Essential Plant Nutrients and their Functions

Idupulapati M. Rao

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I.   Introduction

The supply and absorption of chemical compounds needed for growth and metabolism may be defined as nutrition and the chemical compounds required by an organism termed nutrients. The study of how plants absorb and assimilate inorganic ions is called mineral nutrition. Mineral elements, those acquired primarily in the form of inorganic ions, continually cycle through all organisms and their environment. The entry point of mineral elements to the biosphere is predominantly through the root systems of plants so that, in a sense, plants act as the "miners" of the earth's crust (Epstein, 1972). The ability of roots to absorb inorganic ions at low concentrations in the soil solution makes plant mineral absorption a very effective process. Following absorption at the roots, the mineral elements are transported to the various parts of the plant where they are utilized in important biological functions.

For more than 2000 years, the beneficial effect of adding mineral elements (e.g., plant ash, lime) to soils to improve plant growth has been known in agriculture. Woodward (1699) was the first to document and demonstrate the value of mineral nutrients to plant growth. He showed that the growth of plants was increased markedly when they were supplied with water from a drain rather than with rain-water. However, the Neolithic Chinese Yang-Shao people of at least 3 to 4 thousand B.C. recognized the value of organic fertilizers. Justus von Liebig (1803-1873) collected and summarized the scattered information concerning the importance of mineral elements for plant growth that contributed toward establishment of mineral nutrition of plants as a scientific discipline.

By 1890, scientists had already established that carbon (C), hydrogen (H), oxygen (O), nitrogen (N), phosphorus (P), sulfur (S), potassium (K), calcium (Ca), magnesium (Mg), and iron (Fe) were required by plants, and that their absence or low availability resulted in either the death of the plant, or very poor plant growth with accompanying visual symptoms. Between 1922 and 1954, additional elements were determined to be essential: manganese (Mn), copper (Cu), zinc (Zn), molybdenum (Mo), boron (B), and chlorine (Cl). The 16 essential elements, their discoverer, and the discoverer(s) of essentiality are shown in Table 1. The discovery of the essentiality of several mineral elements led to a rapid increase in the use of mineral fertilizers in agriculture and horticulture to improve plant growth, development and yield.

Of the 16 essential elements, C, H and O are obtained by the plant from either the atmosphere, as carbon dioxide, during the process of photosynthesis, or from water. These 3 elements combined make up the carbohydrate structure of the plant and comprise about 90% to 95% of the plant dry matter. Carbon enters the plant as carbon dioxide from the atmosphere. The entire purpose of photosynthesis is to get carbon incorporated into organic molecules. Once incorporated, carbon is the "backbone" of all the cellular products. These include sugars, proteins, lipids (fats), and nucleic acids (including DNA). Hydrogen is the most abundant nutrient in plant tissue (total atoms not absolute amount by weight). Plants get hydrogen by removing it from water molecules. Once the two hydrogen atoms are removed from water, oxygen is merely a by-product of the process. Plants need hydrogen for photosynthesis, energy transfer, and many other processes

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within plants. Oxygen is provided by either water or elemental oxygen (O_2). All organisms that conduct aerobic respiration need it. Aerobic respiration is a means by which organisms can very efficiently utilize stored energy to create readily usable energy. Just because plants can create and store chemical energy from photosynthesis this does not mean that they get a free ride the rest of the time. All living cells need energy to continue life.

The remaining 13 elements are obtained from the soil through the root system and they make up the remaining 5% to 10% of the plant dry matter. Legumes are slightly different. The bacteria, called rhizobia, in their root nodules have the ability to make use of atmospheric N which they "fix" and pass-on to the host plant. This fixed N is used by the legume and ultimately returned to the soil when the plant dies or is consumed by animals and excreted.

Other things being equal, the rate of plant growth is determined by the mineral nutrient which is most limiting. This is one expression of Liebeg's famous "Law of the minimum", which states that "plants will use essential elements only in proportion to each other, and the element that is in shortest supply – in proportion to the rest – will determine how well the plant uses the other nutrient elements". This basic law of plant nutrition was formulated in the late 19th century and with the benefit of a further 100 years of research can be modified to allow for the fact that some nutrients do interact. Thus, a nutritional stress due to a limitation of K can be modified to some extent by the application of sodium (Na). Similarly P and S interact as do Ca and Mg. However, these second order effects do not invalidate the essential truth expressed in the Law of the minimum. It is still a good practical guide to understanding the role of plant nutrients.

Now it is widely accepted that higher plants must have access to N, P, K, S, Ca, Mg, Fe, Zn, Mn, Cu, Mo, B, Cl, and Ni in order to meet their essential mineral nutrient needs (Table 2). From the results of many studies using a number of plant species grown with and without Ni, and from detection of this element in plant urease, Ni has been added few years ago to the plant-essential list of mineral elements (Brown et al., 1987). Under most natural conditions, soil provides these 14 mineral elements for growing plants. An important exception is the N_2 provided to leguminous plants through their symbiosis with rhizobia. Some mineral nutrients may be supplied directly to plant foliage from the atmosphere, and under some conditions this source may be a major contributor to plant needs for elements such as S and Cl. Without any one of these essential elements, plants cannot complete their life cycles because each element serves some unique vital role. With the exception of B and Cl, a well-defined and unique physiological function has been established for the essential 14 elements (Marschner, 1995).

There are some agriculturally important plants that require additional elements. For example, Na is required by some crops including sugar beet, fodder beet and mangolds. Similarly legumes cannot fix atmospheric N if Co is deficient. In this case it is the rhizobia rather than the parent plant that has the requirement for Co. The amount required is very small, and most soils have sufficient Co for this purpose, even those which are Co deficient with respect to animal health. There is also some evidence that some tropical

plants have a specific requirement for Si and that vanadium (V) can substitute for Mo in some cases. However, recognized criteria for establishing plant essentiality, i.e., serving uniquely for growth, development, or physiological functions, have not been fully satisfied for these four elements (Co, Na, Si, and V).

The functions that essential mineral elements serve in plants may be related to properties they have at the time of uptake, to changes they undergo during assimilation or to both (Marschner, 1995). This article will be concerned therefore mainly with the functional aspects of essential and beneficial mineral elements. It will also consider the role of mineral nutrients in crop growth, development and yield (Table 3). Crop plants will be used for most examples because there is more information regarding these than for native species.

II.   Definition and classification of mineral elements

Arnon and Stout (1939) proposed that the term essential mineral element (= mineral plant nutrient) should be restricted to those elements which fulfill the following criteria:

- Omission of the element in question must result in abnormal growth, failure to complete the life cycle, or premature death of the plant.
- The element must be specific and not replaceable by another.
- The element must be directly involved in plant metabolism, that is, it must be required for a specific physiological function.

The term does not include those elements which, for example, compensate the toxic effects of other elements. Thus, a mineral element which only stimulates growth but does not satisfy the above criteria cannot be defined as mineral plant nutrient. It can merely be described as a "beneficial" element (Marschner, 1983).

It is still difficult to generalize when discussing which mineral elements are essential for plant growth because of differences between higher and lower plants (Table 4). For higher plants the essentiality of 14 mineral elements is well established, although the known requirement for Cl and Ni is as yet restricted to a limited number of plant species. Most micronutrients are predominantly constituents of enzyme molecules and are thus essential only in small amounts (Romheld and Marschner, 1991). In contrast, the macronutrients either are constituents of organic compounds, such as proteins and nucleic acids, or act as osmotica (Marschner, 1995). These differences in function are reflected in the average concentrations of mineral nutrients in shoots that are sufficient for adequate growth (Table 2). The values can vary considerably depending on plant species, plant age, and concentration of other mineral elements.

Some researchers argue that a macronutrient/micronutrient classification is difficult to justify physiologically. Mengel and Kirkby (1987) have proposed that the essential elements should instead be classified into four groups based on their biochemical behavior and physiological functions (Table 5). The first group includes N and S. These elements are major constituents of organic material. Plants assimilate these nutrients via

biochemical reactions involving oxidation-reduction. The second group includes P, B and Si. These elements are important in energy transfer reactions or in maintaining structural integrity. They can often be found in plant tissues as phosphate, borate and silicate esters in which the elemental group is bound to the hydroxyl group of an organic molecule (i.e., sugar-phosphate). The third group includes K, Na, Mg, Ca, Mn and Cl. These elements are present in plant tissue as either free ions or ions bound to substances such as the pectic acids present in the plant cell wall. Of particular importance are their roles as enzyme cofactors and in the regulation of osmotic potentials. The fourth group includes Fe, Cu, Zn, Mo and Ni. These elements are present as structural chelates or metalloproteins and they enable electron transport by valence change.

Mineral nutrients are also classified on the basis of their mobility within a plant and their tendency to retranslocate during deficiencies (Table 6). When relating deficiency symptoms to the role of an essential element, it is important to consider the extent to which an element can be recycled internally within the plant from older to younger leaves. Some elements such as N, P and K are readily move from leaf to leaf, whereas others such as B, Fe, and Ca are relatively immobile in most plant species. If an essential element is mobile, deficiency symptoms will occur first in older leaves. On the other hand, a deficiency of an immobile essential element will first become evident in younger leaves. Although the precise mechanisms of nutrient mobilization are not well understood, plant hormones such as cytokinins appear to play a key role (Marschner, 1995).

III. Functions of mineral nutrients: Macronutrients

A. Nitrogen

Nitrogen is a major component of proteins, nucleic acids, hormones, chlorophyll, vitamins and enzymes essential for plant life (Blevins, 1989). In green plant material, protein N is by far the largest N fraction and amounts to about 80 to 85% of the total N. The N of the nucleic acids makes up about 10% and the soluble amino N about 5% of the total N present in plant material. The proteins formed are used in the chloroplast, mitochondria, and other structures in which most of chemical reactions in the plant occur. Nitrogen is essential to the use of carbohydrates in plants. Nitrogen metabolism is a major factor in stem and leaf growth (vegetative growth). Nitrogen stimulates vegetative growth and results in a deep dark green colored leaves. Excessive N supply can lead to excessive stem elongation, lodging problems and reduced flower and fruit production. Deficiency of N can reduce yields, could cause yellowing of the leaves and stunted growth. The typical concentration of N in healthy foliage ranges from 10 to 50 g kg^{-1} dry matter.

Nitrogen is the mineral element generally required in greatest amounts by higher plants. From its uptake as NO_3^-, the predominant form in most soils except where conditions limit nitrification, to its most abundant form as peptide linkage in proteins, N undergoes a valence change from +5 to -3. The very stable peptide bond is made possible because of an electronic configuration that allows formation of strong covalent linkages with two adjacent C atoms. The energy of dissociation of C-N bonds is 184 kcal mol^{-1}. To completely cleave the C-N linkages between aminoacids in proteins by chemical

hydrolysis using strong acids (e.g., 6 M HCl) requires heating at elevated temperatures for a minimum of several hours or more, depending on the protein being analyzed.

