, leaf age, leaf position, height of plants from which leaf is sampled, soil conditions, crop management, etc. To avoid these difficulties, a different approach called "Diagnosis and Recommendation Integrated System" (DRIS) was adopted (Beaufils 1973; Walworth and Sumner 1987). DRIS uses nutrient ratios instead of individual nutrient concentrations as a basis of judging nutrient deficiency or sufficiency. The most common ratio is the N–S ratio. For most crops, it should range between 10 and 15. When it exceeds 18, the S becomes limiting in relation to N. The ratios are fairly constant over leaf age, leaf position, growth stage, variety, etc. In addition, ratios take nutrient interactions into consideration. So, ratios are more acceptable than nutrient concentrations or critical nutrient ranges. However, the usage of nutrient ratios has also been criticized on the ground that the same N–S ratio of 10, which indicates a balance between N and S, can be created when both N and S are sufficient, when both are deficient, and when S is deficient. DRIS takes all the nutrient ratios at a time into consideration to calculate DRIS indices.

The DRIS is based on the comparison of crop nutrient ratios with optimum values from a high yielding group (DRIS norms). The DRIS provides a means of simultaneous identifying imbalances, deficiencies, and excesses in crop nutrients and ranking them in order of importance. The major advantage of this approach lies in its ability to minimize the effect of tissue age on diagnosis, thus enabling one to sample over a wider range of tissue age than permissible under the conventional critical value approach.

For basic data based on which DRIS norms are determined: (a) The area for which DRIS norms are to be developed (e.g., region, district, state) is decided; (b) a large number of sites where a particular crop is growing are selected at random in order to represent the whole production area; (c) at each site, plant and soil samples are taken for all essential element analyses; (d) other parameters likely to be related directly or indirectly to yields are also recorded; (e) entire population of

observation is divided into two subpopulation (high and low yielders) on the basis of vigor, quality, and yields; (f) each element in the plant is expressed in as many ways as possible (concentrations and ratios); (g) mean of each type of expression for each subpopulation is calculated; and (h) each form of expression which significantly discriminates between the high and low yielding subpopulation is retained as a useful diagnostic parameter. DRIS norms are originated after the reference population definition; in other words, the relation between all the nutrients pairs and their respective standard deviations or coefficients of variation are obtained. The DRIS indices are calculated after obtaining the DRIS norms. For that the nutrient ratios N/P, N/K, Ca/N, Mg/N, K/P, Ca/P, P/Mg, Ca/K, Mg/K, Mg/Ca, and so on, their mean, and coefficient of variations are calculated first, and then the indices are obtained. The readers are referred to Bangroo et al. (2010) for calculation of DRIS indices and their interpretation.

Considering that DRIS uses the nutritional balancing concept (relationship among nutrients), it is postulated that this method might be more precise than the others in the detection of nutritional deficiency or/and excess. Advantages of DRIS over other diagnosis methods include the following: (1) It presents continuous scale and easy interpretation; (2) it allows nutrient classification (from the most deficient up to the most excessive); (3) it can detect yield limitation due to nutrient unbalance, even when none of the nutrients is below the critical level; and (4) it allows diagnosis of the total plant nutritional balance, through an unbalance index (Baldock and Schulte 1996). An additional advantage of DRIS according to some authors is its less sensitivity to tissue aging (Walworth and Sumner 1987). An important limitation of the DRIS method is that the established standard sampling period, in some annual crops, may occur too late in the growing season, so that fertilizer application will not be effective to correct a nutritional problem, or may not match the sudden symptoms of a nutritional disorder (Walworth and Sumner 1987). For this problem, it would be necessary to get nutritional reference values for several maturation stages, but standards have not yet been established for many crops. The main limitation of the DRIS system is the lack of adequate database for the purpose of comparison. This method is not very useful to small farmers. This procedure is of difficult application (Filho 2004). There is a need for precise definition, at the sampling time, of plant growth stages in the field and communicating this information to the person taking care of the diagnosis so that appropriate norms can be selected and used.

10.21.3 Soil Test Is an Efficient Tool of Fertility Evaluation

A soil test can be an important management tool in developing an efficient soil fertility program as well as monitoring a field for potential soil and water management problems. A soil test provides basic information on the nutrient supplying capacity of the soil.

