4 Potassium

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CONTENTS

4.1 HISTORICAL INFORMATION

Ever since ancient classical times, materials that contained potassium have been used as fertilizers, such as excrement, bird manure, and ashes (1), and these materials certainly contributed to crop growth and soil fertility. However, in those days people did not think in terms of modern chemical elements. Even an excellent pioneer of modern chemistry, Antoine Laurent de Lavoisier (1743–1794), assumed that the favorable effect of animal excrement was due to the humus present in it (2). Humphry Davy (1778–1827) discovered the chemical element potassium and Martin Heinrich Klaproth (1743–1817) was the first person to identify potassium in plant sap (3). Home (1762, quoted in 4) noted in pot experiments that potassium promoted plant growth. Carl Sprengel (1787–1859) was the

first to propagate the idea that plants feed from inorganic nutrients and thus also from potassium (5). Justus Liebig (1803–1873) emphasized the importance of inorganic plant nutrients as cycling between the living nature and the inorganic nature, mediated by plants (6). He quoted that farmers in the area of Giessen fertilized their fields with charcoal burners' ash and prophesied that future farmers would fertilize their fields with potassium salts and with the ash of burned straw. The first potash mines for the production of potash fertilizer were sunk at Stassfurt, Germany in 1860.

4.2 DETERMINATION OF ESSENTIALITY

Numerous solution culture and pot experiments with K^+-free substrates have shown that plants do not grow without K^+. As soon as the potassium reserves of the seed are exhausted, plants die. This condition may also occur on strongly K^+-fixing soils. In contrast to other plant nutrients such as N, S, and P, there are hardly any organic constituents known with K^+ as a building element. Potassium ions activate various enzymes, which may also be activated by other univalent cationic species with a similar size and water mantle such as NH_4^+, Rb^+, and Cs^+ (7). These other species, however, play no major role under natural conditions as the concentrations of Cs^+, Rb^+, and also NH_4^+ in the tissues are low and will not reach the activation concentration required. In vitro experiments have shown that maximum activation is obtained within a concentration range of 0.050 to 0.080 M K^+. Ammonium may attain high concentrations in the soil solution of flooded soils, and ammonium uptake rates of plant species such as rice (*Oryza sativa* L.) are very high. In the cytosol, however, no high NH_4^+ concentrations build up because NH_4^+ is assimilated rapidly, as was shown for rice (8). Activation of enzymes in vivo may occur at the same high K^+ concentration as seen in in vitro experiments, as was shown for ribulose bisphosphate carboxylase (9).

It is assumed that K^+ binds to the enzyme surface, changing the enzymic conformation and thus leading to enzyme activation. Recent research has shown that in the enzyme dialkyl-glycine carboxylase, K^+ is centered in an octahedron with O atoms at the six corners. As shown in Figure 4.1, these O atoms are provided by three amino acyls, one water molecule, and the O of hydroxyl groups of each of serine and aspartate (10). As compared with Na^+, the K^+ binding is very selective because the dehydration energy required for K^+ is much lower than for Na^+. If the latter binds to the enzyme, the natural conformation of the enzyme is distorted, and the access of the substrate to the binding site is blocked. Lithium ions (Li^+) inactivate the enzyme in an analogous way. It is supposed that in most K^+-activated enzymes, the required conformation change is brought about by the central position of K^+ in the octahedron, where its positive charge attracts the negative site of the O atom located at each corner of the octahedron. This conformation is a unique structure that gives evidence of the unique function of K^+. In this context, it is of interest that the difference between K^+ and Na^+ binding to the enzyme is analogous to the adsorption of the cationic species to the

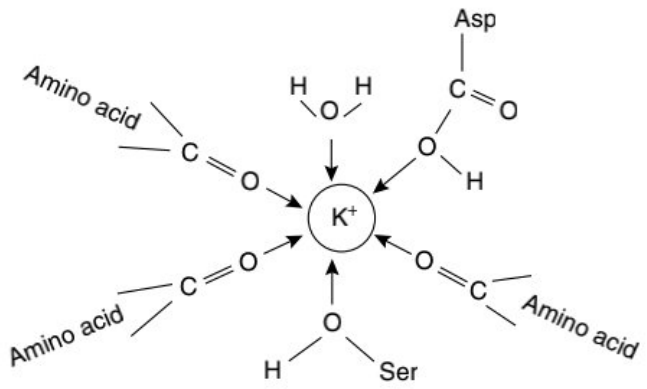

FIGURE 4.1 Potassium complexed by organic molecules of which the oxygen atoms are orientated to the positive charge of K^+. (Adapted from K. Mengel and E.A. Kirkby, *Principles of Plant Nutrition*. 5th ed. Dordrecht: Kluwer Academic Publishers, 2001.)

TABLE 4.1
Effect of Metal Chlorides on the H^+ Release by Roots of Intact Maize Plants

	Treatment of Water or Chloride Salt				
Outer medium	H_2O	K^+	Na^+	Ca^{2+}	Mg^{2+}
H^+ release (μmol/pot)	29.5	128***	46.5*	58.1*	78**

Significant difference from the control (H_2O) at $*P \leq 0.05$, $**P \leq 0.01$, and $***P \leq 0.001$, respectively.

Source: From K. Mengel and S. Schubert, *Plant Physiol.* 79:344–348, 1985.

interlayer of some 2:1 clay minerals, where the adsorption of K^+ is associated with the dehydration of the K^+, thus leading to a shrinkage of the mineral; Na^+ is not dehydrated and if it is adsorbed to the interlayer, the mineral is expanded.

It is not yet known how many different enzymes activated by K^+ possess this octahedron as the active site. There is another enzyme of paramount importance in which the activity is increased by K^+, namely the plasmalemma H^+-ATPase. This enzyme is responsible for excreting H^+ from the cell. As can be seen from Table 4.1 the rate of H^+ excretion by young corn (*Zea mays* L.) roots depends on the cationic species in the outer solution, with the lowest rate seen in the control treatment, which was free of ions. The highest H^+ release rate was in the treatment with K^+. Since the other cationic species had a promoting effect on the H^+ release relative to pure water, the influence of K^+ is not specific. However, a quantitative superiority of K^+ relative to other cations may have a beneficial impact on plant metabolism since the H^+ concentration in the apoplast of root cells is of importance for nutrients and metabolites taken up by H^+ cotransport as well as for the retrieval of such metabolites (11). The beneficial effect of cations in the outer solution is thought to originate from cation uptake, which leads to depolarization of the plasma membrane so that H^+ pumping out of the cytosol requires less energy. This depolarizing effect was highest with K^+, which is taken up at high rates relative to other cationic species. High K^+ uptake rates and a relatively high permeability of the plasmalemma for K^+ are further characteristics of K^+, which may also diffuse out of the cytosol across the plasma membrane back into the outer solution.

4.2.1 Function in Plants

4.2.1.1 Enzyme Activation

The function of potassium in enzyme activation was considered in the preceding section.

4.2.1.2 Protein Synthesis

A probable function of potassium is in polypeptide synthesis in the ribosomes, since that process requires a high K^+ concentration (12). Up to now, however, it is not clear which particular enzyme or ribosomal site is activated by K^+. There is indirect evidence that protein synthesis requires K^+ (13). Salinity from Na^+ may affect protein synthesis because of an insufficient K^+ concentration in leaves and roots, as shown in Table 4.2 (14). Sodium chloride salinity had no major impact on the uptake of ^{15}N-labelled inorganic N but severely depressed its assimilation and the synthesis of labelled protein. In the treatment with additional K^+ in the nutrient solution, particularly in the treatment with 10 mM K^+, assimilation of inorganic N and protein synthesis were at least as good as in the control treatment (no salinity). In the salinity treatment without additional K^+, the K^+ concentrations in roots and shoots were greatly depressed. Additional K^+ raised the K^+ concentrations in roots and shoots to levels that were even higher than the K^+ concentration in the control treatment, and at this high cytosolic K^+ level, protein synthesis was not depressed.

TABLE 4.2
Effect of Na^+ Salinity on the K^+ Concentration in Barley Shoots and on ^{15}N Incorporation in Shoots

Treatment	K (mmol/kg fresh weight)	Total ^{15}N (mg/kg fresh weight)	% of Total ^{15}N in Protein	% of Total ^{15}N in Soluble Amino N	% Total ^{15}N in Inorganic N Compounds
Control	1260	54.4	43.9	53.1	3.0
80 mM NaCl	800	55.4	28.7	51.3	20.0
80 mM NaCl + 5 mM KCl	1050	74.2	39.9	53.8	6.3
80 mM NaCl + 10 mM KCl	1360	74.5	49.0	50.1	0.9

Note: ^{15}N solution was applied to roots of intact plants for 24 h. After pre-growth of plants in a standard nutrient solution for 5 weeks, plants were exposed to nutrient solutions for 20 days differing in Na^+ and K^+ concentrations.

Source: From H.M. Helal and K. Mengel, *Plant Soil* 51:457–462, 1979.

4.2.1.3 Ion Absorption and Transport

4.2.1.3.1 Potassium Absorption

Plant membranes are relatively permeable to K^+ due to various selective K^+ channels across the membrane. Basically, one distinguishes between low-affinity K^+ channels and high-affinity channels. For the function of the low-affinity channels, the electrochemical difference between the cytosol and the outer medium (liquid in root or leaf apoplast) is of decisive importance. The K^+ is imported into the cell for as long as the electrochemical potential in the cytosol is lower than in the outer solution. With the import of the positive charge (K^+) the electrochemical potential increases (decrease of the negative charge of the cytosol) and finally attains that of the outer medium, equilibrium is attained, and there is no further driving force for the uptake of K^+ (15). The negative charge of the cytosol is maintained by the activity of the plasmalemma H^+ pump permanently excreting H^+ from the cytosol into the apoplast and thus maintaining the high negative charge of the cytosol and building up an electropotential difference between the cytosol and the apoplast in the range of 120 to 200 mV. If the plasmalemma H^+ pumping is affected (e.g., by an insufficient ATP supply), the negative charge of the cytosol drops, and with it the capacity to retain K^+, which then streams down the electrochemical gradient through the low-affinity channel, from the cytosol and into the apoplast. Thus in roots, K^+ may be lost to the soil, which is, for example, the case under anaerobic conditions. This movement along the electrochemical gradient is also called *facilitated diffusion*, and the channels mediating facilitated diffusion are known as *rectifying channels* (16). Inwardly and outwardly directed K^+ channels occur, by which uptake and retention of K^+ are regulated (17). Their 'gating' (opening and closure) are controlled by the electropotential difference between the cytosol and the apoplast. If this difference is below the electrochemical equilibrium, which means that the negative charge of the cytosol is relatively low, outwardly directed channels are opened and vice versa. The plasmalemma H^+-ATPase activity controls the negative charge of the cytosol to a high degree since each H^+ pumped out of the cytosol into the apoplast results in an increase of the negative charge of the cytosol. Accordingly, hampering the ATPase (e.g., by low temperature) results in an outwardly directed diffusion of K^+ (18). Also, in growing plants, darkness leads to a remarkable efflux of K^+ into the outer solution, as shown in Figure 4.2. Within a period of 4 days, the K^+ concentration in the nutrient solution in which maize seedlings were grown increased steadily under dark conditions, whereas in light it remained at a low level of <10 µM (19). The outwardly directed channels may be blocked by Ca^{2+} (20). The blocking may be responsible for the so-called *Viets effect* (21), which results in an enhanced net uptake of potassium through a decrease in K^+ efflux (22).

