

1.4 Bioavailability of Soil Potassium

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1.4.1 Introduction

The role of K in soils is prodigious. Of the many plant nutrient-soil mineral relationships, those involving K are of major if not prime significance (Sparks and Huang, 1985).

Since the middle of the 17th century, when J. R. Glauber in The Netherlands first proposed that saltpeter (KNO_3) was the principle of vegetation, K has been recognized as being beneficial to plant growth (Russell, 1961). Glauber obtained large increases in plant growth from addition of saltpeter to the soil that was derived from the leaching of coral soils. The essentiality of K to plant growth has been known since the work of von Liebig published in 1840.

Of the major nutrient elements, K is usually the most abundant in soils (Reitemeier, 1951). Igneous rocks of the Earth's crust have higher K contents than sedimentary rocks. Of the igneous rocks, granites and syenites contain 46 to 54, basalts 7, and peridotites 2.0 g K kg^{-1} . Among the sedimentary rocks, clayey shales contain 30, whereas limestones have an average of only 6 g K kg^{-1} (Malavolta, 1985).

Mineral soils generally range between 0.04 and 3% K. Total K contents in soils range between 3000 and 100,000 kg ha^{-1} in the upper 0.2 m of the soil profile. Of this total K content, 98% is bound in the mineral form, whereas 2% is in soil solution and exchangeable phases (Schroeder, 1979; Bertsch and Thomas, 1985).

Potassium, among mineral cations required by plants, is the largest in nonhydrated size ($r = 0.133$ nm) and the number of oxygen atoms surrounding it in mineral structures is high (8 or 12), which suggests that the strength of each K-O bond is relatively weak (Sparks and Huang, 1985). Potassium has a polarizability equal to 0.088 nm³, which is higher than for Ca^{2+} , Li^+ , Mg^{2+} , and Na^+ but lower than for Ba^{2+} , Cs^+ , NH_4^+ , and Rb^+ ions (Rich, 1968, 1972; Sparks and Huang, 1985). Ions with higher polarizability are preferred in ion exchange reactions. Potassium has a hydration energy of 142.5 kJ g^{-1} ion^{-1} , which indicates little ability to cause soil swelling (Helfferich, 1962).

1.4.2 Forms of Soil K

Soil K exists in four forms in soils: solution, exchangeable, fixed or nonexchangeable, and structural or mineral (Fig. 1.13). Quantities of exchangeable, nonexchangeable, and total K in the surface layer (0–20 cm) of a variety of soils are shown in Table 1.7. Exchangeable K and nonexchangeable K levels comprise a small portion of the total K. The bulk of total soil K is in the mineral fraction (Sparks and Huang, 1985). There are equilibrium and kinetic reactions between the four forms of soil K that affect the level of soil solution K at any particular time, and thus, the amount of readily available K for plants. The forms of soil K in the order of their availability to plants and microbes are solution > exchangeable > fixed (nonexchangeable) > mineral (Sparks and Huang, 1985; Sparks, 1987).

1.4.2.1 Solution K

Soil solution K is the form of K that is directly taken up by plants and microbes and also is the form most subject to leaching in soils. Levels of soil solution K are generally low, unless recent amendments

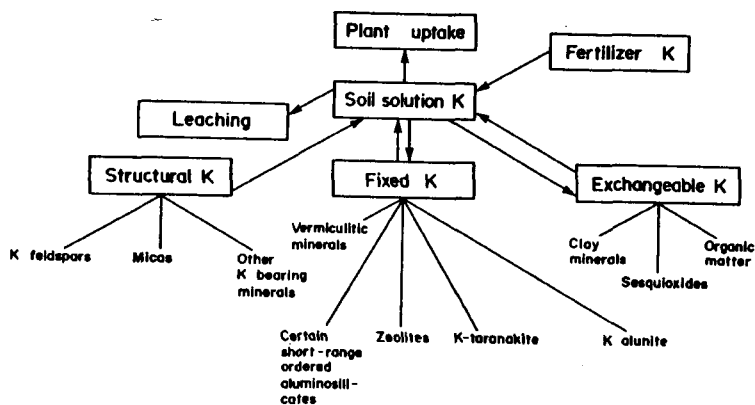


Fig. 1.13 Interrelationships of various forms of soil K [Reprinted from Sparks and Huang, 1985. Munson, (ed.) Potassium in agriculture with permission of the Soil Science Society of America]

of K have been made to the soil. The quantity of K in the soil solution varies from 2 to 5 mg K L⁻¹ for normal agricultural soils of humid regions and is an order of magnitude higher in arid region soils (Haby et al., 1990). Levels of solution K are affected by the equilibrium and kinetic reactions that occur between the forms of soil K, the soil moisture content, and the concentrations of bivalent cations in solution and on the exchanger phase (Sparks and Huang, 1985).

1.4.2.2 Exchangeable K

Exchangeable K is the portion of the soil K that is electrostatically bound as an outer-sphere complex to the surfaces of clay minerals and humic substances. It is readily exchanged with other cations and also is readily available to plants.