Soil tests are used to determine the levels of available nutrients and probability of response to added fertilizers, particularly P, K, and in some instances Mn, Cu, Zn, and Fe. There is growing interest in extending the use of soil testing to assess the potential impact of soils and soil amendments on other sectors of the environment. Understanding many factors, including the soil test extractants used, the methods of soil sampling, handling, and storage, is required to interpret the quantitative results of a soil test. For fertility evaluation, generally the available nutrient levels together with soil texture, pH, and organic matter contents are determined.

Only about a half kilogram of soil is sampled to determine fertility level of a hectare of land having about 2 million kg soil in the furrow slice. Therefore, extreme care must be taken to make the soil sample representative. All sorts of variations in the field must be taken into consideration. The field may need to be separated into different blocks. Usually, it is better to prepare a single soil sample for each block from several subsamples. For large areas, 20–25 subsamples may be taken and mixed together to form a composite sample. A soil probe or auger is ideal for taking soil samples, but a sharp spade, long knife, or trowel can be used. For cereals and other shallow-rooted crops, soil samples from 0 to 15 cm depth may be suitable. For deep-rooted crops, soil sampling depths may be 0–30 or 0–45 cm.

Several soil extractants are used to determine available nutrients of soil. The choice of the extractant will depend on soil properties (pH, organic matter content, cation exchange capacity, etc.) and the overall purpose of soil testing (agronomic vs. environmental, measurement of total vs. soluble vs. plant available, element concentration, and others). Generally, soil and water in 1:2.5 ratio for pH; 1 N KCl solution for NO_3–N, Bray and Kurtz 1, Mehlich 3, and Olsen extractants for available P; 1 N NH_4OAc for exchangeable K, Ca, and Mg; DTPA (diethylenetriaminepentaacetic acid) for Zn, Fe, and B; and calcium phosphate solution for S are used. These methods are described in detail in Page et al. (1982).

Soil test values are classified into low, medium, and high categories (Table 10.13), and fertilizer recommendations are made accordingly, taking yield targets into consideration. At low levels of soil test extractable nutrients, crop yield is limited by nutrient deficiency, and there will be a positive response to added fertilizers. There may be some crop response at medium levels of nutrients, but at high levels, there will usually be no response.

The amount of nutrients extracted by a soil test must be well correlated with plant nutrient uptake by plants for the test to be useful. Pot and field experiments are conducted for calibration of soil test results with crop response.

Table 10.13 Low, medium, and high categories of soil test values

Element	Low	Medium	High
NO$_3$–N[a]	<10	10–20	>20
Olsen P[b]	<10	10–20	>20
Extractable K[a]	<150	150–250	>250
Extractable Ca[a]	<1,000	1,000–2,000	
Extractable Mg[b]	<60	60–300	>300
DTPA extractable Fe[c]	<2.5	2.5–4.5	>4.5
DTPA extractable Zn[c]	<0.5	0.5–1.0	>1.0
DTPA extractable Cu[c]	<0.3	0.3–1.0	>1.0
DTPA extractable Mn[c]	<1.0	1.0–2.5	>2.5

Source: [a]Marx et al. (1999), [b]Horneck et al. (2011), [c]Herrera (2000)

10.21.4 Pot Experiments Are Closely Observed Small-Scale Fertilizer Trials

Pot experiments are often conveniently used to find out the effects of added fertilizer on crop plants and to relate crop response to soil test and plant test values. The soil, for which the need of fertilizer or the effect of added fertilizers will be evaluated, is filled in earthen, plastic, or porcelain pots of appropriate size, and the crop is grown after giving the necessary treatments. The pots can be arranged according to an experimental design in a small area within the lawn, nursery shed or experimental block, in shade or open sunlight as needed under close observation, or at completely controlled environment in the greenhouse. The soil of the pots may be analyzed before planting and after the harvest; plant parts may be analyzed at different growth stage, and yield of the plant can be estimated. Results may be used to infer the effect of the fertilizers and the uptake of nutrients by the crop and to construct the crop response curve.