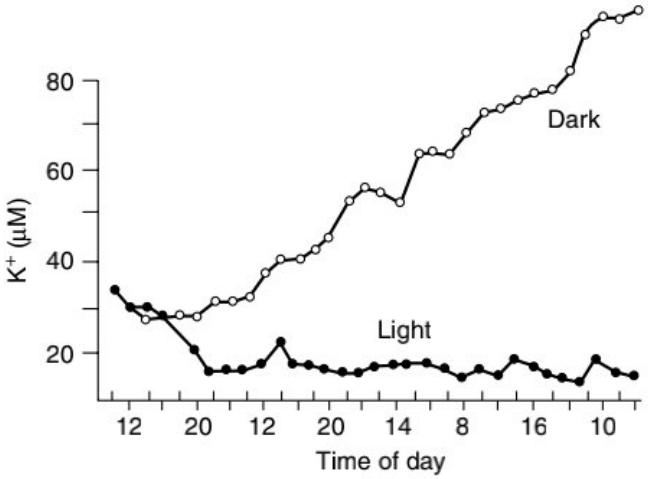

FIGURE 4.2 Potassium concentration changes in the nutrient solution with young intact maize plants exposed to light or dark over 4 days. (Adapted from K. Mengel, in *Frontiers in Potassium Nutrition: New Perspectives on the Effects of Potassium on Physiology of Plants*. Norcross, GA: Potash and Phosphate Institute, 1999, pp. 1–11.)

4.2.1.3.2 Potassium Transport within Tissues

Opening and closure of K^+ channels are of particular relevance for guard cells (23), and the mechanism of this action is controlled by the reception of red light, which induces stomatal opening (24). Diurnal rhythms of K^+ uptake were also found by Le Bot and Kirkby (25) and by MacDuff and Dhanoa (26), with highest uptake rates at noon and lowest at midnight. Energy supply is not the controlling mechanism, which still needs elucidation (26). Owing to the low-affinity channels, K^+ can be quickly transported within a tissue, and also from one tissue to another. This feature of K^+ does not apply for other plant nutrients. The low-affinity channel transport requires a relatively high K^+ concentration in the range of >0.1 mM (17). This action is mainly the case in leaf apoplasts, where the xylem sap has K^+ concentrations > 1 mM (27). At the root surface, the K^+ concentrations may be lower than 0.1 mM, and here high-affinity K^+ channels are required, as well as low-affinity channels, for K^+ uptake.

The principle of high-affinity transport is a *symport* or a *cotransport*, where K^+ is transported together with another cationic species such as H^+ or even Na^+. The K^+–H^+ or K^+–Na^+ complex behaves like a bivalent cation and has therefore a much stronger driving force along the electrochemical gradient. Hence, K^+ present near the root surface in micromolar concentrations is taken up.

Because of these selective K^+ transport systems, K^+ is taken up from the soil solution at high rates and is quickly distributed in plant tissues and cell organelles (28). Potassium ion distribution in the cell follows a particular strategy, with a tendency to maintain a high K^+ concentration in the cytosol, the so-called *cytoplasmic potassium homeostasis*, and the vacuole functions as a storage organelle for K^+ (29). Besides the H^+-ATPase, a pyrophosphatase (V-PPase) is also located in the tonoplast, for which the substrate is pyrophosphate. The enzyme not only pumps H^+ but also K^+ into the vacuole, and thus functions in the cytoplasmic homeostasis (Figure 4.3). This mechanism is an uphill transport because the vacuole liquid is less negatively charged than the cytosol. In Table 4.3, the typical pattern of K^+ concentration in relation to K^+ supply is shown (30). The cytosolic K^+ concentration remains at a high level almost independently of the K^+ concentration in the nutrient solution, whereas the vacuolar K^+ concentration reflects that of the nutrient solution.

4.2.1.3.3 Osmotic Function

The high cytosolic K^+ concentration required for polypeptide synthesis is particularly important in growing tissues; the K^+ in the vacuole not only represents K^+ storage but also functions as an indispensable osmoticum. In most cells, the volume of the vacuole is relatively large, and its turgor is essential for the tissue turgor. The osmotic function is not a specific one as there are numerous

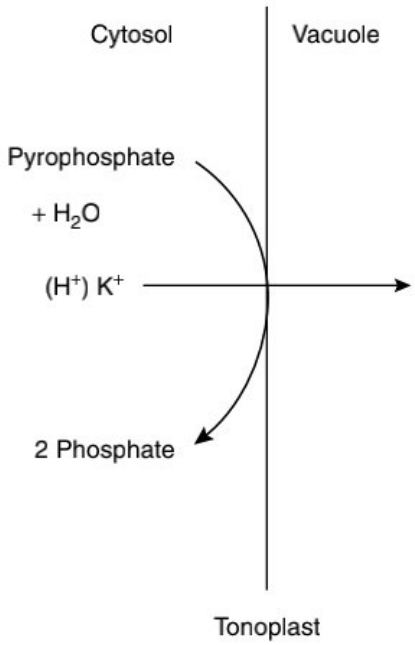

FIGURE 4.3 Pyrophosphatase located in the tonoplast and pumping H^+ or K^+ from the cytosol into the vacuole.

TABLE 4.3
K^+ Concentrations in the Cytosol and Vacuole as Related to the K^+ Concentration in the Outer Solution

	K^+ Concentration (mM)	
Outer Solution	**Vacuole**	**Cytosol**
1.2	85	144
0.1	61	140
0.01	21	131

Source: From M. Fernando et al., *Plant Physiol.* 100:1269–1276, 1992.

organic and inorganic osmotica in plants. There is a question, however, as to whether these can be provided quickly to fast-growing tissues, and in most cases it is the K^+ that is delivered at sufficient rates. In natrophilic species, Na^+ may substitute for K^+ in this osmotic function. The high vacuolar turgor in expanding cells produces the pressure potential required for growth. This pressure may be insufficient ($p < 0.6$ MPa) in plants suffering from K^+ deficiency (31). In Figure 4.4, pressure potentials and the related cell size in leaves of common bean (*Phaseolus vulgaris* L.) are shown. Pressure potentials (turgor) were significantly higher in the treatment with sufficient K^+ compared with insufficient K^+ supply. This higher turgor (ψ_p) promoted cell expansion, as shown in the lower part of Figure 4.4. From numerous observations, it is well known that plants insufficiently supplied with K^+ soon lose their turgor when exposed to water stress. In recent experiments it was found that K^+ increased the turgor and promoted growth in cambial tissue (32). The number of expanding cells derived from cambium was reduced with insufficient K^+ nutrition.

4.2.1.4 Photosynthesis and Respiration

Potassium ion transport across chloroplast and mitochondrial membranes is related closely to the energy status of plants. In earlier work, it was shown that K^+ had a favorable influence on photoreduction and photophosphorylation (33). More recently, it was found that an ATPase located in the

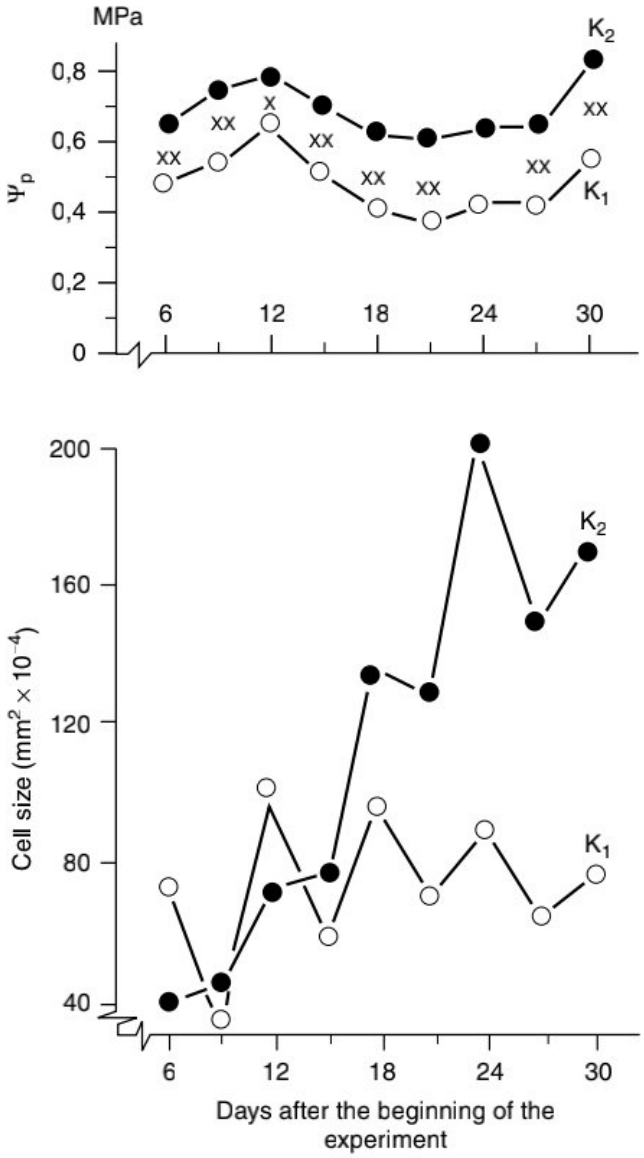

FIGURE 4.4 Pressure potential (ϕ_p) and cell size in leaves of common bean (*Phaseolus vulgaris* L.) insufficiently (K_1) and sufficiently (K_2) supplied with K^+. (Adapted from K. Mengel and W.W. Arneke, *Physiol. Plant* 54:402–408, 1982.)

inner membrane of chloroplasts pumps H^+ out of the stroma and thus induces a K^+ influx into the stroma via selective channels (34). The K^+ is essential for H^+ pumping by the envelope-located ATPase (35). Were it not for a system to pump H^+ from the illuminated chloroplast, the increase in stromal pH induced by the electron flow in the photosynthetic electron-transport chain would quickly dissipate (34). This high pH is a prerequisite for an efficient transfer of light energy into chemical energy, as was shown by a faster rate of O_2 production by photolysis in plants treated with higher K^+ concentration (36). The favorable effect of K^+ on CO_2 assimilation is well documented (37,38). An increase in leaf K^+ concentration was paralleled by an increase in CO_2 assimilation and by a decrease in mitochondrial respiration (38). Obviously, photosynthetic ATP supply substituted for mitochondrial ATP in the leaves with the high K^+ concentration. Thus, K^+ had a beneficial impact on the energy status of the plant.

