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Physiological functions of mineral macronutrients

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Plants require calcium, magnesium, nitrogen, phosphorous, potassium and sulfur in relatively large amounts (>0.1% of dry mass) and each of these so-called macronutrients is essential for a plant to complete its life cycle. Normally, these minerals are taken up by plant roots from the soil solution in ionic form with the metals Ca^{2+}, Mg^{2+} and K^{+} present as free cations, P and S as their oxyanions phosphate (PO_4^{3-}) and sulfate (SO_4^{2-}) and N as anionic nitrate (NO_3^{-}) or cation ammonium (NH_4^{+}).Recently, important progress has been made in identifying transport and regulatory mechanisms for macronutrients and the mechanisms of uptake and distribution. These and the main physiological roles of each nutrient will be discussed.

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Introduction

Plants require 14 essential nutrients of which the macronutrients nitrogen (N) and the minerals potassium (K), calcium (Ca), magnesium (Mg), phosphorous (P) and sulfur (S) are present in plant tissues in relatively large amounts [1]. By contrast, inorganic macronutrients are usually present at low concentrations in the soil and often need to be accumulated against steep concentration gradients. Although generally low, soil availability can fluctuate greatly in both space and time due to factors such as precipitation, temperature, wind, soil type and soil pH. As sessile organisms, plants therefore have had to develop adaptive and flexible strategies for the acquisition of nutrients and these are mechanistically similar for all macronutrients. Further mechanisms are present for (re)distribution throughout the plant. A more detailed description of the availability and distribution can be found elsewhere in this volume for N, P and S [2] and K, Ca and Mg [3].

Issues of availability, uptake and distribution pertain to all macronutrients and it is therefore not surprising that many of the adaptive and molecular mechanisms recur when different nutrients are discussed. For example, uptake mechanisms at the root-soil boundary are typically multiphasic with varying affinities to accommodate different substrate supplies. Localised deficiency or surplus for many nutrients induces morphological root adaptations such as proliferation of lateral roots in the soil. When excess nutrients are available, these are typically stored in the central vacuole and deficiency leads to depletion of vacuolar stores in order to maintain cytoplasmic requirements.

Nitrogen (N)

Occurrence

Around 80% of our atmosphere consists of N. However, the extremely stable form of atomic N (N_2) is not available to plants. Both free living and symbiotic microorganisms are capable of fixing atmospheric N_2 in the form of NH_4^{+} that can be directly taken up by plants or converted into NO_3^{-} by nitrifying bacteria.

The preferred form in which N is taken up depends on soil conditions and plant species [1,4•]. In general, plants adapted to low pH and reducing soil conditions tend to take up NH_4^{+}. At higher pH and in more aerobic soils, NO_3^{-} is the predominant form. Both NO_3^{-} and NH_4^{+} are highly mobile in the soil. By contrast, organic N compounds such as amino acids, are far less mobile but there is growing evidence that these can also form important N sources [4•,5].

N uptake and distribution

Multiple uptake systems contribute to N uptake in plant roots [4•,6]. *Arabidopsis*, which primarily acquires N in the form of NO_3^{-}, contains both high and low affinity transport systems that have affinities in the micromolar and millimolar range. These NO_3^{-} transporters are encoded by genes from the NRT1 and NRT2 families, respectively (Figure 1a). Some are induced by NO_3^{-} which provides a regulatory mechanism that ensures increased uptake when substrate becomes available. NO_3^{-} uptake is also regulated by the plant N status, with glutamine acting as negative feedback signal.

In non-aerobic conditions, NH_4^{+} is often the prevalent form of inorganic N (Figure 1a). Plants grown in submerged environments such as rice, have relatively large numbers of high and low affinity NH_4^{+} transporters encoded by the AMT family. In rice two isoforms, AMT1;1 and 1;2, are detected exclusively in roots, where the large majority of NH_4^{+} is assimilated. Both *Arabidopsis*

[7••] and rice [8] AMT1;1 contain a threonine residue that forms a phosphorylation target that plays a crucial role in the allosteric regulation of this transporter [7••]. Organic N forms are transported throughout the plant often by proton dependent oligopeptide transporters of the POT/PTR family [9,10].

Assimilation and biological functions

N needs to be reduced to its −3 valence state. Two important enzymes, nitrate reductase and nitrite reductase ensure that the prevalent form in which N is taken up (NO_3^-) is converted to ammonium. Nitrate reduction can take place in both roots and shoots but is spatially separated between the cytoplasm where nitrate reduction takes place and plastids/chloroplasts where nitrite reduction happens (Figure 1a) [6,10].