1.4.2.3 Nonexchangeable K

Nonexchangeable or fixed K differs from mineral K in that it is not bonded within the crystal structures of soil mineral particles. It is held between adjacent tetrahedral layers of dioctahedral and trioctahedral micas, vermiculites, and intergrade clay minerals such as chloritized vermiculite (Rich, 1972; Sparks and Huang, 1985; Sparks, 1987). Potassium becomes fixed because the binding forces between K and the clay surfaces are greater than the hydration forces between individual K⁺ ions. This results in a partial collapse of the crystal structures and the K⁺ ions are physically trapped to varying degrees, making K release a slow, diffusion controlled process (Sparks, 1987). Nonexchangeable K also can be found in wedge zones of weathered micas and vermiculites (Rich, 1964). Only ions with a size similar to K⁺, such as NH₄⁺ and H₃O⁺, can exchange K from wedge zones (Section F, Chapter 2). Large hydrated cations, such as Ca²⁺ and Mg²⁺, cannot fit into the wedge zones. Release of nonexchangeable K to the exchangeable form occurs when levels of exchangeable and soil solution K are decreased by crop removal and/or leaching and perhaps by large increases in microbial activity (Sparks, 1980).

Nonexchangeable K is moderately to sparingly available to plants (Mengel, 1985; Sparks and Huang, 1985; Sparks, 1987). Mortland et al. (1956) showed that biotite could be altered to vermiculite by plant removal of K. Schroeder and Dummler (1966) showed that the nonexchangeable K associated with some German soil illites was an important source of K to crops. The ability of plants to take up nonexchangeable K appears to be related to the plant species. Steffens and Mengel (1979) found that ryegrass (*Lolium perenne*) could take up nonexchangeable K longer without yield

Table 1.7 Potassium status of selected soils[†]

Origin of Soil	Exchangeable K	Nonexchangeable K	Total K	Source
----- (cmol _c kg ⁻¹) -----				
<i>Alfisols</i>				
Nebraska, USA	0.40	--	--	<i>Soil Taxonomy</i> (1975)
West Africa	0.46	--	3.07	Juo (1981)
<i>Inceptisols</i>				
California, USA	0.40	--	--	<i>Soil Taxonomy</i> (1975)
Maryland, USA	0.20	--	--	<i>Soil Taxonomy</i> (1975)
<i>Mollisols</i>				
Iowa, USA	0.27	--	--	<i>Soil Taxonomy</i> (1975)
Nebraska, USA	0.40	--	--	<i>Soil Taxonomy</i> (1975)
<i>Ultisols</i>				
Delaware, USA	0.33	0.49	22.5	Parker et al. (1989)
Florida, USA	0.14	0.25	2.71	Yuan et al. (1976)
Virginia, USA	0.11	0.17	6.5	Sparks et al. (1980)
West Africa	0.24	--	8.06	Juo (1981)

[†] Data are for surface soils (0-20 cm depth).

reductions, while red clover (*Trifolium pratense*) could not. This was attributed to the ryegrass having longer root length which would allow it to grow at a relatively low K concentration. A similar concentration would result in a K deficiency in red clover. It may be that the difference in root mass, root length, and root morphology between monocots and dicots explains why monocots feed better from nonexchangeable K than dicots (Mengel, 1985).

1.4.2.4 Mineral K

As noted earlier, most of the total K in soils is in the mineral form, mainly as K-bearing primary minerals such as muscovite, biotite, and feldspars. For example, in some Delaware soils, Sadusky et al. (1987) found that mineral K comprised about 98% of the total K (Table 1.8). Most of the mineral K was present as K feldspars in the sand fractions.

Common soil K-bearing minerals, in the order of availability of their K to plants, are biotite, muscovite, orthoclase, and microcline (Huang et al., 1968; Sparks, 1987). Mineral K is generally assumed to be only slowly available to plants; however, the availability is dependent on the level of K in the other forms, and the degree of weathering of the feldspars and micas constituting the mineral K fraction (Sparks and Huang, 1985; Sparks, 1987). Sadusky et al. (1987) and Parker et al. (1989a,b) have found that a substantial amount of K is released from the sand fractions of Delaware soils that are high in K feldspars. This finding, along with the large quantities of mineral K in these and other Atlantic Coastal Plain soils, could help in explaining the often observed lack of crop response to K

amendments on these soils (Liebhardt et al., 1976; Yuan et al., 1976; Sparks et al., 1980; Woodruff and Parks, 1980; Parker et al., 1989b).

1.4.3 Factors Affecting Potassium Availability

1.4.3.1 Solution-Exchangeable K Dynamics

The rate and direction of reactions between solution and exchangeable forms of K determine whether applied K will be leached into lower horizons, taken up by plants, converted into unavailable forms, or released into available forms.

The reaction rate between soil solution and exchangeable phases of K is strongly dependent on the type of clay minerals present (Sivasubramaniam and Talibudeen, 1972; Sparks et al., 1980; Sparks and Jardine, 1981, 1984; Jardine and Sparks, 1984) and the method employed to measure kinetics of K exchange (Sparks, 1989, 1995; Amacher, 1991; Sparks et al., 1996). Vermiculite, montmorillonite, kaolinite, and hydrous mica vary drastically in their ionic preferences, ion binding affinities, and types of ion exchange reactions. Such fundamental differences in these clay minerals account for the varying kinetics of K exchange.

