2 Plant Mineral Nutrition

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Elements mainly derived from soil in inorganic form are known as **mineral elements**. The three main sources of nutrients for plants are air, water, and soil. Elements obtained from air are known as **non-mineral elements**, such as carbon, oxygen, and hydrogen. Irrigation water is also a source of mineral elements from dissolved salts, mainly NaCl, Na_2SO_4, $NaHCO_3$, $MgSO_4$, $CaSO_4$, $CaCl_2$, KCl, and K_2SO_4. The third environmental source of nutrition for autotrophic plants is soil. Figure 2.1 shows the relative distribution of various elements in the earth's crust, most of which are required for plant growth. Of these, oxygen constitutes about 46.5%, copper being 0.01%, and zinc, nickel, and selenium are present in traces. The relative percentage of some of the well-known macronutrients required for plant growth (calcium, potassium, magnesium, and phosphorus) is in the range of 3.6–0.12%. Phosphorus is the least abundant among the four elements. Among macroelements, nitrogen is the most abundant (44%) followed by potassium, calcium, magnesium, phosphorus, and sulfur. Iron is the most abundant (51%) microelement followed by manganese, boron, zinc, and copper. Mineral elements are essentially used in the synthesis of a variety of important organic compounds. They also play a variety of roles as ions or as components of inorganic compounds (Table 2.1). Mineral nutrients continually cycle through all living organisms. However, they enter biosphere primarily through the roots. Elemental composition of plants reflects the composition of soil. In soil, more than 60 elements are present, but not all are absorbed by the plants. At the same time, many of the ions absorbed by the plants remain in ionic state inside the cells for an indefinite period. Many of these ions are incorporated either into the structure of more complex molecules, such as storage proteins, calcium oxalate, glycosides, etc., or into the protoplasm or cell walls. Some mineral elements are utilized in one organ of a plant and get subsequently released by disintegration of cellular constituents. These are further translocated to other organs of the plant for reutilization. Redistribution of minerals which have accumulated in cells but have not been actually utilized is also common in plants. Plants have the ability to accumulate **essential elements** and exclude

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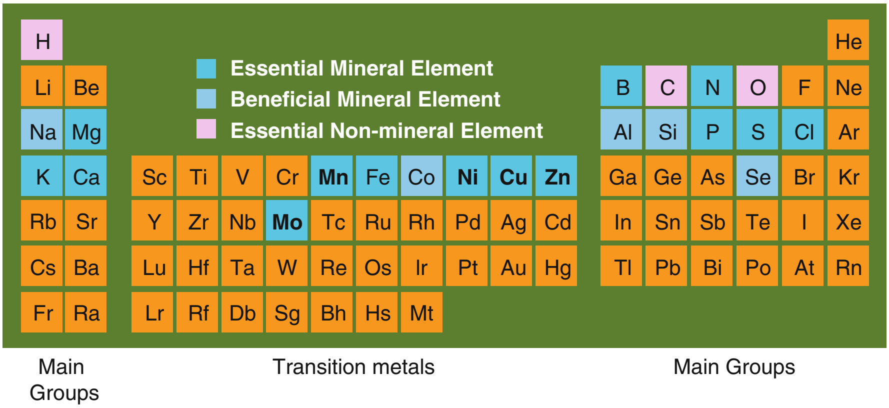


Fig. 2.1 Distribution of essential and beneficial mineral elements. All, except molybdenum, are among the 30 lightest elements. Elements in bold letters are hyperaccumulators in plants

Table 2.1 The roles of various mineral nutrients in plant cells

Mineral nutrients	Role in metabolism
As a constituent of organic compounds	
Nitrogen	Amino acids, proteins, purines and pyrimidines, chlorophyll, and many coenzymes
Phosphorus	Nucleic acids, phospholipids, ADP, ATP, NAD, NADP, and phosphate esters of sugars
Sulfur	Amino acids like cysteine and methionine, vitamin (thiamine and biotin)
As enzyme activators	
Iron	Cytochromes, peroxidases, catalases, and metalloflavoproteins
Calcium	Hydrolysis of ATP and phospholipids
Magnesium	Enzymes involved in carbohydrate metabolism and synthesis of DNA, RNA
Manganese	Nitrite reductase and hydroxylamine reductase
Molybdenum	Nitrate reductase, nitrogenase (in symbiotic association)
Zinc	Alcohol dehydrogenase, glutamic dehydrogenase, lactic dehydrogenase, and alkaline phosphatase
Copper	Cytochrome oxidase, ascorbic acid oxidase, polyphenol oxidase, and plastocyanin
Other roles	
K^+ and Na^+	Increase membrane permeability
Ca^{2+} and Mg^{2+}	Reduce permeability
Calcium	As calcium pectate in cell wall
Magnesium	Component of chlorophyll molecule and pectate in the middle lamellae

nonessential elements. Some minerals are required in minute quantities, e.g., plant requires 60 million times less molybdenum than hydrogen (Box 2.1). Such minute quantities could not be detected by the crude methods which were used earlier. In

Box 2.1: Mineral Nutrition: Historical Background

Aristotle (384–322 BC) and his student **Theophrastus** (371–285 BC) observed that plants require soil for their growth as it provides nutrition to the plants. Aristotle considered soil as vast stomach for the plants that prepares and supplies food to the plants. This observation was referred to as "humus theory of plant nutrition." According to this theory, humus provides carbon to the plants. However, according to **Thales of Miletus** (460–547 BC), "If water can change into ice and air then perhaps under some circumstances it changes into a tree or a rock." In 1648, **Van Helmont** noticed the requirement of inorganic nutrition in plants. In an experiment carried with willow plants, he observed that after 5 years, weight of dry soil decreased by 2 oz., while weight of the plant increased by 3 oz. He further observed that 61 pounds of gases and 1 pound of ash were produced when he burned 62 pounds of oak charcoal. He concluded that weight of plant increased by water only. In 1656, **Glauber** observed promotion of plant growth when potassium nitrate was added to the soil. He concluded that potassium nitrate is an "essential principle of vegetation." Later in 1699, **Woodward** observed that the plants grow better in muddy water as compared to rainwater. Thus, besides water, something else was believed to be contributing to the growth of plants. Water was only acting as a vehicle to transport nutrients from soil to the plants. In 1804, **Nicolas Théodore De Saussure** provided foundation for present knowledge of mineral nutrition. He rejected the theory of humus and demonstrated that plants obtain minerals from the soil through their root system and gases from air. **Sprengel** and **Boussingault** examined the relationship between fertilizer application and crop yield. Boussingault is also credited for providing the first evidence that legumes have the unique capacity to assimilate atmospheric nitrogen. **Sachs** and **Knops** started liquid culture of plants to study the nutrient requirements of the plants. They identified ten elements which are essential for the plant growth, viz., C, H, O, N, P, K, Ca, S, Mg, and Fe. **Justus von Liebig** was pioneer of agricultural chemistry and proposed the **law of minima** which states that productivity depends on the amount of deficient minerals. He stressed upon the importance of replenishing the mineral nutrients by fertilizer application. He analyzed ash composition of many plants and recorded 109 mineral elements to be present. Out of these, 20 elements were present in all plants, and these elements were called as **essential elements. J.B. Lawes** and **J.H. Gilbert** successfully converted insoluble rock phosphate into soluble phosphate (called superphosphate) by treating with sulfuric acid. **Arnon** and **Stout** in 1939 gave three criteria for an element to be considered as essential element.

addition to seven **ash elements** (the incombustible fraction of plant tissue), all elements which are required in large quantity (except for iron) are now known as **macronutrients.** There is another group of minerals, the **micronutrients**, needed in only minute quantities. It includes molybdenum, copper, zinc, manganese, boron, chlorine, and nickel**.**

In addition to essential elements, there is a small group of **beneficial elements** (sodium, silicon, aluminum, selenium, and cobalt) required by some plants. Sodium is essential for animals but is also required by C_4 plants. Although aluminum is found in both plants and animals, it is not essential for either of them. It is toxic to plants and may even be detrimental to animals. In some plants, aluminum acts as a functional element. For example, it is beneficial for the growth of tea plants and combats heavy metal toxicity. Accumulation of some micronutrients leads to toxicity in plants. Toxicity of elements generates reactive oxygen species which causes cellular damage. Some highly toxic elements, like lead and cadmium, are not distinguishable by the roots, and they enter the food web via nutrient uptake. Plants utilize various strategies for mobilization and uptake of nutrients. Soil properties like humidity, soil pH, and aeration are responsible for the availability of nutrients to the plants (Box 2.2). Most plants grow in nutrient-limited soils by changing root structure and increasing overall surface area to increase nutrient acquisition. They may exhibit elongation of the root system to access new nutrient sources. The most common change is inhibition of primary root growth (often associated with phosphorus deficiency). Other changes include increase in lateral root growth and density (during nitrogen, phosphorus, iron, and sulfur deficiency) and increase in root hair growth and density (during iron and phosphorus deficiency). An element present at a low level in the soil may cause deficiency symptoms in plants, while the same element at a higher level may cause toxicity. Sometimes, symptoms of deficiency of one element are similar to symptoms of toxicity of another element. Furthermore, abundance of one nutrient may cause deficiency of another nutrient. For example, lower availability of SO_4^{2-} can affect the uptake of NO_3^-, and K^+ uptake can be influenced by the amount of available NH_4^+. In certain plants, abnormal growth can be attributed to mineral deficiency, e.g., **"heartrot"** of sugar beet (boron), **"die-back"** in citrus tree (copper), **"whiptail"** of cauliflower (molybdenum), and **"little leaf"** of apple (zinc). All these are visible symptoms and can also be treated. This chapter emphasizes on inorganic plant nutrition requirement and their roles in plant growth and development and also on their deficiency symptoms.

Box 2.2: Soil-Nutrients Relationship

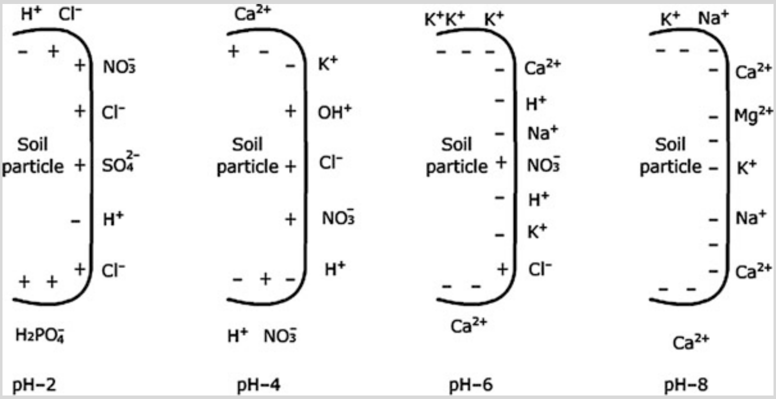
The concentration of free ions in the soil solution is generally low. The major portion of the cations is absorbed on the negatively charged sites of clay micelle and organic material in the soil**.** Anions, such as nitrate and sulfate, usually occur as free ions in the soil solution, whereas phosphate is firmly bound to the clay particles and is found at low concentrations in the soil solution. Anions are absorbed from the soil solution, but cations are exchanged directly between roots and soil particle by cation exchange. The soil cations essential for plant growth include ammonium, calcium, magnesium, and potassium ions. There are three additional cations which are not essential plant elements but affect soil pH. These include sodium, aluminum, and hydrogen. Soil cations are further divided into two categories. Ammonium, calcium, magnesium, potassium, and sodium are known as *base cations*, whereas aluminum and hydrogen are known as *acid cations*. When soil particles have a negative charge, they attract and retain cations. Most of the soils are negatively charged and attract cations. The ability or capacity of the soil colloid to hold cations is called **cation exchange capacity** (CEC). Cations in the soil compete with one another for a spot on the basis of CEC. However, some cations are attracted and held more strongly than other cations. Holding strength order of cations as held by soil particles is $Al^{+3} > H^{+} > Ca^{+2} > K^{+} > Na^{+}$. This is directly dependent on the amount of charge on the soil colloid. The number of cations a soil can hold is dependent upon the quality and composition of soil, pH of soil, and the presence of hydrous oxides of iron and aluminum. CEC is expressed as milliequivalents per 100 g of soil. CEC is indicative of nutrient-holding capacity of a soil. Addition of lime and how often it should be added are determined by CEC. In tropics, many highly weathered soils retain anions, rather than cations. The anions that are held by soil particles include phosphate, sulfate, nitrate, and chlorine (in order of decreasing strength). In comparison with soils with CEC, soils with an anion capacity have net positive charge. Soils that have an **anion exchange capacity** (AEC) typically contain weathered kaolin (hydrated aluminum silicate) minerals, iron and aluminum oxides, and amorphous materials. AEC is also dependent upon the pH of the soil and increases as the pH of the soil decreases. Base saturation is a measurement that indicates the relative amounts of base cations in the soil. It is the percentage of calcium, magnesium, potassium, and sodium cations that make up the total CEC. For example, a base saturation of 25% means that 25% of the CEC is occupied by the base cations. If soil does not exhibit AEC, then remaining 75% of the CEC will be occupied by acid cations. Generally, the base saturation is relatively high in moderately weathered soil that is formed from the basic igneous rocks. The pH of soil increases as base saturation increases. In contrast, highly weathered and acidic soils tend to have low base saturation. Whenever there is depletion of any free ions from the soil solution, respective ions are released from clay particles into the soil solution to maintain the equilibrium.

(continued)

Box 2.2 (continued)

This is achieved by a process called ion exchange process. This may be due to contact ion exchange mechanism or by carbonic acid ion exchange mechanism. Roots respire and liberate significant quantities of CO_2, which when dissolved in soil water produces carbonic acids.

Contact ion exchange mechanism: Plant roots are in contact with soil clay particles which have colloidal dimensions. Root cells, which are living, secrete hydrogen ions. Hydrogen ions displace cations like K^+, Na^+ ions that are bound to clay particles. Order of the strength of adsorption of cations by the soil is $Al^{+3} > H^+ > Ca^{+2} = Mg^{+2} > K^+ > NH^{4+} > Na^+$. This is called the *lyotropic series* or *Hofmeister series*. It is a classification of ions in the order of their ability to salt out or salt in water. The sequence of ions is determined by their charge, size, and hydration. It lists the common soil cations in order of their strength of bonding to the cation exchange surface.