The foremost function of N is to provide amino groups in amino acids. N is also prolific in nucleotides, where it occurs incorporated in the ring structure of purine and pyrimidine bases. Nucleotides form the constituents of nucleic acids but also have many important functions in their own right such as in energy homeostasis, signalling and protein regulation. In addition, N is essential in the biochemistry of many non-protein compounds such as co-enzymes, photosynthetic pigments, secondary metabolites and polyamines. When in ample supply, NO_3^- is deposited in the vacuole where it significantly contributes to turgor generation.

Phosphorus (P)

Occurrence

More than 90% of soil P is normally fixed and cannot be used by plants. Another part of insoluble P, the 'labile fraction', exchanges with the soil solution. The inorganic P (Pi) released from the labile compartment can be taken up by plants. However, this release is extremely slow and thus P deficiency is widespread. The form in which Pi is found in the soil solution is pH dependent but at typical soil solution pH, Pi consists almost exclusively as $H_2PO_4^-$ and this is the form in which plants take up Pi. The low P availability means that in agricultural settings, P is replenished with large amounts of P fertiliser derived from phosphate rock, a finite source material.

Pi uptake and distribution

The limited provision of P has led to the evolution of various adaptations in plants to satisfy requirements: Over 90% of plant species form mycorrhizal symbioses that improve acquisition of scarce minerals (Figure 1b). The fungal hyphae can deliver up to 80% of plant P albeit at a considerable cost to the plant in the form of reduced carbon [11•,12]. Several plant species form socalled protoid roots in the case of P deficiency. These dense clusters of fine lateral roots not only increase the invaded soil volume but also extrude large amounts of chelators in the form of organic acids to dissolve the sparingly soluble calcium phosphates.

Expression of high and low affinity Pi transporters greatly depends on P supply [13,2]. The presence of mycorrhizal associations also impacts on expression of specific transporters [14]. Vacuolar sequestration of P is particularly important during seed development when large amounts of P and other minerals are stored in complex myo-inositol salts such as phytate. These are contained in globoid inclusion bodies within seed protein storage vacuoles and hence require two transmembrane transport steps.

Assimilation and biological functions

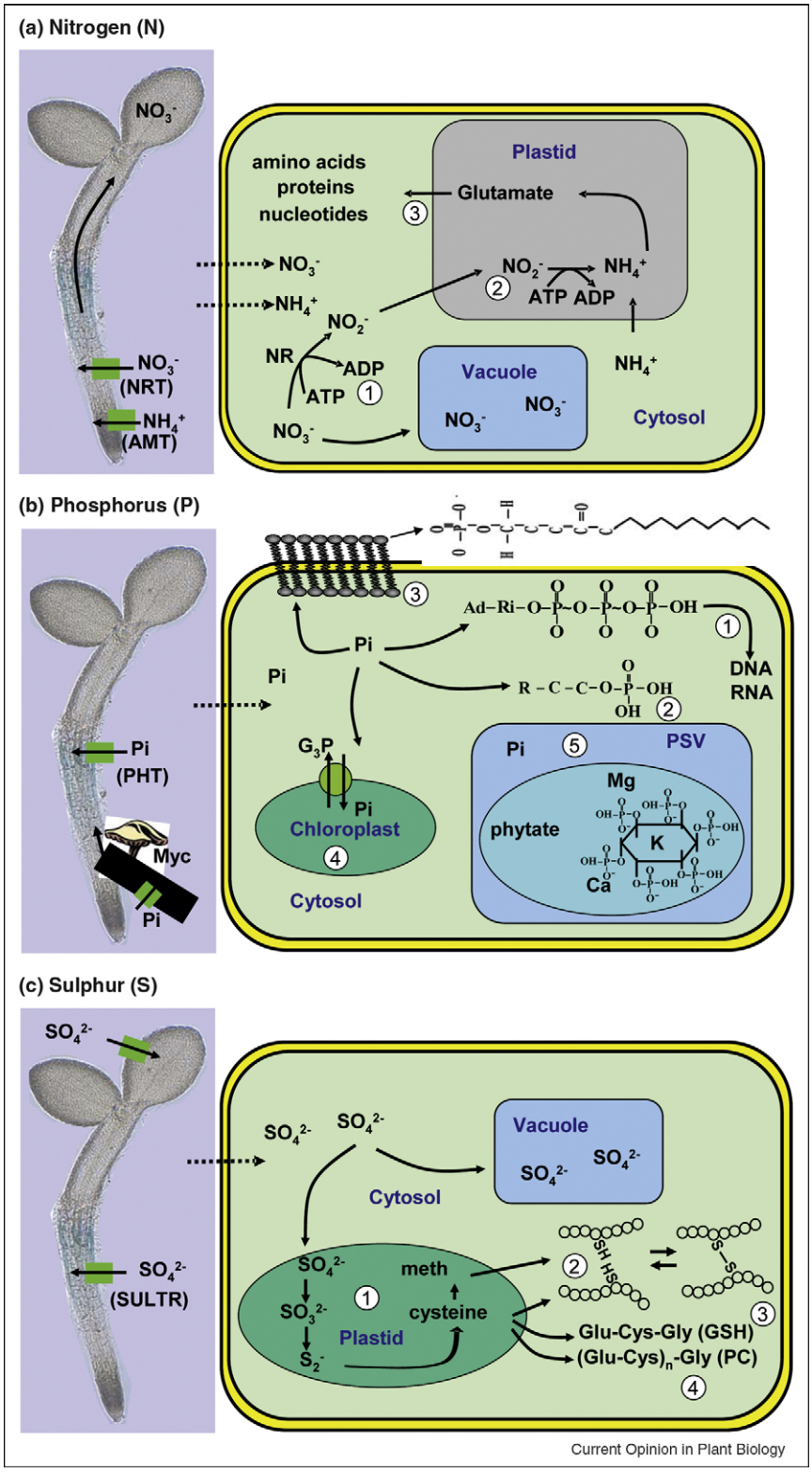
Unlike N and S, P remains in its oxidised form. As inorganic P it is either found as soluble Pi (orthophosphate) or as PP (pyrophosphate). Organic P is mainly bound to hydroxyl groups of sugars and alcohols via esterification [1]. Alternatively, Pi binds to other phosphate groups via pyrophosphate bonds (Figure 1b). Formation and disruption of the pyrophosphate bond is one of the central mechanisms in cellular energy homoeostasis: ATP releases energy of around 50 kJ/mol its pyrophosphate bond is hydrolysed. ATP also is the basis of many pathways such as those for synthesis of nucleic acids. Similar energy rich phosphonucleotides are UTP, CTP and GTP that all play roles in nucleic acid metabolism. UTP is also a building block of sucrose, starch and cellulose formation whereas CTP acts as energy rich compound during phospholipid biosynthesis.

