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Chapter 7
Considering Soil Potassium Pools with Dissimilar Plant Availability

Michael J. Bell, Michel D. Ransom, Michael L. Thompson, Philippe Hinsinger, Angela M. Florence, Philip W. Moody, and Christopher N. Guppy

Abstract Soil potassium (K) has traditionally been portrayed as residing in four functional pools: solution K, exchangeable K, interlayer (sometimes referred to as "fixed" or "nonexchangeable") K, and structural K in primary minerals. However, this four-pool model and associated terminology have created confusion in understanding the dynamics of K supply to plants and the fate of K returned to the soil in fertilizers, residues, or waste products. This chapter presents an alternative framework to depict soil K pools. The framework distinguishes between micas and feldspars as K-bearing primary minerals, based on the presence of K in interlayer positions or three-dimensional framework structures, respectively; identifies a pool of K in neoformed secondary minerals that can include fertilizer reaction products; and replaces the "exchangeable" K pool with a pool defined as "surface-adsorbed" K, identifying where the K is located and the mechanism by which it is

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held rather than identification based on particular soil testing procedures. In this chapter, we discuss these K pools and their behavior in relation to plant K acquisition and soil K dynamics.

7.1 Introduction

Traditionally, soil potassium (K) has been depicted as occurring in four pools—soil solution K, exchangeable K, interlayer K, and mineral or structural K (Barber 1995). Various publications have estimated the relative sizes of these traditional K pools (for example, Öborn et al. 2005; Hinsinger 2006) with K in primary minerals (90–98% of total soil K) the dominant form of soil K. The K most readily available for plant uptake [exchangeable K (1–2%) and solution K (0.1–0.2%)] represents only a very small fraction of the total soil K, although interlayer K in secondary minerals can also be a significant proportion (1–10%, depending on mineralogy). However, this terminology creates some confusion for a number of reasons. In particular, exchange reactions between the solid and the soil solution phases can result in reversible K movement to or from both surface and interlayer positions of clay minerals, while interlayer K can be found in both primary minerals (e.g., micas) as well as in secondary minerals (e.g., illite). Furthermore, soils with a history of repeated applications of high-K waste materials and/or high rates of band-applied compound fertilizers containing K may also contain neoformed secondary K minerals with poorly understood behavior in terms of K bioavailability.

These considerations have led to the development of an alternative framework to depict soil K pools (Fig. 7.1). There are three key characteristics of this conceptual diagram that differ from the traditional four-pool model. The first is the distinction between micas and feldspars as K-bearing primary minerals, which is based on the presence of K in interlayer positions between mineral layers in phyllosilicate minerals (micas and partially weathered micas) or in the three-dimensional structural frameworks of tectosilicates (feldspars). The flux from structural K in feldspars and micas to soil solution K is unidirectional. However, the flux from interlayer K to soil solution K can be bidirectional for partially weathered micas. The second characteristic is the identification of a pool of K in neoformed secondary minerals that can include fertilizer reaction products. The third characteristic is the replacement of the "exchangeable" K pool with a pool defined as "surface-adsorbed" K. The "surface-adsorbed K" concept clearly identifies where the K is located and the mechanism by which it is held. It avoids ascribing possible locations (surfaces, wedge, and interlayer positions) on the basis of particular soil testing procedures.

Quantification of K in these different K pools, particularly in relation to K available for plant acquisition in time frames relevant to individual crop or pasture seasons (i.e., K bioavailability, Chap. 4), is challenging. This is due to both the limitations of current diagnostic soil testing methods (Chap. 8) and the need to consider crop, season, and soil-specific factors that regulate root dynamics, rhizosphere conditions, and soil moisture dynamics (Chap. 4). In this chapter, we will

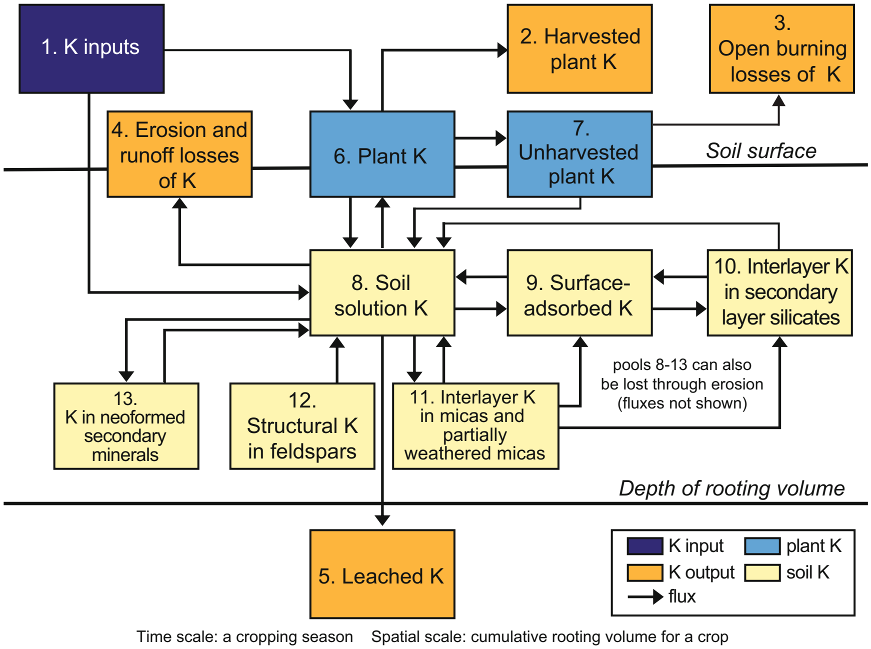


Fig. 7.1 Diagrammatic representation of the K cycle, identifying the soil K pools (rectangles) discussed in this chapter. The arrows denote fluxes of K in soil–plant systems

discuss these K pools and their behavior in relation to plant K acquisition and soil K dynamics.

7.2 Solution Potassium and Potassium Activity

Soil solution K is *the quantity of K dissolved in the aqueous liquid phase of the soil* (Soil Science Glossary Terms Committee 2008). Unless mineral soils have been recently fertilized or amended with manure, soil solution K concentrations are typically low (100–1000 μM) because of selective adsorption of K by some clay minerals (Hinsinger 2006). Leaching losses of K are usually low, but they may occur when K inputs exceed the sum of K holding capacity and plant uptake (Chap. 3) or where preferential flow of water occurs.

As the monovalent cation, K^+ in the soil solution is the form taken up directly by plants (Sparks 1987), with concentrations determined by reactions with solid-phase forms of soil K and with other cations on the exchange complex and in the soil solution, and by soil moisture content (Sparks and Huang 1985). The small amount of K^+ present in the soil solution in all except recently fertilized soils suggests that the rate of K uptake from this pool is likely to be limited as solution K^+ stocks are rapidly depleted (Barrow 1966). Therefore, factors that control solution K concentration ultimately influence uptake rates. These factors include the rates of K diffusion in the soil solution from surrounding, undepleted soil, and the quantity of readily desorbable K on the exchange complex (Evangelou et al. 1994; Barber 1995). The moderating effects of other major soil solution cations (Ca, Mg, and Na) on the kinetics of soil solution K replenishment and subsequent uptake of K by plant roots have been the subject of extensive research, reviewed by Sparks (1987) and Evangelou et al. (1994). This research has shown that the complex interactions among soil solution chemistry, rooting density, and the subsequent competition for K uptake make extrapolation beyond the specific conditions of individual experiments difficult (Barber 1995). There is, however, a general recognition of the importance of cation exchange capacity (CEC) on both the ability of the soil to buffer soil solution K (sometimes measured as buffer capacity, BC_K) and also on K supply to the root (Barber 1981). As CEC increases, there is less K available for plant uptake, even in soils with the same concentrations of exchangeable K (Bell et al. 2009). These relationships have currently not been well defined.