The charged soil particle with adsorbed cations and anions at different pH

2.1 Plant Nutrition

On the basis of modes of nutrition, living organisms have been classified into **autotrophs** (Greek: auto, self; trophe, nourishing) and **heterotrophs** (Greek: hetero, different; trophe, nourishing). Green plants obtain energy from sunlight and synthesize their own food using raw material by the process known as photosynthesis and are hence called as autotrophs. Since green plants use light to synthesize their food, they are called **photoautotrophs**. Heterotrophs are those living organisms which cannot synthesize their own food. The heterotrophic plants are further categorized into three main groups, viz., **saprophytes** (Greek: sapros, rotten; phyton, plants), **parasites**, and **insectivorous/carnivorous plants,** which

Box 2.3: Mineral Nutrition of Carnivorous Plants

Plant carnivory is an adaptation strategy to unfavorable conditions, mostly low-nutrient availability in wet and acidic soils. There are about 600 terrestrial and 50 aquatic or amphibious species of carnivorous plants (CPs). Some of the common CPs are *Nepenthes* sp. (pitcher plant), *Drosera* sp. (sundew), *Dionea* sp. (Venus flytrap), and *Utricularia* sp. (bladderwort). All CPs are green and are able to fix CO_2 (autotrophy) but are partly dependent on organic carbon uptake from prey (*facultative heterotrophy*). Nearly all plants with glandular hairs are potentially carnivorous. Foliar nutrient uptake from prey is "ecologically significant" for CPs. The glandular hairs contain phosphatase, phosphodiesterase, and protease activities. They are generally present in nitrogen-deficient soil and use insects as a source of nitrogen. CPs are classified into three main ecophysiological groups. The first group of plants is "nutrient-requiring species" which increase their growth due to both soil and leaf nutrient supply. CPs in the group of "root-leaf nutrient competitors" grow better and accumulate more nutrients because of both root and leaf nutrient uptake, resulting in a competition between the root and leaf nutrient uptake. CPs in the third group of "nutrient modest species" have roots with very low nutrient uptake capacity. Therefore, they depend on leaf for their nutrient supply. However, terrestrial CPs have considerably lower content of macroelements per dry weight as compared to aquatic CPs. Nutrient uptake from prey is advantageous because animal prey is relatively rich in mineral nutrients. The total nutrient contents found in insects ($g.kg^{-1}$ DW) are N, 99–121; P, 6–14.7; K, 1.5–31.8; Ca, 22.5; and Mg, 0.94.

eat insects. Saprophytic plants grow on dead decaying matter of plant and animal origin. They release extracellular enzymes which break down complex organic compounds into simpler forms. Parasitic plants derive food from the host by penetrating their **haustoria** into the phloem of the host plants, for example, *Cuscuta*. There are certain autotrophic plants which derive nutrition from insects to supplement the deficiency of a specific mineral in the soil. Such plants are called insectivorous or carnivorous plants (Box 2.3).

2.2 Essential Elements

At present the list of essential elements includes 13 elements which are essential for all angiosperms and gymnosperms. Adding carbon, hydrogen, and oxygen makes it 16, and after the addition of nickel (a trace element), it makes a total of 17 essential elements. The known essential elements have interesting distribution in periodic table (Fig. 2.1). All, except molybdenum, are among the 30 lightest elements and are clustered in such a way that every essential element (except hydrogen) lies adjacent to another horizontally or vertically placed element. Only molybdenum is present diagonally to manganese.

2.2.1 The Criteria of Essentiality

The **dry matter** residue from any plant tissue obtained after desiccation can be separated into **combustible** and **incombustible** fractions. The combustible fraction represents organic matter, while incombustible element is called **ash**. Ash roughly corresponds to the mineral salts absorbed by the plant from the soil. Nitrogen is not included in ash because it is released during combustion process along with carbon, hydrogen, and oxygen. The mineral elements occur as oxides in the ash. Hence, the ash content of a plant tissue gives a crude estimation of mineral content of the tissue. The presence of a particular element in plant ash does not necessarily mean that it is an important element for plant growth and development. Roots absorb around 60 elements from the soil, but not all are required for plant growth. The nutrients or elements necessary for growth or completing life cycle of a plant are considered as essential elements. Only 16 elements are essential for most of the plants. Criteria to find out the essentiality of microelements are difficult. The criteria of essentiality of elements are as follows:

- Deficiency of essential elements prevents completion of life cycle and produces deficiency symptoms in the plant.
- They cannot be replaced by another element with similar properties.
- They are directly involved in plant metabolism.
- In the absence of essential elements, plants are unable to produce viable seeds.
- Essential elements should be constituents of some essential plant metabolites, e.g., Mg^{2+} is a constituent of chlorophyll molecule.

2.2.2 Roles of Essential Elements

Essential elements play two major roles in plants: (i) structural role and (ii) activators of enzymes. There is no sharp distinction between their roles because many elements form structural components of essential enzymes and help to catalyze the chemical reactions in which enzymes participate. Carbon, hydrogen, oxygen, nitrogen, sulfur, and magnesium perform both the functions. Magnesium is a structural constituent of chlorophyll molecules and it also activates many enzymes. A number of elements also regulate osmotic potential. Monovalent ions, potassium and chloride, control osmotic potential as well as act as activators of certain enzymes (Table 2.1). Depending upon the role played by essential elements, they can be broadly classified as:

Framework/Structural Elements These elements are components of biomolecules present in protoplasm, cell wall, and storage products in plants, e.g., sulfur in proteins, phosphorus in nucleoproteins and lecithins, magnesium in chlorophyll, and calcium in calcium pectate. Carbon (C), hydrogen (H), and oxygen (O) are elements which make the structural framework of plants.

Colloidal Elements Cations and anions such as calcium, magnesium, and chloride ions influence the degree of hydration of the colloidal micelles in the protoplasm and affect the permeability of the membrane. In general, potassium and sodium enhance cell permeability, whereas divalent ions, such as calcium and magnesium, reduce membrane permeability.

Elements Associated with pH Modulation and Buffering Action The mineral salts absorbed from the soil influence the pH of cell sap. The metabolic activity of the cell depends on its pH. Two important buffer systems found in the plants are the phosphate and carbonate systems.

Balancing Elements They minimize the toxic effects of heavy elements, e.g., Ca^{2+}, Mg^{2+}, and K^{+}.

Activator, Cofactor, or Constituent of Enzyme Elements like iron, copper, and molybdenum are constituents of many enzymes. Some minerals are either the components of enzymes or are constituents of cofactors or they act as activators of the enzymes, e.g., Ca^{2+}, Mg^{2+}, K^{+}, Mn, Cu, Ni, Zn, etc. Calcium is required as a cofactor or enzyme activator for hydrolytic enzymes involved in hydrolysis of ATP and phospholipids hydrolysis. Magnesium is required by a large number of enzymes involved in phosphate transfer. Manganese is involved in the activity of some dehydrogenases, decarboxylases, kinases, and peroxidases.

Osmotic Pressure and Turgor Movements The osmotic pressure of the cell sap is due to the presence of dissolved mineral salts. The difference in osmotic pressure in different cells is responsible for intercellular transport. For example, expansion and contraction of guard cells involve rapid K^{+} fluxes across the cell.

2.3 Macroelements and Microelements

2.3.1 Macroelements or Macronutrients

These are mineral nutrients consumed in larger quantities and are present in plant tissue in quantities ranging from 0.2% to 4.0% on dry matter weight basis. The **primary macronutrients** are nitrogen, phosphorus, and potassium, while **secondary macronutrients** include calcium, sulfur, and magnesium. Usually, potassium, calcium, and magnesium are grouped together as they are present as cations (K^+, Ca^{2+}, Mg^{2+}). Similarly, nitrogen, phosphorus, and sulfur are grouped together because they are present as anions (NO_3^-, SO_4^-, and $H_2PO_4^-$).

2.3.2 Microelements or Micronutrients

These are the mineral nutrients present in plant tissue in quantities measured in parts per million (ppm), ranging from 5 to 200 ppm or less than 0.02% of dry weight. Micronutrients or trace minerals are boron, chlorine, manganese, iron, zinc, copper, molybdenum, and nickel. Microelements are present as inorganic ions, oxyanions (anion with one or more oxygen atom), or undissociated molecules of boron or as organic compound complexes (chelates).

2.4 Beneficial or Functional Elements

Mineral elements which either stimulate growth, but are not essential, or which are essential only for certain plant species under given conditions are referred to as beneficial or functional elements. In addition to 17 essential elements, some plants require certain other elements for their growth. In some cases, a particular element may substitute an essential element when that element is deficient and thus produces its beneficial effects. Alternatively, it may stimulate absorption and transport of an essential element which is in limited supply or inhibit uptake and distribution of an element that is present in excess. Sodium is required for regeneration of phosphoenolpyruvate from pyruvate in chloroplast in CAM and C_4 plants. It was first observed in bladder saltbush (*Atriplex vesicaria*) in which the absence of sodium resulted in reduced growth, **chlorosis**, and **necrosis** of the leaves. Silicon is the second most abundant element in the earth's crust. Higher plants differ characteristically in their capacity for silicon uptake. Depending on their silicon content, they can be divided into three major groups: (1) wetland Gramineae, which includes wetland rice and horsetail (10–15%); (2) dryland Gramineae, which includes sugarcane, most of the cereal species and few dicotyledon species (1–3%); and (3) most of dicotyledons including legumes (<0.5%).

The long distance transport of silicon in plants is confined to xylem. Therefore, its distribution within the shoot is determined by transpiration rate. Silicon can stimulate growth and yield of plants due to several indirect actions. These include decrease in mutual shading by improving leaf erectness and decrease in susceptibility to lodging and preventing manganese and iron toxicity. It strengthens cell wall and thus improves drought and frost resistance and boosts the immune system of the plants. It is responsible for improvement of root mass and density and hence results in an increase in biomass as well as yield. It is an essential element for plant growth and development (except for specific plant species, such as sugarcane, and members of the horsetail family). Silicon is considered a beneficial element in many countries due to its numerous benefits to various plant species. Silicon is currently under consideration by the Association of American Plant Food Control Officials (AAPFCO) for its elevation to the status of a "plant beneficial substance." Cobalt is essential for some plants, such as legumes, where it is required by nitrogen-fixing bacteria rather than the host plant. When legumes are provided with nitrates, cobalt is not required. In nonleguminous plants, it is beneficial.

2.5 Micronutrient Toxicity

Micronutrient toxicity is the result of accumulation of high levels of trace elements (primarily iron and manganese) in plant tissues. The critical concentrations (above which plants exhibit toxic effects) of copper and zinc are 20 and 200 $\mu g.g^{-1}$ dry weight, respectively; critical toxicity level of manganese is 200 $\mu g.g^{-1}$ dry weight in corn, while it is 5300 $\mu g.g^{-1}$ dry weight for sunflower. Root growth is the first one to be affected by micronutrient toxicity. In vineyards and orchards, excess use of copper-containing fungicides and subsequent soil pollution lead to copper toxicity. Acidic soils increase zinc toxicity. The most common symptoms of zinc toxicity are interveinal chlorosis, necrotic speckling, and leaf deformity. It usually occurs in older or lower leaves and in mature tissues. The toxicity symptoms are difficult to predict as an excess of one nutrient may induce deficiency of another nutrient, e.g., the toxicity symptoms of manganese (due to MnO_2) are brown spots surrounded by chlorotic veins. Excess of manganese also induces deficiency of iron, magnesium, and calcium. Manganese competes with iron and magnesium for their uptake. It also competes with magnesium for binding sites in some enzymes. It inhibits calcium translocation into the shoot apex and induces deficiency commonly known as "crinkle leaf" (leaf cups upward and is smaller in size and has chlorotic edges). The symptoms resemble those of calcium deficiency. Now it has been shown that these symptoms are due to manganese-induced calcium deficiency. Therefore, the symptoms of manganese toxicity overlap with the deficiency symptoms of iron, magnesium, or calcium. Moist, organic soils under acidic conditions are especially susceptible to manganese toxicity. Manganese toxicity results in the "sudden crash" syndrome of watermelon which results in wilting and death of plant. When the soil pH drops below 5.2, manganese minerals become highly soluble and perhaps toxic. Manganese oxide gets solidified and becomes unavailable to plants, while manganese ions are soluble and are readily available for plant uptake.

$$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$$

Farmers may reduce manganese toxicity by liming and aerating the soil. Plants fertilized with ammonium-nitrogen (NH_4^+-N) salts may exhibit NH_4^+ toxicity symptoms, accompanied with carbohydrate depletion and reduced plant growth. Excess phosphorus, manganese, or zinc can cause iron deficiency (chlorosis in young leaves) and symptoms of nutrient toxicity (old leaves). High nickel concentrations can also cause iron displacement. Tolerance to aluminum varies among plant species. Certain crops, such as sugarcane, pineapple, and corn, can tolerate relatively high levels of aluminum. Aluminum toxicity inhibits root development and limits crop growth. It occurs readily under acidic conditions, especially when pH values are equal to or less than 5.4. In acidic soils of the tropics, aluminum toxicity may become a serious problem and limit crop yield. Management of soil pH is a key factor in avoiding aluminum toxicity. Tea plants exhibit a high degree of tolerance for aluminum toxicity and their growth is stimulated by its application. The possible reason is the prevention of copper, manganese, or phosphorus toxicity effects. There have been reports that aluminum may serve as a fungicide against certain types of root rot. Plants have homeostatic mechanisms to cope with changing concentrations of toxic inorganic ions (Box 2.4). A variety of naturally produced organic acids released in soil also play a crucial role in mineral nutrient acquisition by plants.

Box 2.4: Metal Homeostasis

In plant cells, the major sinks of micronutrient metal cations are chloroplasts and mitochondria (50% of copper and 80% of iron are present in the chloroplasts of leaf), whereas the major repository for toxic ions in roots as well as shoots is vacuoles. Therefore, it is very important to have efficient mechanism of transport of these toxin ions through cytoplasm to organelles. The transport of metal ions through cytoplasm is facilitated by proteins that act as **metallochaperones.**

Metallothioneins act as metallochaperones and control toxic ion concentrations in plant cells. These are also present in mycorrhizal fungi. There are molecules that routinely detoxify or chelate reactive metals. In general, glutathione and amino/carboxylic acids perform these functions in plant cells.