4.2.1.5 Long-Distance Transport

Long-distance transport of K^+ occurs in the xylem and phloem vessels. Loading of the xylem occurs mainly in the root central cylinder, where protoxylem and xylem vessels are located adjacent to xylem

parenchyma cells. The K^+ accumulates in the parenchyma cells (Figure 4.5) and is transported from there across the plasmalemma and the primary cell wall and through pits of the secondary cell wall into the xylem vessels (39). There is evidence that the outward-rectifying channels allow a K^+ flux (facilitated diffusion) from the parenchyma cells into the xylem vessel (40,41). The release of K^+ into the xylem sap decreases its water potential and thus favors the uptake of water (42). The direction of xylem sap transport goes along the transpiration stream and hence from root to leaves. The direction of the phloem sap transport depends on the physiological conditions and goes toward the strongest sinks. These may be young growing leaves, storage cells of roots, or fleshy fruits like tomato.

Phloem sap is rich in K^+, with a concentration range of 60 to 100 mM (43). Potassium ions are important for phloem loading and thus phloem transport. It was shown that K^+ particularly promotes the uptake of sucrose and glutamine into the sieve cells at high apoplastic pH (44). These metabolites presumably are taken up into the sieve vessels via a K^+ cotransport (Figure 4.5). This process is important, since in cases in which insufficient H^+ are provided by the plasmalemma H^+ pump, and thus the apoplastic pH is too high for a H^+ cotransport of metabolites, K^+ can substitute for H^+ and the most important metabolites required for growth and storage, sucrose and amino compounds, can be transported along the phloem. Hence the apoplastic K^+ concentration contributes much to phloem loading (Figure 4.5). This occurrence is in line with the observation that the phloem flow rate in castor bean (*Ricinus communis* L.) was higher in plants well supplied with K^+ than in plants with a low K^+ status (43). The favorable effect of K^+ on the transport of assimilates to growing plant organs has been shown by various authors (45).

Potassium ions cycle via xylem from roots to upper plant parts and via phloem from leaves to roots. The direction depends on the physiological demand. During the vegetative stage, the primary meristem is the strongest sink. Here, K^+ is needed for stimulating the plasmalemma ATPase that produces the necessary conditions for the uptake of metabolites, such as sucrose and amino acids. High K^+ concentrations are required in the cytosol for protein synthesis and in the vacuole for cell expansion (Figure 4.4). During the generative or reproductive phase, the K^+ demand depends on whether or not fruits rich in water are produced, such as apples or vine berries. These fruits need K^+ mainly for osmotic balance. Organs with a low water content, such as cereal grains, seeds, nuts, and cotton bolls, do not require K^+ to a great extent. Provided that cereals are well supplied with K^+ during the vegetative stage, K^+ supply during the generative stage has no major impact on grain formation (46).

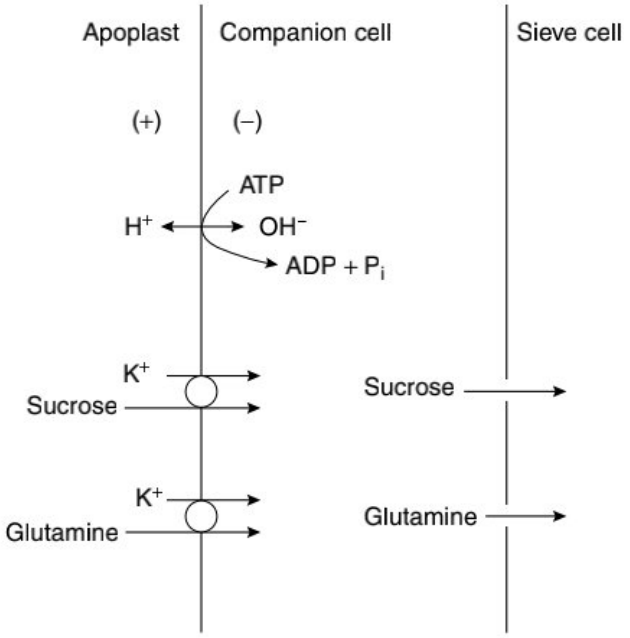

FIGURE 4.5 Cotransport of K^+/sucrose and K^+/glutamine from the apoplast into the companion cell, and from there into the sieve cell, driven by the plasmalemma ATPase.

However, for optimum grain filling, a high K^+ concentration in the leaves is required for the translocation of assimilates to the grains and for protein synthesis in these grains (47).

The generative phase of cereal growth requires hardly any K^+, but still appreciable amounts of N. In such cases, nitrate uptake of the plants is high and K^+ uptake low. The K^+ is recycled via the phloem from the leaves to the roots, where K^+ may enter the xylem again and balance the negative charge of the NO_3^- (48). Both the ionic species, K^+ and nitrate, are efficient osmotica and are thus of importance for the uptake of water into the xylem (49). In the phloem sap, K^+ balances the negative charge of organic and inorganic anions.

In storage roots and tubers, K^+ is required not only for osmotic reasons, but it may also have a more specific function. From work with sugar beet (*Beta vulgaris* L.) roots, a K^+-sucrose cotransport across the tonoplast into the vacuole, driven by an H^+/K^+ antiport cycling the K^+ back into the cytosol, was postulated (50).

4.3 DIAGNOSIS OF POTASSIUM STATUS IN PLANTS

4.3.1 Symptoms of Deficiency

The beginning of K^+ deficiency in plants is growth retardation, which is a rather nonspecific symptom and is thus not easily recognized as K^+ deficiency. The growth rate of internodes is affected (51), and some dicotyledonous species may form rosettes (52). With the advance of K^+ deficiency, old leaves show the first symptoms as under such conditions K^+ is translocated from older to younger leaves and growing tips via the phloem. In most plant species, the older leaves show chlorotic and necrotic symptoms as small stripes along the leaf margins, beginning at the tips and enlarging along leaf margins in the basal direction. This type of symptom is particularly typical for monocotyledonous species. The leaf margins are especially low in K^+, and for this reason, they lose turgor, and the leaves appear flaccid. This symptom is particularly obvious in cases of a critical water supply. In some plant species, e.g., white clover (*Trifolium repens* L.), white and necrotic spots appear in the intercostal areas of mature leaves, and frequently, these areas are curved in an upward direction. Such symptoms result from a shrinkage and death of cells (53) because of an insufficient turgor. Growth and differentiation of xylem and phloem tissue is hampered more than the growth of the cortex. Thus, the stability and elasticity of stems is reduced so that plants are more prone to lodging (54). In tomato (*Lycopersicon esculentum* Mill.) fruits insufficiently supplied with K^+, maturation is disturbed, and the tissue around the fruit stem remains hard and green (55). The symptom is called *greenback* and it has a severe negative impact on the quality of tomato.

At an advanced stage of K^+ deficiency, chloroplasts (56) and mitochondria collapse (57). Potassium-deficient plants have a low-energy status (58) because, as shown above, K^+ is essential for efficient energy transfer in chloroplasts and mitochondria. This deficiency has an impact on numerous synthetic processes, such as synthesis of sugar and starch, lipids, and ascorbate (59) and also on the formation of leaf cuticles. The latter are poorly developed under K^+ deficiency (15). Cuticles protect plants against water loss and infection by fungi. This poor development of cuticles is one reason why plants suffering from insufficient K^+ have a high water demand and a poor *water use efficiency* (WUE, grams of fresh beet root matter per grams of water consumed). Sugar beet grown with insufficient K^+, and therefore showing typical K^+ deficiency, had a WUE of 5.5. Beet plants with a better, but not yet optimum, K^+ supply, and showing no visible K^+ deficiency symptoms, had a WUE of 13.1, and beet plants sufficiently supplied with K^+ had a WUE of 15.4 (60). Analogous results were found for wheat (*Triticum aestivum* L.) grown in solution culture (61). The beneficial effect of K^+ on reducing fungal infection has been observed by various authors (54,61,62). The water-economizing effect of K^+ and its protective efficiency against fungal infection are of great ecological relevance.

Severe K^+ deficiency leads to the synthesis of toxic amines such as putrescine and agmatine; in the reaction sequence arginine is the precursor (63). The synthetic pathway is induced by a low

cytosolic pH, which presumably results from insufficient pumping of H^+ out of the cell by the plasmalemma H^+-ATPase, which requires K^+ for full activity. The reaction sequence is as follows:

- Arginine is decarboxylated to agmatine
- Agmatine is deaminated to carbamylputrescine
- Carbamylputrescine is hydrolyzed into putrescine and carbamic acid

4.3.2 Symptoms of Excess

Excess K^+ in plants is rare as K^+ uptake is regulated strictly (64). The oversupply of K^+ is not characterized by specific symptoms, but it may depress plant growth and yield (65). Excess K^+ supply has an impact on the uptake of other cationic species and may thus affect crop yield and crop quality. With an increase of K^+ availability in the soil, the uptake of Mg^{2+} and Ca^{2+} by oats (*Avena sativa* L.) was reduced (66). This action may have a negative impact for forage, where higher Mg^{2+} concentrations may be desirable. The relationship between K^+ availability and the Mg^{2+} concentrations in the aerial plant parts of oats at ear emergence is shown in Figure 4.6 (66). From the graph, it is clear that the plants took up high amounts of Mg^{2+} only if the K^+ supply was not sufficient for optimum growth. High K^+ uptake may also hamper the uptake of Ca^{2+} and thus contribute to the appearance of bitter pit in apple (*Malus pumila* Mill.) fruits (67) and of blossom-end rot in tomato fruits, with strong adverse effects on fruit quality (55).

The phenomenon that one ion species can hamper the uptake of another has been known for decades and is called *ion antagonism* or *cation competition.* In this competition, K^+ is a very strong competitor. If it is present in a relatively high concentration, it particularly affects the uptake of Na^+, Mg^{2+}, and Ca^{2+}. If K^+ is not present in the nutrient solution, the other cationic species are taken up at high rates. This effect is shown in Table 4.4 for young barley (*Hordeum vulgare* L.) plants grown in solution culture (68). In one treatment with the barley, the K^+ supply was interrupted for 8 days, having a tremendous impact on the Na^+, Mg^{2+}, and Ca^{2+} concentrations in roots and shoots as compared with the control plants with a constant supply of K^+. The sum of cationic equivalents in roots and shoots remained virtually the same. This finding is explained by the highly efficient uptake systems for K^+ as compared with uptake of the other cationic species. Uptake of K^+ leads to a partial depolarization of the plasmalemma (the cytosol becomes less negative due to the influx of K^+). This depolarization reduces the driving force for the uptake of the other cationic species, which are

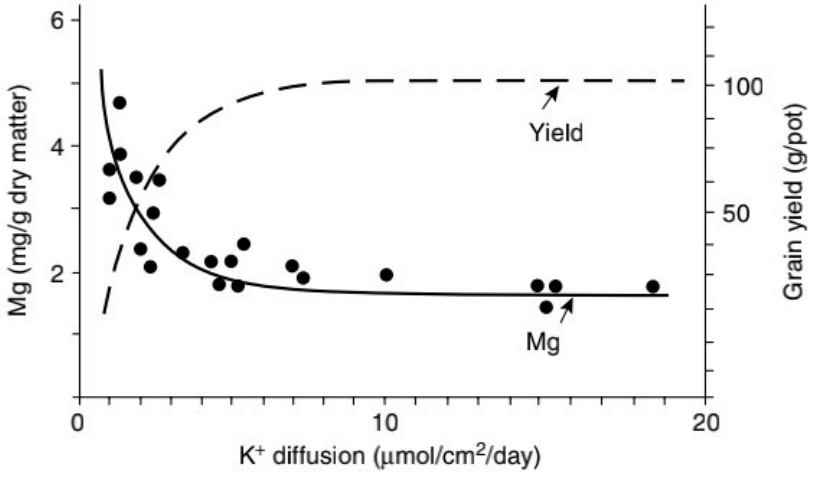

FIGURE 4.6 Effect of K^+ availability expressed as K^+ diffusion rate in soils on the Mg concentration in the aerial plant parts of oats at ear emergence and on grain yield (Adapted from H. Grimme et al., *Büntehof Abs.* 4:7–8, 1974/75.)