All aspects of plant growth and development depend upon enzymes which are proteinaceous complexes. In vegetative tissues of many plants, the enzyme catalyzing the linkage of CO_2 to ribulose 1, 5-bisphosphate (RuBP), RuBP carboxylase oxygenase (RUBISCO), accounts for a significant fraction of the N present. In leaves of potato and of wheat, RUBISCO accounts for 40.8 and 23.7 percent, respectively, of the total soluble proteins (Ku et al., 1979). These values are in contrast to the value of 7.8% of total soluble proteins as RUBISCO in leaves of maize, a species with the more efficient C4 photosynthetic mechanism.

Chemical linkages involving N also account for physiological functions served by non proteinaceous metabolites. In the reduced form, by donating unshared electrons, N may behave as a fairly strong Lewis base. Thus it can bind metal ions, such as linking to Mg in chlorophyll, and can also produce changes in molecular configuration necessary for certain reactions of intermediary metabolism. Oxidation of NADH can occur by the release of electrons from the reduced N present in the nicotinamide ring. By forming complexes with metal ions, lower molecular weight organic N compounds, such as aminoacids, and amides aid ion transport in the xylem (White et al., 1981).

Depending upon the kind of plant and conditions of growth, the amounts of N plants need to absorb to meet the requirements for growth and to complete their life cycle, vary widely. High yields of crops growing under favorable growing conditions require amounts on the order of 20 g m^{-2} and more. Plant factors influencing the efficient use of N for growth, development and yield include the effectiveness of N uptake and assimilation mechanisms (Moll et al., 1982) and transport processes. These factors function independently and are related to carbon metabolism.

During the vegetative period of growth, N generally accumulates in plants at a greater rate than does the accumulation of dry matter. The accumulation of N in the leaves of plants grown in soils high in available N may extend the vegetative phase of growth. This accumulation may provide a larger pool of N to be used subsequently during the reproductive stage of growth. But in cereals, for example, it may decrease the physiological efficiency of N use under adverse conditions that impair remobilization and translocation during grain fill. An opposite effect, a delay in the onset of the reproductive stage, may result from N deficiency in some species. At high N supply from soil, a lower proportion of the total N absorbed may be partitioned into storage organs or fruit.

Because of the high requirement of crop plants for elemental N and its numerous important roles in growth and development, N is the mineral nutrient element that most often limits crop productivity (Below, 2002). Both between and within species, there are large and complex differences in the relationship between the acquisition of N and its use by plants. Using conventional and molecular breeding approaches, crop genotypes that use soil N more effectively in the production of dry matter and grain yield are being developed. Interrelationships between plant parts as sources and sinks during

reproductive growth stages are the main contributing factors toward improved N use efficiency.

Plants which are stressed due to N deficiency cannot produce sufficient chlorophyll and hence are pale green and in the extreme yellowish. The choruses will be more marked in the older tissues as the plant mobilizes its limited N supplies to the new growth. N-deficient plants typically lack vigor and remain stunted as a result of their inability to capture energy from sunlight. They will also have a lower protein content and hence have a lower food-value for either humans (e.g., as in cereals) or animals (e.g., as in pasture herbage). Thus, N affects both quantity and quality of plant material. An excess of N can result in over-stimulating plant growth causing problems such as lodging in cereals and the production of otherwise unnecessary vegetative growth. This can result in the onset of secondary diseases (e.g., rust).

B. Phosphorus

Phosphorus is essential not only as a constituent of various organic compounds but also inorganic phosphorus (Pi) exerts important regulatory functions in energy transfer and storage in plants (Marschner, 1995). Adenosine di- and triphosphates are the most important forms of phosphate and these are involved in the energy transfer processes. The uptake of nutrients and their translocation throughout the plant are tied to these energy transfer processes. Also, P is important in many proteins, coenzymes, nucleic acids, and metabolic substrates in plants. Phosphorus is a component of phospholipids which play specific roles within the cell membranes. Phosphorus has been shown to increase root growth which increases the ability of the plant to take up water and nutrients. Phosphorus is necessary for seed germination, photosynthesis, protein formation and almost all aspects of growth and metabolism in plants. It is essential for flower and fruit formation. Deficiency of P markedly reduces crop yield. For the plants to acquire P, it must be applied close to root system. Healthy plants foliage contains 1 to 4 g kg^{-1} dry matter.

Phosphorus taken up by roots from soils is in anionic forms as $H_2PO_4^-$ and HPO_4^{2-} (Barber, 1995). The anionic forms of P involve linkages to O by covalent bonding. P is more electronegative than N and S, and its linkage to O is retained in plant tissues. P atoms link to C and to each other through O bonds, as in ATP and ADP. These polyphosphate complexes are a vital part of the energy conversion processes in plants. They are water-stable, but when properly configured, and in the presence of an appropriate kinase, P-O linkages are broken and the energy released is used for a number of metabolic reactions. The amounts of energy (8 kcal mol^{-1}) in these P-O linkages, often referred to as "high-energy bonds", are not large compared to most covalent bonds. The effective transfer of the energy in the linkage to drive metabolic reactions depends not only on the amount, but also upon the physiological regulation of the rate at which this energy is released. Turnover times for the individual P atoms are very rapid. Bieleski (1976) estimated that each inorganic P ion entering a plant cell makes an average of 60 passages through ATP and the metabolic cycle before it is withdrawn in growth, storage, or transport.

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Phosphorus serves vital functions other than as a component of ADP and ATP. It undergoes reversible esterification with many sugars and other compounds involved in photosynthesis and respiration. P atoms provide bridges between the ribonucleoside units of RNA and DNA. The amounts of P in these nucleic acids account for about the same proportion of the total P in vegetative tissue as the amounts in P-esters, typically ranging from 10 to 25% of total P. P is an essential component of RUBISCO, but this enzyme with a molecular weight of about 500,000, accounts for only a very small fraction of the total P in plants.

Amounts of P provided for optimum plant growth must exceed the needs for assimilation into organic forms so that a substantial portion of that present in the plant tissues is in inorganic forms. The cytoplasmic pool of inorganic P (Pi) "appears to be the hub of all cellular P metabolism and of the whole P economy of the plant "(Bieleski and Ferguson, 1983). If adequate levels of inorganic phosphate are not present, RUBISCO activity of intact spinach chloroplasts is impaired, and 3-phosphoglycerate or dihydroxyacetone phosphate will not substitute for this need (Held et al., 1978). During maturation, the ratio of Pi to phosphorylated compounds in the cytoplasm depends on reproductive sink demands, indicating an important role of Pi in sink size to source activity relationships (Plaut et al., 1987).

The P needs of roots and shoots during the early stages of plant growth are provided by phytic acid (P-ester of inositol) stored in seeds. This storage form accounts for a major fraction (in some cases over 50%) of the total amount of P present in the seeds of many plants. The amounts of P that crops need to absorb to meet the requirements for growth and development vary widely, and depend upon other conditions of growth as well as on amounts of P in soils.

One of the earliest symptoms of P deficiency is a specific inhibition of leaf expansion and leaf surface area (Rao, 1996). The effects of P deficiency on photosynthesis are less severe than on shoot growth (Rao and Terry, 2000). By contrast to the effects on shoot growth, root growth is much less inhibited (Rao et al., 1999). P deficiency results in poor seedling establishment, stunted top growth, spindly stalks, delayed maturity and poor seed and fruit set. Thus not only low yields but also poor quality fruits and seeds are obtained from P deficient crops. Legumes will have poor nodule formation. Reddish-purplish coloration of the stem and the older leaves can often be observed if the deficiency is extreme. Leaves may have a dark-green appearance with reddening of the mid-rib.

C. Potassium

Potassium is important as a regulatory nutrient in photosynthesis, energy metabolism, starch synthesis, nitrate reduction, sugar degradation, carbohydrate and sugar translocation, protein synthesis and cell division in roots and other parts of the plant (Glass, 1989). A main feature of K^+ is the high rate and efficient means by which it is taken up and translocated throughout the plant. Accumulation by roots is achieved by plasmamembrane transporters which are able to adjust quickly to the wide range of K^+ in solution (Maathuis and Sanders, 1996). The distribution of K^+ within the cell is strictly

controlled whereby a constantly high K^+ concentration is maintained in the cytosol whereas the K^+ in the vacuole may alter depending on K^+ supply to the tissue. Potassium is highly mobile in plants and long-distance transport takes place in xylem and phloem. A basic function of K^+ is its impact on proton pumps. ATPase is stimulated by K^+ which favors the process of H^+ pumping by the dephosphorylation of the ATPase subunit. The activating effect of K^+ on ATPase is not only of relevance to meristematic growth, but also to electron transport in photosynthesis and to phloem loading.

Potassium is different to the other nutrients in that it is not incorporated into any organic compounds but remains as a positively charged ion in the plant. It is part of the cytoplasmic solution and helps to lower the osmotic potential resulting in lower water loss from the leaves and better water uptake by the plant roots. Potassium increases the growth of underground structures such as tubers and bulbs. It helps improve the plants ability to resist diseases and insect problems. It increases the strength of the stems resulting in less lodging problems. It also improves the color and flavor of fruits and vegetables along with the color of flowers. Deficiency of K results in low yields, mottled, spotted or curled leaves, scorched or burned look to leaves. Typical concentrations of potassium in healthy foliage range from 10 to 40 g kg^{-1} of dry matter.

With a few exceptions (halophytes), K is the most important inorganic solute in plants. This explains at least in part the particular role of K in osmoregulation and in water relations in plants as well as in enzyme activation. The functions served by K in meeting plant needs have little in common with those for N, S, and P. Except under severe K deficiency or saline conditions, K^+ is the main counterion for balancing the negative charges of sulfate, nitrate, phosphate, chloride, and organic ions. The NH^{4+} in plant cells also serves this role, but the quantity generally present is too low to contribute significantly to the maintenance of ionic balance. Unlike N, S, and P, the atomic structure of K is not conducive to covalent bonding and thus does not form stable coordination complexes. Like P, but unlike N and S, K undergoes no change in redox state during assimilation, remaining entirely in the same ionic form as absorbed.

Several reviews have been published on specific roles of K in enzyme catalysis (Suelter, 1985), protein metabolism (Blevins, 1985), photosynthesis (Huber, 1985), structural features (Beringer and Nothdurft, 1985), assimilate transport (Mengel, 1985), and plant water relations (Hsiao and Lauchli, 1986). K ions have a marked effect on cell water potentials and turgor. As the major osmotic component in leaf guard cells, the transfer of K in and out of these cells regulates stomatal opening and closing (Fischer, 1968). Thus, the supply of K to plants affects several physiological processes, including loss of water and uptake of CO_2 through the stomates (Terry and Ulrich, 1973; Peoples and Koch, 1979). The high mobility of K in transport through membranes enables it also to act as counterion for anions both in short- and long-distance transport and in ATPase-stimulated proton efflux, for example at the plasmalemma of root cells. This proton-coupled K transport has consequences for both the pH and osmotic pressure in the cell and its compartments. The role of K in water balance of higher plants is shown to be directly related to its function in regulating osmotic pressure of the guard cells and thus stomatal movement (Raschke, 1979).