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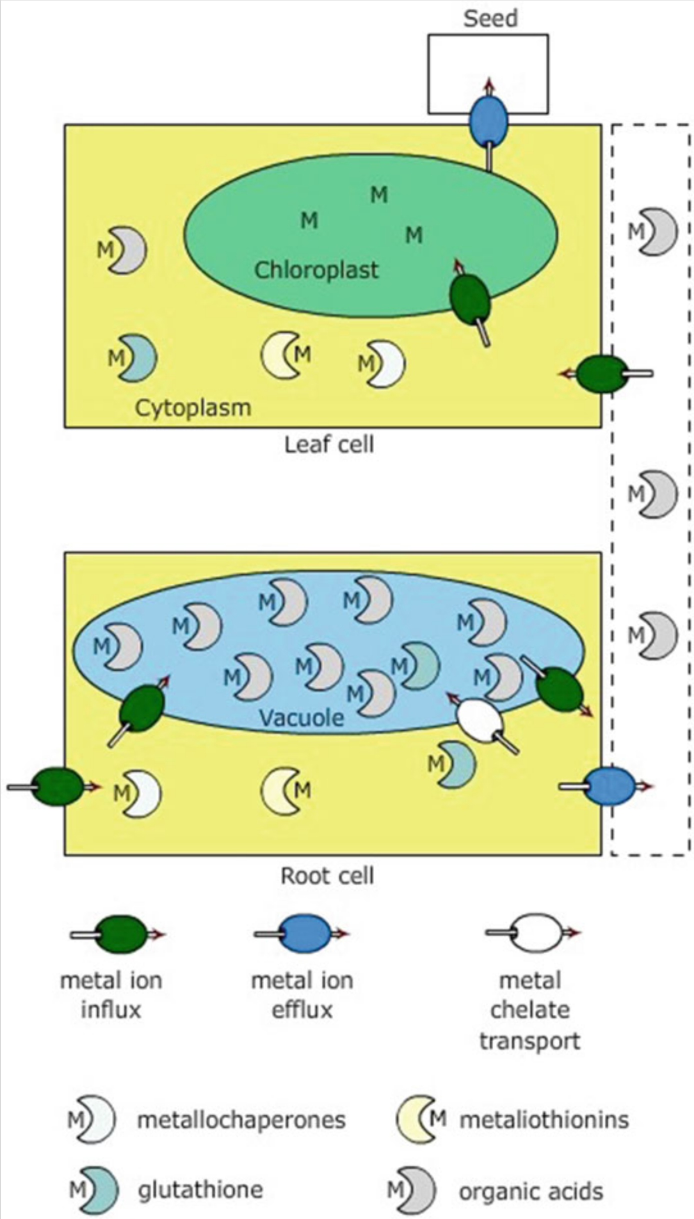
Box 2.4 (continued)



Mechanism of metal homeostasis in plants

2.6 Deficiency Symptoms of Mineral Elements in Plants

Plants respond to inadequate supply of essential mineral elements by exhibiting deficiency symptoms (Table 2.2). The characteristic deficiency symptoms can be correlated with specific deficient mineral element using "hydroponics," but under natural environment conditions, this correlation becomes difficult to observe (Box 2.5). Inadequate supply of an element can be due to its low concentration in soil, the presence of an element in the form that the plant cannot access, or the influence of other factors, such as soil pH, aeration, water status, or high concentration of antagonistic elements. Under natural conditions, these symptoms are the indicators of mineral deficiencies in the soil. Most of the symptoms appear on the shoot system and are easily observed (Fig. 2.2). Deficiency symptoms are of many types (Table 2.3):

Table 2.2 Deficiency symptoms of different nutrient elements in plants

Elements	Deficiency symptoms	Symptoms due to excess supply
Nitrogen	Lateral bud dormancy, wrinkled cereal grains	Dark bluish-green leaves; high shoot/root ratio; new growth will be succulent and susceptible to disease; insect infestation and drought stress; flower abort and lack of fruit set
Phosphorus	Premature leaf fall and flower bud; delay in seed germination; chlorosis; and necrosis first in older leaves	No direct effect on the plant, but will show deficiency symptoms of Zn, Fe, Mn, or Ca; maturity often delayed; poor vascular tissues; shoot growth is less and root growth is more
Potassium	Loss of apical dominance; interveinal chlorosis first in older leaves; scorched leaf tips; short internodes; and dieback	Excess of potassium causes Mg and Ca deficiency
Calcium	Stunted growth; degeneration of meristems, especially root meristem; growing tips of roots and leaves will turn brown and die; fruit quality will be affected; decay of the conductive tissue in lower region of stem wilt easily	Deficiency symptoms of magnesium can be seen, and if concentration further increases, potassium deficiency may also occur
Magnesium	Interveinal chlorosis and anthocyanin pigmentation appear; older leaves affected first; premature leaf abscission	Occurs rarely; results in cation imbalance; plant shows calcium and/or potassium deficiency
Sulfur	Chlorosis first in young leaves; reduced nodulation in legumes, stunted and delayed growth; anthocyanin accumulation; defoliation in tea	Premature senescence of leaves
Iron	Interveinal chlorosis appearing first in young leaves, slow growth of the plant	Occurs rarely; results in bronze-colored leaves with brown spots;

(continued)

Table 2.2 (continued)

Elements	Deficiency symptoms	Symptoms due to excess supply
		symptoms frequently seen in rice leaves
Manganese	Interveinal chlorosis with gray spots on young leaves; malformed leaves, white streaks on the leaves of some plants; plant growth is slow	Older leaves show brown spots surrounded by a chlorotic zone; tree fruits, referred to as measles
Zinc	Upper leaves show interveinal chlorosis; stunted growth; dieback; internodes will be short and plants will be stunted	Fe deficiency develops; toxicity is severe; plants severely stunted and eventually die
Copper	Leaf tip necrosis; blackening of potato tubers; bark becomes rough and splits; loss of apical dominance	Fe deficiency may be induced with very slow growth; root tips may die
Boron	Death of root and shoot tips; abscission of flowers; reduced nodulation in legumes; interveinal chlorosis with marginal necrosis and in folding; pollination is reduced; no internode elongation giving a compressed appearance	Leaf tips and margins turn brown and die; stunted growth toxic to many plants
Molybdenum	Similar to nitrogen; slight retardation of growth; chlorosis and necrosis of old and middle leaves; sometimes leaf margins get rolled, new growth is malformed, and flower formation is restricted	Not of common occurrence
Chlorine	Bronze color in leaves; wilting of leaves; swollen root tips; stunted root growth	Premature yellowing of the lower leaves with burning of leaf margins and tips; wilting and leaf abscission in woody plants

1. *Chlorosis*—it refers to yellowing of leaf tissue due to lack of chlorophyll. Poor drainage in soil, damaged roots, compact roots, high alkalinity, and nutrient deficiencies are some of the reasons for yellowing of leaves. The affected plants or leaves are unable to manufacture carbohydrate and they ultimately die.
2. *interveinal chlorosis*—yellowing in between leaf veins though veins remain green.
3. *Necrosis*—the affected plant tissue usually turns brown to black in color. It is caused due to the death of plant cells. Necrotic symptoms could appear in any part of the plant, such as in storage organs, green tissues, or woody tissues.
4. *Cessation of growth* or terminal growth resulting in rosette appearance.
5. *Pigmentation*—when sugars are not metabolized in the plant cells, it results in the accumulation of anthocyanin. The leaves may become purple because of anthocyanin (glycosylated form of anthocyanidins) accumulation. Reduction in

nitrogen or phosphorus level favors anthocyanin accumulation in various plant parts. This symptom can be particularly difficult to diagnose because low temperatures, disease, drought, and even maturation of some plants can also cause anthocyanin to accumulate.

6. *Stunting* or reduced growth.
7. *Premature fall of leaves and buds.*
8. *Delayed flowering*.

Box 2.5: Hydroponics

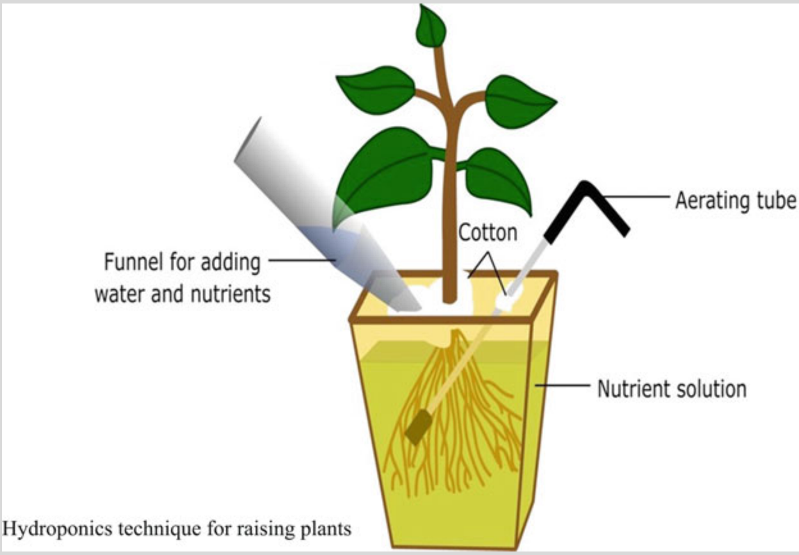
In 1880, two German botanists Julius von Sachs and Knop working independently demonstrated that plants can absorb minerals from solution as well. The plants were grown in Knop's nutrient solution which consisted of potassium nitrate, calcium nitrate, potassium dihydrogen phosphate, magnesium sulfate, and an iron salt. This technique of growing plants in nutrient solution without soil is known as **hydroponics**. Inert materials like vermiculite, sand, coir, etc. can be used as supporting material. Vigorous air bubbling is done to provide oxygen to the root system.

The most common solution used in hydroponics is **Hoagland's solution**. It consists of all the essential elements in the correct proportion necessary for growth of almost all plants. The concentration of minerals in most nutrient solutions is many times greater than in soils in order to maintain continuous supply of nutrients. The most commonly encountered problem with hydroponics is providing air to roots. The absence of oxygen in solution culture can result in **anoxia** or **hypoxia** in plant roots. Iron absorption poses another challenge as it needs to be provided in chelated form for ready absorption by the roots. Hydroponics offers the following advantages: (1) soil-less raising of plants, (2) the water stays in the system and can be reused, (3) it is possible to control the nutrition levels in the system, and it reduces nutrients loss, (4) no nutritional pollutants are released into the environment because of the controlled system, (5) plants show uniform growth and high yields, (6) pests and diseases are easily eradicated as compared to plants growing in soil, (7) ease of harvesting, and (8) no pesticide used and consequently no damage to the plants. However, some of the hurdles experienced in hydroponics are as follows: (1) any failure in the system that leads to rapid plant death, (2) the need to replace the solution after every few days in order to achieve good growth (this is because the composition of nutrient solution changes as certain ions are absorbed more rapidly as compared to others), and (3) selective uptake of ions that also changes the pH of the medium. For example, when nitrogen is given as nitrate, it is rapidly absorbed by the plants along with H^+ resulting in a rapid rise of pH. At high pH, iron and other elements precipitate as hydroxides

(continued)

Box 2.5 (continued)

and hence are not available to the plant. It can be minimized by adding ammonium salt. Pathogen attack is associated with hydroponics, and overwatering of soil-based plants can lead to wilting, e.g., damp-off due to *Verticillium* wilt caused by the high moisture levels. The mineral requirement of each plant is different. Therefore, it is important to find optimal medium required for growth of different plants.

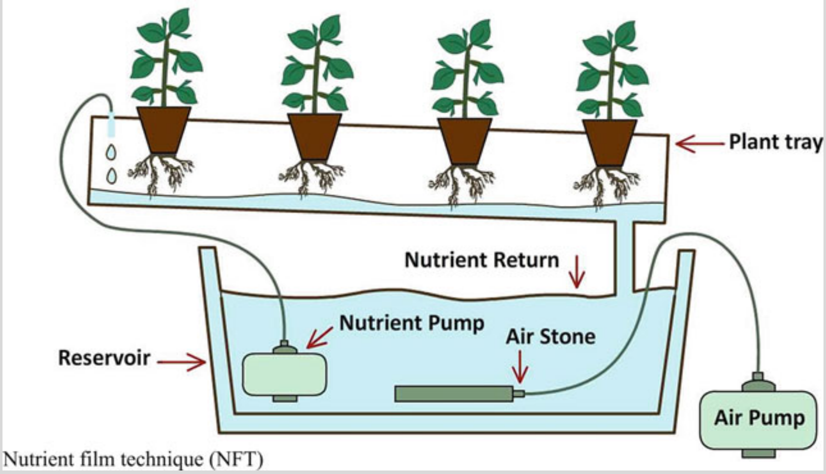


Hydroponics technique for raising plants

Two main types of hydroponics are **solution culture** and **solid culture**. There are three types of solution cultures, viz., **static solution culture**, **continuous-flow solution culture**, and **aeroponics.** **(i) Static solution culture:** Plants are grown in containers with nutrient solution. If it is unaerated, the solution level is kept low enough so that enough roots are above the solution and can get adequate oxygen. Aeration in the medium can also be provided by a small pump. The nutrient solution is changed either on a schedule, such as once per week, or when the concentration of nutrients drops below a certain level, which can be monitored with an electrical conductivity meter. **(ii) Continuous-flow solution culture**: In this method, the nutrient solution constantly flows past the roots. It is much easier to automate than the static solution culture because sampling and adjustments for the temperature and nutrient concentrations can be made in a large storage tank that has potential to serve thousands of plants. **Nutrient film technique** (**NFT**) is a popular

(continued)

Box 2.5 (continued)
variation of continuous-flow culture, in which a very shallow stream of water containing all the dissolved nutrients required for plant growth is recirculated around a thick root mat. Subsequent to this, an abundant supply of oxygen is provided to the roots of the plants. The main advantage of the NFT system over other forms of hydroponics is that the plant roots are exposed to adequate supply of water, oxygen, and nutrients. **(iii) Aeroponics:** This method requires no substrate. Roots are suspended in growth chamber with the roots periodically wetted with a fine mist of atomized nutrients. Aeroponics technique is commercially successful for micropropagation, seed germination, seed potato production, tomato production, and leafy crops.