Kinetics of K exchange on kaolinite and montmorillonite are usually quite rapid (Malcolm and Kennedy, 1969; Sparks and Jardine, 1984). An illustration of this is shown in Fig. 1.14. In the case of kaolin clays, the tetrahedral layers of adjacent clay layers are held tightly by H bonds; thus, only planar

Table 1.8 Potassium status of Delaware soils and sand fractions [From Sadusky et al. 1987. Soil Sci. Soc. Am. J. 51:1460-1465 with permission of the Soil Science Society of America]

Horizon	Depth cm	Soils				Sand fractions	
		CaCl ₂ extractable	HNO ₃ extractable	Mineral K [‡]	Total K	Total K [§]	K feldspars [¶] frequency %
		cmol kg ⁻¹					
<i>Kenansville loamy sand</i>							
Ap	0-23	0.25	0.42	35.02	35.69	30.88	9.5
Bt2	85-118	0.25	0.49	45.30	46.04	33.86	12.0
<i>Rumford loamy sand</i>							
Ap	0-25	0.33	0.49	21.67	22.51	18.62	6.7
BC	89-109	0.21	0.54	23.39	23.96	16.76	8.2
<i>Sassafras fine loamy sand</i>							
Ap	0-20	0.35	0.56	43.54	44.45	28.95	16.0
C1	84-99	0.13	0.36	45.99	46.68	36.69	24.0

[‡] Mineral K = [(total K) - (CaCl₂ ext. K + HNO₃ ext. K)].

[§] These data represent the amount of total K in the sand based on a whole soil basis.

[¶] Determined through petrographic analyses of the whole sand fractions and represents the percentage of total point counts in a given sample that were K feldspars. The remaining minerals in the sand fractions were quartz, plagioclase, and opaques.

external surface and edge sites are available for ionic exchange. With montmorillonite, the inner peripheral space is not held together by H bonds, but instead is able to swell with adequate hydration, and thus allow for rapid passage of ions into the interlayer space. Malcolm and Kennedy (1969) found that the rate of Ba exchange on kaolinite and montmorillonite was rapid with 75% of the total exchange occurring in three s.

Kinetics of K exchange on vermiculitic and micaceous minerals tend to be extremely slow. Both are 2:1 phyllosilicates with peripheral spaces that impede many ion exchange reactions. Micaceous minerals typically have a more restrictive interlayer space than vermiculite since the area between layer silicates of the former is selective for certain types of cations (e.g., K^+ , Cs^+). Bolt et al. (1963) theorized the existence of three types of binding sites for K exchange on a hydrous mica. The authors hypothesized that slow kinetics were due to internal exchange sites, rapid kinetics to external planar sites, and intermediate kinetics to edge sites.

1.4.3.2 Potassium Fixation

The phenomenon of K fixation or retention significantly affects K availability. The fact that fixation processes are limited to interlayer ions such as K^+ has been explained in terms of the good fit of K^+ ions (the crystalline radius and coordination number are ideal) in an area created by holes and adjacent oxygen layers (Barshad, 1951). The important forces involved in interlayer reactions in clays are electrostatic attractions between the negatively charged layers and the positive interlayer ions, and expansive forces due to ion hydration (Kittrick, 1966).

The degree of K fixation in clays and soils depends on the type of clay mineral and its charge density, the degree of interlayering, the moisture content, the concentration of K^+ ions as well as the concentration of competing cations, and the pH of the ambient solution bathing the clay or soil (Rich, 1968; Sparks and Huang, 1985).

The major clay minerals responsible for K fixation are montmorillonite, vermiculite, and weathered micas. In acid soils, the principal clay mineral responsible for K fixation is dioctahedral

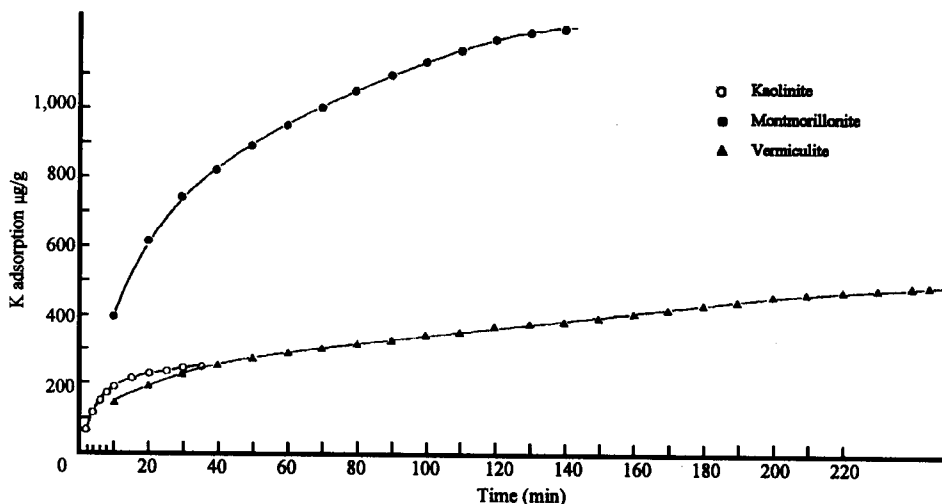


Fig. 1.14 Potassium adsorption versus time in pure systems [Reprinted from Sparks and Jardine, 1984. Comparison of kinetic equations to describe K-Ca exchange in pure and mixed systems. Soil Sci. 138:115-122 with permission of Williams and Wilkins, Baltimore, MD]