7.3 Surface-Adsorbed Potassium

Surface-adsorbed K is *the quantity of K associated with negatively charged sites on: soil organic matter; planar surfaces of phyllosilicate minerals; and surfaces of iron and aluminum oxides*. However, the location of those charge surfaces and the specificity of those sites for K varies greatly. An example of the contrasting sites was provided by Mengel (1985) for a weathered grain of mica (Fig. 7.2). The **p-position** is *a site on the planar surfaces of phyllosilicate minerals where hydrated* K^+ *is adsorbed*. In these positions, K ions tend to retain a hydration shell, be weakly and nonspecifically bound, and be in rapid dynamic equilibrium with soil solution K. Exchange reactions in response to altered soil solution concentrations occur very quickly. For example, cation exchange reactions on montmorillonite have been measured to be complete in less than 10^{-1} s (Tang and Sparks 1993), but modelled to be complete much faster, less than 5×10^{-10} s (Bourg and Sposito 2011). As a result, this K pool is considered to be in a form immediately available for movement into the soil solution in response to depletion by plant root uptake (Barber 1995).

Planar surface sorption sites, along with carboxylate and phenolate groups in soil organic matter and negatively charged sites on the surfaces of iron and aluminum oxides, tend to show a greater affinity for divalent cations like Ca^{2+} and Mg^{2+} (Hinsinger 2006). This means that application of soil amendments (lime, limestone, or dolomite), or even frequent rainfall or irrigation in well-drained soils, can result in displacement of surface-adsorbed K from the charged surface by other cations and possible loss from the rooting zone through leaching. Other sorption sites illustrated in Fig. 7.2, the e- and i-positions, show greater affinity for K and a slower interaction with components of the soil solution. These sites are discussed below.

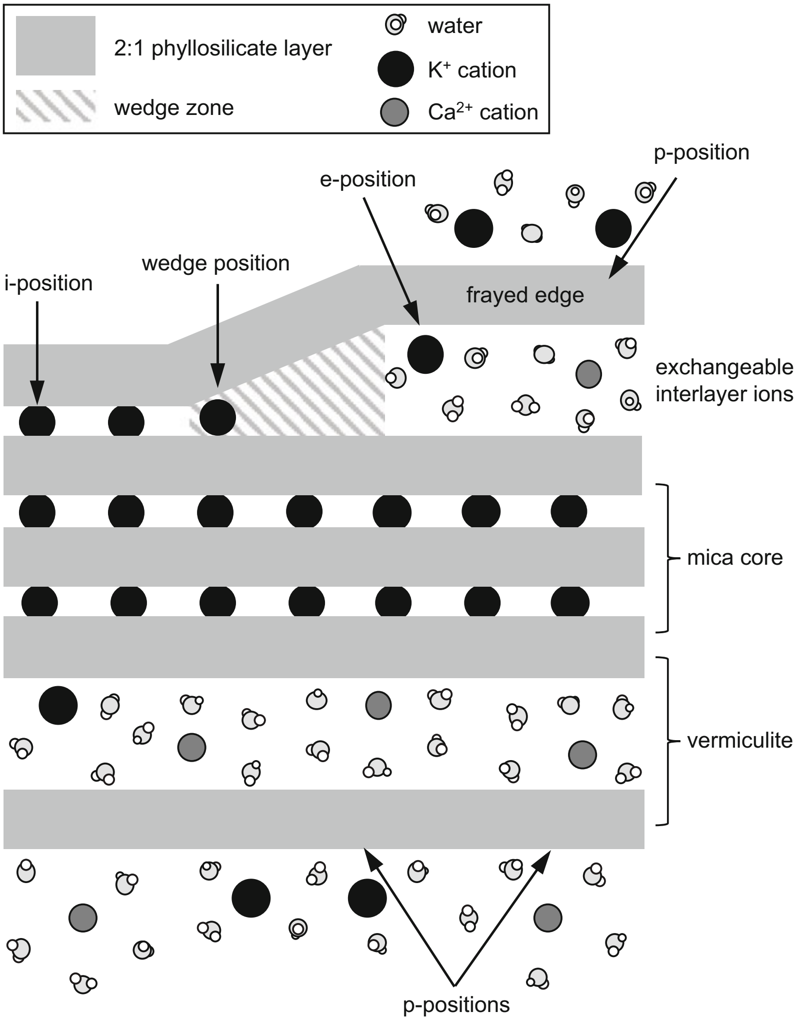
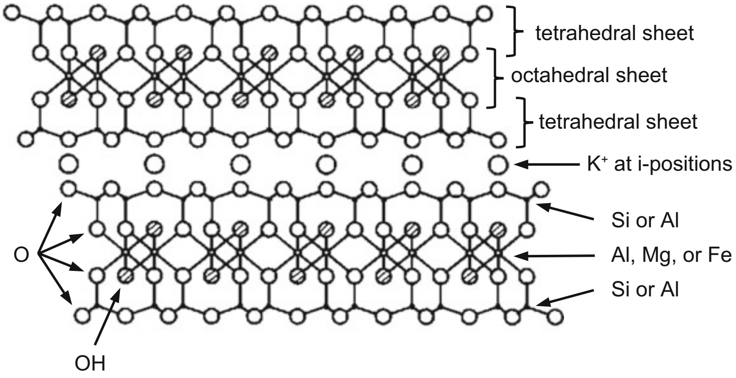


Fig. 7.2 Diagrammatic representation of K adsorption positions for mica, a frayed edge of mica, and an outer layer where mica has transformed to vermiculite. Planar surface (p-position), interlayer (i-position), edge (e-position), and wedge positions are shown. (adapted from Mengel 1985; Mei et al. 2015; Rich 1968)

7.4 Interlayer K in Micas and Partially Weathered Micas

Interlayer K is *the quantity of K bound between layers of phyllosilicate minerals.* Micas are phyllosilicate minerals with each mineral layer composed of two tetrahedral sheets bound on either side of one octahedral sheet (2:1 layer silicates, Fig. 7.3a). Layers carry a net negative charge and are bound together by K^+ ions. Away from the edges of the crystal, these K^+ ions do not have a hydration shell.

a) Dioctahedral mica (2:1 phyllosilicate mineral)



b) Dioctahedral smectite and vermiculite (2:1 phyllosilicate minerals)

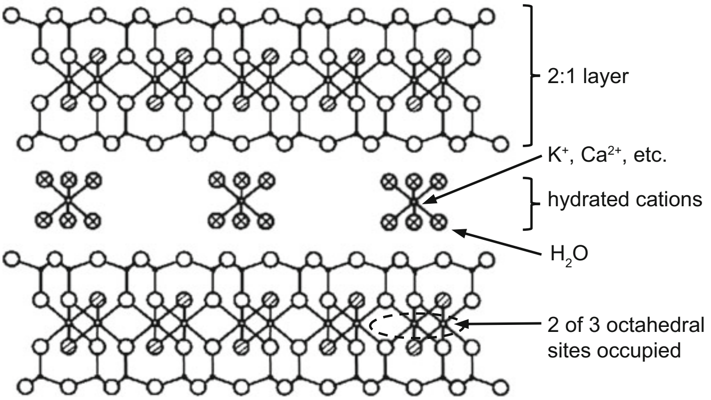


Fig. 7.3 Diagrammatic representation of the structure of (**a**) a dioctahedral mica, and (**b**) vermiculite and smectite. (adapted from Schulze 1989)

They are dehydrated and occupy the ditrigonal cavities in the tetrahedral sheets above and below them in adjacent 2:1 layers (Fig. 7.3a). Muscovite and biotite are two common micas. Pure muscovite is a dioctahedral mica in which two-thirds of the cation positions in the octahedral sheet are filled with trivalent Al^{3+}. Biotite is a trioctahedral mineral in which all the cation positions in the octahedral sheet are filled with divalent cations such as Fe^{2+} and Mg^{2+}. The negative layer charge in these minerals is derived primarily from isomorphic substitution of Al^{3+} for Si^{4+} in the tetrahedral sheets. The layer charge of both muscovite and biotite is close to 1 mol of charge per 10-oxygen formula unit (Thompson and Ukrainczyk 2002).