However, pot experiments have several limitations. Pot soils behave differently from field soils. Pot soils tend to remain loose at the onset of the experiment and get compacted at the end. Root growth in pots is often restricted by the size of the pot. Aeration, water movement, and water saturation in pot soils are very different from field soils. Yield of potted crops often becomes magnified and, without correlating to results of a field trial in the soil where the crop will be ultimately grown, cannot give useful results. Therefore, as the conditions of pot experiments are different from those in the field, the results are not always directly applicable to large-scale farming.

10.21.5 Field Trials Are Large-Scale Fertilizer Experiments

Once the soil test or plant test values are obtained, they are correlated with crop response from field trials. By field trials, we get how much fertilizers will be needed by a particular crop in a particular soil. The expected response of the crop at any given soil test level is what determines the recommended level of each nutrient. The amount of fertilizer recommended is determined from many field trials on different soils over many years. The approach is based on a research data base that adequately predicts a crop response under good or normal conditions. The research base must be sufficient for each crop on the existing soil types under most of the prevailing weather conditions. Let us think of a field trial with six fertilizer combinations preconceived from reference database. We have to take at least three replications. A suitable area of the field or the entire field will then be divided into 18 equal plots, may be in 3 blocks. Six fertilizer dozes will be randomly and separately assigned to each of the plots. This is a randomized complete block field design. A crop will be grown in the plots with equal management inputs. After harvest the dose of fertilizer for the maximum economic yield will be selected for that crop in that and similar soils. Maximum economic yield may differ from maximum yield.

Field experiments are the more reliable methods, but being time-consuming and expensive, they are conducted mainly by the research farms and research organizations. Farmers wishing to use field experiments as a valid means of determining the fertility status of their soils should seek the advice of agronomists.

Crops, Soils, and Human Nutrition
Humans get carbohydrates, proteins, vitamins, alkaloids, and mineral nutrients mainly from plant products. Only 17 plant species provide approximately 90% of human food requirement. Eight cereal grains including wheat, corn (maize), rice, barley, sorghum, oats, rye, and millet provide 56% of the food energy and 50% of the protein consumed on earth. Three cereals: wheat, maize, and rice together comprise at least 75% of the world's grain production. Cereals, the main sources of carbohydrates, lack a number of nutrients which are essential for human health and well-being. They contain numerous vitamins and minerals with low biological availability (Cordain 1999). Fruits and vegetables supplement necessary vitamins and minerals to humans. Besides carbon, nitrogen, hydrogen, and oxygen, humans need 29 mineral nutrients, including aluminum, arsenic, boron, bromine, calcium, chlorine, chromium, cobalt, copper, fluorine, germanium, iodine, iron, lead, lithium, magnesium, manganese, molybdenum, nickel, phosphorus, potassium, rubidium, selenium, silicon, sodium, sulfur, tin, vanadium, and zinc, for their life processes (McDowell 2003). Food materials, including cereals, vegetables, fruits, nuts, meat, and fish, contain minerals in widely

(continued)

varying amounts. Since plant materials constitute more than 90% of the food, they are the main sources of mineral nutrients to human. Plants absorb these nutrients from the soil. Therefore, soil is the principal source of human nutrients as well. But during analysis of plant and soil samples in the laboratory, we hardly remember this fact; we only consider essential nutrients for plants. Some examples of how deficiency of minerals in soil affects human health are noted here. Iodine deficiency is the leading cause of brain damage and mental retardation in the world. Iodine deficiency also causes endemic goiter, cretinism, dwarfism, and muscular disorder. More than 300 million people are suffering from goiter in the South Asian region including Bangladesh. Although coastal saline areas of this country are sufficient, the alluvial and piedmont soils away from the Bay of Bengal are deficient in iodine. Iodine deficiency is met by iodine supplementation in common salt in Bangladesh (Yusuf et al. 2008). Again, selenium deficiency to human occurs in the regions of the world containing low-selenium soils. These regions include Keshan Province in China (from which the name of the Keshan disease was taken), New Zealand, and Finland. Although "Keshan" disease was eliminated from China in the 1970s by an aggressive selenium supplementation program, Se deficiency still occurs in many parts of China (Sunde 2006). Serious Se deficiency in soils, crops, and serum samples of human has been reported from Yugoslavia (Maksimovic et al. 1992).