vermiculite. Weathered micas fix K under moist as well as dry conditions, whereas some montmorillonites fix K only under dry conditions (Rich, 1968).

The degree of K fixation is strongly influenced by the charge density on the layer silicate. Those with high charge density fix more K than those with low charge density (Walker, 1957). Weir (1965) noted that K fixation by montmorillonites is limited unless the charge density of the clays is high. Low charge montmorillonite (Wyoming) stays at 1.5 nm when K saturated unless it is heated (Laffer et al., 1966). Schwertmann (1962a,b) noted that soil montmorillonites have a greater capacity to fix K than do many specimen montmorillonites. Soil montmorillonites have higher charge density and a greater probability of having wedge positions near mica-like zones where the selectivity for K is high (Rich, 1968).

The importance of interlayer hydroxy Al and hydroxy Fe³⁺ material on K fixation was first noted in the classic work of Rich and Obenshain (1955). They theorized that hydroxy Al and hydroxy Fe³⁺ interlayer groups acted as props to decrease K fixation. This theory was later corroborated in the work of Rich and Black (1964) who found that the introduction of hydroxy Al groups into Libby vermiculite increased the Gapon selectivity coefficient (k_G) from 5.7 to $11.1 \times 10^{-2} \text{ L mmol}^{-1/2}$.

Wetting and drying and freezing and thawing can significantly affect K fixation (Hanway and Scott, 1957; McLean and Simon, 1958; Cook and Hutcheson, 1960). The degree of K fixation or release on wetting or drying is dependent on the type of colloid present and the level of K⁺ ions in the soil solution.

Potassium fixation by 2:1 clay minerals may be strongly influenced by the kind of adsorbed cations or the anions within the system. In studies with the silicate ion, Mortland and Gieseking (1951) found that montmorillonite clays dried with K₂SiO₃ were altered in their swelling properties and fixed K in large amounts. Hydrous mica clays also fixed large amounts of K that could not be removed with boiling HNO₃.

Volk (1934) observed a marked increase in K fixation in soils where pH was raised to about 9 or 10 with Na₂CO₃. Martin et al. (1946) showed at pH values up to 2.5 there was no fixation; between pH 2.5 and 5.5, the amount of K fixation increased very rapidly. Above pH 5.5, fixation increased more slowly. These differences in K fixation with pH were discussed by Thomas and Hipp (1968). At pH values > 5.5, Al³⁺ cations precipitate as hydroxy polycations, which increase in the number of OH groups as pH increases until they have a form like gibbsite (Thomas, 1960). At this pH (~ 8), Al³⁺ does not neutralize the charge on the clay and cannot prevent K fixation. Below pH 5.5, Al³⁺ and Al(OH)_x species dominate. Below pH 3.5, H₃O⁺ predominates (Coleman and Harward, 1953; Thomas and Hipp, 1968).

The increase in K fixation between pH 5.5 and 7.0 can be ascribed to the decreased numbers of Al(OH)_x species which decrease K fixation (Rich and Obenshain, 1955; Rich, 1960, 1964; Rich and Black, 1964). At low pH, the lack of K fixation is probably due to large numbers of H₃O⁺ and their ability to replace K as well (Rich, 1964; Rich and Black, 1964).

1.4.3.3 Potassium Release

The release of K from micas proceeds by two processes: (1) the transformation of K-bearing micas to expansible 2:1 layer silicates by exchanging the K with hydrated cations, and (2) the dissolution of the micas followed by the formation of weathering products. The relative importance of these two mechanisms depends on the stability of micas and the nature of soil environments (Sparks and Huang, 1985).

Release of K from feldspars appears to involve a rapid exchange with H, which creates a thin layer of hydrolyzed aluminosilicate. This residual layer ranges in thickness from several to a few tens of nm and seems to cause the initial nonstoichiometric release of alkali and alkaline earths relative to Si and Al. Following this step, there is continued dissolution, which removes hyperfine particles. After these

are removed, further dissolution breaks down the outer surface of the residual layer at the same rate that alkalis are replaced by H at the interface between fresh mineral surfaces and the residual layer. This releases all constituents to the solution. Release is now stoichiometric. Thus, the weathering of feldspars appears to be a surface-controlled reaction (Sparks, 1989).