During mica weathering, the layer charge of these minerals declines and interlayer K leaves from the edges of the particles (Scott and Smith 1967; Barber 1995; Hinsinger 2006). As the net negative charge in the layers decreases, not only is K released from some interlayer positions near the edge of the particles but the space

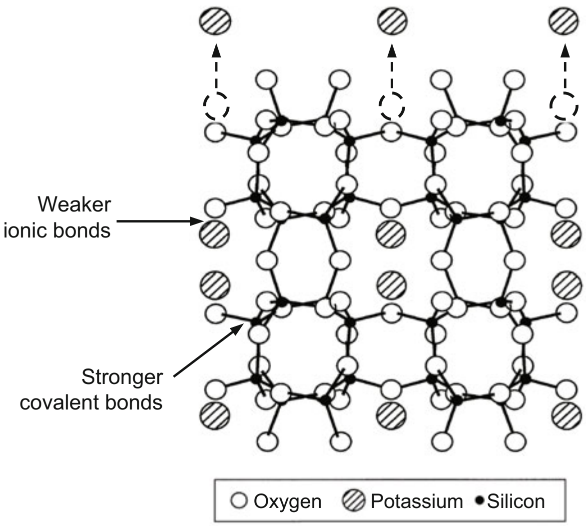


Fig. 7.4 An example structure of a potassium feldspar (orthoclase) and the types of bonds present. Arrows indicate the desorption of K^+ cations from their original positions at the outer surface of the tectosilicate structure, indicated by circles with dotted lines. (adapted from Fenter et al. 2000)

between the layers opens at those locations (Fig. 7.2). These changes allow for freer movement of other cations into that portion of the interlayer region and facilitate exchange reactions. In general, weathering of micas leads to loss of layer charge and transformation to vermiculite, and then to smectite (Wilson 1999; Thompson and Ukrainczyk 2002) (Fig. 7.4).

As micas weather, interlayer adsorption sites become differentiated (Fig. 7.2). The **e-position** is *an interlayer adsorption site where hydrated* K^+ *is preferentially adsorbed and where* K^+ *can rapidly diffuse short distances out of the crystal lattice and into the soil solution.* Potassium in this position is rapidly exchangeable with NH_4^+, and NH_4^+ is also preferentially adsorbed at these sites (Bolt et al. 1963; Mengel 1985). The **i-position** is *an interlayer adsorption site where dehydrated* K^+ *is preferentially adsorbed and where* K^+ *diffuses more slowly into the soil solution.* A **wedge zone** is *the interlayer volume at the nexus where two adjacent phyllosilicate mineral layers separate farther due to solvation forces*. A **wedge site** is *an interlayer adsorption site at the point where two adjacent layers begin to separate farther due to solvation forces*. Wedge sites on illite are most selective for the dehydrated cesium cation (Cs^+) but are also selective for dehydrated K^+ (Lee et al. 2017).

Hinsinger (2006) noted that while adsorption/desorption of K can occur in the e-positions in frayed edges of weathered clay minerals, this process was considerably slower than that at the planar surfaces discussed in Sect. 7.3. Even slower release can occur with K in the i-positions, because the ionic radius of K^+ and its low hydration energy allow it to dehydrate and fit perfectly into cavities created by the basal plane of oxygen ions in the tetrahedral sheets of phyllosilicates. While adsorption/desorption reactions may still occur under particular circumstances, they are very slow.

Mengel (1985) differentiated K adsorption positions by their Gapon selectivity coefficients. The **Gapon coefficient** is *a factor that quantifies the selectivity for one ion over another at adsorption sites*. The higher the Gapon coefficient is, the greater the selectivity. Using the selectivity for K^+ over Ca^{2+} (Bolt et al. 1963), Mengel (1985) reported that the Gapon coefficients differed by an order of magnitude between adsorption positions. The p-positions had the lowest selectivity for K (Gapon coefficients less than 10), the e-positions had an intermediate selectivity (Gapon coefficients approximately equal to 100), and the i-positions had the highest selectivity for K (Gapon coefficients greater than 1000).

As a mica weathers, transformations occur within very short distances. **Interstratification** is *the occurrence of both high-charge layers of mica and layers with lower charge in the same mineral domain*. In phyllosilicate clays, the high-charge, K-bearing core is typically illite, i.e., a clay mica. Core illite layers are often continuous with near-edge layers where weathering has lowered the charge sufficiently to be classified as vermiculite. The difference in the structural charge of domain cores and of layers near domain edges is usually ignored in the literature, and such particles are lumped into the term “illites.” Potassium that is held in the core interlayers (i-positions) is not surface-adsorbed, is not exchangeable with ammonium, and is not likely to be bioavailable to plants unless subjected to the unique conditions of the rhizosphere (Chap. 4). Indeed, K^+ cations in those positions can be extremely stable. In contrast, the lower-charge interlayer positions near domain edges, e-positions in Fig. 7.2, may retain K from fertilizer amendments and release it back slowly to the soil solution. Because the layer charge there is lower than in unweathered mica layers, K^+ ions are held less tightly and are more susceptible to subsequent release. It should be noted that both primary micas and the high-charge core of illite domains will yield a 1.0-nm *d*–spacing in X-ray diffraction patterns. It is difficult to quantitatively differentiate a primary mica from illite by using routine X-ray diffraction procedures.

7.5 Interlayer Potassium in Secondary Layer Silicates

Secondary layer silicates are *phyllosilicate minerals that are weathering products of primary minerals*. The interlayer compositions of these minerals are variable and can contain a variety of cations and quantities of water. Figure 7.3b shows an example structure that represents two different types of secondary minerals important to K behavior in soils: smectite and vermiculite. A key feature of these minerals is the presence of hydrated cations in the interlayer. The presence of water facilitates the diffusion of cations in and out of the interlayer, making cation exchange possible. Soil tests that rely on cation exchange to measure K will measure some K from interlayers of these minerals.

7.6 Structural Potassium in Feldspar and Feldspathoids

Structural K in feldspars is *the quantity of K in structures of tectosilicate minerals*. Making up nearly 31% of the Earth's crust, feldspars (specifically, orthoclase and microcline) and feldspathoids (e.g., leucine) represent the dominant form of structural K in many soils, with the quantities in soil determined by the intensity of weathering and also erosional and depositional factors (Sparks 1987; Barber 1995). While feldspars are commonly present in the silt and sand fractions of younger and moderately weathered soils (Sparks 1987), alkali feldspars have also been found in the clay fractions of moderately weathered soils (Huang and Lee 1969).