Since triphosphate nucleotides form the backbone of DNA and RNA, P is an indispensible component of nucleic acids [1,15•]. In these macromolecules Pi acts as a bridge between each nucleotide base by coupling C3 and C5 of two adjacent riboses via esterification. A second area where P plays a structural role is in cellular membranes [16]. Membranes are largely made up of phospholipids where Pi links the lipophilic glycerol-fatty acid part to the hydrophilic choline part of the lipid. The negative charge on the phosphate group makes this part of the lipid strongly hydrophilic and therefore helps a proper orientation in the membrane. The negative charges are compensated by electrostatic binding of divalent cations, in particular of Ca^{2+}.

Reversible protein phosphorylation is one of the most prominent mechanisms for the modulation of protein activity and is mediated by the action of kinases that transfer Pi to Ser or Thr residues of proteins, and phosphatases that release Pi. Such reactions are normally highly specific using particular kinases or phosphatases and are strictly controlled in space and time.

The essential role of P in many aspects of cellular metabolism is also evident from the large amounts of P that are stored in seeds to enable embryo development, germination and seedling growth [1]. P is typically stored in protein storage vacuoles as inositol-hexa-phosphate

Figure 1



The major functions of anionic macronutrients. **(a)** Nitrogen is predominantly taken up as inorganic NO_3^- and NH_4^+. NO_3^- uptake is mediated by high affinity H^+ coupled symporters from the NRT family whereas NH_4^+ uptake is mediated by AMT transporters that function as ion channel or possibly NH_3:H^+ symporters. Most NO_3^- reduction and assimilation occurs in the shoot. The first reductive step (1) occurs in the cytoplasm by the enzyme nitrate reductase (NR) and nitrite is further reduced to NH_4^+ in chloroplasts (2). Reduced N is assimilated into the amino acid glutamate. Surplus N is

(IP_6). IP_6 or phytic acid is an excellent chelator of cations and thus contains the bulk of cationic minerals found in seeds such as Ca^{2+}, Mg^{2+} and K^+ (Figure 1b) [16]. Phytate also sequesters micronutrients like Fe^{2+} and Zn^{2+}.