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K ions also have other attributes suiting them for specific physiological functions. They are relatively small in size even in the hydrated state, and they are highly mobile since they do not readily bond to other cellular components. Thus, they are ideally suited to aid the intercellular and intracellular transport of inorganic and organic ions. K ions influence the conformation of proteins and thus contribute to the effectiveness of some enzymes in catalyzing metabolic reactions. Potassium also plays a vital role in maintaining the electrical balance in the plant. Plants can take up nutrients as anions (negatively charged) or cations (positively charged). The plant by either excreting K or taking up more K, maintains electrical neutrality. This is one of the reasons why plants sometime take up far more K than they require for normal functioning. This phenomenon is called luxury consumption.

Plants typically require amounts of K similar to needs for N. Varietal differences are important in the uptake of K. Like P, K is mobile within the plant and when it is in short supply the plant moves the available K to the new tissues. Thus, K deficiency symptoms are first seen in the older leaves. Initially there is a yellowing of the margins and tips of the older leaves which progresses to white-brownish spots at the leaf margin and finally to what looks like "scorching"of the outer edges of the leaf. Plant stalks are typically brittle and lodge easily. Fruit and seed are shriveled and dry.

Plant K nutritional status can strongly affect the "quality" of crop plants and its organs not only for human and animal nutrition, but also as substrate for parasitic attack. When K supply is inadequate, for example, the synthesis of highly polymerized compounds (starch, proteins) is inhibited and the resulting plant composition is of lowered "quality" from the agricultural and horticultural view point. However, the corresponding increase in low molecular weight compounds (sugars, amino acids) in K deficient plants increases its "quality" for various parasites, fungi, bacteria or insects (Perrenoud, 1977).

D. Calcium

Calcium plays a key role in plant growth and development (Hanson, 1984). It is an important component of plant cell walls and in the structure and permeability of cell membranes. The elongation and division of cells requires calcium. Calcium aids in the uptake of N and seems to increase the uptake of K over Na. Once deposited in plant tissue, Ca is immobile (non-translocatable) so there must be a constant supply of Ca for plant growth. Calcium deficiency can prevent the terminal buds and apical root tips from forming resulting in no new growth. Thus deficiency of Ca could cause stunting of new growth in stems, flowers and roots. Symptoms of Ca deficiency range from distorted new growth to black spots on leaves and fruit. Yellow leaf margins may also appear. Typical Ca concentrations in foliage range from 2 to 10 g kg^{-1}.

Although not a constituent of cell membranes, Ca ions are of fundamental importance for membrane permeability and transport and the maintenance of cell integrity (Bush, 1995). Much of the Ca in plants occurs as intermolecular linkages in cell walls and membranes, and it thus contributes to the structural stability and cell-to-cell movement of various metabolites. The regulating effect of Ca at the plasmalemma on influx and efflux of other ions and selectivity in ion uptake have been thoroughly investigated for the past three

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decades. It is now well established that ion uptake studies, for example with plant roots in the absence of externally supplied Ca^{2+}, are of rather limited value.

As much as 50 to 60% of the total Ca in plant roots is present in cell walls (Rossignol et al., 1976). The manner in which Ca links to molecules, particularly carboxylases and phosphates, in cell walls and membranes is unique and vital, but details on these linkages are relatively less understood. Adequate Ca supply helps plants to avoid stress effects due to the presence of heavy metals or salinity. Ca also reacts with various other cellular components to form insoluble salts. Thus, under some conditions, a significant fraction of the total Ca in vacuoles and organelles may be present as precipitates of organic acids, particularly oxalates, and as phosphates. Marschner (1986) demonstrated that in mature sugar beet leaves, up to 90% of the total Ca is bound to oxalate.

The Ca-activated protein calmodulin, first noted in animals but subsequently also found in pea plants (Anderson and Cormier, 1978), plays a major role in a number of metabolic reactions involving Ca. The main functions of calmodulin include activation of the photosynthetic enzyme NAD-kinase and roles in protein phosphorylation and phytochrome responses. The ATPases involved in the transport of Ca into and out of cellular compartments through membranes have a high degree of specificity for Ca.

The role of Ca^{2+} for membrane stability, and thus compartmentation of a single cell or a plant tissue, has consequences for several processes other than ion transport. It affects the efflux rate of sugars from plant roots or leaf segments into the external solution, as well as the flux rate of endogenous respiratory substrates from the vacuole to the respiratory enzymes in the cytoplasm. An increase in the Ca content of a tissue therefore decreases the respiration rate (Faust and Klein, 1974). Typical features of senescence include an increase in the rate of respiration together with enhanced permeability and thus leading to a decline in compartmentation. Ca is thus directly involved in the regulation of senescence in addition to the role played by phytohormones such as ethylene or cytokinins (Poovaiah, 1979).

The role of Ca^{2+} in fruit development and ripening was investigated because of the widespread occurrence of calcium-related physiological disorders (Bangerth, 1979). Fruit ripening as a special case of senescence is correlated with increased ethylene production. Fruit ripening is stimulated in Ca-deficient tissue and can be depressed by Ca treatment of the fruit. It certainly requires removal of part of the Ca from the middle lamella (bound Ca). Comparative studies conducted using a ripening and a non-ripening mutant (rin) of tomato documented the causal involvement of Ca in the process of ripening (Poovaiah, 1979).

Ca in the middle lamella is not only important for the structure of pectins itself, but also for the resistance of the tissue to fungal infections. Plant cell walls containing a high proportion of Ca pectates should therefore be expected to show increased resistance to fungal infections (Sharples and Johnson, 1977).

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The data from field studies for the total amounts of Ca needed for plant growth are limited (Bar-Yosef and Kafkafi, 1972; Karlen et al., 1982). There are considerable genotypic differences in the demand for Ca at a cellular level, causally connected with differences in cation exchange capacity (CEC) of the cell wall system (middle lamella) i.e., amount of free carboxylic groups of pectins (polygalacturonic acid). This dicots, as compared to monocots, are characterized by both higher CEC and also much higher Ca demand. Genotypic differences to Ca deficiency within a certain species may also be related to differences in uptake, long- and short-distance transport and/or compartmentation within the cells.

Deficiency of Ca causes brown spotting. Calcium is relatively immobile and hence these symptoms appear in the new growing tips. Foliage can be abnormally green and the stems brittle. Terminal buds die and root tips appear swollen. Premature dropping of blossom and buds occur.

E. Magnesium

The main functions of Mg in plants are related to its capacity to interact with strongly nucleophilic ligands (e.g., phosphoryl groups) through ionic bonding, and to act as a bridging element and/or form complexes of different stabilities (Marschner, 1995). It is a critical structural component of the chlorophyll molecule and is necessary for functioning of plant enzymes to produce carbohydrates, sugars and fats. Most energy processes involving ATP require Mg. Magnesium is also a component of ribosomes in plants. It is used for fruit and nut formation and essential for germination of seeds. Magnesium-deficient plants appear chlorotic, show yellowing between veins of older leaves; leaves may droop. Typical concentration of Mg in healthy foliage range from 1 to 4 g kg^{-1}.

Generally, most of the Mg in plants is present as divalent cations. The characteristics of this element relative to its main functions in plants are intermediate between K and Ca. Mg is sufficiently abundant and mobile as the soluble ion to serve with K and other cations as an important counterion for various inorganic and organic anions. Thus it is an important contributor to the physiological processes in which properties of celluar environments such as ionic strength and water potential gradients are involved.

The resemblance of Mg to Ca is in its divalency and its ability to form chemical linkages that are somewhat stable, but generally Mg bonds are less tenacious than those of Ca. Mg in chlorophyll is linked to N of four porphyrin groups by partial covalent bonds and it accounts for about 15 to 20% of the total Mg in plants.

Many reactions of intermediary metabolism involve activation of N bases and phosphoryl groups by linkage to Mg, for example, to aid nutrient flux across the plasmalemma. Formation of an ATP-Mg complex is necessary before the energy in -P--O-P- bonds can be released and then used for driving metabolic reactions and for synthesizing metabolites. Mg is known to activate fixation of CO_2 by RUBISCO.

Other ions, for example, Mn have been found to be capable of substituting for Mg as enzyme substrate activators; they are generally much less effective, however. Chemical

attributes of Mg that account for its uniqueness in serving most effectively in this role are its relatively small size, high energy of hydration, and strong electrophilic properties (Clarkson and Hanson, 1980). Ca might be expected to behave similarly, but with an ionic radius about 50% greater than Mg, its energy of hydration is less and it does not link to O as tenaciously as Mg.

The amount of Mg taken up for growth of crops is generally somewhat lower than for Ca (Karlen et al., 1982). Magnesium is relatively mobile and is transferred from the older to the younger leaves when limited in supply. Thus symptoms appear on the older leaves first. The interveinal area becomes mottled with yellowish spots while the veins remain green. The leaves can become abnormally thin. Brilliant orange red or purple colorations may occur and the leaves may curl at the margins.

F. Sulfur

Sulfur is a structural component of aminoacids, proteins, vitamins and enzymes and is essential to produce chlorophyll (Schmidt and Jäger, 1992). Sulfur is found in proteins/enzymes that regulate photosynthesis and also nitrogen fixation. In proteins, sulfur serves the role of forming disulfide bonds between the polypeptide chains. It imparts flavor to many vegetables. Deficiency of S shows as light green leaves. Healthy plant foliage contains around 1.5 to 4.5 g kg^{-1} of dry matter with high values of 11 to 17 g kg^{-1} in plants belonging to the family Cruciferae.

Sulfur is similar to N in some functions it serves in plant metabolism, but there are also important differences. Most often S is absorbed by plants as SO_4^{2-} and, like N when absorbed as NO3, must undergo an 8-electron change during assimilation in order to serve its quantitatively most important role as a protein component.

Like N, the chemical structure of S permits the formation of stable covalent bonds, especially with C and other S atoms. The bonding to C as in cysteine (-C-SH), methionine (-C-S-CH3), and cystine (-C-S-S-C-) in proteins, accounts for most of the S in plants. Plants deficient in S become chlorotic, similar to N-deficient plants, because of impaired biosynthesis of proteins that form complexes with chlorophyll in chloroplasts.

The C-S linkage is very stable, with an energy dissociation of 167 kcal mol^{-1}. The S-S linkage is relatively weaker (102 kcalmol^{-1}), and the reversible transformation of the disulfide functional group (-C-S-S-C-) of cystine to the sulfhydryl functional group (-C-SH) of cysteine is an important redox system. Glutathione helps to maintain S-containing amino acids metabolically active by keeping them in a reduced form. S linked to Fe in metallo proteins also serves as a redox system. The presence of S in coenzyme A provides a reactive site for reversible oxidation-reduction reactions.