The K in feldspars occurs throughout the mineral structure (Fig. 7.3). In K-feldspars, silicon (Si)-oxygen, and aluminum (Al)-oxygen bonds are stronger, covalent bonds, but K is held in the tectosilicate structure by weaker, ionic bonds (Fogler and Lund 1975). When feldspars weather, the K in the outer layer of the structure is released first, causing structural relaxation of the remaining bonds in the surrounding structure (Fenter et al. 2000). The result is an irreversible dissolution of the mineral's silicate framework during weathering (Sparks 1987; Barber 1995; Hinsinger 2006). While K feldspars can be present in only small quantities or are completely absent in some strongly weathered soils (Sparks 1987), the rates of weathering and subsequent K release may be slowed by the formation of a noncrystalline Si-Al-O skin on the mineral surface (Rich 1972). Rich (1968) found that the rates of K release from feldspars were typically slower than that from micas, although Song and Huang (1988) noted that this order may be altered in the presence of organic acid anions (oxalate and citrate) that can be exuded by roots of some plant species into their rhizospheres.

There is evidence to suggest that feldspars can contribute significant quantities of bioavailable K to plants, with these contributions potentially originating from sand-sized fractions rather than clay-sized fractions. Examples include the work of Rehm and Sorensen (1985), who conducted a 4-year trial that varied fertilizer application rates of K and magnesium (Mg) in a factorial combination on an irrigated Valentine loamy fine sand with aeolian sand parent material. Application rates of fertilizer K ranged from 0–269 kg K ha^{-1}. Based on the levels of ammonium acetate extractable K, Rehm and Sorensen expected maize (*Zea mays* L.) yield to increase when fertilized with K; however, no increase was observed over the study period. They attributed the lack of maize response to the added K to the presence of bioavailable K in feldspars in the fine sand and very fine sand size fractions. Sautter (1964) characterized the Valentine soil as having up to 23% K feldspars in the upper 28 cm (inferred from Fig. 7.1 in that paper). Sadusky et al. (1987) measured K release rates from three US Atlantic Coastal Plains soils that had high quantities of feldspars in the sand fractions, ranging from 6.7–16.0% in the surface horizons and 8.2–24.0% in the subsurface horizons. Potassium release rates were studied for a period of up to 30 days in the presence of both oxalic acid and a cation exchange resin. Because the resin provided a continuous sink for K and kept solution K levels lower than did the oxalic acid, approximately two orders of magnitude more K were released with the resin than with oxalic acid. Most of the K was released in the first 16 days (inferred from Fig. 7.1 in that paper). After 30 days, the total quantities of K released by the resin ranged from 67–92 mg K kg^{-1} soil in the surface horizon samples.

This type of evidence suggests that blanket statements about coarser-textured sandy soils providing little bioavailable K to plants can be inaccurate. The observations of Niebes et al. (1993) that a substantial portion of K had been extracted by rape (*Brassica napus* L.) grown in the coarse (silt and sand) fractions of soils from two long-term fertilizer experiments in Europe support this conclusion. Despite the short duration of this experiment (8 days of plant growth), they found for the coarse silt and sand fractions that 80–100% of the bioavailable K was not originating in the ammonium-exchangeable pool. The mineralogical composition and the K-supplying power of a given particle size fraction must be considered, and future K recommendations need to consider the possible contribution of K feldspars.

7.7 Neoformed Potassium Minerals

Neoformed K minerals are *newly formed minerals created from the reaction of soil solution K with other soil solution ions*. Neoformed K minerals do not include primary or secondary layer silicate minerals, but are considered to be a possible byproduct of fertilizer use in intensive cropping areas, especially where compound fertilizers that include K are applied in bands with high in-band concentrations (e.g., the result of wideband spacings in sugarcane or row crops). Such minerals are probably rare in soils, but they may form under certain conditions.

As an example, we consider the neoformation of potassium taranakite ($K_3Al_5H_6(PO_4)_8 \cdot 18H_2O$) or its noncrystalline analogs. Du et al. (2006) coapplied monocalcium phosphate with KCl on an acid (pH 4.6) soil. They hypothesized that some of the added K displaced Al^{3+} from exchange sites, leading to precipitation of K, P, and Al as a noncrystalline analog of potassium taranakite. Formation of potassium taranakite was also observed by Lindsay (1962) after adding saturated solutions of monocalcium phosphate or monopotassium phosphate to an acidic (pH 4.9) Hartsells fine sandy loam soil. The formation of potassium taranakite with only monocalcium phosphate indicates that to form this precipitate, K may not need to be added but simply needs to be present in solution or in a position (probably the p-position) where it can be readily displaced into solution by fertilizer addition. Potassium taranakite was present at 15 min and 3 h after fertilizer addition, but not after 3 days. When Lindsay added those same saturated fertilizer solutions to a basic (pH 8.3) Webster silty clay loam soil, no taranakite formed. Acid conditions where Fe and Al are present are necessary for potassium taranakite formation.

How the formation of taranakite or other neoformed minerals changes K bioavailability during the growing season of plants has not been well researched and is currently not well known.

7.8 Fixation and Release of Interlayer Potassium

The processes by which K is adsorbed or desorbed from interlayer positions of weathered micas, vermiculite, and high-charge smectite are referred to as fixation and release. In **potassium fixation**, *hydrated* K^+ *ions move to interlayer positions in phyllosilicate minerals, then dehydrate as the mineral layers contract. In this position, the* K^+ *is unavailable to plants*. **Potassium release** is when *mineral layers expand,* K^+ *ions rehydrate, and move to the soil solution, becoming bioavailable to plants*. In addition to environmental factors such as pH, redox potential and temperature, fixation and release are governed by the soil solution concentrations of K and competing cations. The actions of plant root uptake (depletion) or fertilizer application (enrichment) determine the net impact of fixation and release on the dynamics of interlayer K (Schneider et al. 2013). The processes of K interlayer fixation have been studied extensively, due to the focus on exchangeable K as a proxy of the pool of soil K that is bioavailable to plants and the apparent inefficient use of applied K fertilizer in soils where K fixation occurs (e.g., Kovar and Barber (1990)), but there has been less research focus on the release process. Sparks (1987), Barber (1995), Öborn et al. (2005), Hinsinger (2006), and Zörb et al. (2014) provide detailed reviews of much of this work (see also Chap. 4).

In some ways, K fixation can be conceptualized as the reversal of mica weathering (Fig. 7.5). When micas weather, their interlayers expand, and K is released. Even though layer charge declines, there is an increase in CEC because more surface area is available to exchange with cations in extractant solutions used to measure CEC. This greater surface area comes from interlayer positions that have