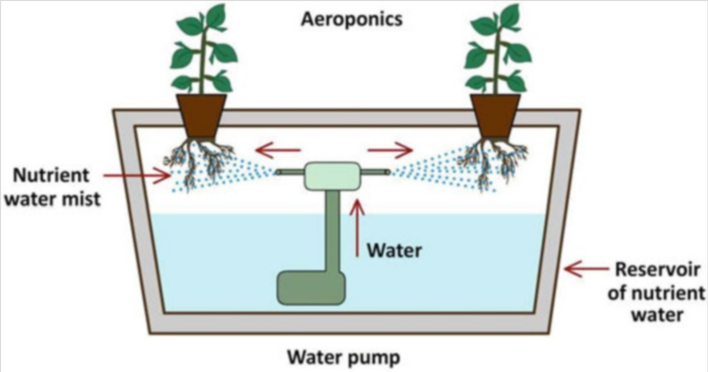


Nutrient film technique (NFT)

The limitation of conventional hydroponics is aeration of roots. One kilogram of water can only hold 8 milligrams of air, no matter whether aerators are utilized or not, but excellent aeration is achieved only by aeroponics. Almost all species of plants can be grown in a true aeroponics system because the microenvironment around the plants can be finely controlled. However, in conventional hydroponics, only certain species of plants can survive due to waterlogged conditions. Plants receive adequate oxygen for the roots which accelerates biomass growth and reduces rooting time. NASA research has shown that plants grown using aeroponics have an 80% increase in dry weight biomass (essential minerals) as compared to plants grown by using conventional hydroponics. Aeroponic-grown plants do not suffer from transplant shock when transplanted to soil and are less prone to diseases.

(continued)

Box 2.5 (continued)



Advantage of aeroponics over conventional hydroponics

Solid Medium Culture

This method uses solid media for the roots and is named on the basis of the type of medium used, as discussed below:

Vermiculite: Vermiculite is a hydrated magnesium, aluminum, and silicate mineral which resembles mica in appearance. Vermiculite has a natural "wicking" property to draw water and nutrients in a passive hydroponic system. Vermiculite improves aeration, slightly raises pH, enhances drainage, and does not interfere nutrient availability to the plants.

Sand: Sand is easy to recharge with nutrients and can be washed easily. However, it is heavy and does not hold water very well. It is recommended for growing succulents, sand-loving trees, drought-tolerant plants, and *Euphorbia* species.

Gravel: Gravel, as used in aquarium, can be used after washing. Plants are grown in a typical traditional gravel filter bed, with water circulated using electrically powered head pumps. Gravel drains well and does not get waterlogged. However, it is heavy, and, if not kept wet, the plant roots may dry out.

Polystyrene packing peanuts: These are standard packing peanuts used in shipping industry. Polystyrene packing peanuts have excellent drainage for growing plants. Biodegradable packing peanuts, however, decompose into sludge, and plants may absorb styrene and may cause health risk to their consumers.

Wood fiber: It is a very efficient organic substrate for hydroponics. For organic farming the wood fiber is the best medium to supply nutrients. It maintains its structure for a very long time. However, it reduces the effect of

(continued)

Box 2.5 (continued)
plant growth regulators and is biodegradable. It is not possible to sterilize it; therefore, it attracts many pests.

The techniques used to raise plants in solution and solid cultures have been modified to cater to the needs of different plants. It is difficult to find out the requirement of trace elements by the above mentioned techniques. Requirement for molybdenum, nickel, copper, zinc, and boron is difficult to be demonstrated for the species with large seeds. Since large seeds contain enough of these elements, their deficiency symptoms for these elements cannot be observed.

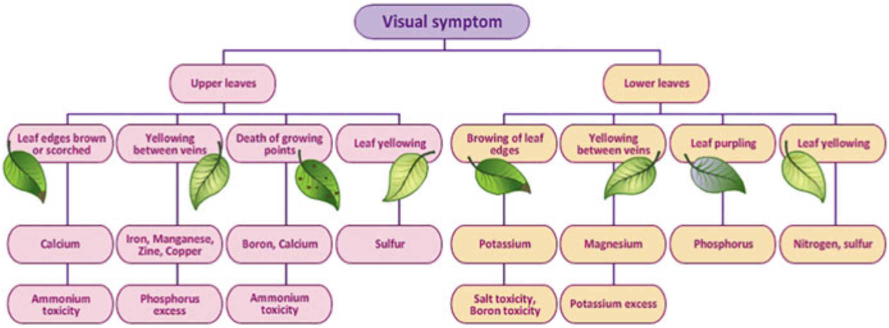


Fig. 2.2 Major diagnostic features to identify the nutritional status of different mineral nutrients in plants

Table 2.3 Different types of deficiency symptoms and the elements responsible for those symptoms

Deficiency symptoms	Elements showing the symptom
Chlorosis	K, Mg, N, S, Fe, Mn, Zn, Mo
Necrosis	P, K, B, Cu
Lack of new growth or terminal growth resulting in rosette	N, K, S, Mo
Anthocyanin formation	N, P, S, Mg
Stunted/retarded plant growth	N, P, K, Zn, Ca
Premature fall of leaves and buds	K, P
Delayed flowering	N, S, Mo

It is, however, not easy to diagnose elemental deficiency symptoms. For example, chlorosis of leaves can be caused by the deficiency of iron or nitrogen or due to low light intensity or insect or fungal infestations, albinism, and senescence. Visual symptoms of elemental deficiencies have limited use in field crops because they appear only when deficiency is severe. Appearance of these symptoms depends upon the role played by these elements or upon their mobility (Table 2.4). Depending on the mobility of the element, leaf symptoms can occur in the upper, middle, or lower

Table 2.4 Mobility patterns of elements essential for plant growth

Essential element	Mobility pattern
Boron (Bo)	Mobile in phloem, degree of mobility varies in plants
Calcium (Ca)	Mobile through xylem (and not phloem)
Copper (Cu)	Poorly mobile element
Iron (Fe)	Mobile as ferrous ions (Fe^{3+})
Magnesium (Mg)	Good mobility in plants, transported through phloem
Manganese (Mn)	Less mobile
Molybdenum (Mo)	Relatively less mobile and least abundant microelement
Nitrogen (N)	Mobile in the form of nitrates across ammonium transporter
Phosphorus (P)	Least mobile, taken up in inorganic form (P_i)
Potassium (K)	Highly mobile element due to potassium channel
Sodium (Na)	Mobile
Sulfur (S)	Mobile
Zinc (Zn)	Immobile

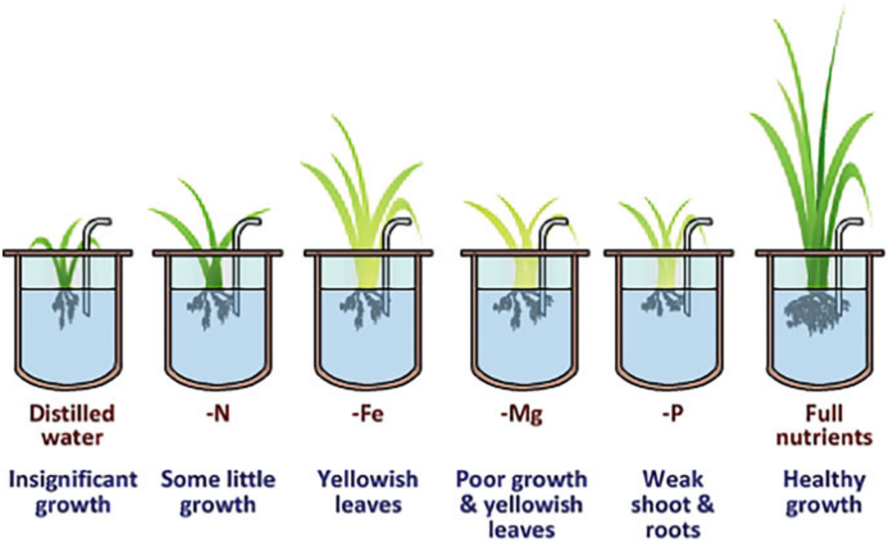


Fig. 2.3 The experiment to demonstrate the role of inorganic nutrients in plant growth. Plants are grown in solution with all nutrients (minus one) and compared with plants grown in full nutrient medium and distilled water

sections of a plant**.** This can be demonstrated by adding all the nutrients in solution culture and then transferring plants to solution culture lacking one element each time (Fig. 2.3). If older leaves remain normal, while the newer leaves develop the deficiency symptoms, then the deficient element is immobile. On the other hand, if the deficiency is there in old leaves as well, then the element is mobile. In other words, those elements which are translocated fast are called **mobile elements** and those which are not translocated are called as **immobile elements.** Mobile nutrients include nitrogen, phosphorus, potassium, magnesium, and molybdenum. Immobile nutrients include calcium, sulfur, boron, copper, iron, manganese, and zinc.

2.6.1 Mineral Deficiencies in Older Tissues

Magnesium is highly mobile within the plant. It is a component of chlorophyll molecule and its deficiency results in less chlorophyll formation. During magnesium deficiency, older leaves first turn yellow, and gradually yellowing occurs in younger leaves as well. Mobile elements like nitrogen, magnesium, phosphorus, chlorine, molybdenum, cobalt, or potassium satisfy local shortages, particularly in new shoots or developing seeds**.** When one of these mobile elements is deficient, older leaves are first to be depleted and show symptoms.

2.6.2 Mineral Deficiencies in Younger Tissues

Some deficiency symptoms appear first in younger parts and move elsewhere with difficulty. Less mobile elements, such as iron, copper, boron, zinc, sulfur, or calcium, do not move readily from older to younger tissues. So, when these elements are deficient, symptoms appear in the newer or upper leaves or in the flowers or seeds. The most important diagnostic feature of nutritional disorder symptoms is to find out the location and pattern of the symptoms**.** Nutritional deficiency symptoms generally develop in specific organs, such as leaves, roots, shoots, or growing points. These symptoms include the following: (1) symptoms that are initially restricted to leaves of particular age, i.e., young-, old-, or intermediate-aged leaves, and are closely related to leaf venation; (2) nutritional deficiencies that cause defects in cell functions and rarely cause mechanical disruption of the cuticle (outer layer) of the leaf (thus, any damage to the surface of a leaf is not likely to be caused by nutritional deficiency); and (3) changes in leaf color and tissue death. Visible changes in a crop, such as yellowing of leaves, development of small leaves, and poor seed set, are due to breakdown in cell functioning and nutritional disorder. For example, the distortion of new tissues or flowers or the death of growing points is typical of boron deficiency. Similarly, the leaves of nitrogen- or magnesium-deficient plants are pale because nitrogen and magnesium are components of chlorophyll. The nature of symptoms is a useful guide to identify the nutritional disorder. Diagnostic features help in identifying deficiencies, but sometimes it is difficult to identify them because of the following reasons:

- Sometimes a disorder is quite advanced before clear visual symptoms appear and this results in loss of yield or quality.
- The absence of symptoms in a plant does not mean that nutrition is adequate. “Hidden hunger” is the condition in which yield is poor due to inadequate nutrition, but no symptoms can be observed.

- Visual symptoms can be unreliable when more than one element leads to same deficiency symptoms.
- Some symptoms may appear due to modification in some environmental stress.

2.7 Role, Deficiency Symptoms, and Acquisition of Macronutrients and Micronutrients

2.7.1 Macronutrients

2.7.1.1 Carbon

Carbon and oxygen account for almost 90% of the dry weight of higher plants. Carbon forms bonds in the shape of a tetrahedron and is the backbone of many biomolecules, like starch and cellulose. It is fixed as photoassimilate through photosynthesis using carbon dioxide drawn from the atmosphere. Nearly, all the complex molecules of living organisms have carbon.

2.7.1.2 Hydrogen

It plays a central role in plant metabolism and is necessary for the synthesis of sugars. In its oxidized form, it is responsible for creating proton gradient which in turn regulates electron transport chain in photosynthesis and respiration. Protons are ubiquitous and are important for maintaining ionic balance.

2.7.1.3 Oxygen

Like carbon, oxygen is present in all organic compounds of living organisms. Free oxygen is primarily involved as an electron acceptor in respiration. It functions as a substrate in reactions involving oxidases. Some hydroxylation reactions use free oxygen instead of hydroxyl ions. Plants produce oxygen during photosynthesis and form glucose, while they undergo aerobic cellular respiration by the breakdown of glucose to generate ATP. The role of oxygen as an inhibitor of metabolism (photo-respiration) has more problem than its deficiency.

2.7.1.4 Nitrogen

Nitrogen is the most abundant gas (80%) in the atmosphere, but only certain bacteria and cyanobacteria can utilize gaseous nitrogen directly. It exists in a number of oxidized and reduced forms and cycles in the atmosphere between organic and inorganic pools. A number of plant species can fix nitrogen by having symbiotic association with diazotrophic microorganisms. Nitrate and ammonium ions are two sources of nitrogen in nonleguminous plants. Most of the nitrogen taken up by the plants is derived from the soil in the form of nitrate (NO^{3-}), which is then converted into nitrite by nitrate reductase in the cytosol. Nitrite is transported to plastids and is then converted into NH_4^+, by the action of nitrite reductase. Soluble forms of nitrogen are transported as amines and amides. Nitrogen is a constituent of all proteins, enzymes, and various metabolic processes involved in the synthesis and

Table 2.5 Roles of macronutrients in plants

Nutrients	Functions in cell metabolism	Functions at whole-plant level
Nitrogen	Constituent of amino acids, nitrogenous bases, cofactors, alkaloids, coenzymes, and chlorophyll, including some hormones (IAA)	Enhanced seed and fruit production; improved leaf and forage crop production
Phosphorus	Required as phosphate in sugar; as ester in DNA, RNA; as phospholipids in membrane and is constituent of ATP	Rapid growth; encourages blooming and root growth
Potassium	As an activator of enzymes; essential ion for protein synthesis; manufacture of sugar and starches	Regulates opening and closing of stomata
Sulfur	Constituent of amino acids (cysteine and methionine); vitamins (thiamine and biotin); coenzyme A (required in respiration); formation of sulpholipids	Improves root growth and seed production; helps with vigorous plant growth and resistance to cold
Calcium	Cell wall formation; maintenance of membrane structure and permeability; cell signaling	Regulates fruit quality, protects against heat stress and disease
Magnesium	Constituent of chlorophyll molecules and required as an enzyme activator; essential for binding of ribosome subunit	Nutrient uptake control, root formation

transfer of energy. It is also a constituent of many other important biomolecules, such as hormones (indole-3-acetic acid and cytokinins) and chlorophyll. Some plants, such as corn (*Zea mays*), require very high dosage of nitrogen as compared to other plants. It facilitates rapid plant growth and helps increase seed and fruit production (Table 2.5).