Oxidized S as SO_4^{2-} also serves metabolic functions. Of the total S in higher plants, one-third to one-half must be present as SO_4^{2-} for the optimum growth. For its reduction and assimilation, SO_4^{2-} ions must be present at reduction sites at adequate levels. For proper functioning of cells and membranes in plant tissues, SO_4^{2-} ions along with a number of

other cations and anions are necessary. Sulfate ions linked to organic metabolites confer greater solubility these complexes due to its hydrophilic nature.

In Brassicaceae the content of glucosinolates and their volatile metabolites is closely related to sulfate supply. A number of S-substituted cysteines and S-esters impart aroma and taste to plant components, and these characteristics may play a role in plant survival and competitiveness. Forage legumes generally have relatively high S requirements to attain maximum growth.

A drastic decrease in chlorophyll content of leaves is a typical feature of S deficiency. Symptoms of S deficiency are very similar and often mistaken for N deficiency. However, S deficiency appears first in young tissues whereas N deficiency is seen initially in the older parts of the plant. The young leaves are light green to yellowish in color with lighter colored veins. Symptoms also include small leaves and shortened and "hard"stems. Legumes in particular are sensitive to S deficiency.

IV. Functions of mineral nutrients: Micronutrients

Compared with macronutrients, micronutrients are required for growth in lower amounts, and serve mainly as constituents of prosthetic groups in metalloproteins and as activators of enzyme reactions (Romheld and Marschner, 1991; Welch, 1995; Fageria et al., 2002). Micronutrients catalyze redox processes by electron transfer (Fe, Mn, Cu, and Mo), form enzyme-substrate complexes by coupling enzyme and substrate (Fe and Zn), or enhance enzyme reactions by influencing the molecular configuration of an enzyme or substrate (Zn). Two micronutrients, B and Cl, are nonmetals for which there are no well-defined element-containing enzymes or other essential organic compounds.

A. Iron
Iron is used in chlorophyll synthesis and in electron transfer processes. It is found in several of the peroxidase, catalase, cytochrome enzymes that are involved in oxidation-reduction reactions. Iron is an essential part of the enzyme nitrogenase that plays a key role in nitrogen fixation. It is essential for young growing parts of plants. Deficiency of Fe results in pale leaf color of young leaves followed by yellowing of leaves and large veins. Typical plant concentrations range from 50 to 250 mg kg^{-1}.

The most ubiquitous role of Fe in plants is to undergo reversible oxidation-reduction while linked to a variety of ligands vital to reactions of intermediary metabolism. One large group of such metabolites are the heme and nonheme Fe proteins. Heme proteins are also called porphyrins since the skeletal structure to which the protein becomes linked is porphine. Cytochromes are the examples of this group in which Fe is centered in the heme complex linked to four N atoms. Chlorophyll is another example of porphyrin in which the central linkage is to Mg rather than Fe. Cytochromes function in coupled electron transfer reactions through which the energy needs of plants are provided, with bound Fe atoms serving as redox loci. The redox potential of Fe in the porphyrin structure differs from that of Fe present as free ions.

Nonheme Fe also performs important physiological functions. In ferredoxin it is linked to S and through this linkage to another Fe atom. The structure of this complex varies among different kinds of organisms. Ferredoxin in plants is involved, in some cases with thioredoxin, in a number of oxidation-reduction reactions, notably those that are light-activated (Buchanan, 1984). Some Fe is present in a soluble form and some is membrane-bound. The latter has a lower molecular weight (ca. 8000) and contains more (4 versus 2) Fe atoms than the soluble form. In chloroplasts the Fe in Ferredoxin is present in both divalent and trivalent forms, and under illumination a portion of the Fe^{3+} accepts electrons and becomes reduced (Boardman, 1975).

Iron deficient plants exhibit distinctive pattern of chlorosis on the younger leaves. While over one-half of the total Fe present in plants may be located in chloroplasts, just what specific function Fe serves that results in chlorotic leaves is not fully understood. Various ways in which Fe might be directly involved in chlorophyll biosynthesis or in reactions associated with biosynthetic pathways have been proposed (Terry and Abadia, 1985). Iron deficiency stress affects not only the amounts of several photosynthetic pigments in the chloroplast, but a reduction in photosynthetic electron transport as well. Iron deficiency also impairs the biosynthesis of thylakoid galactolipids. This impairment could have an adverse effect on the development of thylakoid membranes, and thus may affect chloroplast function.

Because of its greater solubility and mobility, Fe^{2+} is more metabolically active than Fe^{3+}. Significant amounts of the trivalent form occur as inorganic precipitates. Chelates such as citrate help mobilize Fe from these insoluble forms.

Plant needs for Fe are comparable to those for Mn. In shoots, the first visible symptom of Fe deficiency is chlorosis of young leaves. The critical deficiency concentrations of Fe in leaves range from 30 to 50 mg kg^{-1} dry weight basis. Deficient plants exhibit interveinal chlorosis in the leaves especially the younger tissues. Affected leaves become whitish due to lack of chlorophyll and there may be scorching at the leaf margins. The veins remain green. These symptoms are similar to those caused by Mg and N but will generally only occur on alkaline soils.

B. Manganese

Manganese is involved in enzyme activity for photosynthesis, respiration, and nitrogen metabolism. Deficiency of Mn in young leaves may show a network of green veins on a light green background similar to Fe deficiency. In the advanced stages of Mn deficiency, the light green parts become white, and leaves are shed. Brownish, black, or grayish spots may appear next to the veins. Typical concentrations in healthy foliage range from 30 to 200 mg kg^{-1} dry weight basis.

Manganese generally occurs in plants as a divalent ion. Since the amounts of Mn present are low compared to Mg, Ca, and K, it has much less influence than these three cations on the ionic strength and osmotic properties of the cytosol. Manganese would become phytotoxic if it were present at concentrations high enough to be an important contributor to osmotic properties of cells.

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The best-documented role of Mn in plants is its involvement in O_2 evolution during photosynthesis, in conjunction with the transfer of electrons from H_2O (Clarkson and Hanson, 1980). The redox potential of Mn is also a likely factor determining its participation in photosynthetic oxygen evolution. In its biochemical functions Mn^{2+} resembles Mg^{2+}. Both ion species bridge ATP with the enzyme complex (phosphokinases and phosphotransferases). Activities of a number of plant enzyme systems are influenced by the presence of Mn. In some of these systems, other elements, most often Mg, can serve equally well as Mn. An absolute requirement for Mn was found in a number of C4 plants in which fixed CO_2 is transferred to the bundle sheath cells as aspartate (Hatch and Kagawa, 1974).

The Mn nutritional status of plants is reflected in their Mn concentration. The critical deficiency level for most plant species is in the range of 10 to 20 mg Mn/kg in the dry matter of mature leaves. Below this level dry matter production, net photosynthesis and chlorophyll content are markedly affected (Ohki, 1981) whereas rates of respiration and transpiration are largely unaltered.

C. Copper

Copper is concentrated in roots of plants and plays a part in N metabolism. It is a component of several enzymes and may be part of the enzyme systems that use carbohydrates and proteins. Deficiency of Cu causes die back of the shoot tips, and terminal leaves develop brown spots. Typical concentrations in healthy foliage range from 5 to 20 mg kg^{-1}.

The amount of Cu necessary to meet plant needs is the least of any of the essential elements taken up as cations. Copper is a vital component in the functioning of a number of enzyme systems involving oxidation-reduction reactions. The complex stability constant of Cu is greater than that of Mn.

A major portion of the Cu in plants occurs in chloroplasts. This metal provides reducing equivalents to photosystem I as a component of plastocyanin, the terminal protein in the electron transport chain during photosynthesis. Another group of Cu-containing enzymes, also present primarily in chloroplasts, are the superoxide dismutases. These enzymes aid in ameliorating the effects of superoxide radicals generated in photorespiration (Sandmann and Boger, 1983).

A Cu containing enzyme, cytochrome c oxidase functions in respiratory processes, catalyzing the transfer of electrons to O_2 to form H_2O. An assay of Cu-containing oxidase enzyme has been suggested as an effective means of diagnosing Cu nutrition of plants (Loneragan et al., 1982). Insufficient Cu impairs biosynthesis of another Cu containing metalloprotein enzyme, diamino oxidase (Delhaize et al., 1986).

The symptoms of Cu deficiency are not very specific. Generally plants appear "bleached" and growth is stunted. These symptoms are more noticeable in the younger leaves. Insufficient Cu in leaves and stems leads to abnormal morphological features. Distortion

of leaves is related to the lower amounts of lignin in cell walls because of reduced activity of phenolase in Cu-deficient tissues (Robson et al., 1981).

Total uptake of Cu by plants is the least of the heavy metals.

D. Zinc

Zinc is a component of enzymes or a functional cofactor of a large number of enzymes including auxins. It is essential to carbohydrate metabolism, protein synthesis and internodal elongation (stem growth). Deficiency of Zn results in mottled leaves with irregular chlorotic areas. Zinc deficiency leads to Fe deficiency causing similar symptoms. Typical concentrations in the plant range from 25 to 150 mg kg^{-1}.

Zinc has been implicated in the functioning of a large number of enzymes, mostly in animal systems. One of the plant enzyme systems with which Zn is associated is carbonic anhydrase. This enzyme activity is severely impaired in some Zn-deficient plants.

The amounts of Zn needed to complete a growth cycle of many plants are comparable to those for Mn. Deficient plants exhibit interveinal chlorosis particularly in the lower leaves.

E. Nickel

Nickel has been shown to be essential in many plants (Brown et al., 1987). It has been found to be used with the urease enzyme which breaks down urea into ammonium and CO_2 preventing toxic levels of urea to accumulate in legumes. Also, in grains it has been shown to be essential for certain enzymes which are involved in grain filling and seed viability. Seeds need Ni in order to germinate. Nickel is required for iron absorption. Plants grown without additional Ni will gradually reach a deficient level about the time they mature and begin reproductive growth. If Ni is deficient plants may fail to produce viable seeds. The concentration in plants ranges from 1 to 10 μg kg^{-1}.

F. Molybdenum

Molybdenum is a structural component of the enzymes nitrogenase and nitrate reductase. It is essential for nitrogen metabolism in plants. Without Mo, the synthesis of proteins is blocked and plant growth ceases. Root nodule (nitrogen fixing) bacteria also require Mo. Seeds may not form completely, and N deficiency may occur if plants are lacking Mo. Deficiency signs are pale green leaves with rolled or cupped margins. Typically, the concentration of Mo in plants is less than 1 mg kg^{-1}.

Molybdenum serves two vital functions in N nutrition of plants. It is a component of nitrogenase, an enzyme necessary for plants that depend upon fixation of N_2 by their symbiotic relationship with rhizobia. To serve this role, Mo needs to be present only in root nodules where N_2 is converted to NH_3.

A second function, for plants using NO_3^- to meet N needs, is as a constituent of molybdoflavoprotein enzyme, NO_3^- reductase, which catalyzes the reduction of N.