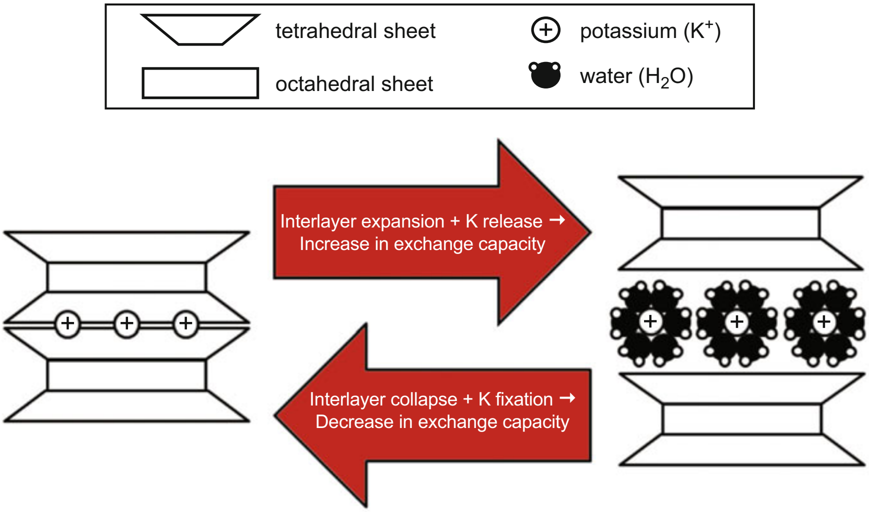


Fig. 7.5 Model of the processes of K fixation and release

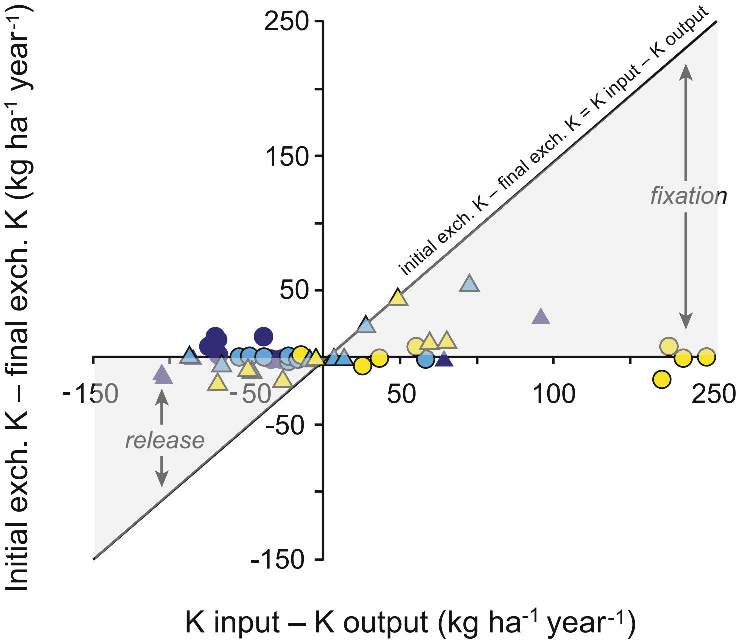


Fig. 7.6 Annual change in exchangeable K (exch. K) in response to annual K budgets in several long-term fertilizer trials in Europe. Potassium inputs are from organic and inorganic K fertilizers, and K outputs occur in harvested produce. The general lack of equivalent changes in exchangeable K in response to surpluses or deficits in K budgets have been interpreted as evidence of K fixation or release, respectively. (Hinsinger 2002)

become available for ion exchange upon interlayer hydration and expansion. When K is fixed between the layers of expanded 2:1 layer silicates, the layers contract, trapping dehydrated K^+ ions in ditrigonal voids in adjacent tetrahedral sheets. The dehydration and contraction of interlayers prevent ion exchange, and an equivalent decrease in CEC is observed. Fixed K becomes nonexchangeable, or at least not exchangeable with NH_4^+ in the 1 M ammonium acetate extractant commonly used to measure CEC and exchangeable cations. For decades, the fixation process has been studied in laboratory settings (Barshad 1948, 1951, 1954; Jackson 1963; Reichenbach and Rich 1975; Wear and White 1951), and its effects can be observed at the field level in some long-term fertilized treatments, for example, at the Rothamsted site discussed by Blake et al. (1999) and other sites in Europe (Hinsinger 2002, Fig. 7.6). At the same time, the unfertilized or negative K balance treatments in long-term studies have demonstrated that there can be significant net release of nonexchangeable K in unfertilized plots (Velde and Peck (2002), Fig. 7.6). However, whether K was released from feldspars, from primary or partially weathered micas, or from secondary phyllosilicate minerals, or simply depletion of unsampled subsoil layers (Kuhlmann and Barraclough 1987; Prasad 2009), was rarely determined.

Potassium ions, in addition to those of other monovalent cations such as NH_4^+, rubidium (Rb^+), and Cs^+, are all fixed in a similar manner (Barshad 1954; Meunier and Velde 2004; Šucha and Širáňová 1991), while ions of monovalent sodium (Na^+) and the divalent cations calcium (Ca^{2+}), magnesium (Mg^{2+}), barium (Ba^{2+}), and strontium (Sr^{2+}) are not fixed to any appreciable extent. This is because monovalent cations have relatively weak energies of hydration compared to the divalent cations and so they are more likely to shed water molecules from the hydration sphere as they enter the charged space of the interlayer region. Furthermore, because of their size, K^+, NH_4^+, Rb^+, and Cs^+ ions can be positioned more stably in the ditrigonal cavities in the tetrahedral sheet than can other monovalent ions like Na^+ or lithium (Li^+) (Reichenbach and Rich 1975). Staunton and Roubaud (1997) reported that the order of increasing affinity of monovalent cations for montmorillonite and illite was generally $Na < K < NH_4 < Cs$, arguing that the strong retention of Cs may be the result of the more covalent nature of the Cs–clay interaction compared to the electrostatic interactions of the other ions.

7.8.1 Contractive and Expansive Forces

At the molecular scale, most K fixation by 2:1 layer silicates can be thought of most simply as the force of lattice contraction exceeding the forces of lattice expansion with K^+ ions in the interlayer space (Fig. 7.7). Contraction is a result of the attraction of negatively charged sites on the silicate surface for the positively charged cation. Expansion occurs when the layer charge is insufficient to overcome the energies of hydration of the cations in the interlayer (Hurst and Jordine 1964; Kittrick 1966; Kaufhold and Dohrmann 2010). The repulsion of the strong dipoles of the oxygen ions that are fixed in place on the basal planes of the minerals also contribute to repulsion of the layers from one another.

Clay layers may also collapse when there are no interlayer molecules or ions (i.e., water, metal hydroxyl complexes, organic cations, and molecules) to prevent the approach of adjacent layers close enough for van der Waals forces of attraction to exceed the forces of expansion. The strength of van der Waals forces lies in the proximity of clay layers to each other, and the proximity is controlled by the coulombic force of attraction of interlayer cations for interlayer surfaces. The greater the attraction, the closer the cation is held to the interlayer surface. The closer the cation is held, the closer an adjacent clay layer can approach. The closer adjacent clay layers become, the stronger van der Waals attractive forces become. When van der Waals attractive forces exceed the forces of expansion, the clay layers will collapse. Hence, cations with high energies of hydration and large hydrated ionic radii (e.g., Ca^{2+} and Mg^{2+}) are not appreciably fixed because it is difficult to overcome the distance that these hydrated cations place between clay layers and the energy with which they hold onto their surrounding water molecules (Fig. 7.7).