Nitrogen is a mobile element. Therefore, older leaves exhibit chlorosis and necrosis earlier than younger leaves during nitrogen deficiency. During severe nitrogen deficiency, leaves become completely yellow and fall off. Nitrogen deficiency causes stunted and slow growth because cell division is inhibited and lateral buds become dormant. Chlorosis and purple appearance on the stems as well as petiole and underside of leaves are also caused by nitrogen deficiency. Some plants, such as tomato and maize, also accumulate anthocyanins which accompany nitrogen deficiency. Plants grown in the presence of excess nitrogen produce dark green leaves and vigorous foliage as root system is highly reduced resulting in high shoot/root ratio. In nitrogen deficiency, reverse situation is evident, i.e., low shoot/root ratio. Potato plants grown in the presence of abundant nitrogen exhibit more foliage and small tubers. Flower and seed formation are highly reduced due to high nitrogen in the soil. Excess nitrogen also results in the splitting of tomato fruits as they ripen. The crops become susceptible to disease, insect infestation, and drought stress, leading to lodging, when nitrogen content is high. Soils are usually deficient in nitrogen as compared to other elements. In addition to atmosphere, the primary source of nitrogen is often provided to cultivated plants from fertilizer application.

2.7.1.5 Phosphorus

It is required in young meristematic cells as it is utilized in the formation of nucleoproteins and other phosphorus-containing compounds in the growing tissues. Requirement of phosphorus in the annual plants is more during the first few weeks of germination and again near the end of their life cycle (fruit and seed development). Addition of phosphates in the soil also promotes root development. Like nitrogen, phosphorus is essential for the process of photosynthesis. It is needed as the structural component of ATP which is synthesized during light reaction of photosynthesis. It is an essential component of many sugars involved in photosynthesis, respiration, and other metabolic processes. Organic phosphates play an important role in metabolism. For example, in the metabolism of sugars (which have hydroxyl groups, -OH), phosphate esters are often formed as intermediate compounds. In plants, phosphorus is mainly present as phosphate esters which include sugar phosphates. Phosphate esters are needed for the synthesis of DNA, RNA, and phospholipids present in the membrane. Phosphorus plays an important role in membrane biochemistry in the form of phospholipids. Phosphorus is also a constituent of ATP, ADP, AMP, and pyrophosphate (PP_i), which are important components of energy metabolism (Table 2.5). It participates in signal transduction pathway by phosphorylation and dephosphorylation of receptors, secondary messengers, and target enzymes. Modification of activity of various enzymes requires phosphorylation and is also used for cell signaling as inositol triphosphate (IP_3). IP_3 is a secondary messenger involved in signal transduction and lipid signaling. In many species, the amount of phosphorus and nitrogen regulates plant maturation process. Excess nitrogen delays maturation, while abundant phosphorus speeds up the process of maturation. Phosphate is withdrawn from older senescing leaves and is redistributed in different plant organs. As a result, first symptoms of phosphorus deficiency appear in older leaves. It results in stunted growth, poor vascular tissue formation, dark green coloration in leaves, and necrosis of leaves. Plant may show premature fall of leaves and flower buds (Fig. 2.4).

Phosphorus is present in various forms in the earth's crust. It is present in mineral deposits, as inorganic and organic phosphorus in soil and water and in different organisms. Although it can react with other elements to make hydrides, halides, sulfides, and metal phosphides, it is present in neutral state in combination with oxygen as phosphates. Unlike nitrates and sulfates, phosphates are not reduced in plants during assimilation. It remains in its oxidized state forming phosphate esters in a wide range of organic compounds. It combines with hydrogen and oxygen to form phosphoric acid. Phosphoric acid is tribasic (having three replaceable hydrogen atoms) and can form monophosphate, diphosphate, and triphosphate salts in which one, two, or three of the hydrogens of the acid are replaced, respectively. Because replaceable hydrogen remains in monophosphates and diphosphates, they are called acid phosphates. The most important inorganic phosphate is calcium phosphate [$Ca_3(PO_4)_2$]. It makes up the larger part of phosphate rock, a mineral that is abundantly distributed throughout the world. Since calcium phosphate is only slightly soluble in water, it is not very suitable as a source of phosphorus. However,

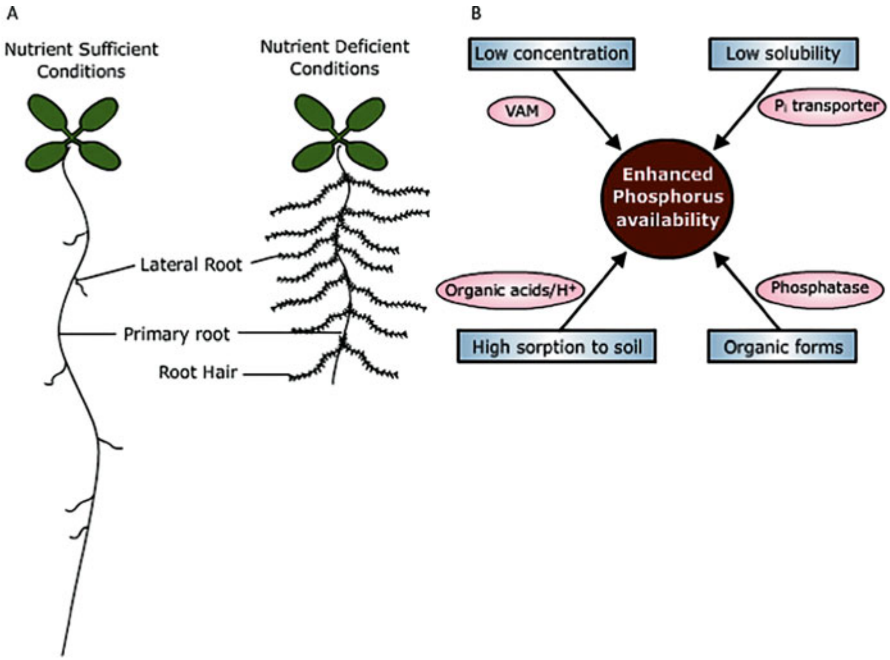


Fig. 2.4 (**a**) Plant roots exhibiting change in response to phosphorous deficiency. The deficiency induces inhibition of primary root elongation and increase in growth and density of lateral roots and root hairs. (**b**) Plants can increase phosphorous availability by secreting phosphatase, organic acids, protons, or via involving Pi transporters or gets associated with vesicular arbuscular mycorrhiza (VAM) to

by treating it with sulfuric acid, the soluble calcium acid phosphate known as superphosphate [$Ca(H_2PO_4)_2$] is formed. Other important inorganic phosphates include ammonium phosphate, which is an important fertilizer.

Phosphorus is readily absorbed in the form of monovalent anion $H_2PO_4^-$ and less rapidly in the form of divalent anion, HPO_4^{2-}. Below pH 7, phosphorus is absorbed as monovalent anion $H_2PO_4^-$ and above pH 7 as divalent anion HPO_4^{2-}. Most cations (except Na^+, K^+, NH_4^+, and Li^+) form insoluble salts with phosphorus leading to nonavailability of phosphorus for plant growth. Thus, in soils rich in iron and aluminum, most of the phosphates are not available to the plants. Addition of chelating agent releases inorganic phosphate (P_i) from aluminum and iron. The concentration of phosphorus in root cells is in the millimolar range, whereas in soil the concentration is 1 μM or less.

In addition to high-affinity transporters, two groups of low-affinity transporter have been identified for intracellular transfer of inorganic phosphate across membranes. During sufficient supply of phosphorus, more than 85% of the inorganic phosphate is stored in vacuoles. However, when there is deficiency of phosphorus, vacuolar P_i is mobilized to maintain cytosolic P_i homeostasis. The import of P_i is inhibited until vacuolar reservoir is over. Availability and acquisition of phosphorus from soil are very low. It is because of low solubility, low concentrations in soil (>1 μM), presence of Al^{3+} and/or Fe^{2+}, and conversion of soil P_i to organic forms. Phosphorus starvation response is observed at whole-plant level. As phosphate starvation occurs, there is an increased expression of high-affinity transporters. Phosphorus deficiency also activates several purple acid phosphatases (PAPase) and ribonucleases (RNase) which accelerate movement of phosphorus from old tissues to new tissues. Under P_i-deficient conditions, root diameter decreases, and the number of root hairs as well as their length increases which enhances P_i uptake by increasing the root-soil contact area. Plants release phosphatases, organic acids, and protons to solubilize P_i. The other strategy adopted by the plants is mycorrhizal-mediated phosphorus acquisition with the help of **arbuscular mycorrhizal fungi** (Box 2.6).

Box 2.6: Plants and Mycorrhizae

Plant growth is highly dependent on bacteria and saprophytic and mycorrhizal fungi which facilitate the cycling and mobilization of nutrients. In addition to bacteria, more than 80% of plants have symbiotic relationship with fungi (mycorrhizae). This association is mainly of two types and these are *endomycorrhizae* and *ectomycorrhizae.* Endomycorrhizae are those fungi which develop the association by penetrating into the cortical cells of the roots of the host plants. On the other hand, ectomycorrhizae develop the association by developing a vast hyphae network between cortical cells without penetrating the host plants. A variety of plant species develop the endomycorrhizal association with *arbuscular mycorrhizal fungi* (AMF) also known as *vesicular-arbuscular mycorrhiza* (VAM). Plants release chemicals which induce the germination of mycorrhizal spores present in the soil. The germinating spores form a network of hyphae which penetrate the cortical cells of the roots of host plants forming a highly branched structure called arbuscule. This symbiotic association facilitates phosphorus uptake from the soil by increasing root absorptive area of the host plant. The ectomycorrhizal fungi form symbiotic association with many tree species. The fungi form extensive hyphal growth around compatible root cap forming a *hartig net* surrounding the cells within the root cortex and provide phosphorus and nitrogen to the host plants. The ectomycorrhizae produce enzymes that digest organic material present in the litter and mobilize the nutrients to the hartig net, making it available to the plant. This interaction is essential for the trees, as the nutrients present in the litter are otherwise not available to long deep roots of the trees. Absorption of nutrients around the roots depletes nutrients and results in nutrient depletion zone in the region of the soil near the plant roots. Root association with mycorrhizal fungi helps plants to overcome this problem by moving the nutrients from high concentration zone to the depletion zone. The benefit to the fungal partners in this relationship involves transfer of

(continued)

Box 2.6 (continued)
carbohydrates from the plant to the microorganism. The symbiotic fungi obtain water and nutrients, primarily S, P_i, and N, from the soil and translocate them to the host plants helping their growth and development. The presence of AMF enhances sulfur uptake in maize, clover, and tomato. At molecular level AMF can influence the expression of plant sulfate transporters which improves the sulfur status of the host plant. Additionally, inoculation with AMF has been shown to increase both root colonization and the magnitude of the sulfonate mobilizing bacterial community in the rhizosphere. Whenever there is lack of readily available sulfate in soil, it leads to reduction in plant exudates, and as a consequence, soil microbial activity decreases due to reduced availability of photosynthate as a source of carbon. Inoculation practices, therefore, have huge potential to sustainably increase crop yield in areas where sulfur is becoming a limiting factor for plant growth.

Under P_i deficiency, plants need to minimize the production of new shoot branches and direct limited P_i resources to already existing shoots while maximizing P_i acquisition from the soil. AMF spores treated with root exudates from plants grown under P_i starvation have more hyphal branching activity than those treated with exudates from P_i-sufficient plants. Moreover, increased soil P_i levels resulted in a decreased AMF colonization of the roots. Subsequently, a stimulant of hyphal branching and root colonization of symbiotic AMF was isolated. This stimulant was found to be a terpenoid lactone derived from carotenoids and was named *strigolactones* (SLs). It was originally derived from plant root exudates and recognized as germination stimulant for root parasites such as *Striga*, *Orobanche*, and *Phelipanche.* SLs play a dual role in the modulation of P_i acquisition and utilization under P_i-deficient conditions. P_i deficiency stimulates SL biosynthesis in roots and exudation to soil. Elevated SLs (acting as endogenous hormones) act locally by modifying root system to increase root coverage that provides more surface area to explore more soil volumes and allow higher P_i uptakes. SLs are also transported through the xylem to suppress shoot branching (a means to reduce P_i utilization). SL exudation into the soil serves as a rhizosphere signal for symbiotic interaction between some host plants and arbuscular mycorrhizal fungi (AMF), a means to increase P_i acquisition. More recently, it has been demonstrated that SLs act as long-distance signaling molecules that can be transported from roots to shoots for their specific functional control on shoot branching. The transport of SLs from roots to shoots is partly mediated by ATP-binding cassette (ABC) transporters. Nutrient uptake soon depletes nutrients near the roots and forms nutrient depletion zone in the region of the soil near the plant roots. Root associations with mycorrhizal fungi help the plant to overcome this problem.

2.7.1.6 Potassium

The name potassium is derived from “pot ash.” Plant ash mainly contains potassium, which constitutes nearly 50% of its total weight. It is absorbed by plants in larger amounts than any other mineral element except nitrogen. It occurs in plants mainly as soluble inorganic salts. Cytoplasmic potassium concentration varies from 80 mM to 200 mM. It varies considerably in subcellular compartments. This fluctuation of potassium levels is regulated by its accumulation in the vacuoles of plant cells. Vacuolar potassium can be exchanged against sodium to maintain potassium concentration in cytosol. The young and active regions of the plants, especially buds, young leaves, and root tips, are rich in potassium. Older tissues, such as wood, contain much less potassium. It is supplied to plants from soil minerals, organic materials, and fertilizers. Potassium is not used in the building up of any cell constituents. However, it mainly has catalytic and regulatory roles. It is an activator of enzymes used in photosynthesis and respiration. It is used to build cellulose and aids in photosynthesis by the formation of a chlorophyll precursor. K^+ is highly mobile and helps in balancing the anion charges within the plant. K^+-Na^+ pumps facilitate active transport. K^+ regulates the opening and closing of stomata by regulating the activity of potassium ion pumps. It also reduces water loss from the leaves, increases drought tolerance, and maintains turgidity of the cell. Potassium helps in the buildup of proteins and fruit quality and disease resistance. Starch and protein syntheses are also affected by potassium ions (Table 2.5).