The amount of Mo needed by plants is very low. Uptake of Mo of 1 mg m^{-2} is sufficient. Legumes deficient in Mo show typical symptoms of N deficiency with pale yellow leaves and stunted growth. Other plants, especially vegetables, may show chlorosis on the leaf margins with a distinctive upward curling. Brassicas are particularly sensitive and leaf tissue develops irregularly producing long narrow leaves. The flower fails to develop.

G. Boron

Boron is necessary for cell wall formation, membrane integrity, Ca uptake and may aid in the transport of sugars. Boron affects at least 16 functions in plants. These functions include flowering, pollen germination, fruiting, cell division, starch formation, carbohydrate synthesis, nucleic acid synthesis, water relationships and the synthesis and movement of hormones. Boron must be available throughout the life of the plant. It is not translocated and deficiencies kill terminal buds leaving a rosette effect on the plant. Leaves are thick, curled and brittle. Fruits, tubers and roots are discolored, cracked and flecked with brown spots. Plant concentration will vary from 6 to 60 mg kg^{-1}.

Boron is unique compared to the other essential elements in that under most conditions it is taken up largely, not as an ion, but as undissociated boric acid. Although it can be readily shown in growth experiments that B is essential for plants, a vital physiological role of B has not yet been clearly defined. Several researchers reported marked effects of B supply on metabolism and translocation of carbohydrates.

A need for B in phenol metabolism has been proposed to account for abnormalities in cell walls and membranes, and in root growth elongation (Hirsch et al., 1982). Impaired root development due to B deficiency was attributed to decreased synthesis of DNA or its precursors (Krueger et al., 1987).

Once inside plants, much of the B absorbed becomes immobile, not moving readily from older to younger, growing plant parts. Total uptake of B in some crops is comparable to that for Zn and Cu. Concentrations of B in dicots are generally much greater than in monocots, by about an order of magnitude (Mengel and Kirkby, 1982). Deficiency of B is expressed differently in different crops. In Lucerne young leaves are yellow, while the older leaves may have reddish tints. In brassicas and particularly turnips, Swedes and beets, B deficiency causes "brown heart"- the root may have a brown water-soaked appearance and, with the stem, may be hallow.

H. Chlorine

Chlorine is involved in osmosis (movement of water or solutes in cells), the ionic balance necessary for plants to take up mineral elements and in photosynthesis. Deficiency symptoms include wilting, stubby roots, chlorosis and bronzing. Odors in some plants may be decreased. Chloride is the ionic form of chlorine used by plants. Some plants may show signs of toxicity if levels are too high. Typical concentrations in healthy plants range from 2.0 to 20 g kg^{-1}.

Similar to B, chlorine has been established as an essential element based on growth experiments, but a vital physiological function has not been conclusively identified.

There is evidence that Cl⁻ is necessary for the evolution of O_2 in photosynthesis. However, the expected impairment of photosynthetic activity was not observed in Cl-deficient sugar beet leaves (Terry, 1977). Thus it is questionable whether there is a general need for Cl in higher plants. It is important to note that methods used in preparing experimental material for demonstrating Cl essentiality in photosynthesis can affect other plant components and could result in artifacts (Anderson et al., 1984).

Phytotoxic concentrations of Cl are a frequent cause of salinity stress on plants.

V.   Functions of beneficial mineral elements

Beneficial elements are the mineral elements which either stimulate growth but are not essential or which are essential only for certain plant species, or under specific conditions. It is difficult to make the distinction between beneficial and essential in the case of some trace elements.

A. Sodium

Sodium is involved in osmotic (water movement) and ionic balance in plants. Sodium is essential for certain halophytes, and is considered also as a micronutrient at least for C4 plant species (Brownell, 1979). Sodium has been shown to be used in place of K for certain plant functions in halophytes that can grow in sodic soils. Concentrations vary greatly from 0.1 to 100 g kg⁻¹ in plants with most plants growing with lower concentrations.

B. Silicon

Silicon is an essential mineral element for certain lower plants. It is also well established as a beneficial mineral element for higher plants, the monocots in particular. Silicon is found as a component of cell walls. Plants with supplies of soluble Si produce stronger, tougher cell walls making them a mechanical barrier to piercing and sucking insects. This significantly enhances plant heat and drought tolerance. Tests have also found that Si can be deposited by the plants at the site of infection by fungus to combat the penetration of the cell walls by the attacking fungus. Concentration of Si in plants vary greatly from 0.2 to 100 g kg⁻¹ with monocots having the highest values while dicots having lower values.

Uptake of Si is closely related to the rate of transpiration and is deposited mainly in the cell walls of the epidermal layers, and causes an increase in mechanical resistance and also resistance to fungal infections (Hutton and Norrish, 1974; Volk et al., 1958). The deposition of Si also increases the rigidity of leaf blades and therefore leaf angle and light utilization for photosynthesis (Yoshida et al., 1969). Improved leaf erectness, stem strength and prevention or depression of Fe and Mn toxicity have all been noted as effects from Si. Since one of the effective role of Si is suppression of Mn toxicity (Vlamis and Williams, 1967), growth stimulation by Si is often limited to conditions of excessive Mn supply (Horst and Marschner, 1978).

The situation with Si seems to be similar to that of Na, where classification as either an essential or beneficial mineral element depends upon the genotypes.

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C. Cobalt

Cobalt is required for N_2 fixation in legumes and in root nodules of nonlegumes. The demand for cobalt is much higher for N_2 fixation than for ammonium nutrition. Deficient leaves could result in N deficiency symptoms. Concentrations of Co in plants vary from 0.02 to 0.5 mg kg^{-1}.

The essentiality of cobalt is well documented for certain higher and lower plants. For cobalt this essentiality is coupled with the mode of N supply, as this metal is a constituent of the vitamin B_{12} and thus essential for all higher and lower plants which rely on N_2-fixation for their N supply. For the same plant species supplied with bound N either in organic or inorganic form, cobalt does not have the characteristics of a beneficial mineral element.

D. Selenium

The chemistry of selenium (Se) has features in common with sulfur. Sulfate and selenate compete for common uptake sites in the roots and, thus, selenate uptake can be strongly decreased by high sulfate supply (Terry et al., 2000). Plant species differ very much in Se uptake and accumulation in the shoots and also in their capacity to tolerate high Se concentrations in the rooting medium or in the shoot tissue or in both. The large differences between plant species in tissue tolerance to Se are causally related to differences in the detoxification of Se.

Many species of the genera *Astragalus*, *Xylorrhiza* and *Stanleyea* are typical selenium-accumulators, and capable of growing on high Se soils without any detrimental effect on plant growth and reaching shoot Se contents as high as 20 to 30 mg g^{-1} dry matter. Members of the Cruciferae family such as black mustard and broccoli also accumulate relatively large amounts of Se and might contain, and tolerate, several hundred μg Se g^{-1} shoot dry matter (Terry et al., 2000). On the other hand, most agricultural and horticultural crops are nonaccumulators of Se and can be sensitive to Se at very low concentrations such as 10 μg Se g^{-1} dry mater (e.g., wheat). These large differences between plant species in tissue tolerance to Se are causally related to differences in the detoxification of Se.

In contrast to higher plants, Se is an essential mineral element for animals and humans. In both animals and humans the only well-established function of Se is its role as cofactor in glutathione peroxidase. The function of the Se-containing glutathione peroxidase in animals and humans is comparable to that of the glutathione reductase in higher plants, for example, in chloroplasts.

E. Aluminum

Aluminum (Al) concentrations in mineral soil solutions are usually much below 1 mg L^{-1} (about 37 μM) at pH values higher than 5.5, but rise sharply at lower pH. Aluminum toxicity is frequently found on acid soils. There is no convincing evidence that Al is an essential mineral element even for Al accumulator species (Marschner, 1995). Marked growth stimulation has been observed with the tea plant, which is one of the most Al-tolerant crop species, at Al concentrations as high as 1000 μM (Matsumoto et al., 1976).

However, a major problem of studies with high Al concentrations in nutrient solutions has been a high proportion, or nearly all, of the Al added is presumably lost by precipitation (e.g., with phosphate), or by polymerization and complexation. In nonaccumulator species, the nature of beneficial effects of Al on plant growth is not clear. Asher (1991) provided substantial evidence that this is often a secondary effect, brought about by alleviation of toxicity caused by other mineral elements, particularly P and Cu.

The first observable effect of Al on plants is a limitation in root growth. Root tips and lateral roots become thickened and turn brown. The restriction of root growth is associated with the formation of callose. Aluminum may be particularly accumulated in the root tips where it is mainly bound in the apoplast. Crossbinding of Al in the pectate moiety of meristematic cell walls may affect the extensibility and water permeability of cell walls (Horst, 1994). Aluminum inhibits the formation of microtubules and actin and microfilaments in the transition zone of root tips of Al sensitive cultivar of maize thus affecting the development of cytoskeleton (Sivaguru et al., 1999).

F. Other mineral elements

The requirement of other mineral elements such as iodine and vanadium is fairly well established for certain lower plant species, including marine algae (iodine) and fungi and fresh water algae (vanadium). However, the reports on beneficial effects of these elements and titanium on higher plants have been rare and vague (Marschner, 1995). Supply of rare earth elements such as lanthanum (La) and cerium (Ce) in the range of micronutrients could enhance plant growth. In China, mixtures of both elements are used on a large-scale as foliar sprays or seed treatment of agricultural and horticultural crops to improve growth and yield (Asher, 1991; Marschner, 1995). There is no convincing evidence for beneficial effects of heavy metals such as cadmium, chromium, lead, and mercury, in higher plants.

VI. Mineral nutrition and crop yield

Mineral nutrition is central to modern agriculture and environmental protection. High agricultural yields depend strongly on fertilization with mineral elements. In fact, yields of most crop plants increase linearly with the amount of fertilizer that they absorb through the large surface area of roots (Loomis and Conner, 1992). World consumption of the primary fertilizer mineral elements – nitrogen, phosphorus, and potassium – rose steadily from 112 million metric tons in 1980 to 143 million metric tons in 1990 in order to meet increased demand for food (Lauriente, 1995). Crop plants, however, typically use less than half of the fertilizer applied (Loomis and Conner, 1992).

Nutrient supply and acquisition are two of the most important factors that control crop productivity and diversity, as growth is generally limited by the availability of inorganic nutrients in the soil. From a biochemical point of view, all crops should need the same quantity of nutrients to construct a given amount of plant tissue. However, differences do exist in tissue concentrations because of heterogeneous distribution of nutrients in the soil and varying uptake efficiency. In addition, crop plants respond differently to

environmental variability, including shortage, and have different physiological needs that cause differences in metabolism and constitution (Marschner, 1995).