10.22 Fertilizer Application Methods Depend on Crops and Fertilizers

The time and methods of fertilizer application vary with the kind of fertilizers and the type of crops. For example, broadcasting may be suitable for basal dressings and closely growing crops but unsuitable for orchards. Liquid fertilizers may be applied by spraying over foliage or injecting into the soil or with irrigation water. Bulky organic manures should be applied well ahead of sowing so that the preliminary decomposition takes place before the seeds germinate. Otherwise, decomposing microorganisms may compete with the crop plants for nutrients. Considerable immobilization may take place after addition of partially decomposed manures and composts. Failing pre-sowing application, they may be applied any time after the seedlings have established themselves and in growing perennial crops. On the basis of time of application, fertilizers may be applied as basal dressing and top dressing:

1. *Basal dressing*: It is the application of fertilizers during field preparation or together with the seed. During field preparation, all the phosphate and potash fertilizers and a part of nitrogen fertilizer are applied through broadcasting and incorporated with the soil by harrowing. Fertilizers may be applied along with the seed by seed and fertilizer drillers.

2. *Top dressing*: It is the application of fertilizers to a standing crop. A part of nitrogen fertilizers is applied during maximum vegetative growth stage, and another part is given prior to flowering. Application of nitrogen fertilizers in such splits is known as split application. The top dressing of P and K is ordinarily done only in orchards and pasture lands which occupy the land for several years. In some countries, airplanes are employed for fertilizer application in hilly terrains, where large amount are to be applied and where deficiency develops over large tracts of land. In such application, fertilizer and pesticides may be combined together. It saves labor and time but may be expensive. On the basis of application in field, methods of fertilizer application may be of several types:

(a) *Broadcasting*: Spreading of fertilizers by hand or mechanical spreaders over the entire surface of field during cultivation, prior to sowing of seeds, or in a standing crop is termed as broadcasting. Broadcasting may be as basal dressing or top dressing. Broadcasting distributes large amounts of fertilizers, usually N, P, and K, evenly throughout the field. However, broadcasting micronutrient fertilizers has the risk of uneven distribution due to their small amounts.

(b) *Placement*: When fertilizers are not distributed throughout the whole field but are restricted to a place with reference to the seed or root is known as fertilizer placement. There are several placement methods:

  (i) *Plow-sole placement*: The fertilizer is placed in a continuous band on the bottom of the furrow during the process of plowing. Each band is covered as the next furrow is turned. By this method, fertilizer is placed in moist soil where it can become more available to growing plants during dry seasons. It results in less fixation of P and K than that which occurs normally when fertilizers are broadcast over the entire soil surface.

  (ii) *Deep placement or subsurface placement*: In this method, fertilizers are placed in the reduction zone as in paddy fields, where it remains available to the crop during the active vegetative period. It ensures better distribution in the root zone and prevents any loss by surface runoff. Fertilizers may be applied under the plow furrow in the dry soil before flooding the land and making it ready for transplanting.

(iii) *Localized placement*: It refers to the application of fertilizers into the soil close to the seed or root. It is usually employed when relatively small quantities of fertilizers are to be applied. It has some advantages. The roots of the young plants are assured of an adequate supply of nutrients; localized placement promotes a rapid early growth, and it reduces loss of applied fertilizers. It may have some limitations too. Seeds or roots may be damaged and the application may need special equipment.

(iv) *Combined drilling placement*: It refers to the drilling of seed and fertilizer together while sowing. It places the seed and small quantities of fertilizers in the same row. This is found useful in cereal crops, cotton, and grasses but not for pulses and legumes. This may affect the germination of the seed, particularly in legumes, due to excessive concentration of soluble salts.

3. *Band placement*: Fertilizer is placed in narrow bands which may be continuous or discontinuous to the side of seedling, some distances away from it and either at level with the seed, above the seed level, or below the seed level. There are two types of band placement: It includes hill and row placement. Hill placement is practiced in widely spaced (row to row about 1 m) crops. Row placement is done when plants are sown in close rows.