TABLE 4.4
Effect of Interrupting the K^+ Supply for 8 Days on the Cationic Elemental Concentrations in Roots and Shoots of Barley Plants

	Elemental Concentration (me/kg dry weight)			
	Roots		Shoots	
Element	Control	Interruption	Control	Interruption
K	1570	280	1700	1520
Ca	90	120	240	660
Mg	360	740	540	210
Na	30	780	trace	120
Total	22,050	1920	2480	2510

Source: From H. Forster and K. Mengel, Z. *Acker-Pflanzenbau* 130:203–213, 1969.

otherwise taken up by facilitated diffusion. In the roots, the absence of K^+ in the nutrient solution promoted especially the accumulation of Na^+, and the shoots showed remarkably elevated Ca^{2+} and Mg^{2+} concentrations. Owing to the increased concentrations of cations except K^+, the plants were able to maintain the cation–anion balance but not the growth rate. The interruption of K^+ supply for only 8 days during the 2-to-3-leaf stage of barley significantly depressed growth and yield; the grain yield in the control treatment was 108 g/pot, and in the K^+-interrupted treatment was 86 g/pot. This result shows the essentiality of K^+ and demonstrates that its function cannot be replaced by other cationic species.

In this context, the question to what degree Na^+ may substitute for K^+ is of interest. The osmotic function of K^+ is unspecific and can be partially replaced by Na^+, as was shown for ryegrass (*Lolium* spp.) (69) and for rice (70). The Na^+ effect is particularly evident when supply with K^+ is not optimum (71). A major effect of Na^+ can be expected only if plants take up Na^+ at high rates. In this respect, plant species differ considerably (72). Beet species (*Beta vulgaris* L.) and spinach (*Spinacia oleracea* L.) have a high Na^+ uptake potential, and in these species Na^+ may substitute for K^+ to a major extent. Cotton (*Gossypium hirsutum* L.), lupins (*Lupinus* spp. L.), cabbage (*Brassica oleracea capitata* L.), oats, potato (*Solanum tuberosum* L.), rubber (*Hevea brasiliensis* Willd. ex A. Juss.), and turnips (*Brassica rapa* L.) have a medium Na^+ uptake potential; barley, flax (*Linum usitatissimum* L.), millet (*Pennisetum glaucum* R. Br.), rape (*Brassica napus* L.), and wheat have a low Na^+ potential and buckwheat (*Fagopyrum esculentum* Moench), corn, rye (*Secale cereale* L.), and soybean (*Glycine max* Merr.) a very low Na^+ uptake potential. However, there are also remarkable differences in the Na^+ uptake potential between cultivars of the same species, as was shown for perennial ryegrass (*Lolium perenne* L.) (73). The Na^+ concentration in the grass decreased with K^+ supply and was remarkably elevated by the application of a sodium fertilizer. In sugar beet, Na^+ can partially substitute for K^+ in leaf growth but not in root growth (74). This effect is of interest since root growth requires phloem transport and thus phloem loading, which is promoted by K^+ specifically (see above). The same applies for the import of sucrose into the storage vacuoles of sugar beet (50). Also, Na^+ is an essential nutrient for some C4 species, where it is thought to maintain the integrity of chloroplasts (75). The Na^+ concentrations required are low and in the range of micronutrients.

4.4 CONCENTRATIONS OF POTASSIUM IN PLANTS

Potassium in plant tissues is almost exclusively present in the ionic form. Only a very small portion of total K^+ is bound by organic ligands via the e^- pair of O atoms. Potassium ions are

dissolved in the liquids of cell walls, cytosol, and organelles such as chloroplasts and mitochondria and especially in vacuoles. From this distribution, it follows that the higher the K^+ content of a tissue the more water it contains. These tissues have a large portion of vacuole and a low portion of cell wall material. Plant organs rich in such tissues are young leaves, young roots, and fleshy fruits. Highest K^+ concentrations are in the cytosol, and they are in a range of 130 to 150 mM K^+ (76). Vacuolar K^+ concentrations range from about 20 to 100 mM and reflect the K^+ supply (30). The high cytosolic K^+ concentration is typical for all eukaryotic cells (29), and the mechanism that maintains the high K^+ level required for protein synthesis is described above.

If the K^+ concentration of plant tissues, plant organs, or total plants is expressed on a fresh weight basis, differences in the K^+ concentration may not be very dramatic. For practical considerations, however, the K^+ concentration is frequently related to dry matter. In such cases, tissues rich in water show high K^+ concentrations, since during drying the water is removed and the K^+ remains with the dry matter. This relationship is clearly shown in Figures 4.7a to 4.7c (77). In Figure 4.7a, the K^+ concentration in the tissue water of field-grown barley is presented for treatments with or without nitrogen supply. Throughout the growing period the K^+ concentration remained at a level of about 200 mM. In the last phase of maturation, the K^+ concentration increased steeply because of water loss during the maturation process. The K^+ concentrations in the tissue water were somewhat higher than cytosolic K^+ concentrations. This difference is presumably due to the fact that in experiments the water is not removed completely by tissue pressing. In Figure 4.7b, the K^+ concentration is based on the dry matter. Here, in the first phase of the growing period the K^+ concentration increased, reaching a peak at 100 days after sowing. It then declined steadily until maturation, when the concentration increased again because of a loss of tissue water. In the treatment with nitrogen supply, the K^+ concentrations were elevated because the plant matter was richer in water than in the plants not fertilized with nitrogen. Figure 4.7c shows the K^+ concentrations in the tissue water during the growing period for a treatment fertilized with K^+ and a treatment without K^+ supply. The difference in the tissue water K^+ concentration between both treatments was high and remained fairly constant throughout the growing period, with the exception of the maturation phase.

From these findings, it is evident that the K^+ concentration in the tissue water is a reliable indicator of the K^+ nutritional status of plants, and it is also evident that this K^+ concentration is independent of the age of the plant for a long period. This fact is an enormous advantage for analysis of plants for K^+ nutritional status compared with measuring the K^+ concentrations related to plant dry matter. Here, the age of the plant matter has a substantial impact on the K^+ concentration, and the optimum concentration depends much on the age of the plant.

Until now, almost all plant tests for K^+ have been related to the dry matter because dry plant matter can be stored easily. The evaluation of the K^+ concentration in dry plant matter meets with difficulties since plant age and also other factors such as nitrogen supply influence it (77). It is for this reason that concentration ranges rather than exact K^+ concentrations are denoted as optimum if the concentration is expressed per dry weight (see Table 4.6). Measuring K^+ concentration in the plant sap would be a more precise method for testing the K^+ nutritional status of plants.

Figure 4.7c shows the K^+ concentration in tissue water during the growing period for treatments with or without K fertilizer. There is an enormous difference in tissue water K^+ concentration since the treatment without K has not received K fertilizer since 1852 (Rothamsted field experiments). Hence, potassium deficiency is clearly indicated by the tissue water K^+ concentration. The increase in K^+ concentration in the late stage is due to water loss.

If the K^+ supply is in the range of deficiency, then the K^+ concentration in plant tissue is a reliable indicator of the K^+ nutritional status. The closer the K^+ supply approaches to the optimum, the smaller become the differences in tissue K^+ concentration between plants grown with

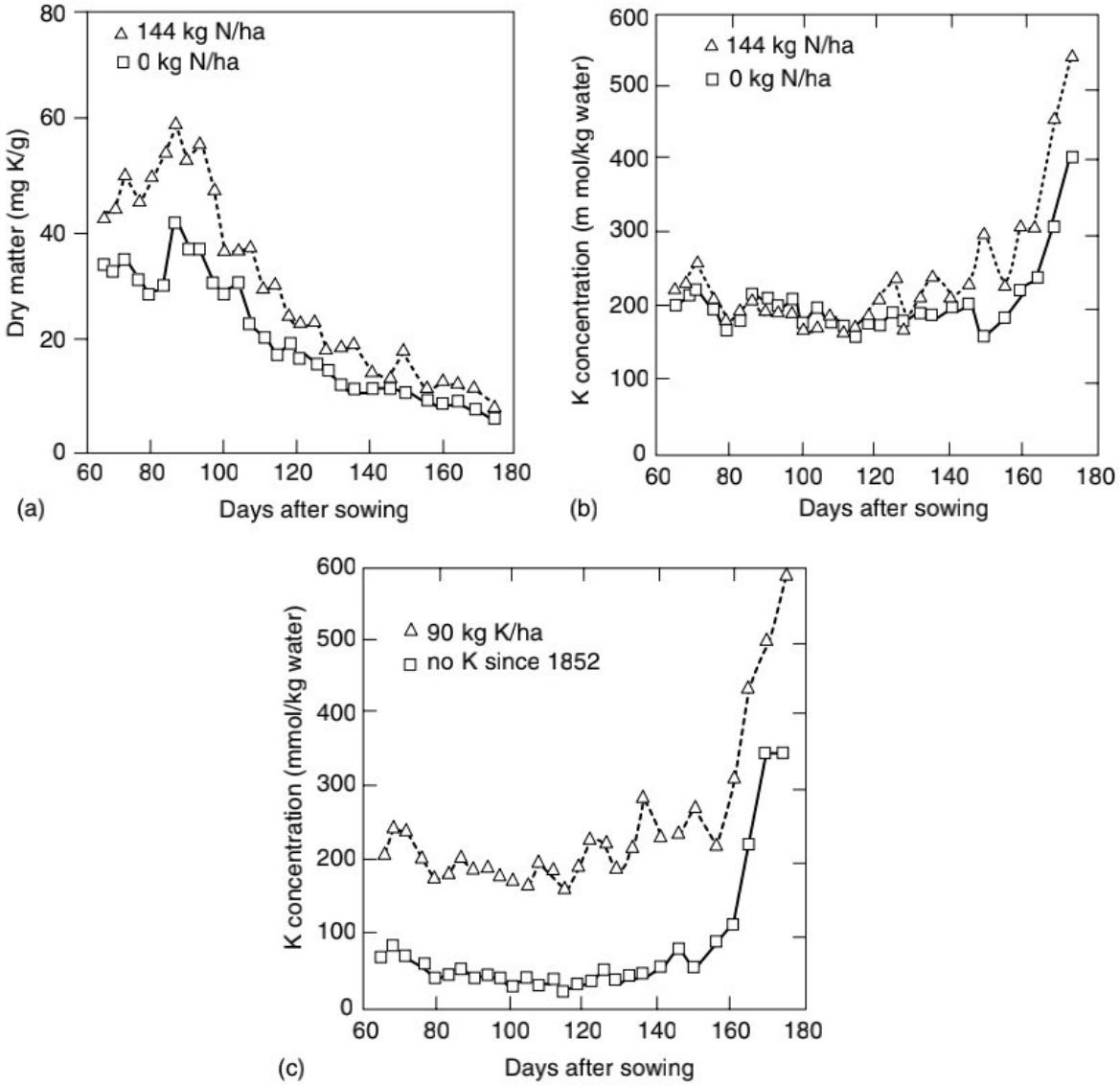

FIGURE 4.7 Potassium concentration in aboveground barley throughout the growing season of treatments with and without N supply (a) in the dry matter, (b) in the tissue water, and (c) in the tissue water with or without fertilizer K. (Adapted from A.E. Johnston and K.W. Goulding, in *Development of K Fertilizer Recommendations*. Bern: International Potash Institute, 1990, pp. 177–201.)

suboptimum and optimum supply. Such an example is shown in Table 4.5 (65). Maximum fruit yield was obtained in the K2 treatment at K^+ concentrations in the range of 25 to 35 mg K/g dry matter (DM). In the K^+ concentration range of 33 to 42 mg K/g DM, the optimum was surpassed.