P deficiency causes a rapid decrease in photosynthetic rates. This may be due to many of the intermediate steps during carbon fixation involving sugar phosphates. Thus, chloroplast Pi demand is high and normally fulfilled by the Pi triosephosphate translocator in the chloroplast envelope.

Sulfur (S)

Occurrence

Soils contain inorganic and organic forms of S. In saline and sodic soils inorganic salts are predominant. In aerobic conditions, inorganic S is present mainly as sulfate (SO_4^{2-}) and this is also the form in which plants take up most S (Figure 1c). However, the reducing environment created by flooding can give rise to sulfides such as FeS, FeS_2 and H_2S. In addition to soil S, plants can also extract S from the atmosphere where it occurs as SO_4^2 and H_2S.

S uptake, distribution and assimilation

S is largely taken up as SO_4^{2-} via dedicated sulfate transporters that are energised by the H^+ gradient [17,18,2]. In roots, members of the 'Sultr' family constitute uptake mechanisms that are located in the epidermal and cortical plasma membranes and transcription of this type of mechanism is induced or de-repressed when S becomes deficient [19,20•]. SO_4^{2-} is highly mobile and rapidly transported through the xylem to shoot tissues where the majority is reduced. Surplus S is deposited in vacuoles as SO_4^{2-} (Figure 1c). Although some SO_4^{2-} may be reduced in root plastids, it is believed the bulk of reduced S is produced in shoot chloroplasts. S assimilation involves reduction of SO_4^{2-} to SO_3^{2-} and subsequently to S^{2-} that is incorporated into the amino acid cysteine. This means that roots derive most reduced S via the phloem primarily in the form of the tripeptide glutathione (Glu-Cys-Gly). Both intracellular and long-distance transport of glutathione is likely to involve oligo peptide transporters [21].

Biological functions

Most S is found in reduced form in the amino acids cysteine and methionine. In cysteine, S appears in the sulfhydryl (–SH or thiol) group that can undergo reversible oxidation and hence the formation of a covalent –S–S– bond if a second –SH group is present. The formation and disruption of these S bridges impact on tertiary and quaternary protein structure and therefore protein activity (Figure 1c).

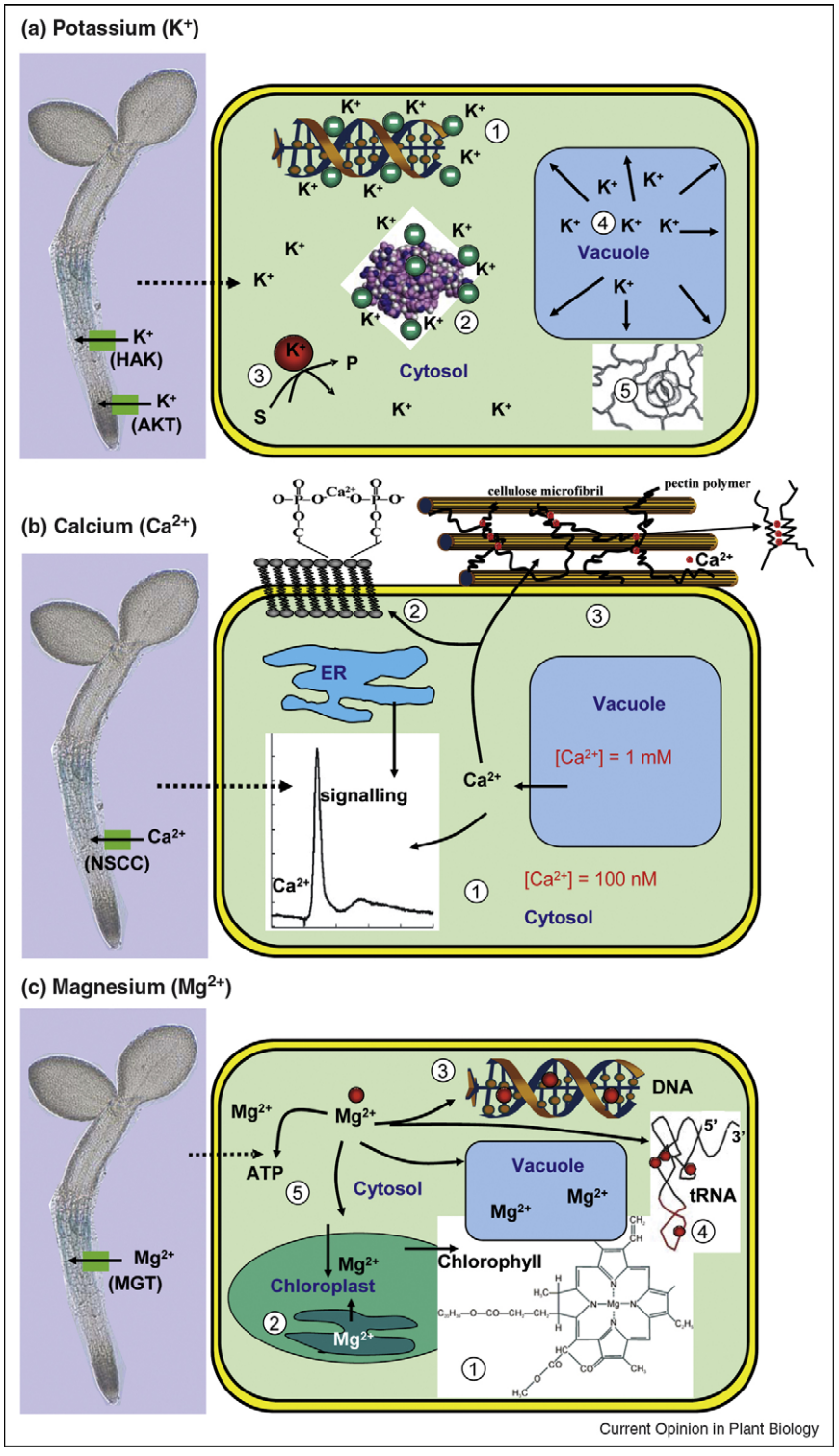
The production of glutathione serves as a mobile carrier of reduced S but glutathione also acts as a general redox buffer for instance as a reductant in the detoxification of reactive oxygen species [22]. The glutathione-based phytochelatins (PCs) have a general structure of (Glu-Cys)*n*-Gly, where *n* is typically 2–5. The high affinity of PCs for heavy metals and arsenic helps detoxify these compounds [22] and there is a strong correlation between heavy metal stress and sulfate uptake [23]. Recently much effort has been spent to increase PC production, not only to make (crop) plants more tolerant to pollutants such as arsenic and Cd^{2+} but also to improve the phytoremediation potential [23]. More recently, evidence has emerged that PCs may also be involved in non-stress metal homeostasis: in *Arabidopsis*, reduction of PC synthesis affected root Zn^{2+} accumulation and overall homeostasis of this essential micronutrient [24••]