4. *Pellet placement*: In this method, mainly urea is applied in the form of pellets 2.5–5.0 cm deep between the rows of paddy crop. Fertilizer is mixed with soil in the ratio of 1:10 and made into dough. Small pellets of a convenient size are then made and deposited in the soft mud of paddy fields.

5. *Foliar application*: Roots are the main absorbing organs of the plants, but however, they can absorb small amount of nutrients from dilute solutions sprayed on their leaves. Sometimes fertilizers, particularly micronutrient fertilizers which are needed in small quantities, are applied as foliar sprays. Foliar sprays are a convenient way to apply additional nutrients to plants, supplementing those taken up from the soil. Foliar sprays also provide a quick means to help overcome an existing nutrient deficiency. When insecticides and fungicides are sprayed, fertilizers may be added in the same spray. The application of fertilizer with insecticides and fungicides reduces labor costs and machinery costs leading to less cost of crop production.

6. *Fertigation*: Fertigation is the application of fertilizer to standing crops together with irrigation water preferably in drip and sprinkler irrigation systems. Fertilizers are dissolved in irrigation water in appropriate concentrations, and the water is released at a controlled rate to keep pace with the nutrient uptake rate of the crop. Principal advantages of fertigation are increase in yield by 25–30%, saving fertilizer by 25–30%; precise application and uniform distribution of fertilizers, reducing nutrient losses; and major- and micronutrients may be applied at the same time, saving of cost, labor, energy, and risk of environmental contamination. Sandy soils can be brought under cultivation in this system. The system needs careful monitoring of the concentration of nutrients in solution and requires sophisticated control and distribution systems which may not be affordable by small farm holders.

Study Questions

1. What do you mean by soil fertility and productivity? How do they differ? What are the criteria of essentiality of elements to plants? What are the forms of nutrients that are absorbed by plants?
2. Discuss the physiological roles of N, P, and Mg. All of them affect carbohydrate metabolism—how? Mention the sources of N and P in soils. How do the pools of P in soil interact?
3. Discuss the environmental impacts of N and P fertilizers. How can we minimize fertilizer loss from soils? Sandy soils can be effectively fertilized by fertigation—explain.
4. Sandy, acid, and calcareous soils are prone to micronutrient deficiency—why?
5. What do you mean by availability of nutrients? How can you evaluate fertility of soil by soil test methods? Discuss fertilizer placement.

References

Amesz J (1993) The role of manganese in photosynthetic oxygen evolution. Biochem Biophys Acta 726:1–12

Anderson G (1980) Assessing organic phosphorus in soils. In: Khasawneh FE et al (eds) The role of phosphorus in agriculture. ASA/CSSA/SSSA, Madison

Arnon DI, Stout PR (1939) The essentiality of certain elements in minute quantity for plants with special reference to copper. Plant Physiol 14:371–375

Auld DS (2001) Zinc coordination sphere in biochemical zinc sites. Biometals 14:271–313

Bai C, Reilly CC, Wood BW (2006) Nickel deficiency disrupts metabolism of ureides, amino acids, and organic acids of young pecan foliage. Plant Physiol 140:433–443

Baldock JO, Schulte EE (1996) Plant analysis with standardized scores combines DRIS and sufficiency range approaches for corn. Agron J 88:448–456

Bangroo SA, Bhat MI, Ali T, Aziz MA, Bhat MA, Wani MA (2010) Diagnosis and Recommendation Integrated System (DRIS) – a review. Int J Cur Res 10:84–97

Beaufils ER (1973) Diagnosis and recommendation integrated system (DRIS). Soil Science Bulletin no. 1. University of Natal, Natal

Blevins DG, Lukaszewski KM (1998) Boron in plant structure and function. Ann Rev Plant Physiol Plant Mol Biol 49:481–500

Bonilla I, Blevins D, Bolaos L (2009) Boron functions in plants: looking beyond the cell wall. In: Taiz L, Zeiger EA (eds) Companion to plant physiology, 4th edn. Sinauer Associates Inc., Sunderland

Brady NC, Weil RR (2002) The nature and properties of soils, 13th edn. Pearson Education Inc., New Delhi