A number of physiochemical and mineralogical factors govern the release of K from micas by both cation exchange reactions and dissolution processes. These include tetrahedral rotation and cell dimensions, degree of tetrahedral tilting, hydroxyl orientation, chemical composition, particle size, structural imperfections, degree of K depletion, layer charge alterations and associated reactions, hydronium ions, biological activity, inorganic cations, wetting and drying, and other factors (Sparks and Huang, 1985). This review will focus on the latter four factors.

Biological activity promotes K release from micas (Mortland et al., 1956; Boyle et al., 1967; Weed et al., 1969; Sawhney and Voight, 1969). The organisms deplete the K in the soil solution, and their action may be analogous to that of tetraphenylboron (TPB) in artificial weathering of micas. Furthermore, the overall action of organisms is more complex when organic acids are produced (Boyle et al., 1967; Spyridakis et al., 1967; Sawhney and Voight, 1969).

The importance of organic acids in weathering of rock-forming minerals has been recognized for a long time (Sprengel, 1826; Bolton, 1882; Huang and Keller, 1970). All soils contain small but measurable amounts of biochemical compounds such as organic acids. Furthermore, since the time required for soil formation can extend over a period of centuries, the cumulative effect in a soil of even very small quantities of chelating agents will be considerable. The influence of oxalic and citric acids on the dynamics of K release from micas and feldspars was studied by Song and Huang (1988). They found that the sequence of K release from K-bearing minerals by oxalic and citric acids is biotite > microcline orthoclase > muscovite.

The activity of K^+ ions in soil solution around mica particles greatly influences the release of K from micas by cation exchange. When the K level is less than the critical value, K is replaced from the interlayer by other cations from the solution. On the contrary, when the K level is greater than the critical value, the mica expands and takes K from the solution. The critical K level is highly mineral dependent, being much higher for the trioctahedral minerals (Scott and Smith, 1967; Newman, 1969; von Reichenbach, 1973; Henderson et al., 1976). The critical levels for muscovite are so low that even the K impurities in laboratory chemicals or dissolved from glassware are often sufficient to prevent any K release (Scott and Smith, 1967).

The nature and concentration of the replacing cations also influences the critical K level of the cations tested in Cl^- solutions. Rausell-Colom et al. (1965) found the critical K levels decreased in the order $Ba^{2+} > Mg^{2+} > Ca^{2+} \approx Sr^{2+}$ for the same concentration of these ions and with a constant mica particle size. The activity of all of these replacing ions in the solution phase must be much greater than that of the K for significant K release to occur. The activity of various cations in the soil solution is governed by other minerals in the soil systems, by pedogenic processes, and by anthropogenic activities.

The release of K upon drying a soil is related to the clay fraction (Scott and Hanway, 1960). When a soil is dried, the degree of rotation of weathered soil minerals, such as micas, may be changed. Thus, the K-O bond may be modified. Dehydration of interlayer cations may permit a redistribution of interlayer cations, because Ca could now compete with K for wedge sites. This seems to account for the release of K from soils upon drying. Rich (1972) found that Virginia soils, which contain hydroxy Al interlayers and appreciable amounts of K, did not release K upon drying. The presence of the hydroxy Al interlayers may block or retard the interlayer diffusion of K ions and may change the b dimension of micas, the degree of tetrahedral rotation, and the length and strength of the K-O bond.

Other factors that can affect K release from soils are leaching, redox potential (Eh), and temperature. Leaching promotes the K release from K-bearing minerals by carrying away the reaction products. Therefore, leaching accelerates the transformation of minerals, e.g., micas, to expandable 2:1 layer silicates and other weathering products if the chemistry of leaching water favors the reaction.

Redox potential of soils could influence K release from micas since it has been pointed out that the tenacity with which K is held by biotite is greater after oxidation of its structural Fe. It appears that, other factors being equal, the extent of the K release from biotite should be less in soil environments that oxidize Fe than in soil environments that reduce it. Major elements in K-bearing feldspars do not exist in more than one valence state, thus the prevailing Eh of a soil may not be of direct concern to chemical weathering of the feldspars. However, the weatherability of feldspars can be affected by complexing organic acids that are vulnerable to oxidation. Therefore, the stability of feldspars may be indirectly related to the prevailing Eh of a soil.

Increasing temperature has been shown to increase the rate of K release from biotite (Rausell-Colom et al., 1965) and K feldspars (Rasmussen, 1972). Under conditions of leaching of biotite with 0.1 mol NaCl L⁻¹, the rate of K release appears directly proportional to temperature in the range of 293 to 323 K (Mortland, 1958). Under similar leaching conditions, Mortland and Ellis (1959) observed that the log of the rate constant for K release from fixed K in vermiculite was directly proportional to the inverse of the absolute temperature.

Preheating of micas to high temperatures (1273 K) prior to TPB extraction (Scott et al., 1973) was found to enhance the rate of K extraction from muscovite, to decrease the rate for biotite, and to have little effect on phlogopite, except at very high temperatures. The decrease in K release from biotite by preheating is presumably because of oxidation of Fe at high temperatures. The more rapid rate with muscovite following heating remains unexplained.