The optimum K^+ concentration range for just fully developed leaves of 25 to 35 mg K/g DM, as noted for tomatoes, is also noted for fully developed leaves of other crop species, as shown in Table 4.6 (52). For cereals at the tillering stage, the optimum range is 35 to 45 mg K/g DM. From Table 4.5, it is evident that stems and fleshy fruits have somewhat lower K^+ concentrations than other organs. Also, roots reflect the K^+ nutritional status of plants, and those insufficiently supplied with K^+ have extremely low K^+ concentrations. Young roots well supplied with K^+ have even higher K^+ concentrations in the dry matter than well-supplied leaves (see Table 4.5). The K^+ concentrations for mature kernels of cereals including maize ranges from 4 to 5.5 mg/g, for rape seed from 7 to 9 mg/g, for sugar beet roots from 1.6 to 9 mg/g, and for potato tubers from 5 to 6 mg/g.

TABLE 4.5
Potassium Concentrations in Tomato Plants Throughout the Growing Season Cultivated with Insufficient K (K1), Sufficient K (K2), or Excess K (K3)

		Harvest Date					
		May 7	June 30	July 14	July 28	Aug 11	Aug 28
Plant Part		Potassium Concentration (mg K/g dry weight)					
Leaves	K1		10	13	15	10	11
	K2	29	25	34	31	30	35
	K3		33	41	40	39	41
Fruits	K1		22	22	23	18	18
	K2		28	30	28	26	26
	K3		27	27	33	29	28
Stems	K1		14	13	12	8	7
	K2	28	26	26	28	24	24
	K3		26	31	34	32	32
Roots	K1		8	12	6	4	5
	K2	17	47	44	22	27	43
	K3		43	52	44	37	39

Source: M. Viro, *Büntehof Abs*. 4:34–36, 1974/75.

TABLE 4.6
Range of Sufficient K Concentrations in Upper Plant Parts

Plant Species	Concentration Range (mg K/g DM)
Cereals, young shoots 5–8 cm above soil surface	
Wheat (*Triticum aestivum*)	35–55
Barley (*Hordeum vulgare*)	35–55
Rye (*Secale cereale*)	28–45
Oats (A*vena sativa*)	45–58
Maize (*Zea mays*)[a] at anthesis near cob position	20–35
Rice (*Oryza sativa*)[a] before anthesis	20–30
Dicotyledonous field crops	
Forage and sugar beets (*Beta vulgaris*)[a]	35–60
Potatoes (*Solanum tuberosum*)[a] at flowering	50–66
Cotton (*Gossypium*), anthesis to fruit setting	17–35
Flax (*Linum usitatissimum*), 1/3 of upper shoot at anthesis	25–35
Rape (*Brassica napus*)[a]	28–50
Sunflower (*Helianthus annuus*)[a] at anthesis	30–45
Faba beans (*Vicia faba*)[a] at anthesis	21–28
Phaseolus beans (*Phaseolus vulgaris*)	20–30
Peas (*Pisum sativum*)[a] at anthesis	22–35
Soya bean (*Glycine max*)	25–37
Red clover (*Trifolium pratense*)[a] at anthesis	18–30
White clover (*Trifolium repens*) total upper plant part at anthesis	17–25
Alfalfa (*Medicago sativa*) shoot at 15 cm	25–38
Forage grasses	
Total shoot at flowering 5 cm above soil surface, *Dactylis glomerata*, *Poa pratensis*, *Phleum pratense*, *Lolium perenne*, *Festuca pratensis*	25–35

TABLE 4.6 (*Continued*)

Plant Species	Concentration Range (mg K/g DM)
Vegetables	
Brassica species[a] *Brassica oleracea botrytis*, *B. oleracea capita*, *B. oleracea gemmifera*, *B. oleracea gongylodes*	30–42
Lettuce (*Lactuca sativa*)[a]	42–60
Cucumber (*Cucumis sativus*)[a] at anthesis	25–54
Carrot (*Daucus carota sativus*)[a]	27–40
Pepper (*Capsicum annuum*)[a]	40–54
Asparagus (*Asparagus officinalis*) fully developed shoot	15–24
Celery (*Apium graveolens*)[a]	35–60
Spinach (*Spinacia oleracea*)[a]	35–53
Tomatoes (*Lycopersicon esculentum*)[a] at first fruit setting	30–40
Watermelon (*Citrullus vulgaris*)[a]	25–35
Onions (*Allium cepa*) at mid vegetation stage	25–30
Fruit trees	
Apples (*Malus sylvestris*) mid-positioned leaves of youngest shoot	11–16
Pears (*Pyrus domestica*) mid-positioned leaves of youngest shoot	12–20
Prunus species[a], mid-positioned leaves of youngest shoots in summer *P. armeniaca*, *P. persica*, *P. domestica*, *P. cerasus*, *P. avium*	20–30
Citrus species[a], in spring shoots of 4–7 months, *C. paradisi*, *C. reticulata*, *C. sinensis*, *C. limon*	12–20
Berry fruits[a]	
From anthesis until fruit maturation *Fragaria ananassa*, *Rubus idaeus*, *Ribes rubrum*, *Ribes nigrum*, *Ribes grossularia*	18–25
Miscellaneous crops	
Vine (*Vitis vinifera*), leaves opposite of inflorescence at anthesis	15–25
Tobacco (*Nicotiana tabacum*)[a] at the mid of the vegetation season	25–45
Hop (*Humulus lupulus*)[a] at the mid of the vegetation season	28–35
Tea (*Camellia sinensis*)[a] at the mid of the vegetation season	16–23
Forest trees	
Coniferous trees, needles from the upper part of 1- or 2-year-old shoots, *Picea excelsa*, *Pinus sylvestris*, *Larix decidua*, *Abies alba*	6–10
Broad-leaved trees[a] of new shoots, species of *Acer*, *Betula*, *Fagus*, *Quercus*, *Fraxinus*, *Tilia*, *Populus*	12–15

[a]Youngest fully developed leaf.

Source: W. Bergmann, Ernährungsstörungen bei Kulturpflanzen, 3rd ed. Jena: Gustav Fischer Verlag, 1993, pp. 384–394.

4.5 ASSESSMENT OF POTASSIUM STATUS IN SOILS

4.5.1 Potassium-Bearing Minerals

The average potassium concentration of the earth's crust is 23 g/kg. Total potassium concentrations in the upper soil layer are shown for world soils and several representative soil groups in Table 4.7 (78). The most important potassium-bearing minerals in soils are alkali feldspars (30 to 20 g K/kg), muscovite (K mica, 60 to 90 g K/kg), biotite (Mg mica, 36 to 80 g K/kg), and illite (32 to 56 g K/kg). These are the main natural potassium sources from which K^+ is released by weathering and which feed plants. The basic structural element of feldspars is a tetrahedron forming a Si—Al–O framework in which the K^+ is located in the interstices. It is tightly held by covalent bonds (79). The weathering of the mineral begins at the surface and is associated with the release of K^+. This process is promoted by very low K^+ concentrations in the soil solution in contact with the mineral surface, and these low concentrations are

TABLE 4.7
Total K Concentrations in Some Soil Orders

Soil Order	Concentration of K (mg/g soil)
Entisols	26.3 ± 0.6
Spodosols	24.4 ± 0.5
Alfisol	11.7 ± 0.6
Mollisol	17.2 ± 0.5

Source: P.A. Helmke, in M.E. Sumner ed., *Handbook of Soil Science*, London: CRC Press, 2000, pp. B3-B24.

produced by K^+ uptake by plants and microorganisms and by K^+ leaching. The micas are phyllosilicates (80) and consist of two Si-Al-O tetrahedral sheets between which an M-O-OH octahedral sheet is located. M stands for Al^{3+}, Fe^{2+}, Fe^{3+}, or Mg^{2+} (81). Because of this 2:1 layer structure, they are also called 2:1 minerals. These three sheets form a unit layer, and numerous unit layers piled upon each other form a mineral. These unit layers of mica and illite are bound together by K^+ (Figure 4.8). K^+ is located in hexagonal spaces formed by O atoms, of which the outer electron shell attracts the positively charged K^+. During this attraction process, the K^+ is stripped of its hydration water. This dehydration is a selective process due to the low hydration energy of K^+. This action is in contrast to Na^+, which has a higher hydration energy than K^+; the hydrated water molecules are bound more strongly and hence are not stripped off, and the hydrated Na^+ does not fit into the interlayer. The same holds for divalent cations and cationic aluminum species. This selective K^+ bond is the main reason why K^+ in most soils is not leached easily, in contrast to Na^+. Ammonium has a similar low hydration energy as K^+ and can, for this reason, compete with K^+ for interlayer binding sites (82,83). This interlayer K^+ is of utmost importance for the release and for the storage of K^+. Equilibrium conditions exist between the K^+ concentration in the adjacent soil solution and the interlayer K^+. The equilibrium level differs much between biotite and muscovite, the former having an equilibrium at about 1 mM and the latter at about 0.1 mM K^+ in the soil solution (84). For this reason, the K^+ of the biotite is much more easily released than the K^+ from muscovite, and hence the weathering rate associated with the K^+ release of biotite is much higher than that of muscovite. The K^+ release is induced primarily by a decrease of the K^+ concentration in the adjacent solution caused by K^+ uptake of plant roots, or by K^+ leaching, or by both processes. The release of K^+ begins at the edge positions and proceeds into the inner part of the interlayer. This release is associated with an opening of the interlayer because the bridging K^+ is lacking. The free negative charges of the interlayer are then occupied by hydrated cationic species (Ca^{2+}, Mg^{2+}, Na^+, cationic Al species). From this process, it follows that the interlayer K^+ is exchangeable. The older literature distinguishes between p (planar), e (edge), and i (inner) positions of adsorbed (exchangeable) K^+ according to the sites where K^+ is adsorbed, at the outer surface of the mineral, at the edge of the interlayer, or in the interlayer. It is more precise, however, to distinguish between hydrated and nonhydrated adsorbed K^+ (79), the latter being much more strongly bound than the former. With the exception of the cationic aluminum species, hydrated cationic species may be replaced quickly by K^+ originating from the decomposition of organic matter or inorganic and organic (slurry, farm yard manure) K fertilizer. The dehydrated K^+ is adsorbed and contracts the interlayers and is thus 'fixed.' The process is called *K^+ fixation*. Fixation depends much on soil moisture and is restricted by dry (and promoted by moist) soils.