Bray RH, Kurtz LT (1945) Determination of total, organic, and available forms of phosphorus in soils. Soil Sci 59:39–45

Chen C, Huang D, Liu J (2009) Functions and toxicity of nickel in plants: recent advances and future prospects. Clean 37(4–5):304–313

Chen W, He ZL, Yang XE, Mishra S, Stoffella PJ (2010) Chlorine nutrition of higher plants: progress and perspectives. J Plant Nutr 33(7):943–952

Collard JM, Corbisier P, Diels L, Dong Q, Jeanthon C, Mergeay M, Taghavi S et al (1994) Plasmids for heavy-metal resistance in Alcaligenes-eutrophus Ch34 – mechanisms and applications. FEMS Microbiol Rev 14(4):405–414

Conrad R (1996) Soil microorganisms as controllers of atmospheric trace gases (H_2, CH_4, OCS, N_2O and NO). Microbiol Rev 60:609–640

Cordain L (1999) Cereal grains: humanity's double-edged sword. In: Simopoulos AP (ed) Evolutionary aspects of nutrition and health. Diet, exercise, genetics and chronic disease. World Rev Nutr Diet Basel Karger 84:L19–73

Cowan CE, Zachara JM, Resch CT (1991) Cadmium adsorption on iron-oxides in the presence of alkaline-earth elements. Environ Sci Technol 25:437–446

Cui Y, Zhao N (2011) Oxidative stress and change in plant metabolism of maize (*Zea mays* L.) growing in contaminated soil with elemental sulfur and toxic effect of zinc. Plant Soil Environ 57(1):34–39

Deak S (1985) Health hazards from nitrates in drinking water. Report on a WHO meeting, Copenhagen, 5–9 March 1984. WHO, Geneva

Ewing MC, White RMM (1951) Cyanosis in infancy from nitrates in drinking water. Lancet 260:931

Fageria VD (2001) Nutrient interactions in crop plants. J Plant Nutr 24(8):1269–1290

Filho FAAM (2004) DRIS: concepts and applications on nutritional diagnosis in fruit crops. Sci Agricn (Piracicaba Braz) 61(5):550–560

Fixen PE, Grove JH (1990) Testing soils for phosphorus. In: Westerman RL (ed) Soil testing and plant analysis. SSSA, Madison

Foth HD (1990) Fundamentals of soil science, 8th edn. Wiley, New York

Frolking SE, Mosier AR, Ojima DS, Li C, Parton WJ, Potter CS, Priesack E, Stenger R, Haberbosch C, Dorsch P, Flessa H, Smith KA (1998) Comparison of N_2O emissions from soils at three temperate agricultural sites: simulations of year-round measurements by four models. Nutr Cycl Agroecosyst 52:77–105

Freundlich H (1926) Colloid and capillary chemistry. Methuen, London

Goldbatch HE, Huang L, Wimmer MA (2007) Boron functions in plants and animals: recent advances in boron research and open questions. Adv Plant Anim Boron Nutr Part 1:3–25. Springer

Griffin RA, Jurinak JJ (1974) Kinetics of the phosphate interaction with calcite. Soil Sci Soc Am Proc 38:75–79

Hall SJ, Huber D, Grimm NB (2008) Soil N_2O and NO emissions from an arid, urban ecosystem. J Geophys Res 113. doi:10.1029/2007JG000523

Hepler PK (2005) Calcium: a central regulator of plant growth and development. Plant Cell 17:2142–2155

Herrera E (2000) Soil test interpretations. Guide A-122. http://aces.nmsu.edu/pubs/_a/a-122.pdf. Accessed 22 Dec 2011

Hingston FJ, Posner AM, Quirk JP (1974) Anion adsorption by goethite and gibbsite. 2. Desorption of anion from oxide surfaces. J Soil Sci 25:16–26

Hopkins B, Ellsworth J (2005) Phosphorus availability with alkaline/calcareous soil. Western Nutr Manage Conf 6:88–94

Horneck DA, Sullivan DM, Owen JS, Hart JM (2011) Soil test interpretation guide. http://www.sanjuanislandscd.org/Soil_Survey/files/page18_3.pdf. Accessed 3 Jan 2012

http://www.montmorillonite.org/Mulders%20chart.htm. Accessed 27 Aug 2011

IPCC (1992) Climate change 1992: the supplementary report to the IPCC scientific assessment. Cambridge University Press, Cambridge