A third role of inorganic S is in sulfolipids. These are normally found in a small proportion in chloroplast thylakoids. Why membranes of photosynthetic membranes require such lipids is not entirely clear but it has been suggested that they are essential for the stabilisation of photosystem components [25]. However, levels of sulfolipids are not static. For example, phosphorous deficiency can increase this fraction: non-specific phospholipases and phosphatases are responsible for degradation of phospholipids to increase the Pi pool [15•,25] while at the same time transcription of the sulfolipid synthetase *SQD1* is rapidly increased in response to P starvation [26]. Other environmental factors also influence the ratio between phospho- and sulfo-lipids. In several halophytes (*Aster tripolium* and *Sesuvium portulacastrum*) sulfolipid content increased after exposure to salt whereas it remained unaltered in the glycophyte *Arabidopsis*, suggesting in may confer some adaptive advantage [25].

S toxicity is rare but can occur in saline soils with high levels of SO_4^{2-} salts. Atmospheric SO_4^{2-} derived from

(Figure 1 Legend Continued) typically stored in the central vacuole as NO_3^- (3). **(b)** Phosphorus is often growth limiting and many plants associate with mycorrhizal fungi (Myc) that improve P nutrition in return for reduced carbon. P is taken up directly as inorganic PO_4^{3-} (Pi) through H^+-coupled high affinity transporters. Cellular Pi is essential in cellular energy homeostasis since it readily forms high-energy pyrophosphate (1) and ester (2) bonds. Phosphate groups form the lipophilic component of many membrane lipids (3) and are therefore essential for membrane composition and integrity. Chloroplast P, necessary for synthesis of high-energy bonds in photosynthesis, enters the chloroplast (4) in exchange for glyceraldehyde-3-phosphate (G_3P). In storage tissues (5), P is sequestered in the protein storage vacuole (PSV) as phytate together with minerals. **(c)** Soil sulfur is predominantly taken up as SO_4^{2-} through H^+-coupled high affinity transporters. However, S may also be taken up through leaves. Reduction of SO_4^{2-} takes place in plastids where it is assimilated in cysteine. Cysteine can be directly incorporated into proteins or, converted into methionine (1). Cysteine contains SH (thiol) groups that are essential for protein functioning through the formation and disruption of sulfur bridges (2). Reduced S (3) is mainly distributed around the plant as the tripeptide glutathione (GSH). During many stresses glutathione based phytochelatins (PCs) are synthesised (4) which detoxify metals and metalloids.