It is generally believed that H^+ released by roots also contributes much to the release of K^+ from K-bearing minerals. This process, however, is hardly feasible since in mineral soils the concentration of free protons is extremely low and is not reflected by the pH because of the very efficient H^+ buffer systems in mineral soils (85). It is the decrease of the K^+ concentration in the adjacent solution that mainly drives the K^+ release (86,87). Only high H^+ concentrations ($pH < 3$) induce a remarkable release of K^+, associated with the decomposition of the mineral (88). A complete removal of the

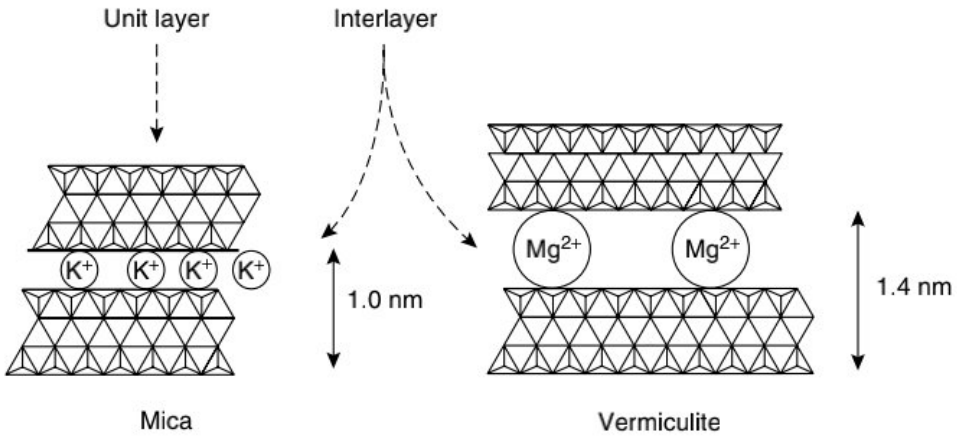

FIGURE 4.8 Scheme of a K^+-contracted interlayer of mica or illite and of vermiculite interlayer expanded by Mg^{2+}. (Adapted from K. Mengel and E.A. Kirkby, *Principles of Plant Nutrition*. 5th ed. Dordrecht: Kluwer Academic Publishers, 2001.)

interlayer K^+ by hydrated cations, including cationic aluminum species, leads to the formation of a new secondary mineral as shown in Figure 4.8 for the formation of vermiculite from mica (15). In acid mineral soils characterized by a relatively high concentration of cationic aluminum species, the aluminum ions may irreversibly occupy the interlayer sites of 2:1 minerals, thus forming a new secondary mineral called chlorite. By this process, the soil loses its specific binding sites for K^+ and hence the capacity of storing K^+ in a bioavailable form.

Under humid conditions in geological times, most of the primary minerals of the clay fraction were converted into secondary minerals because of K^+ leaching. The process is particularly relevant for small minerals because of their large specific surface. For this reason, in such soils the clay fraction contains mainly smectites and vermiculite, which are expanded 2:1 clay minerals. In soils derived from loess (Luvisol), which are relatively young soils, the most important secondary mineral in the clay fraction is the illite, which is presumably derived from muscovite. Its crystalline structure is not complete, it contains water, and its K^+ concentration is lower than that of mica (89). Mica and alkali feldspars present in the silt and sand fraction may considerably contribute to the K^+ supply of plants (90,91). Although the specific surface of these primary minerals in the coarser fractions is low, the percentage proportion of the silt and sand fraction in most soils is high and, hence, also the quantity of potassium-bearing minerals.

Cropping soils without replacing the K^+ removed from the soil in neutral and alkaline soils leads to the formation of smectites and in acid soils to the decomposition of 2:1 potassium-bearing minerals (92). Smectites have a high distance between the unit layers, meaning that there is a broad interlayer zone occupied mainly by bivalent hydrated cationic species and by adsorbed water molecules. For this reason, K^+ is not adsorbed selectively in the interlayers of smectites. The decomposition of K^+-selective 2:1 minerals results also from K^+ leaching. In addition, under humid conditions, soils become acidic, which promotes the formation of chlorite from K^+-selective 2:1 minerals. Thus, soils developed under humid conditions have a poor K^+-selective binding capacity and are low in potassium, for example, highly weathered tropical soils (Oxisols).

Organic soil matter has no specific binding sites for K^+, and therefore its K^+ is prone to leaching. Soils are generally lower in potassium, and their proportion of organic matter is higher. Soils with a high content of potassium are young soils, such as many volcanic soils, but also include soils derived from loess under semiarid conditions.

4.5.2 Potassium Fractions in Soils

Fractions of potassium in soil are (a) total potassium, (b) nonexchangeable (but plant-available) potassium, (c) exchangeable potassium, and (d) water-soluble potassium. The total potassium comprises the

mineral potassium and potassium in the soil solution and in organic matter. Soil solution potassium plus organic matter potassium represent only a small portion of the total in mineral soils. The total potassium depends much on the proportion of clay minerals and on the type of clay minerals. Kaolinitic clay minerals, having virtually no specific binding sites for K^+, have low potassium concentrations in contrast to soils rich in 2:1 clay minerals. Mean total K^+ concentrations, exchangeable K^+ concentrations, and water-soluble K^+ are shown Table 4.8 (93). Soils with mainly kaolinitic clay minerals have the lowest, and those with smectitic minerals, which include also the 2:1 clay minerals with interlayer K^+, have the highest potassium concentration. The K^+ concentration of the group of mixed clay minerals, kaolinitic and 2:1 clay minerals, is intermediate. Water-soluble K^+ depends on the clay concentration in soils and on the type of clay minerals. As can be seen from Figure 4.9, the index of soluble K^+ decreases linearly with an increase in the clay concentration in soils and the level of soluble K^+ in the kaolinitic soil group is much higher than that of the mixed soil group and of the smectitic soil group (94).

The determination of total soil potassium requires a dissolution of potassium-bearing soil minerals. The digestion is carried out in platinum crucibles with a mixture of hydrofluoric acid, sulfuric acid, perchloric acid, hydrochloric acid, and nitric acid (95). Of particular importance in the available soil potassium is the exchangeable K^+, which is obtained by extracting the soil sample with a 1 M NH_4Cl or a 1 M NH_4 acetate solution (96). With this extraction, the adsorbed hydrated K^+ and some of the nonhydrated K^+ (K^+ at edge positions) is obtained. In arable soils, the exchangeable K^+ ranges between 40 to 400 mg K/kg. Soil extraction with $CaCl_2$ solutions (125 mM) extracts somewhat lower quantities of K^+ as the Ca^{2+} cannot exchange the nonhydrated K^+, in contrast to NH_4^+ of the NH_4^+-containing extraction solutions. For the determination of the nonexchangeable K^+, not obtained by the exchange with NH_4^+ and consisting of mainly interlayer K^+ and structural K^+ of the potassium feldspars, diluted acids such as 10 mM HCl (97) or 10 mM HNO_3 are used (98). These extractions have the disadvantage in that they extract a K^+ quantity and do not assess a release rate, the latter being of higher importance for the availability of K^+ to plants.

The release of K^+ from the interlayers is a first-order reaction (83) and is described by the following equations (99):

- Elovich function: $y = a + b \ln t$
- Exponential function: $\ln y = \ln a + b \ln t$
- Parabolic diffusion function: $y = b\, t^{1/2}$

where y is the quantity of extracted K^+, a the intercept on the Y-axis, and b the slope of the curve.

In this investigation, soils were extracted repeatedly by Ca^{2+}-saturated ion exchangers for long periods (maximum time 7000 h). Analogous results are obtained with electro-ultra-filtration (EUF), in which K^+ is extracted from a soil suspension in an electrical field (100). There are two successive extractions; the first with 200 V and at 20°C (first fraction) and a following extraction (second fraction)

TABLE 4.8
Representative K Concentrations in Soil Fractions Related to Dominating Clay Minerals

	K Concentration in Clay Types (mg K/kg soil)		
K Fraction	**Kaolinitic (26 Soils)**	**Mixture (53 Soils)**	**2:1 Clay Minerals (23 Soils)**
Total	3340	8920	15,780
Exchangeable	45	224	183
Water-soluble	2	5	4

Source: From N.C. Brady, and R.R. Weil, *The Nature and Properties of Soils*. 12th ed. Englewood Cliffs, NJ: Prentice-Hall, 1999.

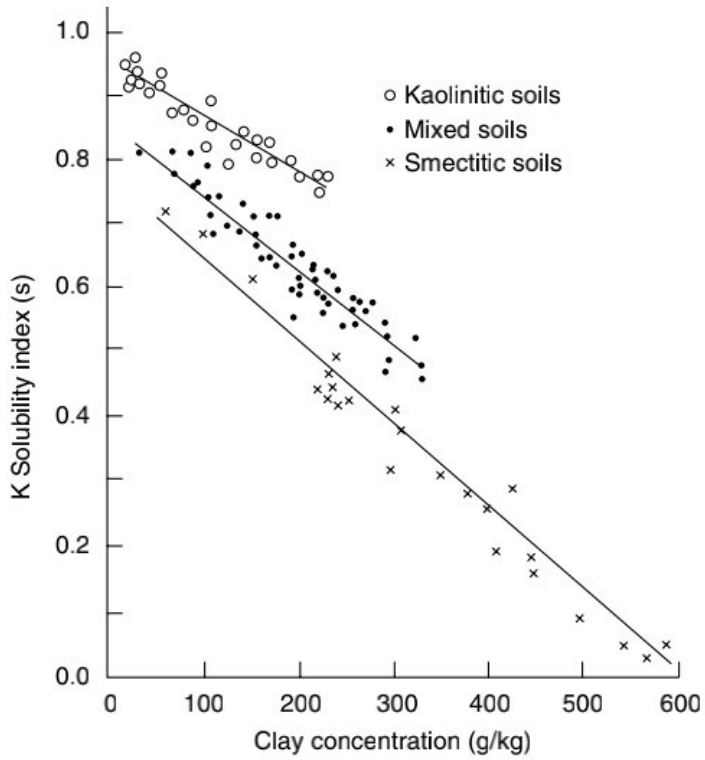

FIGURE 4.9 Potassium solubility of various soils related to their type of clay minerals (Adapted from A.N. Sharpley, *Soil Sci.* 149:44–51, 1990.)

with 400 V at 80°C. The first fraction contains the nonhydrated adsorbed K^+ plus the K^+ in the soil solution, whereas the second fraction contains the interlayer K^+. The extraction curves are shown for four different soils in Figure 4.10, from which it is clear that the K^+ release of the second fraction is a first-order reaction (101). The curves fit the first-order equation, the Elovich function, the parabolic diffusion function, and the power function, with the Elovich function having the best fit with $R^2 > 0.99$.