IPCC (1995) Climate change 1994: radiative forcing of climate change and an evaluation of the IPCC IS92 emission scenarios. Cambridge University Press, Cambridge

Jiang BF, Gu YC (1989) A suggested fractionation scheme of inorganic phosphorus in calcareous soils. Sci Agric Sin 22(3):58–66 (in Chinese)

Kuo S (1996) Phosphorus. In: Sparks DL (ed) Methods of soil analysis: Part 3 Chemical methods. SSSA, Madison

Langmuir I (1918) The adsorption of gases on plane surfaces of glass, mica and platinum. J Am Chem Soc 40:1361–1402

Maksimovic ZJ, Djujic I, Jovic V, Rsumovic M (1992) Selenium deficiency in Yugoslavia. Biol Trace Elem Res 33(1–3):187–196

Manitoba Provincial Soil Testing Laboratory (1987) http://www1.agric.gov.ab.ca/$department/deptdocs.nsf/all/agdex3791/$file/540-.pdf?OpenElement. Accessed 23 Dec 2011

Marschner H (1993) Mineral nutrition of higher plants, 2nd edn. Academic, London

Marx ES, Hart J, Stevens RG (1999) Soil test interpretation guide. http://ir.library.oregonstate.edu/xmlui/bitstream/handle/1957/14361/ec1478.pdf;jsessionid=3B8749E2C71F904D46997A5669BF6029?sequence=1. Accessed 12 Jan 2012

McBride MB (2000) Chemisorption and precipitation reactions. In: Sumner ME (ed) Handbook of soil science. CRC Press, Boca Raton

McDowell LR (2003) Minerals in animal and human nutrition, 2nd edn. Elsevier, Amsterdam

McKenzie R (1992) Micronutrient requirement of crops. Alberta Agriculture, Food and Rural Development http://www1.agric.gov.ab.ca/$department/deptdocsf/all/agdex713/$file/531-1.pdf?OpenElement. Accessed 25 Jan 2012

Mehlich A (1953) Determination of P, Ca, Mg, K, Na, and NH4. North Carolina Soil Test Division (Mimeo), Raleigh, NC

Mehlich A (1984) Mehlich 3 soil test extractant: a modification of Mehlich 2 extractant. Commun Soil Sci Plant Anal 15:1409–1416

Mendel RR, Hansch RJ (2002) Molybdoenzymes and molybdenum cofactor in plants. J Exp Bot 53(375):1689–1698

Mishra SN, Jaiwal PK, Singh RP, Srivastiva HS (1999) Rhizobium-legume association. In: Srivastava HS, Singh RP (eds) Nitrogen nutrition and plant growth. NH Science Publishers, Inc., Enfield

Mulder (1953) Les elements mineurs en culture fruitière, presented at the 1° Congegno Nazionale de Frutticotura, Montan de Saint Vincent. http://www.apal.com.au/site/DefaultSite/filesystem/documents/APAL%20PLANT%20NUTRIENT%20INTERACTIONS%20July%2008.pdf. Accessed 24 Oct 2011

Nakagawa H, Jiang C-J, Sakakibara H, Kojima M, Honda I, Ajisaka H, Nishijima T, Koshioka M, Homma T, Mander LN, Takatsuji H (2005) Overexpression of a petunia zinc-finger gene alters cytokinin metabolism and plant forms. Plant J 41:512–523

Olsen SR, Cole CV, Watanabe FS, Dean LA (1954) Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA Circ 939

Page AL, Miller RH, Keeney DR (1982) Methods of soil analysis. Part 2. Chemical and microbiological properties, 2nd edn. American Society of Agronomy Inc./Soil Science Society of America Inc., Madison

Pierzynski GM, Sims JT, Vance GF (2005) Soils and environmental quality. CRC Press, New York

Powlson DS (1997) Integrating agricultural nutrient management with environmental objectives – current state and future prospects. The Fertiliser Society, York