1.4.3.4 Leaching of Potassium in Soils

Soil solution K is either leached or sorbed by plants or soils. A number of factors influence the movement of K in soils, including the CEC, soil pH and liming, method and rate of K application, and K absorption by plants (Terry and McCants, 1968; Sparks, 1980).

The ability of a soil to retain applied K is very dependent on the CEC of the soil. Thus, the amount of clay and SOM in the soil strongly influences the degree of K leaching. Soils with higher CEC have a greater ability to retain added K, whereas leaching of K is often a problem on sandy soils (Sparks and Huang, 1985).

Retention of K can often be enhanced in sandy, Atlantic Coastal Plain soils after application of lime, since in such variable charge soils, the CEC is increased as soil pH is increased. Nolan and Pritchett (1960) found that liming a Lakeland fine sand soil (thermic, coated Typic Quartzipsamment) to pH 6 to 6.5 caused maximum retentivity of applied K. Potassium was replaced by Ca on the exchange complex at higher levels of limestone application. Less leaching of K occurred at pH 6.0 to 6.5 due to enhanced substitution of K for Ca than for Al, which was more abundant at low pH. Lutrick (1963) found that K leaching occurred on unlimed but not on limed areas when 112 to 224 kg K ha⁻¹ was applied on a Eustis loamy fine sand (sandy, siliceous, thermic Psammentic Paleudult).

Movement of applied K has been related to the method of application. Nolan and Pritchett (1960) compared banded and broadcast placement of KCl applied at several rates to an Arredondo fine sand (loamy, siliceous, hyperthermic Grossarenic Paleudult) in lysimeters under winter and summer crops. For the low rate of application, cumulative K removal for both placements was only about 5.0 kg ha⁻¹.

A number of investigations have been conducted to determine the relationship of crop uptake and rate of K application to leaching of K. Jackson and Thomas (1960) applied up to 524 kg K ha⁻¹ prior to planting sweet potatoes (*Ipomoea batatas* L.) on a Norfolk sandy loam (fine loamy, siliceous,

thermic Typic Paleudult). At harvest time, soil and plant K exceeded applied K at the 131 and 262 kg K ha⁻¹ rates. However, at the 524 kg K ha⁻¹ rate, 38 kg K was unaccounted for by soil and plant K. This deficiency of K was attributed to leaching below sampling depths. During a two-year study with corn (*Zea mays* L.) on two Dothan (Typic Paleudult) soils of Virginia, Sparks et al. (1980) found that 83 and 249 kg of applied K ha⁻¹ increased the exchangeable K in the E and B2t horizons of the two soils. These increases were ascribed to leaching of applied K. The magnitude of leaching varied directly with rate of K application. No accumulation of K was found in the top 0.76 m of a Leon sand (sandy, siliceous, thermic Aeric Haplaquod) after 40 yr of heavy K fertilization (Blue et al., 1955).

1.4.4 Assessing Potassium Extractability and Availability

The extractability and availability of soil and plant K can be assessed by using chemical extractants to quantify the various forms of soil K, soil test extractants, quantity/intensity (Q/I) analyses, and plant analysis.

1.4.4.1 Chemical Extractants for Soil K Forms

Methods to determine total K and the other alkali elements in soils use acids or a high temperature fusion to decompose the soil. The most widely employed digestion techniques for total elements in soils and minerals have used combinations of HF and either H₂SO₄ or HClO₄ (Helmke and Sparks, 1996).

Exchangeable K is that K which is typically extracted with a neutral normal salt, usually 1.0 M NH₄OAc minus the water soluble K (Knudsen et al., 1982). In soils that are not saline, levels of water soluble K are minimal and can be ignored. However, in saline soils, the levels of water soluble K should be determined from a saturated extract or some similar extract and subtracted from the amount of K determined using NH₄OAc.

It should be noted that in soils that contain weathered vermiculitic and micaceous minerals wedge zones can be present that contain K. This K is not accessible to large index cations such as Ca and Mg, but can be extracted by NH₄⁺, which is of similar size to K. For example, in soils that contain wedge zones, NH₄OAc will extract more K than an extractant like 1 M CaCl₂. It is debatable whether this K is truly exchangeable. Thus, in soils containing wedge zones exchangeable K could be overestimated with NH₄OAc (Sparks and Huang, 1985; Helmke and Sparks, 1996).

There are a number of chemical methods that can be employed to extract nonexchangeable K. These include boiling HNO₃, H₂SO₄, hot HCl, electroultrafiltration, Na tetraphenylboron with EDTA, and ion exchange resins such as H and Ca saturated resins (Hunter and Pratt, 1957; Martin and Sparks, 1985; Helmke and Sparks, 1996).

The most commonly used method for extraction of nonexchangeable K is the boiling HNO₃ technique. Most researchers that use this method boil the soil in M HNO₃ for 10 min over a flame, transfer the slurry to a filter, leach the soil with dilute HNO₃, and then determine the concentration in the filtrate. One of the problems with boiling for only 10 minutes over a flame is that it is difficult to be precise about the correct boiling time, the time it takes for boiling to occur, and the vigor of boiling (Martin and Sparks, 1985). Some workers have attempted to diminish these problems by using a 386 K oil bath for 25 minutes, including heating time (Pratt, 1965). This modification is particularly useful when large numbers of samples are being analyzed. Of course, one of the major concerns with using a boiling HNO₃ procedure is the potential to cause partial dissolution of mineral forms of K.