4.5.3 Plant-Available Potassium

Several decades ago it was assumed that the 'activity ratio' between the K^+ activity and the Ca^{2+} plus Mg^{2+} activities in the soil solution would describe the K^+ availability in soils according to the equation (102)

$$AR = K^+/\sqrt{(Ca^{2+}\ Mg^{2+})}$$

In diluted solutions such as the soil solution, the K^+ activity is approximately the K^+ concentration. It was found that this activity ratio does not reflect the K^+ availability for plants (103). Of utmost importance for the K^+ availability is the K^+ concentration in the soil solution. The formula of the AR gives only the ratio and not the K^+ activity or the K^+ concentration. The K^+ flux in soils depends on the diffusibility in the medium, which means it is strongly dependent on soil moisture and on the K^+ concentration in the soil solution, as shown in the following formula (104):

$$J = D_1\ (dc_1/dx) + D_2(dc_2/dx) + c_3v;$$

where J is the K^+ flux toward root surface, D_1 the diffusion coefficient in the soil solution, c_1 the K^+ concentration in the soil solution, D_2 the diffusion coefficient at interlayer surfaces, c_2 the K^+ concentration at the interlayer surface, x the distance, dc/dx the concentration gradient, c_3 the K^+ concentration in the mass flow water, and v the volume of the mass flow water.

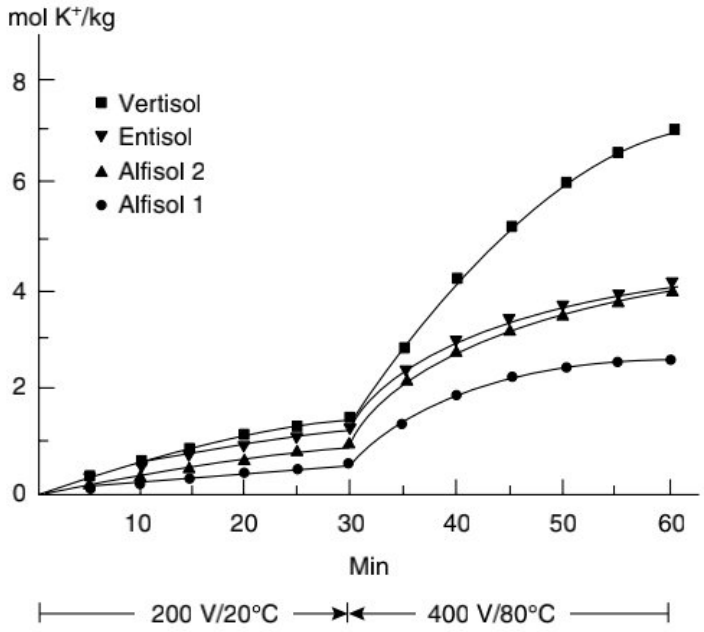

FIGURE 4.10 Cumulative K^+ extracted from four different soils by electro-ultra-filtration (EUF). First fraction extracted at 200 V and 20°C and the second fraction at 400 V and 80°C. (Adapted from K. Mengel and K. Uhlenbecker, *Soil Sci. Soc. Am. J.* 57:761–766, 1993.)

The hydrated K^+ adsorbed to the surfaces of the clay minerals can be desorbed quickly according to the equilibrium conditions, in contrast to the nonhydrated K^+ of the interlayer, which has to diffuse to the edges of the interlayer. The diffusion coefficient of K^+ in the interlayer is in the range of 10^{-13} m^2/s, whereas the diffusion coefficient of K^+ in the soil solution is about 10^{-9} m^2/s (105). The distances in the interlayers, however, are relatively short, and the K^+ concentrations are high. Therefore, appreciable amounts of K^+ can be released by the interlayers. The K^+ that is directly available is that of the soil solution, which may diffuse or be moved by mass flow to the root surface according to the equation shown above.

Growing roots represent a strong sink for K^+ because of K^+ uptake. Generally the K^+ uptake rate is higher than the K^+ diffusion, and thus a K^+ depletion profile is produced with lowest K^+ concentration at the root surface (106), as shown in Figure 4.11. This K^+ concentration may be as low as 0.10 µM, whereas in the equilibrated soil solution K^+, concentrations in the range of 500 µM prevail. Figure 4.11 shows such a depletion profile for exchangeable K^+. From this figure it is also clear that higher the value of dc/dx the higher the level of exchangeable K^+ (106). The K^+ concentration at the root surface is decisive for the rate of K^+ uptake according to the following equation (107):

$$Q = 2\pi a \alpha c t$$

where Q is the quantity of K^+ absorbed per cm root length, a the root radius in cm, α the K^+-absorbing power of the root, c the K^+ concentration at the root surface, and t the time of nutrient absorption.

The K^+-absorbing power of roots depends on the K^+ nutritional status of roots; plants well supplied with K^+ have a low absorbing power and vice versa. In addition, absorbing power depends also on the energy status of the root, and a low-energy status may even lead to K^+ release by roots (19). The K^+ concentration at the root surface also depends on the K^+ buffer power of soils, which basically means the amount of adsorbed K^+ that is in an equilibrated condition with the K^+ in solution. The K^+ buffer power is reflected by the plot of adsorbed K^+ on the K^+ concentration of the equilibrated soil solution, as shown in Figure 4.12. This relationship is known as the Quantity/Intensity relationship.

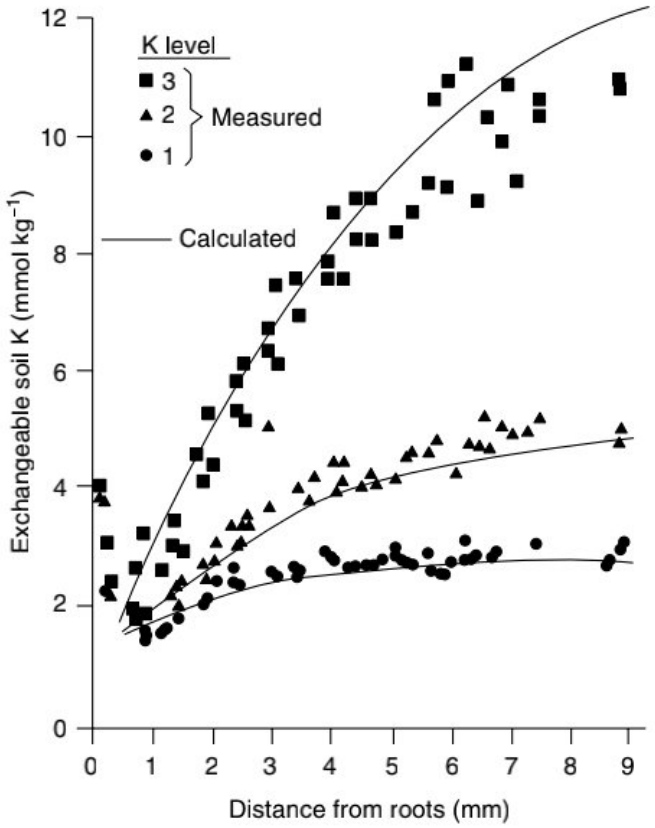

FIGURE 4.11 Potassium depletion profile produced by young rape roots in a Luvisol with three K^+ levels. (Adapted from A.O. Jungk, in *Plant Roots, the Hidden Half*. New York: Marcel Dekker, 2002, pp. 587–616.)

(Q/I relationship) in which the quantity represents the adsorbed K^+ (hydrated + nonhydrated K^+), and the intensity represents the K^+ concentration in the equilibrated soil solution. As can be seen from Figure 4.12, the quantity per unit intensity is much higher for one soil than the other, and the 'high' soil has a higher potential to maintain the K^+ concentration at the root surface at a high level than the 'medium' soil.

4.5.4 Soil Tests for Potassium Fertilizer Recommendations

The most common test for available K^+ is the exchangeable K^+ obtained by extraction with 1 M NH_4Cl or NH_4 acetate. This fraction contains mainly soil solution K^+ plus K^+ of the hydrated K^+ fraction and only a small part of the interlayer K^+. Exchangeable K^+ ranges between 40 and about 400 mg/kg soil and even more. Concentrations of <100 mg K/kg are frequently in the deficiency range; concentrations between 100 and 250 mg K/kg soil are in the range of sufficiently to well-supplied soils. Since one cannot distinguish between interlayer K^+ and K^+ from the hydrated fraction, this test gives no information about the contribution of interlayer K^+. The interpretation of the exchangeable soil test data therefore requires some information about further soil parameters, such as clay concentration and type of clay minerals. But even if these are known, it is not clear to what degree the interlayer K^+ is exhausted and to what degree mica of the silt fraction contributes substantially to the crop supply (90). Available K^+ is determined also by extraction with 1 mM HCl, by which the exchangeable K^+ and some of the interlayer K^+ are removed. Furthermore, with this technique the contribution of the interlayer K^+ also is not determined. The same is true for soil extraction with a mixture of 0.25 mM Ca lactate and HCl at a pH of 3.6 (108). Quantities of K^+ extracted with this technique are generally somewhat lower than the quantities of the exchangeable K^+

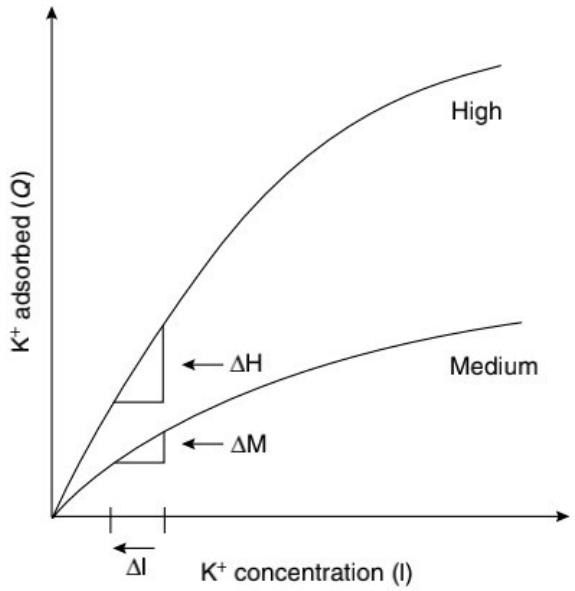

FIGURE 4.12 Potassium buffer power of a soil with a high or a medium buffer power [quantity–intensity (Q/I) ratio].

fraction. With the EUF technique, a differentiation between the nonhydrated exchangeable K^+ and the interlayer K^+ is possible, as shown in Figure 4.10. In the EUF, routine analysis extraction of the adsorbed hydrated K^+ lasts 30 minutes (200 V, 20°C); for the second fraction (400 V, 80°C), the soil suspension is extracted for only 5 minutes. The K^+ extracted during this 5-minute period is a reliable indicator of the availability of interlayer K^+ and is taken into consideration for the recommendation of the potassium fertilization rates. This EUF technique is nowadays used on a broad scale in Germany and Austria with much success for the recommendation of K fertilizer rates, particularly to crops such as sugar beet (109). With the EUF extraction procedure, not only are values for available K^+ obtained but the availability of other plant nutrients such as inorganic and organic nitrogen, phosphorus, magnesium, calcium, and micronutrients are also determined in one soil sample.