The coulombic force of attraction of interlayer surfaces for interlayer cations is a function of layer charge, charge location, and bond geometries in the layer silicate

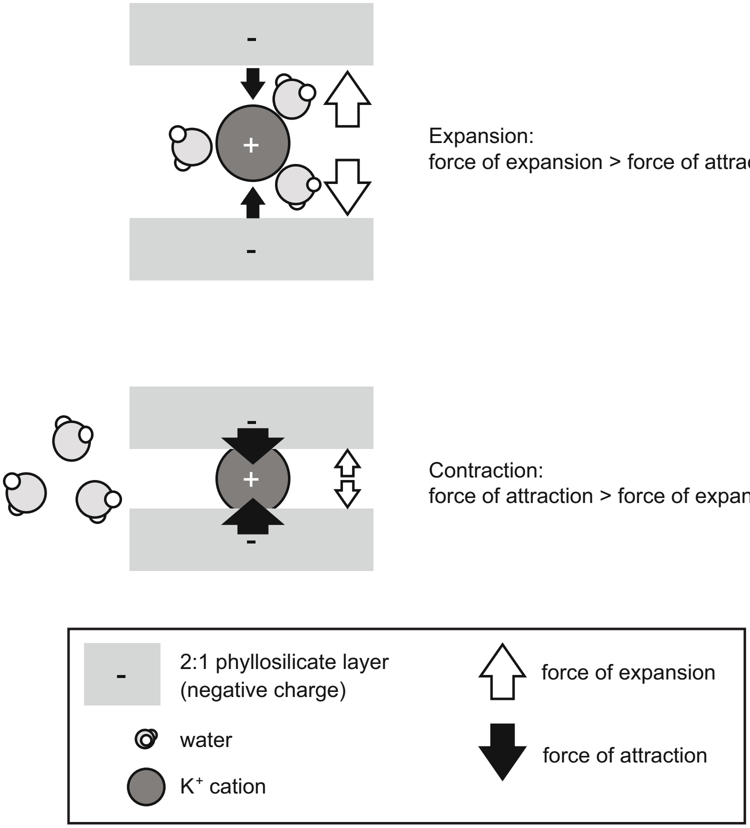


Fig. 7.7 Conceptual model of how the force of attraction and force of expansion contributes to contraction or expansion of 2:1 phyllosilicate layers. (Kaufhold and Dohrmann 2010)

crystal. Increased layer charge equates with increased attraction between interlayer cations and interlayer surfaces. Tetrahedrally derived negative charge is more effective than octahedrally derived negative charge at attracting interlayer cations as a result of its proximity to the basal layer surface. Similarly, bond geometries, particularly the hydroxyl group orientations in the octahedral sheet that are largely a function of cationic occupancies in the octahedral sheet, affect the attraction of interlayer cations for interlayer surfaces by controlling how closely interlayer cations can approach negative layer charge sites.

7.8.2 *Factors Affecting Potassium Fixation and Release*

Soil mineralogy is the key to understanding K fixation and release because only 2:1 layer silicates fix and release K in interlayer positions. Potassium can be fixed by mica weathering products, i.e., vermiculites and high-charge smectites (Barshad 1951, 1954, Ranjha et al. 1990, Rich 1968, Martin and Sparks 1985). Some authors indicate that K can be fixed by micas per se, but this is not likely. Micas are defined by having a high layer charge (near 1 mol of charge per 10-oxygen formula unit). Once the layer charge declines to a point where K can be reversibly or temporarily "fixed," the mineral is no longer considered a true mica, although it has been derived from mica. These are partially weathered micas that cannot be distinguished from primary micas as previously discussed. Where K-fixing minerals predominate in the clay-sized fraction of the soil, K fixation is often related to the clay content of the soil (Shaviv et al. 1985). However, K fixation has also been documented in silt-sized and even very fine sand-sized vermiculite and hydrobiotite (Harris et al. 1988; Murashkina et al. 2007a, b). The effects of soil type and soil horizon on K fixation occur primarily because the amounts and types of 2:1 layer silicates vary among soil types and soil horizons. Particle size distribution and possible artifacts related to sample grinding are important for assessing the degree of K fixation because they affect the accessibility of interlayer spaces. Smaller particles generally mean easier access to interlayer spaces. In general, however, smaller particles mean more edge area per particle and therefore easier access of K to interlayer spaces where it might be fixed.

The degree to which 2:1 layer silicates fix K is largely a function of layer charge and the distribution of that charge in the octahedral and tetrahedral sheets. Layer charge affects the electrostatic attraction of the layers for K^+ ions (Rich 1968). Other factors being equal, greater layer charge is often correlated with greater potential for fixation (Barshad 1954; Bouabid et al. 1991). Murashkina et al. (2007a) speculated that K fixation in some soils dominated by smectite may be due to high-charge smectites that are transitional to vermiculite. Charge location, however, also influences K fixation. Potassium-fixation capacity has been found to be well correlated with isomorphic substitution in tetrahedral sheets, but poorly correlated with isomorphic substitution in octahedral sheets (Bouabid et al. 1991). This is likely because negative charge originating in the tetrahedral sheet is closer to K^+ ions in the interlayer space (Reid-Soukup and Ulery 2002).

In acidic soils, the presence of hydroxy Al interlayers in vermiculite and smectite may affect K fixation (Saha and Inoue 1998). The hydroxy Al interlayers act as obstructions between 2:1 layers that restrict the collapse of the interlayer space around the K^+ ions. Blockage of the surface results in a decrease in cation exchange capacity and causes K to become more exchangeable and less likely to be fixed. In addition, hydroxy interlayers may slow the entry and exit of exchanging cations.

Due to the impact of layer charge on K fixation, the redox state of structural Fe in 2:1 layer silicates can also influence K fixation. The chemical reduction of structural Fe in both smectites and vermiculites has been shown to lead to increases in negative layer charge and K fixation. Furthermore, reduced Fe (i.e., Fe^{2+}) in the tetrahedral sheet appears to have a greater impact on K fixation than reduced Fe in the octahedral sheet (Chen et al. 1987; Dong et al. 2003; Favre et al. 2006; Florence et al. 2017; Stucki et al. 1984, 2000). This is likely due to increased coulombic attraction

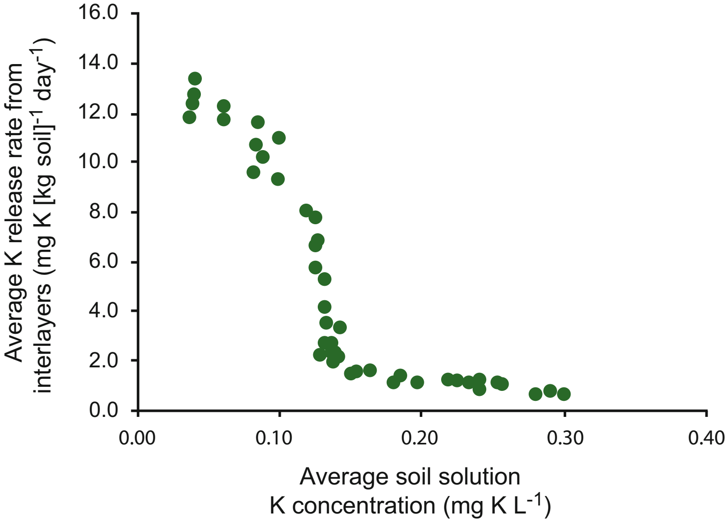


Fig. 7.8 The effect of solution K concentration on the rate of release of nonexchangeable K from a moderately weathered Luvisol derived from loess; reproduced from Hinsinger (2002) and adapted from Springob and Richter (1998)

between interlayer surfaces and K^+ ions, facilitating interlayer dehydration and collapse.

The oxidation of structural Fe^{2+} in the octahedral sheets of micas may lead to interlayer expansion and K release. Conversely, the reduction of structural Fe^{3+} in expanded 2:1 layer silicates can lead to interlayer collapse and K fixation (Scott and Amonette 1988). Note that the oxidation of structural Fe in micas can either stabilize or destabilize interlayer K, depending on both the pH of the environment and on whether oxidation leads to the ejection of the Fe atoms from the octahedral sheet (Thompson and Ukrainczyk 2002). When the oxidation of octahedral Fe in biotite, for example, leads to Fe ejection, nearby hydroxyl ions tend to orient toward the empty octahedral site, allowing interlayer K ions to nest closer into the ditrigonal cavity and subsequently to be held more tenaciously (Barshad and Khishk 1970). Although redox-driven changes in K fixation and release might explain some temporal fluctuations in soil exchangeable K, more work needs to be done to further test the role of Fe redox processes on K fixation and release.