Other researchers have used continuous leaching of the soil with dilute acids such as 0.01 M HCl or with dilute salts such as 0.1 M NaCl, repeated extractions with 3, 0.3 and 0.03 M NaCl, Sr salts, hot MgCl₂, and sodium cobaltinitrite (Martin and Sparks, 1985).

Cation exchange resins saturated with H or Ca also have been widely used to measure nonexchangeable K. These resins have high CECs and when saturated with an appropriate cation and mixed with soil and with a dilute solution, they will adsorb released K. One of the major advantages of using cation exchange resins to extract K is that they act as a sink for the released K and thus prevent an inhibition of further K release. This is a problem with many batch methods that employ dilute acids and electrolytes. One major disadvantage of cation exchange resins for extracting K is that the resins are expensive and the procedure is time consuming and tedious.

In order for electrolyte and acid solutions and cation exchange resins to be effective in extracting K, the K concentration in the solution phase must be kept very low, or K release is inhibited (Rausell-Colom et al., 1965; Wells and Norrish, 1968; Feigenbaum et al., 1981; Martin and Sparks, 1983, 1985). The critical concentration above which release is inhibited is 4 mg L^{-1} for soils in general, 2.3 to 16.8 mg L^{-1} for trioctahedral micas in dilute solution, and as low as $< 0.1 \text{ mg L}^{-1}$ for muscovite and illite (Smith and Scott, 1966; Martin and Sparks, 1985). A low enough concentration of solution K can be maintained by employing a continuous flowing extracting or exchanging solution, cation exchange resins, or Na tetraphenylboron (Scott et al., 1960).

One can quantitatively analyze for mineral K (K feldspars and micas) by using a selective dissolution method employing $\text{Na}_2\text{S}_2\text{O}_7$ fusion. The technique and method for calculating the quantities of K feldspars and micas can be found in Helmke and Sparks (1996). A semiquantitative approach for measuring mineral K is to subtract the quantity of nonexchangeable K, using the boiling HNO_3 procedure, from the quantity of total K, using the HF digestion method. One also can quantify K feldspars in the sand fraction of soil using petrographic analyses (Parker et al., 1989a).

1.4.4.2 Soil Tests for Potassium

Soil test extractants for K were developed to easily and rapidly measure K in soils and to estimate K availability. Based on the amounts of extractable K, recommendations that are based on field test calibrations can then be made on the amount of K that is needed to maximize plant yields. Soil tests for K usually estimate the quantity of solution and exchangeable K, and since acids are usually employed as extractants, some nonexchangeable and mineral K also is extracted (Wolf and Beegle, 1991). The soil tests used to measure extractable K in the United States include Mehlich I and Mehlich III procedures in the northeastern and southeastern United States, the Morgan and modified Morgan procedures in parts of the northeastern United States, the $1 \text{ M NH}_4\text{OAc}$ at pH 7 procedure in the north central United States, and the ammonium bicarbonate-DTPA extraction in the western United States. Procedures for these soil tests are fully described in Helmke and Sparks (1996) and Section D, Chapter 4.

1.4.4.3 Q/I Analysis

Schofield (1947) proposed that the ratio of the activity of cations such as K and Ca was defined by the relation $a_K/(a_{Ca})^{1/2}$ where a is the ion activity. He appears to have been the first person to apply the concepts of quantity (Q) and intensity (I) to the mineral nutrient status of soils (Schofield, 1955).

Beckett (1964a), following a consideration of the Ratio law (Schofield, 1947), suggested that the I of K in a soil at equilibrium with its soil solution could best be defined by the ratio $a_K/(a_{Ca} + a_{Mg})^{1/2}$ of the soil solution. This equilibrium activity ratio for K or AR^K (Beckett, 1964a) has often been used as a measure of K availability to plants (Sumner and Marques, 1966; le Roux and Sumner, 1968).

Beckett (1964c) suggested that exchangeable K is held by two distinct mechanisms. The majority is held by general force fields comparable with those that hold exchangeable Na or Ca. A small proportion is held at sites offering a specific binding force for K but not for Ca and Mg. The electrochemical potential of exchangeable K in the diffuse double layer dictates the chemical potential

of K in the soil solution. The K activity is also affected by the difference in electrical potential across the diffuse double layer that surrounds the exchange complex. Thus, no simple relationship exists between the activity of K in soil solution and quantity of K on the exchange phase (San Valentin et al., 1973). Moss (1967) and Lee (1973) note that a soil with a given complement of exchangeable K, Ca, and Mg gives rise to an activity ratio for K (AR^K) in the equilibrium soil solution that will be characteristic of that soil and independent of the soil-to-solution ratio and total electrolyte concentration. Moss (1967) noted the ratio depends only on K saturation and the strength of adsorption of cations.