4.6 POTASSIUM FERTILIZERS

4.6.1 Kinds of Fertilizers

The most important potassium fertilizers are shown in Table 4.9 (15). Two major groups may be distinguished, the chlorides and the sulfates. The latter are more expensive than the chlorides. For this reason, the chlorides are preferred, provided that the crop is not chlorophobic. Most field crops are not sensitive to chloride and should therefore be fertilized with potassium chloride (muriate of potash). Oil palm (*Elaeis guineensis* Jacq.) and coconut (*Cocos nucifera* L.) have a specific chloride requirement, with Cl^- functioning as a kind of plant nutrient because of its osmotic effect (110). Potassium nitrate is used almost exclusively as foliar spray. Potassium metaphosphate and potassium silicate have a low solubility and are used preferentially in artificial substrates with a low K^+-binding potential to avoid too high K^+ concentrations in the vicinity of the roots. Potassium silicates produced from ash and dolomite have a low solubility, but solubility is still high enough in flooded soils to feed a rice crop (111). The silicate has an additional positive effect on rice culm stability. Sulfate-containing potassium fertilizers should be applied in cases where the sulfur supply is insufficient; magnesium-containing potassium fertilizers are used on soils low in available magnesium. Such soils are mainly sandy soils with a low cation exchange capacity.

TABLE 4.9
Important Potassium Fertilizers

Fertilizer	Formula	Plant Nutrient Concentration (%)					
		K	K_2O[a]	Mg	N	S	P
Muriate of potash	KCl	50	60	–	–	–	–
Sulfate of potash	K_2SO_4	43	52	–	–	18	–
Sulfate of potash magnesia	K_2SO_4 $MgSO_4$	18	22	11	–	21	–
Kainit	$MgSO_4$+KCl+NaCl	10	12	3.6	–	4.8	–
Potassium nitrate	KNO_3	37	44	–	13	–	–
Potassium metaphosphate	KPO_3	33	40	–	–	–	27

[a]Expressed as K_2O, as in fertilizer grades.

Source: From K. Mengel and E.A. Kirkby, *Principles of Plant Nutrition*. 5th ed. Dordrecht: Kluwer Academic Publishers, 2001.

4.6.2 Application of Potassium Fertilizers

Chlorophobic crop species should not be fertilized with potassium chloride. Such species are tobacco (*Nicotiana tabacum* L.), grape (*Vitis vinifera* L.), fruit trees, cotton, sugarcane (*Saccharum officinarum* L.), potato, tomato, strawberry (*Fragaria x ananassa* Duchesne), cucumber (*Cucumis sativus* L.), and onion (*Allium cepa* L.). These crops should be fertilized with potassium sulfate. If potassium chloride is applied, it should be applied in autumn on soils that contain sufficiently high concentrations of K^+-selective binding sites in the rooting zone. In such a case, the chloride may be leached by winter rainfall, whereas the K^+ is adsorbed to 2:1 minerals and hence is available to the crop in the following season. On soils with a medium to high *cation exchange capacity* (CEC > 120 mgmol/kg) and with 2:1 selective K^+-binding minerals, potassium fertilizers can be applied in all seasons around the year since there is no danger of K^+ leaching out of the rooting profile (Alfisols, Inceptisols, Vertisols, and Mollisols, in contrast to Ultisols, Oxisols, Spodosols, and Histosols). In the latter soils, high K^+ leaching occurs during winter or monsoon rainfall. Histosols may have a high CEC on a weight basis but not on a volume basis because of their high organic matter content. In addition, Histosols contain few K^+-selective binding sites. Under tropical conditions on highly weathered soils (Oxisols, Ultisols), potassium fertilizer may be applied in several small doses during vegetative growth in order to avoid major K^+ leaching.

The quantities of fertilizer potassium required depend on the status of available K^+ in the soil and on the crop species, including its yield level. Provided that the status of available K^+ in the soil is sufficient, the potassium fertilizer rate should be at least as high as the quantity of potassium present in the crop parts removed from the field, which in many case are grains, seeds, tubers, roots or fruits. In Table 4.10 (15), the approximate concentrations of potassium in plant parts are shown. It is evident that the potassium concentrations in cereal grains are low compared with leguminous seeds, sunflower (*Helianthus annuus* L.) and rape seed. Potassium removal by fruit trees is shown in Table 4.11. The concept of assessing fertilizer rates derived from potassium removal is correct provided that no major leaching losses occur during rainy seasons. In such cases, the K^+ originating from leaves and straw remaining on the field may be leached into the subsoil at high rates. Such losses by leaching are the case for Spodosols, Oxisols, and Ultisols. Here, besides the K^+ removed from the soil by crop plants, the leached K^+ must also be taken into consideration. On the other hand, if a soil has a high status of available K^+, one or even several potassium fertilizer applications per crop species in the rotation may be omitted. As a first approach for calculating the amount of available K^+ in the soil, 1 mg/kg soil of exchangeable K^+ equals approximately 5 kg K/ha. In this calculation, interlayer K^+ is not taken into consideration. If the soil is low in available K^+, for most soils higher fertilization rates are required than 5 kg K/ha per mg exchangeable K^+, since with the

TABLE 4.10
Quantities of Potassium Removed from the Field by Crops

Crop and Product	Removal[a]	Crop and Product	Removal[a]
Barley, grain	4.5	Soybeans, grain	18
Barley, straw	12.0	Sunflower, seeds	19
Wheat, grain	5.2	Sunflower, straw	36
Wheat, straw	8.7	Flax, seeds	8
Oats, grain	4.8	Flax, straw	12
Oats, straw	15.0	Sugarcane, aboveground matter	3.3
Maize, grain	3.9	Tobacco, leaves	50
Maize, straw	13.5	Cotton, seed + lint	8.2
Sugar beet, root	2.5	Potato, tubers	5.2
Sugar beet, leaves	4.0	Tomatoes, fruits	3.0
Rape, seeds	11	Cabbage, aboveground matter	2.4
Rape, straw	40	Oil palm, bunches for 1000 kg oil	87
Faba beans, seeds	11	Coconuts	40
Faba beans, straw	21	Bananas, fruits	4.9
Peas, seeds	11	Rubber, dry	3.8
Peas, straw	21	Tea	23

[a]kg K/1000 kg (tonne) plant matter.

Source: From K. Mengel and E.A. Kirkby, *Principles of Plant Nutrition*. 5th ed. Dordrecht: Kluwer Academic Publishers, 2001.

TABLE 4.11
Potassium Removal by Fruits of Fruit Trees with Medium Yield

Fruit	K Removed (kg/ha/year)
Pome fruits	60
Stone fruits	65
Grapes	110
Oranges	120
Lemons	115

Source: From K. Mengel and E.A. Kirkby, *Principles of Plant Nutrition*. 5th ed. Dordrecht: Kluwer Academic Publishers, 2001.

exception of Histosols and Spodosols, sites of interlayer positions must be filled up by K^+ before the exchangeable K^+ will be raised. This problem is particularly acute on K^+-fixing soils. Here, high K fertilizer rates are required, as shown in Table 4.12 (112). From the discussion, it is clear that with normal potassium fertilizer rates, the yield and the potassium concentration in leaves were hardly raised and optimum yield and leaf potassium concentrations were attained with application of 1580 kg K/ha. As soon as the K^+-fixing binding sites are saturated by K^+, fertilizer should be applied at a rate in the range of the K^+ accumulation by the crop.

Plant species differ in their capability for exploiting soil K^+. There is a major difference between monocotyledonous and dicotyledonous species, the latter being less capable of exploiting

TABLE 4.12
Effect of Potassium Fertilizer Rates on Grain Yield of Maize, Potassium Concentrations in Leaves, and Lodging for Crops Grown on a K^+-Fixing Soil

Fertilizer Applied (kg K/ha)	Leaf K (mg K/g dry weight)	Grain Yield (1000 kg/ha)	Water in Grain (%)	Lodging (%)
125	6.4	1.75	31.5	42
275	7.8	2.57	28.7	21
460	8.6	4.66	28.6	18
650	10.3	6.95	29.2	20
835	14.3	7.76	29.7	5
1580	17.1	8.98	29.7	2
2200	18.6	8.88	29.3	2
LSD < 0.05	1.0	0.65	1.5	

Source: From V. Kovacevic and V. Vukadinovic, *South Afr. Plant Soil* 9: 10–13, 1992.

soil K^+, mainly interlayer K^+, than the former. In a 20-year field trial on an arable soil derived from loess (Alfisol), the treatment without potassium fertilizer produced cereal yields that were not much lower than those in the fertilized treatment, in contrast to the yields of potatoes, faba beans (*Vicia faba* L.), and a clover-grass mixture. With these crops, the relative yields were 73, 52, and 84, respectively, with a yield of 100 in the potassium-fertilized treatment (113). This different behavior is particularly true for grasses and leguminous species. Root investigations under field conditions with perennial ryegrass and red clover (*Trifolium pratense* L.) cultivated on an Alfisol showed considerable differences in root morphology, including root hairs and root length, which were much longer for the grass (114). Hence the root–soil contact is much greater for the grass than for the clover. The grass will therefore still feed sufficiently from the low soil solution K^+ concentration originating from interlayer K^+, a concentration that is insufficient for the clover. From this result, it follows that leguminous species in a mixed crop stand, including swards of meadow and pasture, will withstand the competition with grasses only if the soil is well supplied with available K^+.

This difference between monocots and dicots in exploiting soil K^+ implies that grasses can be grown satisfactorily on a lower level of exchangeable soil K^+ than dicots. It should be taken into consideration, however, that a major depletion of interlayer K^+ leads to a loss of selective K^+-binding sites because of the conversion or destruction of soil minerals (92), giving an irreversible loss of an essential soil fertility component.

Table 4.12 shows that the optimum K^+ supply considerably decreases the percentage of crop lodging. This action is an additional positive effect of K^+, which is also true with other cereal crops. As already considered above, K^+ favors the energy status of plants and thus the synthesis of various biochemical compounds such as cellulose, lignin, vitamins, and lipids. In this respect, the synthesis of leaf cuticles is of particular interest (15). Poorly developed cuticles and also thin cell walls favor penetration and infection by fungi and lower the resistance to diseases (115).

Heavy potassium fertilizer rates also may depress the negative effect of salinity since the excessive uptake of Na^+ into the plant cell is depressed by K^+. Table 4.13 presents such an example for mandarin oranges (*Citrus reticulata* Blanco) (116), showing that the depressive effect of salinity on leaf area was counterbalanced by higher potassium fertilizer rates. The higher the relative K^+ effect, the higher is the salinity level.

TABLE 4.13
Effect of Potassium Fertilizer on the Leaf Area of Satsuma Mandarins Grown at Different Salinity Levels Induced by NaCl

	Potassium Applied (g/tree)		
	0	70	150
Salinity (dS/m)	Leaf Area (cm^2/tree)		
0.65	23.2	26.4	31.1
2.00	19.8	23.7	28.2
3.50	16.9	22.2	25.0
5.00	13.2	19.4	23.1
6.50	9.7	16.2	21.2

LSD ($P \leq 0.05$) for the K effect = 0.5.

Source: From D. Anac et al., in *Food Security in the WANA Region, the Essential Need for Balanced Fertilization*. Basel: International Potash Institute, 1997, pp. 370–377.

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