Release of interlayer K is facilitated by the expansion of interlayer spaces when K is replaced by cations with larger hydrated radii (e.g., Ca^{2+} and Mg^{2+}), as illustrated in Fig. 7.2. Adequate soil moisture and low solution K concentrations are prerequisites for the release of interlayer K during the weathering process, with the key role played by solution K concentration, as demonstrated in Fig. 7.8 (Springob and Richter 1998; Hinsinger 2002). Key considerations in assessing the potential contribution of released interlayer K for plant uptake are the following: (1) release of K potentially bioavailable to plants is limited to the effective diffusion distance around roots and root hairs—i.e., the zones of greatest solution K depletion correspond to the rhizosphere, which typically comprises less than about 3% of the soil volume (Hinsinger et al. 2005); and (2) release of K is also favored by a high concentration of H^+ ions (i.e., low pH). This is explained in greater detail in Chap. 4.

7.9 Interpreting "Exchangeable Potassium"

While the strengths and weaknesses of specific soil test procedures are discussed in detail in Chap. 8, the diagnostic tests most commonly associated with the measurement of surface-adsorbed K is termed "exchangeable K." **Exchangeable K** is the *K extracted from a sample of soil* via *cation exchange using a solution of a specified composition under a specific set of conditions*. The quantity of exchangeable K extracted from a given soil therefore varies according to the extracting solution and conditions used. Conditions typically involve displacement of K^+ by NH_4^+ ions. Exchangeable K is generally considered to be bioavailable to plants.

The continuum of sorption positions in soil minerals and organic matter is typically distinguished by the affinity for K and the speed of the chemical reactions with simulated soil solutions in soil testing procedures. Accurate quantification of the K in the surface-adsorbed pool can be difficult, especially in soils where there are significant amounts of weathered mica grains or secondary phyllosilicate minerals. In soils where the charge is predominantly associated with organic matter or kaolinite, exchangeable K determinations are a quantification of surface-adsorbed K. In such contexts, this measure can be a reliable index of the capacity of the soil to supply bioavailable K to plants over an extended period (Obreza and Rhoads 1988).

A common misconception is that K exchangeable with NH_4^+ captures only surface-adsorbed K. When soils contain significant amounts of phyllosilicate minerals with hydrated interlayers (e.g., smectite or vermiculite), NH_4^+ will exchange not only with surface-adsorbed K but also with a variable amount of interlayer K. The presence of water between individual layers allows cations to diffuse in and out of interlayer positions, making cation exchange possible. Ammonium is especially able to replace interlayer K in hydrated layer silicates because its size and hydration energy are similar to those of K.

The rates of exchange with NH_4^+ are variable and difficult to predict, depending on the minerals involved, the proportions of planar, edge, wedge and interlayer adsorption positions, and thus the selectivity of adsorption sites for K (Mengel 1985; Sparks 1987; Lin 2010; Römheld and Kirkby 2010). For example, the rate of K desorption from kaolinite and smectite is usually rapid (Sparks and Jardine 1984), while from vermiculite and micaceous minerals (i.e., illite) it tends to be much slower (Sparks 1987). In these situations, Carey and Metherell (2003), among others, hypothesized that the two-stage extraction of K by tetraphenyl boron could be related to the e-position, including wedge zones (rapid) and i-positions (slow).

In most situations, the volume of soil immediately adjacent to roots is small compared to the entire soil volume, so there is unlikely to be a simple, quantitative relationship between K that is exchangeable with ammonium in a soil test procedure and that acquired by plants during a growing season. However, even in experiments in which soil volumes are small and root density is very high, as is typically the case in nutrient depletion assays, not all ammonium-exchangeable K is bioavailable to plants. Various authors have proposed the concept of a lower accessible limit of the exchangeable K pool, below which plants may not be able to extract K (e.g., Tabatabai and Hanway 1969; Schneider et al. 2016). Termed the "plant minimal exchangeable K" this term could perhaps be more simply described as the "minimal plant-accessible K." The size of this fraction increases with increasing clay and CEC (measured at the pH of the soil (Schneider et al. 2016)), suggesting that as clay content increases the number of K-specific adsorption sites also increases. It may be hypothesized that this fraction of the measured exchangeable K could be a useful predictor of a "plant minimal solution K concentration" below which plants are unable to take up K.

7.10 Mineral Transformations

7.10.1 Reversible Changes in Interlayer Potassium

Long-term K removal in cropping systems can result in accelerated degradation of micas and an increase in secondary phyllosilicate minerals such as vermiculite and smectite (Barré et al. 2008). Conversely, long-term fertilization with K has been shown to increase the apparent concentration of mica-like minerals in soils, even though minerals with layer charges high enough to classify as micas were not being formed (Scheffer et al. 1960; Ross et al. 1989; Meunier and Velde 2004; Barré et al. 2008). Ross et al. (1989) reported such observations after only 4 years of high K fertilization. Indeed, changes in the proportion of collapsed interlayers in clay minerals of rhizosphere soil materials over the course of a single growing season have been reported by Barré et al. (2007b) and by Adamo et al. (2016).

Changes consistent with these reports have been reported from both cropped and pasture systems. For example, a 15-year study of alfalfa (*Medicago Sativa* L.) cropping on a loess-derived soil (De-Cheng et al. 2011) showed topsoil exchangeable K decreased due to alfalfa forage uptake and removal, but total K in the topsoil increased, likely due to K uptake and translocation by the alfalfa roots from deep in the soil. A similar phenomenon of enrichment of illite-like clay in temperate region soils has been hypothesized to result from the redistribution of K from deeper soil horizons to the topsoil horizon through root uptake and plant residue deposition (Barré et al. 2007a, 2009).

7.10.2 Implications for Building and Depleting Soil Fertility

The fixation and release of K from interlayer positions in phyllosilicate minerals represent an important buffering system for plant-available reserves of soil K where those minerals occur. Release of K from interlayers can be particularly important under continuous cropping when rates of added K have been inadequate to replace K removed in harvested crop biomass. There is also evidence that fixation of K in these minerals stores K when it is added to soils at rates that exceed removal or when it is redistributed to surface horizons by crop residue deposition, suggesting a degree of resilience that can be exploited to manage soil fertility in the longer term.

The immediate challenge to the sustainable exploitation of soil K is to develop simple diagnostic indicators of the likely K status of these buffered systems. Candidates for this approach would include assays such as those developed by Cassman et al. (1990) and refined by Murashkina et al. (2007a), in which the extent of fixation of added K fertilizer was ascertained. These assays would not only provide information needed to develop an effective K fertilizer application strategy (discussed in Chap. 12), but could also provide an indicator of the extent of K depletion of the interlayer buffer system. Such knowledge could allow the K buffer system to be exploited when K status was moderate or high, but replenished when K status was low to avoid irreversible degradation of these minerals. Another useful approach could be to develop region- or soil-specific predictions of the minimal plant-accessible K that are based on an easily determined parameter like clay content or CEC.