Figure 2



The major functions of cationic macronutrients. **(a)** Potassium is taken up through high affinity H^+-coupled symporters (HAK) and low affinity ion channels (AKT). Inside the plant, the chaotropic properties of K^+ make it ideal as counter ion for negative charges on nucleic acids (1) and proteins (2). In addition, K^+ activates specific enzymes (3) by acting as a cofactor in enzymatic reactions between substrates (S) and products (P). As the main cation in vacuoles (4), K^+ generates turgor to provide structure and drive cell expansion, plant growth and plant movement such as regulation of stomatal apertures (5). **(b)** Roots take up calcium through non-selective cation channels (NSCCs). Cytoplasmic Ca^{2+} concentrations are extremely low (~100 nM) making Ca^{2+} an ideal secondary messenger (1). In membranes (2), Ca^{2+} maintains integrity by electrostatically binding negative groups of

industry and coal burning frequently reach levels of well over 100 μg/m3. This can be detrimental particularly to forest trees that will show damage whenever levels exceed 50 $\mu g/m^3$.

Potassium (K)

Occurrence

The earth's crust contains around 2.6% potassium. In soils, the majority of K^+ is dehydrated and coordinated to oxygen atoms not available to plants. Typical concentrations in the soil solution vary between 0.1 and 1 mM K^+. K^+ deficiency is rare but plant growth is usually stimulated by additional K^+ supply and potash fertilisation is common practice in many crop producing areas.

K^+ uptake and distribution

As with NO_3^-, K^+ uptake into plant roots has high and low affinity components [27]. Electrophysiological studies suggested that passive transport through ion channels with millimolar K_m and active transport through H^+-cotransporters with micromolar K_m underlie the low-affinity and high-affinity components of K^+ uptake respectively [27,28]. The molecular identity of some of these transporters has been established: In *Arabidopsis*, *AKT1* encodes a K^+ selective inward rectifying channel, expressed in the root cortex (Figure 2a) [29]. Loss-of-function mutations in *AtAKT1* [30] have shown that this channel can also mediate K^+ uptake in the high affinity range but not to the extent that H^+-cotransporters can [31]. *AKT1* transcript level is largely impervious to ambient K^+ conditions, but during K^+ deficiency, a Ca^{2+} signal is recorded by the Ca^{2+} sensors CBL1 and CBL9 that activate the protein kinase CIPK23. CIPK23-mediated phosphorylation of AKT1 increases K^+ uptake via this channel [32]. Members of the *Arabidopsis KUP/HAK* gene family have been found to mediate high-affinity uptake [33,34] particularly HAK5 [35]. A substantial fraction of the K^+ and this is taken up is translocated to the shoot that is mediated by SKOR type channels that release K^+ into the xylem [36]. In addition to the delivery of K^+ to green tissue, a large phloem-mediated shoot to root K^+ flux is maintained. The resulting cycling of K^+ is believed to be important in K^+ homeostasis and to provide a constant supply of cations to accompany anions such as NO_3^- on their way to the shoot.

Biological functions

K^+ is needed for metabolic reactions because of its capacity to activate a multitude of enzymes (Figure 2a). *In vitro*, enzyme activation occurs in the presence of 50–80 mM K^+ activity, a value that agrees nicely with those determined for cytoplasmic K^+ [37,38,39]. Binding of K^+ to enzymes is in its dehydrated form, probably via coordination with six oxygens that may derive from carboxyl, carbonyl and hydroxyl groups and from water molecules. Such binding is very selective for K^+ and cannot be substituted by other similar ions such as Na^+ or Li^+. Specific enzymes that have been shown to be activated by K^+ include vacuolar PPase isoforms that accumulate protons into the vacuolar lumen and are strictly dependent on K^+. In addition many enzymes involved in C-metabolism such as pyruvate kinase, phosphofructokinase and ADP-glucose starch synthase show K^+ dependence [1]. Ribosome mediated protein synthesis is another key process that requires high concentrations of K^+. This biochemical requirement for cellular K^+ has frequently been given as the basis for strict homeostatic K^+ control in the cytosol [27,31]. However this notion has been challenged in some cases where flux analyses suggested a much larger variation in cytosolic K^+ [37]. Plant K^+ status can also affect plant metabolism through transcriptional and post-transcriptional regulation of metabolic enzymes. A recent study in K^+-starved *A. thaliana* plants provided evidence for upregulation of malic enzyme and the GS/GOGAT cycle whereas nitrate uptake and reduction were downregulated.[40,41]. Accumulation of reducing sugars and depletion of organic acids and negatively charged amino acids have also been described as direct consequences of K^+-deficiency [42].