In addition to their different functions (Table 5), nutrients also differ in their concentrations with time during crop growth and development. Those with an active metabolic function (N, P and K) increase when the leaf is developing and decline afterwards, partly because of the increasing proportion of cell wall structures and partly because there is translocation of nutrients out of leaves before senescence. By contrast, nutrients such as Ca and Mg are less mobile and monotonically increase with age.

VII. Summary and future perspectives

Studies of plant nutrition have shown that specific mineral elements are essential for plant growth, development and yield. These are called macronutrients and micronutrients, depending on the relative amounts required. Nutritional disorders occur because nutrients have key roles in plant metabolism. They serve as components of organic compounds, in energy storage, to maintain plant structures, as enzyme cofactors, and in electron transfer reactions.

Soil and plant tissue analysis can provide information on the nutritional status of plants and can suggest corrective actions to avoid mineral deficiencies. To prevent the development of deficiencies, nutrients can be added back as fertilizers. Fertilizers that provide nutrients in inorganic forms are called chemical fertilizers, whereas those that derive from plant or animal residues are considered organic fertilizers. In both cases, plants absorb the nutrients primarily as inorganic ions. To obtain nutrients from the soil, plants develop extensive root systems and often form associations with mycorrhizal fungi. Plants tend to suppress mycorrhizal associations under conditions of high nutrient availability.

The highly variable nutrient environment experienced by plants favors plasticity rather than genetic specialization, and that the ability to grow at both low and high nutrient supply may be an important aspect of adaptation of individual plants to the environment.

During the past 40 years, animal scientists have added many new trace elements (i.e., elements that occur in the organism in 100 μg g^{-1} amounts or less) to their list of essential elements including As, B, Br, Cd, Cr, Pb, Li, Mo, Se, Si, Sn, V, and Ni (Nielsen, 1992; Van Campen, 1991). However, plant scientists have added only one new micronutrient - Ni - (Brown et al., 1987) to their list of essential elements since 1954 when chlorine was added (Asher, 1991). Future research should discover new essential elements for higher plants because modern sensitive analytical instrumentation (e.g., inductively coupled, Ar-plasma, mass spectrometry; laser-probe mass spectrometry; Zeeman effect, carbon furnace, atomic absorption spectrometry) and new plant culture techniques (e.g., chelate-buffered nutrient solutions) have been developed that make it possible for such research to be carried out efficiently at ultra-low trace metal concentrations (Welch, 1995).

The distribution of mineral nutrients between different types of cells within a given tissue also provides important information about function of mineral nutrients. In the last two decades, significant progress has been made by applying techniques such as X-ray microanalysis, NMR (nuclear magnetic resonance), ion selective microelectrodes, or fluorescent dyes, for studies on ion distribution in the cytoplasm and the organelles contained in it (e.g., chloroplasts) and the vacuole. These studies on cellular compartmentation provided several new insights into the functions of mineral nutrients as for example of Ca as a second messenger. In the future, similar progress leading to a better understanding of the functions of mineral nutrients is to be expected from research not only in comparing genotypes or mutants within a plant species but also by introducing modern approaches and techniques of functional genomics and molecular genetics into studies on mineral nutrition, particularly on crop plants. Much remains to be learned about the physiology of mineral nutrient acquisition, mobilization and deposition in crop plants, and about the function they perform in crop growth, development and yield.

Acknowledgements

Further reading

Alloway, B. J. (ed). 2008. Micronutrient Deficiencies in Global Crop Production. Springer, NJ, USA.

Barker, A. V. and D. J. Pilbeam. (eds). 2007. Handbook of Plant Nutrition. CRC Press, Taylor & Francis Group, FL, USA.

Barber, S. A. 1995. Soil Nutrient Bioavailability: A Mechanistic Approach. Second Edition. John Wiley & Sons. Chichester, NY.

Bennett, W. F. 1993. Nutrient Deficiencies and Toxicities in Crop Plants. APS, The American Phytopathological Society, St. Paul, MN.

Benton Jones, J. 1998. Plant Nutrition Manual. Second Edition. CRC Press, FL, USA.

Brady, N. C. and R. R. Weil. 1999. The Nature and Properties of Soils. 12th Edition. Printice-Hall, London.

Epstein, E. and A. J. Bloom. 2004. Mineral Nutrition of Plants: Principles and Perspectives. Second Edition. Sinauer Associates, MA, USA.

Fageria, N. K. 2008. The Use of Nutrients in Crop Plants. CRC Press, Taylor & Francis Group, FL, USA.

Fageria, N. K., V. C. Baligar and R. B. Clark. 2006. Physiology of Crop Production. Food Products Press, NY, USA.

Fageria, N. K., V. C. Baligar and C. A. Jones. 1991. Growth and Mineral Nutrition of Field Crops. Marcel Dekker, New York.

Glass, A. D. M. 1989. Plant Nutrition: An Introduction to Current Concepts. Jones and Barlett Publishers, Boston, MA.

Kabata-Pendias, A. and H. Pendias. 1994. Trace Elements in Soils and Plants. Second Edition. CRC Press, Inc., Boca Raton, FL.

Marschner, H. 1995. Mineral Nutrition of Higher Plants. Second Edition. Academic Press. Harcourt Brace & Company, Publishers, London. 889 pp.

Mengel, K. 1991. Nutrition and Metabolism of Plants. 7th Edition. Gustav Fischer Verlag, Jena.

Mengel, K. and E. A. Kirkby. 2001. Principles of Plant Nutrition. 5th Edition. Kluwer Academic Publishers, Dordrecht, The Netherlands. 849 pp.

Rengel, Z. 2000. Mineral Nutrition of Crops: Fundamental Mechanisms and Implications. Food Products Press, NY, USA.

Pais, I. and J. B. Jones, Jr. 1996. Handbook on Trace Elements in the Environment. St. Lucie Press, Boca Raton, FL.

Literature cited

Anderson, B., C. Critchley, I. J. Ryrie, C. Jansson, C. Larsson and J. M. Anderson. 1984. Modification of the chloride requirement for photosynthetic O_2 evolution. FEBS Lett. 168: 113-117.

Anderson, J. M. and M. J. Cormier. 1978. Calcium dependent regulator of NAD kinase in higher plants. Biochem Biophys Res Comm 85: 595-602.

Arnon, D. I. and P. R. Stout. 1939. The essentiality of certain elements in minute quantity for plants with special reference to copper. Plant Physiol. 14: 371-375.

Asher, C. J. 1991. Beneficial elements, functional nutrients, and possible new essential elements. In: Micronutrients in Agriculture. Pp. 703-723. 2nd edition. Morvedt, J. J., Cox, F. R., Shuman, L. M. and Welch, R. M. eds., Soil Science Society of America, Madison, WI.

Bangerth, F. 1979. Calcium-related physiological disorders of plants. Annu. Rev. Phytopathol. 17: 97-122.

Bar-Yosef, B. and U. Kafkafi 1972. Rates of growth and nutrient uptake of irrigated corn as affected by N and P fertilization. Soil Sci Soc Am Proc 36: 931-936.

Below, F. E. 2002. Nitrogen metabolism and crop productivity. In: M. Pessarakli (ed) Handbook of Plant and Crop Physiology. 2nd Edition. Marcel Dekker, Inc., New york, pp 385-406.

Beringer, H. and F. Northdurft 1985. Effects of potassium on plant and cellular structures. In: R.D. Munson (ed) Potasium in Agriculture. Am. Soc Agron., Crop Sci Soc Am., Soil Sci Soc Am., Madison, WI.

Bieleski, R. L. 1976. Passage of phosphate from soil to plant. In: G. J. Blair (ed) Prospects for improving efficiency of phosphorus utilization. Reviews in Rural Science III. Pp 125-129. University of New England, Armidale, Australia.

Bieleski, R. L. and I. B. Ferguson. 1983. Physiology and metabolism of phosphate and its compounds. In: A. Lauchli and R. L. Bieleski (eds) Encyclopedia of Plant Physiology, New Series, Vol. 15A, pp 422-448.

Blevins, D. G. 1985. Role of potassium in protein metabolism in plants. In: R. D. Munson (ed) Potasium in Agriculture. Am. Soc Agron., Crop Sci Soc Am., Soil Sci Soc Am., Madison, WI, pp 413-424.

Blevins, D. D. 1989. An overview of nitrogen metabolism in higher plants. In: J. E. Poulton, J. T. Romeo and E. C. Conn (eds) Plant Nitrogen Metabolism. Plenum, New York, pp 1-41.

Boardman, N. K. 1975. Trace elements in photosynthesis. In: D. J. D. Nicholas and R. Egan (eds) Trace Elements in Soil-Plant-Animal Systems, pp 199-212. Academic Press, New York.

Brown, P. H., R. M. Welch and E. E. Cary. 1987. Nickel: A macronutrient essential for higher plants. Plant Physiol. 85: 801-803.

Brownell, P. F. 1979. Sodium as an essential micronutrient element for plants and its possible role in metabolism. Adv. Bot. Res. 7: 117-224.

Buchanan, B. B. 1984. The ferredoxin/thioredoxin system: A key element in the regulatory function of light in photosynthesis. BioScience 34: 378-383.

Bush, D. S. 1995. Calcium regulation in plant cells and its role in signaling. Annu. Rev. Plant Physiol. Plant Mol. Biol. 46: 95-122.

Clarkson, D. T. and J. B. Hanson 1980. The mineral nutrition of higher plants. Annu Rev Plant Physiol 31: 239-298.

Epstein, E. 1972. Mineral Nutrition of Plants: Principles and Perspectives. John Wiley & Sons, New York, USA.

Delhaize, E., M. J. Dilworth and J. Webb 1986. The effects of copper nutrition and developmental state on the biosynthesis of diamine oxidase in clover leaves. Plant Physiol 82: 1126-1131.

Fageria, N. K., V. C. Baligar and R. B. Clark 2002. Micronutrients in crop production. Adv. Agron. 77: 185-268.

Faust, M. and J. D. Klein 1974. Levels and sites of metabolically active calcium in apple fruit. J. Am. Soc. Hort. Sci. 99: 93-94.

Fischer, R. A. 1968. Stomatal opening in isolated epidermal strips of *Vicia faba*. 1. Response to light and CO_2 free air. Plant Physiol. 43: 1953-1958.

Hanson, J. B. 1984. The function of calcium in plant nutrition. In: P. B. Tinker and A. Läuchli (eds) Advances in Plant Nutrition. Praeger, New York, pp 149-208.

Hatch, M. D. and T. Kagawa 1974. NAD malic enzyme in leaves with C4-pathway photosynthesis and its role in C4 acid decarboxylation. Arch Biochem Biophys 160: 346-349.

Heldt, H. W., C. J. Chon and G. H. Lorimer. 1978. Phosphate requirement for the light activation of ribulose-1, 5-bisphosphate carboxylase in intact spinach chloroplasts. FEBS Lett. 92: 234-240.

Hirsch, A., W. L. Pengelly and J. G. Torrey 1982. Endogenous IAA levels in boron-deficient and control root tips of sunflower. Bot. Gaz 143: 15-19.