Like nitrogen and phosphorous, K^+ is also easily redistributed from mature to younger organs, so its deficiency symptoms first appear in older leaves. K^+ deficiency causes necrosis or **interveinal chlorosis** and leads to the formation of scorched leaf tips and short internodes. Potassium-deficient plants also exhibit loss of apical dominance and cambial activity because of its high solubility in water, and K^+ leaches out of rocky or sandy soils resulting in potassium deficiency. It may result in higher risk of **pathogen** attack, **wilting**, chlorosis, brown spotting, and chances of damage from frost and heat. In most of the monocots, cells at the tips and margins of leaves become necrotic first, and the symptom moves basipetally along the margins toward younger as well as lower parts of leaf bases. Maize and other cereals develop weak stalk during deficiency. Their roots are easily infected, and plants show root-rotting, leading to lodging of the plants by wind and rain. After nitrogen and phosphorus, potassium is one of the deficient elements in soil. Potassium is generally provided to agricultural crops as potash (potassium carbonate, K_2CO_3). In soil, potassium exists in four different forms, viz., exchangeable, fixed, solution, and hidden, in molecular lattice of clay particles. Potassium is highly mobile in soil as well as in plants. More recent work shows that plants contain different transport systems to acquire potassium from the soil and distribute it within the plants. Plants utilize both high- and low-affinity transport systems (**HATS** and **LATS**, respectively) to acquire potassium from the soil. Low-affinity transport systems generally function when potassium levels in the soil are adequate. This process is mediated by ion channels in the plasma membrane of root cells, allowing passive transport of K^+ from external areas of relatively high concentration. Under low concentration of potassium, plants usually induce high-affinity K^+ transport systems. In both cases, plasma membrane proton pumps are activated to restore membrane potential and generate a proton gradient. High-affinity potassium transport is an active process. This pattern of K^+ uptake was described as dual isotherm and reflects the activity of two families of transporters (Fig. 2.5). In addition to K^+ uptake from root surface, potassium channels are also involved in its loading and unloading in both xylem and phloem. Voltage-gated potassium channels are involved in the regulation of stomatal movement.

2.7.1.7 Sulfur

Sulfur, an essential macroelement, may be supplied to the soil from rainwater. Use of gypsum also increases soil sulfur levels. The global sulfur cycle involves microbial conversion between its oxidized and reduced forms. There are many microorganisms capable of oxidizing sulfides or decomposing organic sulfur compounds. Heavy consumption of fossil fuel and natural phenomena such as hot sulfur springs, volcano, and geysers release large amount of sulfur oxides into the atmosphere. Sulfur dioxide, an environmental pollutant, can be absorbed by stomata in the leaves. It is then converted to bisulfate (HSO_3^-) upon reaction with water in the cells which inhibits photosynthesis and causes chlorophyll destruction. Bisulfate present in air is oxidized to H_2SO_4 which is responsible for acid rain. Sulfur is a structural component of some amino acids (cysteine and methionine), vitamins (thiamine and biotin), and coenzyme A (Table 2.5). It is essential for the biogenesis of chloroplasts. It is important for the structure of certain proteins where disulfide bonds (-S-S-) between neighboring cysteine and methionine residues result in folding of polypeptide chain, producing a tertiary structure. Sulfur improves root growth and seed production and facilitates vigorous plant growth and resistance to cold. It is also present in the form of iron-sulfur protein complexes, such as ferredoxin, in the electron transport chain in photosynthesis. It enhances root development and nodule formation in legumes. Sulfur-containing thiocyanates and isothiocyanates (also known as mustard oils) are responsible for the pungent flavor of mustard, cabbage, turnip, horseradish, and

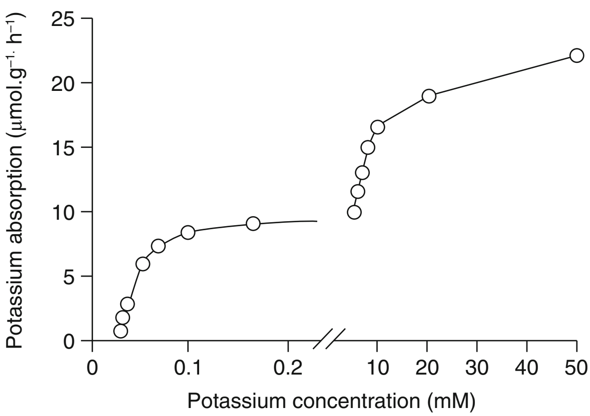


Fig. 2.5 Dual isotherm of K^+ influx reflects the activity of two families of transporters

other members of Brassicaceae. The presence of sulfur in Brassicaceae members makes it fatal for livestock and forms a line of defense against insects and herbivores.

Sulfur deficiency is not very common and it is an immobile element. Therefore, sulfur deficiency symptoms appear first on the younger tissues. Yellowing of leaves, stunted growth, and anthocyanin accumulation are also evident due to its deficiency. In tea plants, sulfur deficiency causes defoliation, and in legumes it leads to reduced nodulation. Approximately 95% of sulfur present in soil is bound in the form of sulfate esters or sulfonates. It is absorbed as divalent sulfate anions (SO_4^{2-}) through roots. Plants and microorganisms assimilate sulfur by reducing sulfate and synthesizing the sulfur-containing amino acid, cysteine, and other organic sulfur compounds. Some of the sulfur is reduced and assimilated in root plastids, but most of the sulfur in plants is transported to shoots. Chloroplasts are sites for light-driven assimilation of sulfate into cysteine, glutathione, and other metabolites. Some sulfate is transported across tonoplast and stored in the vacuoles. Sulfate is taken against electrochemical gradient at the plasma membrane by the proton gradient generated by the plasma membrane H^+-ATPase. It is transported into the cytosol by an electrogenic symport that moves three H^+ per sulfate ions transported. Sulfite, selenate, molybdate, and chromate compete with sulfate for binding to sulfate transporter proteins. The electrochemical gradient favors the diffusion of sulfate into the vacuole. The transfer across the tonoplast occurs through sulfate-specific channels. Multiple transporters with variable affinities for sulfates are present in the roots. In *Arabidopsis*, 14 genes encoding sulfate transporters have been identified. Two of these transporters are high-affinity SO_4^{2-} transporters, SULTR1.1 and SULTR1.2, which are present in the root epidermis and cortex. Four transporters are low-affinity transporters: SULTR1.3, SULTR2.1, SULTR3.5, and SULTR2.2. They are present in the vascular system. SULTR4.1 and SULTR4.2 are tonoplast transporters facilitating the efflux of vacuolar sulfate.

2.7.1.8 Calcium

Calcium is the second most abundant element in plant ash (K^+ being the most abundant). A large proportion of calcium is located in the leaves. In plant cells, calcium is present in central vacuoles, ER, and mitochondria, and it is also bound in cell walls as calcium pectate. High concentration of calcium inhibits cytoplasmic streaming. All organisms maintain low concentration of free Ca^{2+} in the cytosol (~100–200 nM) to prevent formation of insoluble calcium salts of phosphates. In the vacuoles of some plants, calcium gets precipitated as insoluble crystals of calcium oxalate and in some species as insoluble phosphate, sulfate, or carbonate. It is an essential constituent of plant cell wall, and as calcium pectate, it helps in joining the cells together. It plays a key role in transport and retention of other elements and affects the permeability of the cytoplasmic membrane and hydration of colloids in the protoplasm. It is required for normal functioning of the membrane, where it binds phospholipids and membrane proteins. Calcium is supposed to counteract the effect of alkali salts and organic acids within plants. In meristematic tissues, calcium is required for cell division (spindle formation) and cell enlargement. It activates the enzymes required for the growth of root and shoot tip. Calcium regulates the transport of other nutrients into the plants and activates various other enzymes (Table 2.5). Various studies have shown the effect of calcium on diverse developmental processes, such as embryogenesis in sandalwood, cotton fiber elongation, tuberization in potato, and pollen development.

As calcium is not loaded into phloem and is not highly mobile, deficiency symptoms first appear in younger leaves. Meristematic tissues of roots, stems, and leaves are quickly affected by its deficiency as it is required to form middle lamellae in the dividing cells. Deficiency of calcium causes formation of twisted and deformed tissues or stunted growth, leading to rapid death of meristematic tissue especially root meristems. In tomatoes, deficiency of calcium causes degeneration of young fruits. Natural sources of calcium are dolomite, lime, gypsum, and superphosphate. Most soils contain enough calcium, but acidic soils with high rainfall are often supplemented with lime fertilizer (a mixture of CaO and $CaCO_3$) to raise soil pH. Calcium is taken up as divalent cations (Ca^{2+}) due to which it is unable to diffuse through the lipid bilayers without channels or pumps. Calcium entry into root xylem takes place at the apical region of root tip where endodermis has not differentiated. Casparian strips in endodermis block the diffusion of calcium. It is distributed within the plant in free form or complexed with organic acid. Pectin and lignin (both are negatively charged) in the xylem wall do not allow mass flow of calcium. Significant amount of calcium is lost in the form of calcium oxalate. Ca^{2+} serves as a universal second messenger whose cytosolic concentration is tightly regulated by Ca^{2+} transporters. Cells use energy to pump it out across the plasma membrane or into the storage organelles, such as vesicles, vacuole, or the space between the inner and outer nuclear membranes (nuclear membrane lumen). In these organelles, calcium-binding proteins sequester calcium ions to minimize their harmful effects. The low level of calcium in cytosol is sensed by calmodulin (CaM). After binding, it interacts with target proteins, such as protein phosphatases and protein kinases. Vacuolar calcium is released through voltage- or ligand-gated calcium permeable channels in the tonoplast.

2.7.1.9 Magnesium

Plant ash is rich in magnesium. Oilseed crops are richer in magnesium than non-oily seeds. Magnesium is an important constituent of chlorophyll (mainly in the porphyrin moiety) and also acts as an enzyme cofactor for the production of ATP. It is also essential for binding of ribosome subunits. It is also an activator of ribulose bisphosphate carboxylase (Rubisco) and phosphoenolpyruvate carboxylase (PEP carboxylase), two important enzymes involved in dark reaction in photosynthesis. It is also required for the activity of many enzymes of respiration and nucleic acid biosynthesis (Table 2.5). Magnesium is a mobile element. The absence of magnesium results in interveinal chlorosis. It also results in accumulation of anthocyanin pigment in older leaves. Magnesium deficiency results in premature leaf abscission. Magnesium is absorbed as divalent cation (Mg^{2+}) and is transported through the xylem vessels in free or chelated form. It is never limited in soil, but because of soil pH, it is not available to the plants growing in acidic and sandy soils. The concentration of magnesium in soil solutions and cytosol is approximately 0.1–8.5 mM and

0.4 mM, respectively. Entry of magnesium in roots takes place through plasma membrane magnesium channels of the MSR2 family. Movement across tonoplast takes place through MHX Mg^{2+}/H^+ antiporter and TPC1 Mg^{2+}-permeable cation channel.

2.7.2 Micronutrients

2.7.2.1 Iron

Iron is the fourth most abundant element in the earth's crust. It is an essential micronutrient with numerous cellular functions, and its deficiency represents one of the most serious problems in human nutrition worldwide. Plants face two major problems with iron as a free ion, i.e., its insolubility and its toxicity. To ensure iron acquisition from soil and to avoid iron excess in the cells, uptake and homeostasis are tightly controlled. Iron is stored in chloroplasts as iron-protein complexes known as **phytoferritin.** The chemical properties of iron are also responsible for its limited accumulation in plants. Ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions catalyze the reduction of molecular oxygen to damaging ROS (reactive oxygen species). In the symplasm, iron is maintained in a soluble and transportable form. Iron is necessary for the synthesis of many proteins (ferredoxin and cytochromes) that carry electrons during photosynthesis and respiration. Iron is also present as an enzyme cofactor in plants and activates catalase and peroxidase. Iron is not a structural part of chlorophyll but is required for its synthesis (Table 2.6). Iron deficiency in plants is caused largely due to its insolubility in soil rather than its absence. The concentrations of soluble iron optimal for most plants are in the range of 10^{-4}–10^{-8} M (optimal soils are usually slightly acidic). However, 10^{-9} M or lower concentrations of soluble Fe (calcareous or alkaline soils with low bioavailable Fe) are insufficient for plant growth, and plants may develop iron deficiency triggered leaf chlorosis. Iron is one of the most immobile elements in the plants. Its deficiency causes interveinal chlorosis and necrosis, like magnesium, but unlike magnesium, symptoms are first evident in younger leaves. Interveinal chlorosis is followed by chlorosis of the veins, turning the whole leaf yellow. During severe deficiency, young leaves turn white with necrotic lesions. Iron deficiency is most common among the members of Rosaceae, maize, sorghum, and fruit trees. Source of iron for plants is soil, which is available in the form of iron sulfate and iron chelates. Iron undergoes oxidation and reduction, forming Fe^{2+} and Fe^{3+}, alternatively. Both these forms have limited solubility, and in well-aerated soil, their concentration is less than 10^{-15} M. This means, it is not readily available to the plants at physiological pH. Soils with alkaline pH and bicarbonates are deficient in iron. Iron can be solubilized in soil by its detachment from mineral soil particles. Mobilization of iron is a prerequisite for its uptake into the roots. Higher plants can mobilize iron via two distinct strategies (Fig. 2.6).