However, the relation of the amount of exchangeable K to AR^K must be specified to accurately describe the K status of a soil. Beckett (1964b) noted that different soils showing the same value of AR^K may not possess the same capacity for maintaining AR^K while K is removed by plant roots. Therefore, one must include not only the current potential of K in the labile pool but also the form of Q/I or the way in which potential depends on quantity of labile K present. These findings brought about the classic Q/I curves where the ratio of $a_K/(a_{Ca} + a_{Mg})^{1/2}$ is related to the change in exchangeable K to obtain the effect of quantity (exchangeable K) on intensity. The Q/I concept has been widely promulgated in the scientific literature to investigate the K status of soils (Evangelou et al., 1994).

The traditional method for Q/I analyses involves equilibrating a soil with solutions containing a constant amount of $CaCl_2$ and increasing the amounts of KCl (Beckett, 1964a). The soil gains or loses K to achieve the characteristic AR^K of the soil or remains unchanged if its AR^K is the same as the equilibrating solution. The AR^K values are then plotted versus the gain or loss of K to form the characteristic Q/I curve. From the Q/I plot, one can obtain several parameters to characterize the K status of a soil. The AR^K when the Q factor or ΔK equals zero is a measure of the degree of K availability at equilibrium or AR^K_e . The value of ΔK when $AR^K = 0$ is a measure of labile or exchangeable K in soils (ΔK°). The slope of the linear portion of the curve gives the potential buffering capacity of K (PBC^K) and is proportional to the CEC of the soil. The number of specific sites for K (K_x) is the difference between the intercept of the curved and linear portion of the Q/I plot at $AR^K = 0$ (Beckett, 1964b; Sparks and Liebhardt, 1981; Evangelou et al., 1994).

The traditional method described above is too time consuming for routine analyses. Advances in ion selective electrode technology (ISE) have allowed for more rapid Q/I analysis (Evangelou et al., 1994). Parra and Torrent (1983) developed a ISE simplified Q/I method whereby a single K-ISE in an electrochemical cell with liquid junction was employed to quantitate the K concentration (C_K) in equilibrated soil suspensions based on a successive addition procedure. The values of AR^K were estimated based on the expression, $AR^K = (11.5 - 0.3b) C_K + 22 \times 10^{-6}$, where b is the CEC ($cmol_c kg^{-1}$) based on the weight of the soil samples used. The method of Parra and Torrent (1983) is quicker than the traditional Q/I method because equilibration time is reduced to 10 min compared to 24 h for the traditional method. Parra and Torrent (1983) achieved results with their modified procedure that were comparable to the traditional method. Wang et al. (1988) modified the procedure of Parra and Torrent (1983) by making direct measurements of CR_K [concentration ratio: $C_K/(C_{Ca+Mg})^{1/2}$] values with Ca and K-ISEs in an electrochemical cell with or without liquid junction.

1.4.4.4 Plant K Analysis

Plant K analysis will not be discussed in any detail in this review. For extensive discussions on plant analysis, the reviewer is referred to chapters in Westerman (1990). Table 1.9 lists the critical level or concentration of K for various agronomic crops. These levels are usually determined by relating yield (e.g., % of maximum yield or growth rate) to nutrient concentration ($g kg^{-1}$) for a specific plant part sampled at a given stage of development (Munson and Nelson, 1990). This method is based on the principle that if an element such as K is deficient in a plant, growth rates and yield will be decreased.

Table 1.9 Critical K concentrations in agronomic crops [From Westerman, 1990. Soil testing and plant analysis. Soil Science Society of America with permission]

Crop	Time of Sampling	Plant Part	Critical Concentration [‡] g kg ⁻¹
Sugarbeet		Blade	10
Cotton		Leaves	< 9-15
Wheat	Jointing (GS6)	Total tops	20-25
	Early Boot (GS9)	Total tops	15-20
Rice	Flag Leaf to Mid-Tillering		10-14
Corn	At tassel	Ear leaf	19
	At tassel	Leaves	17-27
	At silk	Sixth leaf from base	13
	At silk	Leaf opposite and just below ear shoot	20
Grain sorghum	Full heading	Second blade below apex	18
Alfalfa		Whole top	8-22
Red Clover		Tops	15-22.5
Bermudagrass		Tops	13-15
Orchardgrass		Tops	23-25
Tall Fescue		Tops	24-38
Kentucky Bluegrass		Tops	16-20

[‡] Critical concentration is that nutrient concentration at which plant growth begins to decrease in comparison with plants above the critical concentration.

If one adds increasing amounts of K, the concentration of the element in the plant or plant part increases until an optimum level is attained. Using this approach, growth or yield is expressed as a percentage of the maximum. The zone between the deficient and optimum concentration can be referred to as the transition zone (Ulrich and Hills, 1967). Ulrich and Hills (1967) referred to the transition zone as the zone between nutrient concentrations that produced a 20% reduction in growth or yield and continues to those that cause optimum or 100% in the maximum yield. Dow and Roberts (1982) refer to this latter zone as the critical range where researchers select the yield reduction and nutrient concentrations that are acceptable.

1.4.5 References

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