Power JF, Prasad R (1997) Soil fertility management for sustainable agriculture. CRC Press, London

Reid R (2007) Update on boron toxicity and tolerance in plants. In: Xu F, Goldbach HE, Brown PH, Bell RW, Fujiwara T, Hunt CD, Goldberg S, Shi L (eds) Advances in plant and animal boron nutrition. Springer, Dordrecht

Shikanai T, Muller-Moule P, Munekage Y, Niyogi KK, Pilon M (2003) PPA1, a P-type ATPase of *Arabidopsis*, functions in copper transport in chloroplasts. Plant Cell 15:1333–1346

Sims JT, Hodges SC, Davis J (1998) Soil testing for phosphorus: current status and uses in nutrient management programs. In: Sims JT (ed) Soil testing for phosphorus: environmental issues and implications. Southern Cooperative Series Bulletin no. 389. University of Delaware, Delaware

Solis P, Torrent J (1989) Phosphate fractions in calcareous vertisols and inceptisols of Spain. Soil Sci Soc Am J 53:462–466

Srivastava PC (1997) Biochemical significance of molybdenum in crop plants. In: Gupta UC (ed) Molybdenum in agriculture. Cambridge University Press, New York

Sunde RA (2006) Selenium. In: Bowman BA, Russell RM (eds) Present knowledge in nutrition, 9th edn. ILSI Press, Washington, DC

Sunderman FW, Oskarsson A (1991) Nickel. In: Merian E (ed) Metals and their compounds in the environment. VCH, Weinheim

Takano K (2003) Findings of field-diagnosis based on the Brix of peaches. Kikan Hiryo 94:55–61 (in Japanese)

Tamimi YN, Silva JA, Yost RS, Hue NV (1997) Adequate nutrient levels in soils and plants in Hawaii, Honolulu (HI). University of Hawaii (Agronomy and Soils, AS-3)

Tempkin MI, Pyzhev V (1940) Kinetic of ammonia synthesis on promoted iron catalysts. Acta Physiochim 12:327–356

Tisdale SL, Nelson WL, Beaton JD, Havlin JL (1997) Soil fertility and fertilizers, vol 5. Macmillan Publishing Company, New York

Tran TS, Simard RR (1993) Melich III – extractable elements. In: Carter MR (ed) Soil sampling and methods of analysis. Lewis Publishers, Boca Raton

Turner BL, Paphazy M, Haygarth PM, McKelvie ID (2002) Inositol phosphates in the environment. Philos Trans R Soc Lond Ser B 357:449–469

USEPA (2007) Ground water & drinking water. Consumer fact sheet on nitrates/nitrites. http://www.epa.gov/safewater/contaminants/dw_contamfs/nitrates.html. Accessed 9 Jan 2012

Walworth JL, Sumner ME (1987) The diagnosis and recommendation integrated system (DRIS). In: Stewart BA (ed) Advances in soil science, vol 6. Springer, New York

Wang C, Zhang SH, Wang PF, Hou J, Zhang WJ, Li W, Lin ZP (2009) The effect of excess Zn on mineral nutrition and antioxidative response in rapeseed seedlings. Chemosphere 75(11):1468–1476

Wang J, Liu WZ, Mu HF, Dang TH (2010) Inorganic phosphorus fractions and phosphorus availability in a calcareous soil receiving 21-year superphosphate application. Pedosphere 20(3):304–310

White RE (2006) Principles and practice of soil science: the soil as a natural resource, 4th edn. Blackwell Publishing, Malden

Wild A (1996) Soils and the environment. Low Price edn. Cambridge University Press, Cambridge

Yienger JJ, Levy H II (1995) Empirical model of global soil biogenic NO_x emissions. J Geophys Res 100(11):11447–11464

Yusuf HKM, Rahman AKMM, Chowdhury FP, Mohiduzzaman M, Banu CP, Sattar MA, Islam MN (2008) Iodine deficiency disorders in Bangladesh, 2004–05: ten years of iodized salt intervention brings remarkable achievement in lowering goitre and iodine deficiency among children and women. Asia Pac J Clin Nutr 17(4):620–628

Yruela I (2005) Copper in plants. Braz J Plant Physiol 17(1):145–146