According to strategy I, Fe acquisition is regulated by the availability of iron in the soil and by the developmentally controlled need of the plant. When plants require additional iron, they are able to enhance the activities of the necessary transporters

Table 2.6 Role of micronutrients

Micronutrients	Function in cell metabolism	Function at plant level
Iron	Chlorophyll formation and synthesis of ferredoxin and cytochromes, activates catalase and peroxidase and many enzymes with iron-based cofactor	Provides resistance against plant pathogens
Molybdenum	Nitrogen metabolism and nitrogen fixation	Optimizes plant growth; aids in nodule formation in leguminous crops
Boron	Cell wall formation along with calcium, necessary for sugar translocation	Promotes maturity; essential for pollen grain formation and pollen tube elongation; fruit yield and quality of temperate fruits
Copper	Activates enzymes necessary for photosynthesis and respiration, constituent of cytochrome oxidase and polyphenol oxidase, present in the receptor of ethylene signal	Provides resistance against plant pathogens
Manganese	Acts as a catalyst in growth process; constituent of oxygen evolving complex	Accelerates seed germination and maturity; increases the availability of phosphate and calcium
Zinc	Chlorophyll formation; involved in respiration and nitrogen metabolism; regulates functioning of DNA/RNA polymerase	Provides resistance against plant pathogens
Chlorine	Formation of cytochromes; light reaction of photosynthesis	Regulation of stomatal movement; delayed senescence
Nickel	Constituent of urease	Increases crop yield

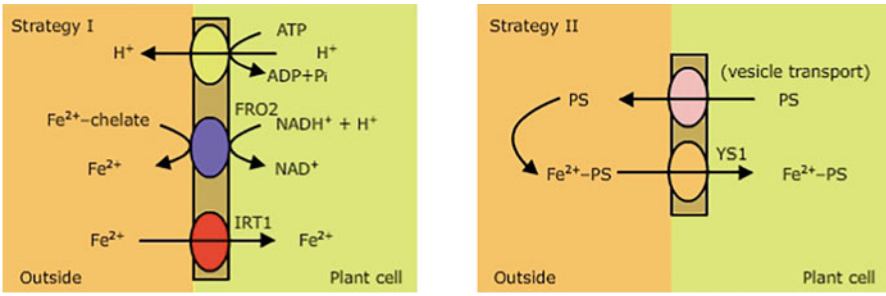


Fig. 2.6 The acquisition of iron by two different strategies in higher plants. Strategy I involves transporters and enzymes, while strategy II involves phytosiderophores

and enzymes performing this strategy. This strategy is found in most monocotyledonous and dicotyledonous plants, except in grasses, and involves the solubilization of iron by soil acidification.

$$Fe(OH)_3 + 3H^+ \leftrightarrow Fe^{3+} + 3H_2O$$

The lowering of pH from 8 to 4 increases the concentration of ferric iron in the soil from 10^{-20} M to 10^{-9} M. This lowering of pH and increase in concentration are carried out by a root plasma membrane bound H^+-ATPase. In *Arabidopsis*, this enzyme is encoded by AHA gene family. Before the uptake of iron by roots, it is essential that Fe^{3+} is reduced to Fe^{2+}. This reduction is catalyzed by an inducible plasma membrane bound ferric reductase oxidase (FRO). This enzyme is encoded by the gene FRO2, which is expressed in iron-deficient epidermal root cells. The enzyme has eight membrane-spanning domains, two histidine-coordinated heme groups, and site for FAD and NADPH. There are other FRO gene families of metal reductases in *Arabidopsis* which are expressed in other cells of the root, vascular tissues, and shoot. Fe^{2+} is then transported into the root cells by IRT1 (iron-regulated transporter1), a member of ZIP metal transporter family (Zn transporter). IRT1 is expressed in the plasma membrane of epidermal cells in iron-deficient roots. Studies with *Arabidopsis* mutants and yeast cells transformed with IRT1 gene have shown that this transporter protein can also transport other divalent metal ions such as zinc, manganese, and cadmium. Strategy II, found in grasses, is based on solubilization of Fe^{3+} by chelation with **phytosiderophores** (Box 2.7). Strategy II is restricted to members of Poaceae family (barley, rice, and maize). According to this strategy, plants release low-molecular-weight phytosiderophores (PSs) of the mugineic acid family. PSs are chelators that bind ferric iron in the rhizosphere and make it available to the roots. This chelation-based response makes it easier for grasses to grow on iron-deficient soils more efficiently as compared to eudicots and other monocots. Mugineic acid and other related PSs are produced from S-adenosyl methionine (SAM). Nicotianamine synthase (NAS) acts upon SAM resulting in the formation of nicotianamine which is a precursor of PS. Nicotianamine is a common chelator for various metal ions found in all plants. The enzyme nicotianamine aminotransferase (NAAT) is specific to grasses and catalyzes the step toward PS production along with a number of other enzymes.

$$3\ \text{SAM} \xrightarrow{\text{nicotianamine synthase}} \text{nicotianamine} \xrightarrow{\text{nicotianamine transferase}} 2'\text{deoxymugineic acid} \xrightarrow{\text{dioxygenase}} \text{mugineic acid}$$

The Fe^{3+}-PS complex is transported into the epidermal cells of iron-deficient roots by high-affinity transporters. These transporters are encoded by YS1 (yellow stripe 1) and have 12 transmembrane domains. YS1 is expressed in a number of tissues. This protein is a proton-coupled symporter for PS and mugineic acid metal chelates. PSs are extruded by the roots and can be reimported as Fe^{3+}-PS complexes. Iron homeostasis is required for building heme and Fe-S prosthetic groups and assembling them correctly to apoproteins. Storage and buffering of iron at subcellular level are very essential to ensure protection against iron toxicity and deficiency. Plastids store iron in the form of **phytoferritin**, a protein molecule that encloses

Box 2.7: Chelation and Mineral Nutrition

The word chelate is derived from the Greek word "chel," meaning a crab's claw. Chelation is a natural process that prevents absorbed nutrients from precipitation. It allows the nutrients to move freely in soil and increases its availability to plants. In plants, proteins, peptides, porphyrins, carboxylic acids, and amino acids act as natural chelating agent. Other naturally occurring organic acids, such as malonic acid and gluconic acid, also play an important role in plant mineral nutrition. Organic acids and amino acids, such as citric acid and glycine, are also naturally occurring chelating agents. Chemically, a chelate is complex of cations with organic compounds resulting in a ring structure. Chelates of glycine with cations, such as iron, zinc, and copper, have been well investigated. They usually contain two moles of ligand (glycine) and one mole of metal. There are also synthetic chelating agents with high stability with divalent and trivalent ions. The proteoid root (clustered roots) in phosphorus-starved plants releases organic acids, mainly citrate and malate. Release of these acids binds aluminum and iron in the soil leading to availability of phosphorus to the plants. A strong chelating agent may bind the mineral too strongly and make it unavailable to plants. On the other hand, a weak chelating agent may not be able to protect the chelated minerals from chemical reactions with other compounds and thereby reduce their availability to plants. A combination of chelating agents can improve product stability and broaden product effectiveness. Organic substances in the soil either applied or produced by plants or microorganisms are the natural chelating agents. The most important compounds exhibiting this nature are hydroxamate siderophores, organic acids, and amino acids. Hydroxamate siderophores are naturally produced by soil microorganisms and are essential in natural ecosystems to solubilize and transport nutrients, especially iron to plant roots. Under iron-deficient conditions, microorganisms produce siderophores to overcome iron starvation. In plant tissue culture, usually Fe-EDTA is added to the medium to improve the availability of the element. Although low concentrations of EDTA stimulate the growth of whole plants in tissue as well as hydroponic cultures, at high concentration tissue may be damaged. For some plant species, EDTA is inhibitory. In a cell, high concentrations of chelating acid are phytotoxic, as they competitively withdraw essential elements from enzymes.

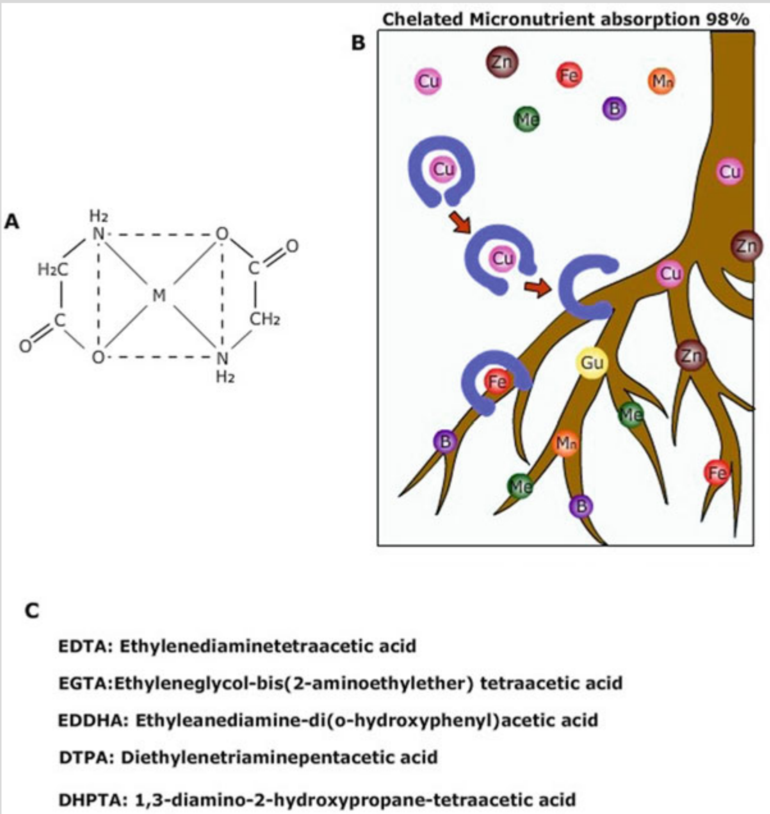
The significance of chelation process are:

- It increases the availability of nutrients, e.g., chelating agent binds relatively insoluble iron in high-pH soil and makes it available to the plants.

(continued)

Box 2.7 (continued)

- Chelation prevents mineral nutrients to form insoluble precipitates. At high pH, iron reacts with hydroxyl group and forms ferric hydroxide which is not available to the plants.
- It reduces toxicity of some metal ions to plants.
- It prevents nutrients from leaching.
- It increases mobility of nutrients.
- It suppresses the growth of plant pathogens.



A. A chelator with two ligand molecules (glycine) around metal ion (M) in the center forms a ring-like structure. **B**. The chelator binds to the nutrients present in the soil and prevents them from precipitating and leaching, thereby increasing their mobility and making them available to root. **C**. Common synthetic chelating agents

4500 Fe^{3+}. *Arabidopsis* encodes four ferritins, viz., FER1, FER2, FER3, and FER4. Root and seeds have FER1 and FER2, respectively, whereas FER3 and FER4 are expressed in shoot tissues. The sensing mechanism of iron deficiency is not yet clearly understood. However, the expression of a transcription factor F1 T1 (Fe-induced deficiency transcription factor) is upregulated as a result of iron deficiency.

2.7.2.2 Molybdenum

Molybdenum is essential to plants but is toxic to animals. Among all the nutrients, molybdenum is required in least concentration. In order to gain biological activity, Mo has to combine with a pyranoprotein, thus forming a prosthetic group named **molybdenum cofactor (Moco)**. It is involved in maintaining the activity of more than 60 enzymes. The crystallographic analysis of molybdenum enzymes made it evident that the cofactor (Moco) is deep seated within the holoenzyme. Thus, Moco could have been added prior to or during the completion of folding and dimerization of the apoprotein monomers. Therefore, during the biosynthesis of enzymes, the formation of molybdenum cofactor is the first step. It is required as a cofactor of enzymes involved in nitrogen metabolism (Table 2.6). Molybdenum is a constituent of nitrate reductase enzyme, which reduces nitrate ions (NO_3^-) to nitrite ions (NO_2^-). The other enzyme used by prokaryotes to reduce atmospheric nitrogen is dinitrogenase, which also contains molybdenum. It plays an important role in the breakdown of purines and is an essential part of an oxidase that converts abscisic acid aldehyde to ABA. Molybdenum also plays a role in sulfur metabolism during oxidation of sulfite (SO_3^{2-}) to sulfate (SO_4^{2-}).

Molybdenum deficiency increases many folds in acidic soils due to precipitation of molybdenum by hydrous iron and aluminum oxides. Molybdenum is highly mobile in xylem and phloem tissues. Therefore, its deficiency symptoms often appear on the entire plant. Only under extreme deficient conditions, molybdenum deficiency symptoms can be observed. The complication in the diagnosis of molybdenum deficiency symptoms is due to its manifestation as nitrogen deficiency symptoms, which are clearly visible in legumes. These symptoms are related to the function of molybdenum in nitrogen metabolism. In legumes, the requirement of molybdenum is higher as compared to other crops. Its deficiency symptoms in legumes are chlorosis, stunted growth, and small root nodules. In other dicotyledonous species, its deficiency leads to drastic reduction in leaf size and yellowing of the leaves. The absence of leaf tissue at the edges of the leaf results in the formation of narrow, distorted leaves that are usually slightly thickened, causing leaf edges to curl upward, a symptom commonly referred as "whiptail." The whiptail disorder is observed in crucifers with cauliflower being the most sensitive to molybdenum deficiency. Twisting of young leaves, which eventually die, can be seen in whiptail of cauliflower and broccoli. Marginal and interveinal necrosis is associated with elevated nitrate concentration indicating a lack of nitrate reductase activity under molybdenum deficiency.

In soils, molybdenum can occur in four different fractions, viz., as dissolved molybdenum in soil solution, with oxides, as a constituent in minerals, and associated with organic matter. The availability of molybdenum for plant growth is highly dependent on soil pH, concentration of adsorbing oxides, soil drainage, and interaction with organic compounds present in the soil colloids. It exists in soil as molybdate (MoO_4^{2-}) and as sulfide (MoS_2). It is absorbed by roots as MoO_4^{2-} under neutral or slightly alkaline conditions. It can be stored as MoO_4^{2-} in vacuoles. However, in acidic soils, the availability of molybdenum is limited due to fixation of MoO_4^{2-} by iron, aluminum, and manganese oxides. Molybdenum uptake increases with liming of soil (addition of lime increases the soil pH). The use of phosphate helps in the release of adsorbed MoO_4^{2-} from iron oxides (phosphate has high affinity for iron oxides) and increases water-soluble MoO_4^{2-} concentration in the soil. There are many chemical similarities in SO_4^{2-} and MoO_4^{2-} acquisition by plants due to which SO_4^{2-} inhibits uptake of MoO_4^{2-} as both compete with each other during root absorption. Fertilizers containing phosphorus and sulfur facilitate higher MoO_4^{2-} uptake. It is highly mobile, and its long-distance transport occurs through xylem and phloem. The high-affinity ABC transporters encoded by the *modA*, *modB*, and *modC* genes are responsible for molybdenum uptake in bacteria. Specific transporters of molybdenum in plants have still not been identified. However, the MoO_4^{2-} behaves similar to SO_4^{2-}, and their uptake is decreased in the presence of high concentrations of SO_4^{2-}. So, it is possible that both these anions use the same transporters.