Horst, W. J. 1994. The role of apoplast in aluminum toxicity and resistance of higher plants: a review. Z. Pflanzenernähr. Bodenk. 158: 419-428.

Horst, W. J. and H. Marschner 1978. Effect of silicon on manganese tolerance of bean plants (*Phaseolus vulgaris* L.). Plant Soil 50: 287-303.

Hsiao, T. C. and A. Lauchli 1986. Role of potassium in plant-water relations. In: B. Tinker and A. Lauchli (eds) Advances in Plant Nutrition Vol 2, pp 281-312. Praegar Scientific, NY.

Huber, S. C. 1985. Role of potassium in photosynthesis and respiration. In: R. D. Munson (ed) Potasium in Agriculture. Am. Soc Agron., Crop Sci Soc Am., Soil Sci Soc Am., Madison, WI, pp 369-396.

Hutton, J. T. and K. Norrish 1974. Silicon content of wheat husks in relation to water transpired. Aust. J. Agric. Res. 25: 203-212.

Karlen, D. L., P. G. Hunt and T. A. Matheny 1982. Accumulation and distribution of P, Fe, Mn, and Zn by selected determinate soybean cultivars grown with and without irrigation. Agron J 74: 297-303.

Krueger, R. W., C. J. Lovatt and L. S. Albert 1987. Metabolic requirement of *Cucurbita pepo* for boron. Plant Physiol 83: 254-258.

Ku, M. S. B., M. R. Schmitt and G. E. Edwards. 1979. Quantitative determination of RuBP Carboxylase-oxygenase protein in leaves of several C3 and C4 plants. J. Exp. Bot. 30: 89-98.

Lauriente, D. H. 1995. World fertilizer overview. In: Chemical Economics Handbook, p. 535: 1000A. Institute, S. R., ed. SRI, Menlo Park, CA.

Loomis, R. S. and D. J. Conner 1992. Crop Ecology: Productivity and Management in Agricultural Systems. Cambridge University Press, Cambridge, UK.

Loneragan, J. F., E. Delhaize and J. Webb 1982. Enzymic diagnosis of copper deficiency in subterranean clover. I. Relationship of ascorbate oxidase activity in leaves to plant copper status. Aust. J. Agric. Res. 33: 967-979.

Lawlor, D. W. 1991. Concepts of nutrition in relation to cellular processes and environment. In: J. R. Porter and D. W. Lawlor (eds.) Plant Growth: Interactions with nutrition and environment. Society for Experimental Biology, Seminar Series 43. Cambridge University Press, Cambridge, U. K. pp 1-32.

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Marschner, H. 1983. General introduction to the mineral nutrition of plants. In: A. Lauchli and R. L. Bieleski (eds) Encyclopedia of Plant Physiology, New Series, Vol. 15, Inorganic Plant Nutrition. Springer-Verlag, Berlin, Germany, pp 5-60.

Marschner, H. 1986. Mineral Nutrition in Higher Plants. Academic Press, London.

Marschner, H. 1995. Mineral Nutrition of Higher Plants. Second Edition. Academic Press. Harcourt Brace & Company, Publishers, London. 889 pp.

Maathuis, F. J. M. and D. Sanders 1996. Mechanism of potassium absorption by higher plants. Physiol. Plant. 96: 158-168.

Matsumoto, H., E. Hirasawa, S. Morimura and E. Takahashi 1976. Localization of aluminum in tea leaves. Plant, Cell Physiology 17: 127-137.

Mengel, K. 1985. Potassium movement within plants and its importance in assimilate transport. In: R. D. Munson (ed) Potasium in Agriculture. Am. Soc Agron., Crop Sci Soc Am., Soil Sci Soc Am., Madison, WI, pp 397-412.

Mengel, K. and E. A. Kirkby. 1987. Principles of Plant Nutrition. International Potash Institute, Berne, Switzerland.

Megel, K. and E. A. Kirkby 1982. Principles of Plant Nutrition. Third Edition. International Potash Institute, Worblaufen-Bern, Switzerland.

Moll, R. H., E. J. Kamprath and W. A. Jackson. 1982. Analysis and interpretation of factors which contribute to efficiency of nitrogen utilization. Agron. J. 74: 562-564.

Nielsen, F. H. 1990. New essential trace elements for the life sciences. Biol. Trace Elem. Res. 26-27: 599-611.

Ohki, K. 1981. Manganese critical levels for soybean growth and physiological processes. J. Plant Nutr. 3: 271-284.

Perrenoud, S. 1977. Potassium and plant health. In: Research Topics. No. 3. pp. 1-118. International Potash Institute, Bern, Switzerland.

Peoples, T. R. and D. W. Koch 1979. Role of potassium in carbon dioxide assimilation in *Medicago sativa* L. Plant Physiol 63: 878-881.

Plaut, Z., M. L. Mayoral and L. Reinhold. 1987. Effect of altered sink:source ratio on photosynthetic metabolism of source leaves. Plant Physiol. 85: 786-791.

Poovaiah, B. W. 1979. Role of calcium in ripening and senescence. Commun. Soil Sci. Plant Anal. 10: 83-88.

Rao, I. M. 1996. Role of phosphorus in photosynthesis. In: M. Pessarakli (ed) *Handbook of Photosynthesis*. Marcel Dekker, Inc., New York, USA, pp. 173-193.

Rao, I.M., D. K. Friesen and M. Osaki. 1999. Plant adaptation to phosphorus-limited tropical soils. In: M. Pessarakli (ed.) Handbook of Plant and Crop Stress. Marcel Dekker, Inc., New York, USA, pp. 61-96.

Rao, I.M., and N. Terry. 2000. Photosynthetic adaptation to nutrient stress. In: M. Yunus, U. Pathre and P. Mohanty (eds), Probing Photosynthesis: Mechanism, Regulation and Adaptation. Taylor & Francis, U.K. pp. 379-397.

Raschke, K. 1979. Movements of stomata. In: W. Haupt and M. E. Feinleib (eds), Physiology of Movements. Vol. 7, Springer, Berlin. pp. 383-441.

Robson, A. D., R. D. Hartley and S. C. Jarvis 1981. Effect of copper deficiency on phenolic and other constituents of wheat cell walls. New Phytol. 89: 361-371.

Romheld, V. and H. Marschner 1991. Function of micronutrients in plants. In: Micronutrients in Agriculture. 2nd Edition. SSSA Book Series, no.4. pp 297-328. Soil Science Society of America, WI.

Rossignol, M., A. Lamant, L. Salsac and R. Heller 1976. Calcium fixation by the roots of calcicole and calcifuge plants: The importance of membrane systems and their lipid composition. In: M. Theiler et al. (eds) Transmembrane Ion Exchanges. Pp 4830490. CNRS, Paris.

Sandmann, G. and P. Boger 1983. The enzymatological function of heavy metals and their role in electron transfer processes in plants. In: A. Lauchli and R. L. Bieleski (eds) Encyclopedia of Plant Physiology, New Series, Vol 15A, Springer-Verlag, NY. pp 563-596.

Schmidt, A. and Jäger, K. 1992. Open questions about sulfur metabolism in plants. Annu. Rev. Plant Physiol. Plant Mol. Biol. 43: 325-349.

Sivaguru, M., S. Baluska, D. Volkmann, H. H. Felle and W. J. Horst 1999. Impacts of aluminum on the cytoskeleton of the maize root apex. Short-term effect on the distal part of the transition zone. Plant Physiol. 119: 1073-1082.

Sharples, R. O. and D. S. Johnson 1977. The influence of calcium on senescence changes in apple. Ann. Appl. Biol. 85: 450-453.

Suelter, C. H. 1970. Enzymes activated by monovalent cations. Science 168: 789-795.

Terry, N. 1977. Photosynthesis, growth, and the role of chloride. Plant Physiol. 60: 69-75.

Terry, N. and A. Ulrich 1973. Effects of potassium deficiency on photosynthesis and respiration of leaves of sugar beet. Plant Physiol. 51: 783-786.

Terry, N. and J. Abadia 1985. Function of iron in chloroplasts. J. Plant Nutr. 9: 609-646.

Terry, N., A. M. Zayed, M. P. de Souza and A. S. Tarun. 2000. Selenium in higher plants. Annu. Rev. Plant Physiol. Plant Mol. Biol. 51: 401-432.

Van Campen, D. R. 1991. Trace elements in human nutrition. In: Micronutrients in Agriculture. Pp. 663-701. 2nd edition. Morvedt, J. J., Cox, F. R., Shuman, L. M. and Welch, R. M. eds., Soil Science Society of America, Madison, WI.

Vlamis, J. and D. E. Williams 1967. Manganese and silicon interaction in the *Gramineae*. Plant Soil 27: 131-140.

Volk, R. J., R. P. Kahn and R. L. Weintraub 1958. Silicon content of the rice plant as a factor influencing its resistance to infection by the blast fungus *Pyricularia oryzae*. Phytopathology 48: 179-184.

Welch, R. M. 1995. Micronutrient nutrition of plants. Critical Reviews in Plant Sciences 14: 49-82.

White, M. C., A. M. Decker and R. L. Chaney. 1981. Metal complexation in xylem fluid. Plant Physiol. 67: 292-300.

Woodward, J. 1699. Thoughts and experiments on vegetation. Philos Trans R Soc London 21: 382-398.

Yoshida, S., S. A. Navasero and E. A. Ramirez 1969. Effects of silica and nitrogen supply on some leaf characters of the rice plant. Plant Soil 31: 48-56.

Table 1. Discoverer and discoverer(s) of essentiality for the essential elements. Adapted from Glass (1989).

Element	Discoverer	Year	Discoverer of essentiality	Year
C	a	a	DeSaussure	1804
H	Cavendish	1766	DeSaussure	1804
O	Priestley	1774	DeSaussure	1804
N	Rutherford	1772	DeSaussure	1804
P	Brand	1772	Ville	1860
S	a	a	von Sachs, Knop	1865
K	Davy	1807	von Sachs, Knop	1860
Ca	Davy	1807	von Sachs, Knop	1860
Mg	Davy	1808	von Sachs, Knop	1860
Fe	a	a	von Sachs, Knop	
Mn	Scheele	1774	McHargue	1922
Cu	a	a	Sommer	1931
			Lipman and MacKinnon	1931
Zn	a	a	Sommer and Lipman	1926
Mo	Hzelm	1782	Arnon and Stout	1939
B	Gay Lussac and Thenard	1808	Sommer and Lipman	1926
Cl	Scheele	1774	Stout	1954

[a] Element known since ancient times.

Table 2. Chemical elements essential for growth and their average content in material from cultivated higher plants, and approximate concentration in the environment (Adapted from Epstein, 1972; Lawlor, 1991; Marschner, 1995).