The dominant role of K^+ in turgor provision and water homeostasis is evident in processes such as pressure-driven solute transport in the xylem and phloem, high levels of vacuolar K^+ accumulation and the large fluxes of K^+ that mediate plant movement. An example includes stomatal aperture changes through uptake and release of K^+ and K^+ provision therefore greatly affects plant water homeostasis [43].

Calcium (Ca)

Occurrence

Like potassium, calcium is very abundant in the lithosphere. Severe weathering and leaching of soils may lead to deficiency in Ca, a condition that is accelerated by low soil pH. Ca^{2+} adsorbed to colloids can be exchanged with the soil solution where much of the 'free' Ca^{2+} forms nearly insoluble compounds with other elements such as phosphorus, thus making P less available.

Ca^{2+} uptake and distribution

Calcium enters the root through Ca^{2+}-permeable channels (Figure 2b). Some of these are Ca^{2+} selective but

(Figure 2 Legend Continued) lipids. A second structural function of Ca^{2+} occurs in cell walls (3) where pectin supplies rigidity to the wall matrix via Ca^{2+} crosslinks. **(c)** Magnesium probably enters the root symplast through MGT type transporters. Cellular Mg^{2+} is indispensible for photosynthesis as transition metal in the porphyrin ring of chlorophylls (1). In the chloroplast, Mg^{2+} is the main charge to counter the build up of a negative thylakoid potential when photosynthesis driven H^+ extrusion occurs (2). Mg^{2+} also binds to negative carboxyl groups in nucleic acid polymers (3) and smaller nucleic acids such as tRNAs (4) to stabilise their configuration.

others are 'non-selective' ion channels [44]. The identity of the specific protein(s) that mediates Ca^{2+} uptake is not known [44].

Within the plant, Ca^{2+} is relatively immobile; the ion tends to be sequestered in the large vacuole of mature cells. This is carried out by members of the CAX H^+:Ca^{2+} antiport family and by ATP-driven P-type ATPases [45]. No transporters have been identified that are responsible for Ca^{2+} xylem loading and a proportion of xylem Ca^{2+} may arrive via the apoplast [46] but in the vascular system too, Ca^{2+} mobility is low. Therefore, Ca^{2+} levels may fall below a critical level in fast-growing tissues causing diseases such as 'black heart' in celery, 'blossom end rot' in tomatoes or 'bitter-pit' in apples.

Biological functions

Cellular functions of Ca^{2+} are structural and as a secondary messenger. Ca^{2+} readily complexes with negative groups of organic compounds such as phosphates and carboxyls of phospholipids, proteins and sugars. This is exemplified in plant cell walls where the cellulose microfibrils are cross-linked by glycans and pectins (Figure 2b). Carboxyl groups from opposing pectins can be electrostatically coordinated by Ca^{2+} that therefore confers rigidity to cell walls. Ca^{2+} plays an analogous role in cell membranes where Ca^{2+} coordinates with phosphate groups from phospholipids. This complexation occurs predominantly at the external face of the plasma membrane. Removal of membrane Ca^{2+}, or its replacement with other cations rapidly compromises membrane integrity. The latter part explains the detrimental effects of salt stress and why heavy metals such as copper induce cellular leakage of electrolytes.

Since Ca^{2+} readily forms insoluble salts with sulfates and phosphates, the free Ca^{2+} concentration in the cytoplasm is kept extremely low at around 100 nM. This makes Ca^{2+} an ideal secondary messenger and a wide range of stimuli has been shown to evoke rapid changes in cytosolic free Ca^{2+} in plants that include responses to biotic and abiotic stress, stomatal regulation and physical damage [43,45].

Magnesium (Mg)

Occurrence

The name magnesium is derived from the Greek 'Magnesia' a region where talc was mined. Soil Mg generally varies between 0.05 and 0.5%. Owing to its small hydration shell, Mg^{2+} adsorption to soil particles is relatively weak which results in high leaching rates and Mg^{2+} deficiency is therefore common [47].