2.7.2.3 Boron

At biochemical and physiological level, the role of boron is not clearly understood. It is only when boron is supplemented to the plant-growth medium/soil that its role becomes evident. It is present in the cell wall and is an important part of pectins. Boron is required for maintaining structural stability of cell wall since primary walls of boron-deficient cells show deformities. Boron plays an important role in the elongation of pollen tubes (Table 2.6). In diatoms, it forms a part of silicon-rich cell wall. It is also involved in sugar translocation and is an essential element for seed and fruit development. It also helps in the use of nutrients and regulates other nutrients. Other secondary roles of boron may be in sugar transport, cell division, and synthesizing certain enzymes. Sources of boron are organic matter and borax. It is absorbed from soil as undissociated boric acid (H_3BO_3) at pH < 8. Its deficiency is not very common, but several disorders related to disintegration of internal tissues result. These include “heartrot” of beets, “stem crack” of celery, “water core” of turnip, and “drought spot” of apples. It causes necrosis in young leaves and also stunting of growth. Boron is involved in nucleic acid synthesis during cell division in apical meristems, resulting in the loss of apical dominance, death of root and shoot tips, abscission of flowers, shortened internodes, and reduced nodulation in legumes.

2.7.2.4 Copper

It is an important component of the electron transport chain in photosynthesis and is also involved in manufacture of lignin. It is a component of oxidase enzymes (cytochrome oxidase) and plastocyanin (chloroplast protein). It also aids in root metabolism and helps in the utilization of proteins. It is absorbed as a divalent cupric ion (Cu^{2+}) in aerated soils or as monovalent ion (Cu^{+}) in wet soils. The browning of freshly cut apple and potato is due to the activity of copper-containing polyphenol oxidases which leads to the production of red or brown-colored polyphenols. Superoxide dismutase (SOD) is another copper-containing enzyme, which is an antioxidant and protects the cell from oxidation from reactive oxygen species. Copper deficiency symptoms are chlorosis, leaf tip necrosis, and the bark becomes rough and splits. Leaves turn dark green and develop necrosis. Citrus orchards show dying young leaves which is commonly referred to as "dieback" disease. In potato, it causes blackening of tubers. The Cu transporter (COPT) mediates Cu^{+} uptake in plants.

2.7.2.5 Manganese

Manganese exists in three oxidation states, viz., Mn^{2+}, Mn^{3+}, and Mn^{4+}, as insoluble oxides as well as in chelated form in soils. It is mostly absorbed as divalent manganese cation (Mn^{2+}) after its release from chelates or reduction in higher valence oxides. Manganese ions (Mn^{2+}) are readily taken up by roots and transported to shoots. The movement of manganese ions from roots to shoots is very rapid due to which it is less toxic to roots as compared with other metals present in the soil. Mn^{2+} is required for chloroplast development and also for activation of many enzymes of photosynthesis, respiration, and nitrogen metabolism. It acts as electron donor for chlorophyll b and is involved in decarboxylation reaction during respiration (Table 2.6). Mn^{2+} deficiency causes interveinal chlorosis and gray spots on leaves. It also results in coloration abnormalities, such as discolored spots on the foliage. Various disorders, such as "gray speck" of oats, "marsh spot" of peas, and "speckled yellows" of sugar beets, are due to Mn^{2+} deficiency. The absence of manganese ions also causes disorganization of thylakoid membranes.

2.7.2.6 Zinc

It is distributed within the cytoplasm (50%), nucleus (30–40%), and cell membrane (10%). It can bind tightly to metalloproteins as a structural component or to metalloenzymes as a cofactor. Zinc binds metallothioneins (MTs) with low affinity, which constitutes about 5–15% of the total cellular zinc pool. It can be compartmentalized into intracellular organelles and vesicles for storage, which serve as a supply for zinc-dependent proteins. Cytosolic free zinc is maintained at very low concentrations. MTs and two zinc transporter families, Zrt- and Irt-like proteins (ZIP) and Zn transporters (ZnT), play crucial roles to maintain this cellular zinc homeostasis. Zinc plays a pivotal role as a structural, catalytic, and signaling component that functions in numerous physiological processes. It participates in chlorophyll formation and prevents its destruction. It is a component of the enzyme carbonic anhydrase (CA). It also regulates the transformation of carbohydrates and consumption of sugars. Zinc has a role in the formation of tryptophan synthase, an enzyme responsible for the synthesis of tryptophan. Tryptophan is a precursor of indole acetic acid (IAA). Thus, zinc has indirect role in IAA synthesis and activates a large number of enzymes, e.g., dehydrogenases (e.g., alcohol dehydrogenase, ADH, and carboxylases). It is also associated with important enzymes, such as SOD. It plays an essential role in maintaining the structure and function of DNA transcription factors, including Zn finger, Zn cluster, and RING finger domains (Table 2.6**).** Zinc deficiency results in malformed or stunted leaves, commonly known as "little leaf" and "rosette" of apples and peaches. It is caused by oxidative degradation of auxin, the growth hormone. Auxin level in zinc-deficient plants is very low. Leaf margins are often distorted and puckered. Other zinc deficiency symptoms include interveinal chlorosis and stunted growth in the leaves of maize, sorghum, beans, and fruit trees. Sources of zinc are soil, zinc oxide, zinc sulfate, and zinc chelates. It is absorbed as divalent cations (Zn^{2+}) from zinc chelates. A group of genes that encode Zn^{2+} micronutrient transporters (ZIPs) have been isolated. ZIP transporters are ubiquitous having been identified in bacterial fungi, mammals, and plants. Most ZIP proteins have eight transmembrane helices, and in many cases, a loop region is present between transmembrane domains 3 and 4 containing a histidine-rich sequence which binds to metal and regulates zinc transport. ZIP1, ZIP3, and ZIP4 are high-affinity zinc transporters which bind to other divalent cations like Cd^{2+} and Cu^{2+}. Both ZIP1 and ZIP3 are expressed in response to zinc deficiency in roots, whereas ZIP4 is expressed in both root and shoot (Box 2.8).

Box 2.8: Hyperaccumulators

Some plants take up high concentration of metal elements from the soil and store them in their aerial tissues. These plants are known as *hyperaccumulators* or *metallophytes*. The elemental concentration in the above ground part ranges from 100- to 1000-fold higher than the observed concentration in non-hyperaccumulators species. They are unique as they can be utilized in biogeochemical and phytoremediation studies. There are around 450 hyperaccumulators plants and nickel is the most accumulated metal. In addition to nickel, arsenic, cobalt, manganese, lead, cadmium, zinc, selenium, and copper too are also being accumulated by the plants. For example, *Brassica* can accumulate up to 30,000 $\mu g.g^{-1}$ zinc and 1300 $\mu g.g^{-1}$ cadmium. The three main characteristic features of hyperaccumulators are:

(i) *Greater capability of heavy metal uptake*: The metal uptake by roots is more because of constituted overexpression of the genes responsible for normal uptake of nutrients. In some species zinc uptake is more because of the overexpression of ZIP (zinc- and iron-regulated protein transporter) family gene coding for plasma membrane cation transporters.
(ii) *Higher root to shoot translocation of metals*: In non-accumulator plants, the metal ions are detoxified by chelation and stored in vacuoles of root cells. On the contrary, the hyperaccumulators rapidly translocate the

(continued)

Box 2.8 (continued)

metals to shoot via xylem. Overexpression of HMA (heavy metal-transporting ATPase) proteins is responsible for rapid loading of metals into xylem.

(iii) *Detoxification and sequestration of metals*: It mainly consists of ligation organic components with metal ions and their removal from metabolically active cytoplasm to non-active compartments of the cell, mainly vacuoles and cell wall. Comparative genomics have shown that overexpression of CDF (cation diffusion facilitator) genes removes divalent metal cations from the cytoplasm to vacuole.

Why should some plant accumulate metals at such high concentration? Most probably hyperaccumulated metals provide defense against herbivores and pathogens. In *Nicotiana caerulescens*, there is significant inhibition of the bacterial pathogen *P. syringae* by zinc accumulation. They also have significant roles in phytoremediation, an eco-friendly method of removal of heavy metals from the polluted soils. Hyperaccumulators also have potential significance in phytomining, recovering, or phytoextraction of metals from plants.

2.7.2.7 Chlorine

Chlorine is universally present in plants in the form of inorganic chlorides. Plants growing in salt marshes and saline soils can tolerate high concentrations of chlorides. Chlorine is essential for photolysis of water leading to oxygen evolution during photosynthesis. It is also essential for roots and for cell division in leaves and maintains ionic balance in cells. It is one of the osmotically active elements in vacuoles. It is involved in transporting cations, such as potassium, calcium, and magnesium, using antiporters. It is required to chemically balance potassium ion concentration that increases during the opening and closing of stomata (Table 2.6). Chloride ions are rarely deficient because of their high solubility and availability in soils as well as in dust or in tiny moisture droplets. Chlorine deficiency causes reduced growth, wilting and bronze coloration of leaves, and swelling of root tips. Leaf mottling and chlorine deficiency in cabbage are marked by the absence of cabbage odor from the plant. Chlorine is absorbed as chloride ions (Cl^{-}) and remains in the same form in approximately 130 organic compounds, but still it is present in trace amounts in plants. Most species absorb 10–100 times more Cl^{-} than required. Asparagus requires sodium chloride for its profuse growth.

2.7.2.8 Nickel

It is an abundant metallic element in soil, absorbed in the form of Ni^{+2} ion. It is present in plant tissues in the range of 0.05–5.0 $mg.kg^{-1}$ dry weight. It is essential for activation of urease, an enzyme involved in nitrogen metabolism. In legumes, removal of nickel from nutrient solutions leads to accumulation of large amount of urea in leaves resulting in necrotic spots. Beneficial effects of nickel on the growth of oats, wheat, and tomato have been reported.

Summary

- Plant nutrition is the study of the nutrients necessary for plant growth and development. Roots absorb around 60 elements from the soil, but not all are required by the plant growth. The nutrients or elements necessary for growth or completing life cycle of a plant are considered as essential elements. There are 17 essential plant nutrients. They mainly serve structural roles, act as enzyme activators, and act as osmotic regulators in plants. The elements which stimulate growth but are not essential, or which are essential only for certain plant species, are referred to as beneficial or functional elements.
- Carnivorous, insectivorous, and parasitic plants are different in acquiring mineral nutrients. Macronutrients are consumed in larger quantities and constitute 0.2–4.0% on a dry matter weight basis. Micronutrients are present from 5 to 200 ppm, or less than 0.02% dry weight, in plant tissues. Most of the micronutrients have very narrow adequate range and very minute change in their concentration leads to symptoms.
- Mobility of nutrients within the soil is related to chemical properties of the soil, such as cation exchange capacity and anion exchange capacity, as well as the soil conditions, such as moisture, pH, etc. The movement of nutrients from soil to root takes place when root comes in physical contact with nutrients. Root hair, along with the rest of the root surface, is the major site for water and nutrient uptake by the plants. The selective permeability features of plasma membrane make it impermeable to certain ions and allow entry of other ions.
- The absence or deficiency of any nutrient causes the development of specific symptoms. Appearance of these symptoms depends on the role played by these elements or upon their mobility in the plants. Depending on the mobility of the element, leaf symptoms can occur in the upper, middle, or lower regions of a plant. When nutrients are mobile, deficiency symptoms are apparent first on the older leaves, e.g., in case of nitrogen, phosphorus, and potassium deficiency. When nonmobile nutrients are deficient, the younger leaves show deficiency symptoms, as the nutrients are utilized in the older leaves and do not move up to the young leaves. This phenomenon is significant in determining which nutrients a plant may be lacking.

Multiple-Choice Questions

1. Which element plays an important role in pollen germination?
   (a) Potassium
   (b) Magnesium
   (c) Zinc
   (d) Boron

2. Which of the following elements is immobile in plants relative to all others listed below?
   (a) Magnesium
   (b) Potassium
   (c) Calcium
   (d) Nitrogen
3. Which of the following cannot be considered as a criterion for essentiality of an element for plants?
   (a) Element must be an essential for normal growth and reproduction.
   (b) Element must be easily absorbed by plant roots.
   (c) Specificity for element's role in plant growth and development.
   (d) Element's direct involvement in plant metabolism.
4. Senescing leaves export much of their mineral content to the younger, healthy leaves. Element most mobilized is:
   (a) Calcium
   (b) Sodium
   (c) Sulfur
   (d) Magnesium
5. The macronutrients potassium, calcium, and magnesium are the examples of:
   (a) Metallic essential elements
   (b) Nonmetallic essential elements
   (c) Nonmetallic nonessential elements
   (d) Metallic nonessential elements
6. Which of the following element is required in least quantity?
   (a) Zn
   (b) Mn
   (c) Mo
   (d) Co
7. Which of the following element is a constituent of biotin and coenzyme A?
   (a) Copper
   (b) Molybdenum
   (c) Sulfur
   (d) Iron
8. An element is considered essential if it:
   (a) Is found in plant ash
   (b) Induces flowering
   (c) Is present in the soil where the plant is growing
   (d) Is not replaceable and is indispensable for the growth of the plant
9. Which of the following mineral nutrients is not involved in redox reactions in plant cells?
   (a) Iron
   (b) Zinc
   (c) Copper
   (d) Sodium

10. The photosynthetic and mitochondrial transports are affected by which of the following three elements?
    (a) Cu, Mn, and Fe
    (b) Co, Mn, and Fe
    (c) Cu, Mg, and Cl
    (d) Zn, Cu, and Fe

Answers

1. d 2. c 3. b 4. c 5. b 6. c 7. c
8. d 9. d 10. a

Suggested Further Readings

Delhaize E, Schachtman D, Kochian L, Ryan PR (2015) Mineral nutrient acquisition, transport and utilization. In: Buchanan BB, Gruissem W, Jones RL (eds) Biochemistry and molecular biology of plants. Wiley Blackwell, Chichester, pp 1101–1131

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Taiz L, Zeiger E (2010) Plant physiology, 5th edn. Sinauer Associates Inc, Sunderland, pp 107–126