Element	Abbreviation	Mass conc. (g dry matter^{-1})	Molar conc. (mmol (kg dry matter)$^{-1}$)	Number of atoms relative to Mo	Conc. in environment (mol m^{-3})	Examples of function in cell
Macro-						
Hydrogen	H	60	60 000	60×10^6	$1\text{-}111 \times 10^3$	Oxidation/reduction, structure in organic molecules
Carbon	C	450	35 000	35×10^6	14×10^{-3}	Structure of cell organic molecules, oxidation/reduction
Oxygen	O	450	30 000	30×10^6	14×10^{-3}	Structure of cell organic molecules, oxidation/reduction
Nitrogen	N	15	1000	1×10^6	1-3	Constituent proteins, nucleic acids, regulation
Potassium	K	10	250	2.5×10^5	1-2	Ionic and osmotic regulation, medium for synthetic processes, e.g., protein synthesis
Calcium	Ca	5	125	1.25×10^5	0.5-1.5	Cell walls, pectinates, regulation of cell metabolism, hormones, membrane stability
Magnesium	Mg	2	80	8×10^4	2-4	Constituent of chlorophyll, enzyme co-factor, control cell metabolism/enzymes
Phosphorus	P	2	60	6×10^4	0.0005-0.002	Constituent of nucleic acids, lipids, essential cellular energetics, co-enzyme regulation
Sulfur	S	1	30	3×10^4	0.3-0.7 0.001-10	Constituents of proteins, sulfolipids, energy transfer

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Table 2. (Continued.)

Element	Abbreviation	Mass conc. (g dry matter^{-1})	Molar conc. (mmol (kg dry matter)$^{-1}$)	Number of atoms relative to Mo	Conc. in environment (mol m^{-3})	Examples of function in cell
Chlorine	Cl	0.1	3	3×10^3	0.001	Chloroplast photosystem II, metabolism, growth
Boron	B	0.02	2	2×10^3	0.001	
Iron	Fe	0.01	2	2×10^3	0.001	Energy transfer proteins, co-enzyme factor for prosthetic groups
Manganese	Mn	0.05	1	1×10^3	0.001	Co-factor in water splitting enzyme, aminopeptidase etc.
Zinc	Zn	0.02	0.3	3×10^2	7×10^{-4}	Enzyme co-factor, carbonic anhydrase, alkaline phosphatase, enzyme regulation
Copper	Cu	0.06	0.1	1×10^2	3×10^{-4}	Constituent of plastocyanin, ascorbic acid oxidase etc.
Molybdenum	Mo	0.0001	0.001	1	5×10^{-4}	Constituent of nitrate reductase
Nickel	Ni		~0.001	1		Constituent of urease

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Table 3. Roles of the essential nutrients in crop development and yield.

Nutrients	Roles
Nitrogen	• Necessary for formation of amino acids, the building blocks of protein • Essential for plant cell division, vital for plant growth • Directly involved in photosynthesis • Necessary component of vitamins • Aids in production and use of carbohydrates • Affects energy reactions in the plant
Phosphorus	• Involved in photosynthesis, respiration, energy storage and transfer, cell division, and enlargement • Promotes early root formation and growth • Improves quality of fruits, vegetables and grains • Vital to seed formation • Helps plants survive harsh winter conditions • Increases water-use efficiency • Hastens maturity
Potassium	• Carbohydrate metabolism and the break down and translocation of starches • Increases photosynthesis • Increases water-use efficiency • Essential to protein synthesis • Important in fruit formation • Activates enzymes and controls their reaction rates • Improves quality of seeds and fruit • Improves winter hardiness • Increases disease resistance
Calcium	• Utilized for continuous cell division and formation • Involved in nitrogen metabolism • Reduces plant respiration • Aids translocation of photosynthates from leaves to fruiting organs • Increases fruit set • Essential for nut development in peanuts • Stimulates microbial activity
Magnesium	• Key element of chlorophyll production • Improves utilization and mobility of phosphorus • Activator and component of many plant enzymes • Directly related to grass tetany • Increases iron utilization in plants • Influences earliness and uniformity of maturity

Table 3. (Continued.)

Nutrients	Roles
Sulfur	• Integral part of amino acids • Helps develop enzymes and vitamins • Promotes nodule formation on legumes • Aids in seed production • Necessary in chlorophyll formation (though it is not one of the constituents)
Boron	• Essential of germination of pollen grains and growth of pollen tubes • Essential for seed and cell wall formation • Promotes maturity • Necessary for sugar translocation • Affects nitrogen and carbohydrate metabolism
Chlorine	• Not much information about its functions • Interferes with P uptake • Enhances maturity of small grains on some soils
Copper	• Catalyzes several plant processes • Major function in photosynthesis • Major function in reproductive stages • Indirect role in chlorophyll production • Increases sugar content • Intensifies color • Improves flavor of fruits and vegetables
Iron	• Promotes formation of chlorophyll • Acts as an oxygen carrier • Reactions involving cell division and growth
Manganese	• Functions as a part of certain enzyme systems • Aids in chlorophyll synthesis • Increases the availability of phosphorus and calcium
Molybdenum	• Required to form the enzyme "nitrate reductase" which reduces nitrate to ammonium in plant • Aids in formation of legume nodules • Needed to convert inorganic phosphates to organic forms in the plant
Zinc	• Aids plant growth hormones and enzyme system • Necessary for chlorophyll production • Necessary for carbohydrate formation • Necessary for starch formation • Aids in seed formation

Table 4. Essentiality of mineral elements for higher and lower plants (Marscner, 1995).

Classification	Element	Higher plants	Lower plants
Macronutrient	N, P, S, K, Mg, Ca	+	+ (Exception: Ca for fungi)
Micronutrient	Fe, Mn, Zn, Cu, B, Mo, Cl, Ni	+	+ (Exception: B for fungi)
Micronutrient and 'beneficial' element	Na, Si, Co	±	±
Micronutrient and 'beneficial' element	I, V	−	±

Table 5. Classification of plant mineral nutrients according to their biochemical role and physiological function (Adapted from Mengel and Kirkby, 1987; Marschner, 1995).

Nutrient element	Form for uptake	Functions in the plant
Group 1		***Nutrients that form the organic compounds of plants***
Nitrogen	Ions in solution (NO_3^-, NH_4^+), or gas in the atmosphere (N_2)	Constituent of aminoacids, amides, proteins, nucleic acids, nucleotides, coenzymes, hexoamines, etc. Many affect carbohydrate utilization due to reducing power requirements for assimilation and loss of TCA cycle intermediates as carbon skeletons for aminoacid biosynthesis, resulting in a drain on carbohydrate reserves.
Sulfur	Ion in solution (SO_4^{2-}), or gas in the atmosphere (SO_2)	Component of cysteine, cystine, and methinine, and proteins. Constituent of lipoic acid, coenzyme A, thiamine pyrophosphate, glutathione, biotin, adenosine-5'-phosphosulfate, and 3-phosphoadenosine. Involved in photosynthetic electron transport as a constituent of several iron-sulfur proteins which are intermediates in the process.
Group 2		***Nutrients that are important in energy storage or structural integrity***
Phosphorus	Ion in solution (PO_4^{3-})	Component of sugar phosphates, nucleic acids, nucleotides, coenzymes, phospholipids, phytic acid, etc. Has a key role in reactions in which ATP is involved.
Boron	Ion in solution (BO_3^{3-})	Complexes with mannitol, mannan, polymannuronic acid, and other constituents of cell walls. Involved in cell elongation and nucleic acid metabolism. Inhibits phenolic synthesis as well as complexing phenolic compounds.
Silicon		Deposited as amorphous silica in cell walls. Contributes to cell wall mechanical properties including rigidity and elasticity.
Group 3		***Nutrients that remain in ionic form***
Potassium	Ion in solution (K^+)	Required as a cofactor for over 40 enzymes. Principal cation in establishing cell turgor and maintaining cell electroneutrality. May be involved in the pumping process by which sucrose is translocated.

Table 5. (Continued.)

Nutrient element	Form for uptake	Functions in the plant
Sodium	Ion in solution (Na^+)	Involved with the regeneration of phosphoenolpyruvate in C_4 and CAM plants. Substitutes for potassium in some functions.
Magnesium	Ion in solution (Mg^{2+})	Constituent of the chlorophyll molecule. Required for ribosome integrity. Involved in phosphorylating reactions of carbohydrate metabolism and phosphate transfers from ATP. Also involved in ion transport mediated by ATPases. Thus, photosynthesis, respiration and N_2 fixation all require Mg.
Calcium	Ion in solution (Ca^{2+})	Constituent of the middle lamella of cell walls. Crosslinks negatively-charged membrane lipid headgroups. Required as a cofactor by some enzymes involved in the hydrolysis of ATP and phospholipids. Acts as a "second messenger" in mitosis, cytokinesis, cytoplasmic streaming, gravitropism and phytochrome responses. May be involved in the action of cytokinin, gibberellin, and auxin.
Manganese	Ion or chelate in solution (Mn^{2+})	Involved in photosynthetic O_2 evolution. Required for activity in many oxidative-reductive processes, and decarboxylation and hydrolysis reactions. Involved in RNA metabolism and influences auxin levels by enhancing IAA oxidase activity.
Chlorine	Ion in solution (Cl^-)	Required for the photosynthetic reactions involved in O_2 evolution. Acts as an osmoregulator.
Group 4		*Nutrients that are involved in electron transfer reactions*
Iron	Ion or chelate in solution (Fe^{2+})	Component of porphyrin molecules such as cytochromes, hemes, hematin, ferrichrome, leghemoglobin, and also non-heme iron proteins (ferredoxin). Involved in photosynthesis, N_2 fixation, respiration and with enzymes of chlorophyll synthesis, organic acid metabolism, catalase, peroxidase and cytochrome oxidase.
Copper	Ion or chelate in solution (Cu^{2+})	Component of ascorbic acid oxidase, tyrosinase, monoamine oxidase, uricase, cytochrome oxidase, phenolase, laccase, and plastocyanin. Involved in photosynthetic electron transport as a component of plastocyanin.

Table 5. (Continued.)

Nutrient element	Form for uptake	Functions in the plant
Zinc	Ion or chelate in solution (Zn^{2+})	Component of alcohol dehydrogense, alkaline phosphatase, glutamic dehydrogenase, carbonic anhydrase, carboxypeptidase B, and other enzymes. Required for auxin synthesis via effect on tryptophan synthesis. May promote synthesis of cytochrome c.
Molybdenum	Ion or chelate in solution (MoO^-)	Component of nitrogenase, nitrate reductase, and xanthine dehydrogenase. Enhances the absorbtion and translocation of iron.
Nickel	Ion or chelate in solution (Ni^{2+})	Component of urease. In N_2 fixing bacteria, it is a component of hydrogenases.

Table 6. Mineral nutrients classified on the basis of their mobility within a plant and their tendency to retranslocate during deficiencies.

Mobile	Immobile
Nitrogen	Calcium
Potassium	Sulfur
Magnesium	Iron
Phosphorus	Boron
Chlorine	Copper
Sodium	
Zinc	
Molybdenum	