Mg^{2+} uptake and distribution

In plants, the free cytoplasmic Mg^{2+} is believed to be in the order of 0.5 mM [48] but total Mg^{2+} levels vary from 0.3 to 1.0% [47] and therefore considerable Mg^{2+} uptake occurs [26]. Mg^{2+} uptake at the root:soil boundary probably proceeds through transporters of the MGT family (Figure 2c) which are homologous to bacterial CorA Mg^{2+} transporters. CorAs forms pentameric, Mg^{2+} selective ion channels so it appears in plants too, Mg^{2+} uptake is passive. Overexpression of the plasma membrane localised AtMGT1 in tobacco led to increased uptake capacity and improved growth during Mg^{2+} deficiency [49]. Most tissue Mg^{2+} resides in the vacuole where it contributes to turgor generation and charge balancing of anions. Vacuolar Mg^{2+} deposition is probably mediated by Mg^{2+}:H^+ antiporters. Given its primary role in chloroplasts, the highest tissue Mg^{2+} is usually measured in shoots.

Biological functions

Mg^{2+} is probably best known for its central position in the chlorophyll molecule where it coordinates covalently with four nitrogen atoms from the porphyrin ring (Figure 2c). Insertion of Mg^{2+} into protoporphyrin is carried out by the enzyme Mg-chelatase, consisting of several subunits that belong to the AAA protein superfamily (ATPases associated with various cellular activities). Recently considerable progress has been made in unravelling the biochemistry of this important process [50,51•] showing that porphyrin induces conformational changes in the BchH subunit that possibly provide the distortion of the porphyrin ring necessary to sequester Mg^{2+} in the molecular structure [52]. Interestingly, protoporphyrin itself is an important signal element in chloroplast development: it accumulates in plastids during stress and negatively impacts on the transcription of photosynthetic genes [53]. Mg^{2+} has further crucial roles in photosynthesis, particularly in its capacity of promoting the light reactions in the stroma. The perception of light and ensuing electron transport leads to the accumulation of H^+ in the thylakoid lumen. The resulting charge separation is countered by Mg^{2+} flux from the thylakoid lumen to the stroma.

The majority of cellular Mg^{2+} has roles as enzyme cofactors and in the stabilisation of nucleotides and nucleic acids. The most prominent type of enzyme reactions where Mg^{2+} is indispensible, are those associated with energy transfer and phosphorylation/dephosphorylation. Much of the cell's energy is stored in the high-energy ester and pyrophosphate bonds of phosphosugars and diphosphate and triphosphate compounds such as ADP and ATP. Release of this energy by enzymes like phosphotransferases and ATPases requires the presence of Mg^{2+} that forms a 'bridge' between the oxygen atoms of two adjacent phosphate groups and a nitrogen atom on the protein catalytic site.

Mg^{2+} also readily binds to nucleic acids. Consequently, DNA melting temperatures are considerably higher in the presence of Mg^{2+} [53]. In RNA, Mg^{2+} has similar roles and helps maintain secondary structure [54]. Thus, gene transcription and translation crucially depend on adequate levels of Mg^{2+}.

Concluding remarks

Plant nutrition impacts on plant growth but also on most other living organisms since plants are the basis of many food chains. Animals and humans require all the minerals discussed above so their abundance and distribution in plants also affects our diets. In agricultural settings, the supply of minerals in the form of fertiliser has large economic and environmental consequences.

Broadly speaking, the primary roles of macronutrient have been well documented and they are unlikely to fundamentally shift. However, many aspects of 'macronutrition' need further clarification especially in light of growing demands for sustainability in agriculture. For example, most studies have focused on the effect of only one mineral whereas interactions between nutrients are little understood. This not only will require experimentation where more than one nutrient is altered but also sophisticated modelling approaches to interpret the complexity of plant nutrition. Large scale depositories (i.e. 'ionomics databases') where nutrient composition data are available from many plants and conditions will be useful in this respect. Nutrient use efficiency, which varies largely between species, is another crucial parameter. Its optimisation in crop species would lessen demand for fertiliser and land. In this respect, the role of the rhizosphere microbial fauna is crucially important and needs further clarification. This is exemplified by work on mycorrhizas that were traditionally believed to primarily aid plants in P delivery but now includes augmentation of plant N, P and S supply [12]. A further hiatus in our understanding concerns the way plants sense nutrient levels both internally and in the external medium. This function impacts on nutrient use efficiency but also on homeostatic mechanisms. Plants have K^+ channels that react to the K^+ gradient [28,29,30] but whether these proteins actually fulfil the role of sensors remains to be seen. For other minerals, equally little is known about the nature of the sensing system or where it takes place. Indeed, for those minerals that are metabolised (P, S, N) any point along the assimilation pathway may be referenced.

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