7.11 Short-Term Transformations in the Rhizosphere

The low concentration of K in soil solutions is thought to be an important driver for the release of K through mineral dissolution and interlayer K release. Plant roots play a key role in depleting soil solution K concentrations in the rhizosphere. Hinsinger (1998) reported that solution K concentrations can decrease by 2–3 orders of magnitude to as little as 2–3 μM in the vicinity of plant roots, and at these concentrations the release of structural and interlayer K can occur at high rates (Springob and Richter 1998, Fig. 7.8). However, it is also clear that this dissolution process is accentuated by root exudates and other rhizosphere characteristics (e.g., low pH). For example, plants can release conjugate bases of a variety of organic acids and those anions complex Al, contributing to dissolution of aluminosilicate framework minerals like feldspars (Chap. 4). Roots of maize (*Zea mays* L.) and rape (*Brassica napus* L.) can release citrate and malate (Hoffland et al. 1989; Pellet et al. 1995), while roots of bak choi (*Brassica rapa* ssp.) (Wang et al. 2000) and radish (*Raphanus raphanistrum* ssp.) (Zhang et al. 1997) have been shown to release tartrate. These ions accelerate the dissolution process at mineral surfaces by complexing and solubilizing Al^{3+} from minerals. Zörb et al. (2014) suggested that the generation of these exudates is driven by the soil solution K concentration and could be initiated when K concentrations fall to less than 10–20 μM. Plants also release hydronium ions, which lower the pH in the zone next to the root and contribute to weathering by creating local charge imbalances when they form new bonds with oxygen ions at mineral surfaces (Brantley 2003). Much more detailed coverage of these and other rhizosphere transformations is presented in Chap. 4.

7.12 Nonexchangeable Potassium as a Functional Pool

Nonexchangeable K is *soil K that is not measured by soil tests that rely on exchange or displacement of K by another cation*. The current lack of analytical techniques that can successfully differentiate between K that resides as structural K in feldspars; interlayer pools in micas, partially weathered micas and secondary clay minerals; or in neoformed K minerals in fertilized soils (pools 9–13 in Fig. 7.1) presents real problems for predicting the size and behavior of sources of K that are potentially bioavailable to plants. Collectively, these pools can make a major contribution to the K uptake by crops. Hinsinger (2006) estimated that this aggregation of K pools could release up to 100 kg K ha^{-1} $year^{-1}$, which is a significant proportion of plant K demand in many agricultural systems. This is substantiated by the K budgets in the treatments without K fertilization of long-term fertilizer trials in Europe (Fig. 7.6). The contributions of interlayer and structural K to crop uptake will obviously vary with soil type and mineralogy. For example, Moody and Bell (2006) demonstrated a significant contribution of nonexchangeable K (measured as the difference between exchangeable K and K extracted using sodium tetraphenyl borate) to plant uptake in some Vertisols, but effectively no contribution in others. Subsequent work indicated that the majority of the nonexchangeable K taken up by different plant species in the 15–30 soils studied was from dissolution of structural K rather than K release from near-edge interlayer positions. The apparent lack of significant release of K from near-edge interlayer positions in this study may reflect the highly weathered nature of the Australian soils. Nonexchangeable, but near-edge, interlayer K could make a significant contribution to plant uptake from less weathered soils in temperate regions where partially weathered micas or vermiculite are present (Barré et al., 2007b, 2008).

The relative strengths and weaknesses of the main analytical methods used to quantify nonexchangeable K (extraction with boiling HNO_3 or sodium tetraphenyl borate) are discussed in detail in Chap. 8. However, given the inability of current analytical soil test methods to differentiate between these nonexchangeable K sources, that is, structural and near-edge interlayer K, Hinsinger (2006) has suggested they could be referred to collectively as “nonexchangeable K.” This term has merit, as it recognizes the current limitations and uncertainty surrounding diagnostic testing and the variability in interpretation of soil test results across soil types with differing mineralogy.

7.13 Classifying Soils According to Their Potassium Behavior

Soil Taxonomy, the system of soil classification used in the United States (Soil Survey Staff 2014) groups soils into classes that have similar behavior, use and management, and productivity. The lowest level of classification is the family level, which emphasizes soil properties relevant to the potential use and management of the soil. Differentiating criteria at the family level include particle size classes, mineralogy classes, and cation activity classes. In the United States, *Soil Taxonomy* is the basis for soil surveys, which are made by the National Cooperative Soil Survey. These surveys are typically intended for general agriculture and land use planning and are made at scales ranging from 1:12,000 to 1:31,680. Although soil surveys are not intended to be used for making fertilizer recommendations, they could be used to group and identify soils with potential for K fixation or release. This would help researchers identify sites for future K fertility trials or help producers and consultants identify soils that need K fertility recommendations designed to compensate for K fixation or release. Currently, *Soil Taxonomy* does not include specific classification criteria for recognizing soils with potential for K fixation or release. However, the system could be modified by extrapolating mineralogical and K-fixation data for horizons at well-studied sites to other land areas.

Effective recognition of K-fixing or K-releasing soils in *Soil Taxonomy* would require knowledge of the particle size distribution, mineralogy, and cation exchange capacity of multiple soil horizons, including the surface horizons that are not currently used in the system's mineralogy classes at the family level. An assessment of the soil's cation exchange capacity (e.g., before and after heating a K-saturated sample of clay fractionated from the soil, as described by Ransom et al. (1988)) could be combined with the properties listed above to identify soils with a significant potential for buffering plant-available K. Additional work would be required to see if a similar procedure could be used to recognize soils with a potential for K-fixation using other soil classification systems such as the World Reference Base for Soil Resources and the Australian Soil Classification System. However, neither soil classification system includes clay mineralogy and cation exchange capacity as classification criteria used to predict soil responses for use and management.

Even without formal revisions to soil classification systems, informal, local models to predict the K-supply characteristics and locations of K-fixing or K-releasing soils could be useful. For example, O'Green et al. (2008) developed a method to classify the K-supply characteristics of soils in vineyards of the Lodi Winegrape District of California in the United States. Their approach correlated readily available soil survey information about parent material age, mineralogy, and weathering intensity with levels of exchangeable K and the K-fixation potential for soils in the region. While their model was specifically designed for this region or for wine-grape cropping systems, it is innovative and the concepts could be applied elsewhere.

7.14 Lessons Learned from Long-Term Experiments

Exhaustive cropping currently remains the most effective way of quantifying the bioavailable fraction of a nonexchangeable K pool, although these results may vary considerably with crop species (and perhaps even genotypes) and experimental conditions. However, long-term experiments offer an opportunity to explore the importance of nonexchangeable soil K reserves, i.e., pools 9–12 in Fig. 7.1. An example that quantifies the long-term impact of different K inputs/balances on soil K content in different K pools at the end of a monitoring period is the study of Blake et al. (1999), with this extended to cover other long-term experiments in France, Germany, and Poland by Hinsinger (2002, 2006, Fig. 7.6). Others have measured the change in soil K stocks in different pools over a defined period between treatment sequences or soil sampling events, e.g., Kaminski et al. (2010) and Madaras et al. (2014). Still others have reported qualitative changes in secondary phyllosilicate minerals in response to either K fertilizer use or unbalanced K removal (Barré et al. 2007b, 2008). Collectively, such studies have been able to demonstrate the dynamic nature of soil K, the importance of mineralogy on K fixation and release (the latter by either desorption or dissolution) and the impact of net K balance on the direction of K fluxes.

Many of these studies cannot conclusively identify the pools of soil K that contribute to the overall K balance of the systems investigated. Some are limited by their soil sampling strategy, which typically focusses on the cultivated layer (0–25 cm) or even the upper 10 cm in minimum and zero-tillage systems. The sources and sinks of K may well be from deeper soil layers, especially in tropical and subtropical environments where soil temperatures do not limit root exploration and access to subsoil moisture. Nutrient stores in deeper layers are keys to productive agricultural systems (Bell et al. 2009), but changes in soil K in these layers are typically not measured (Prasad 2009). Pradier et al. (2017) have measured significant changes of K pools at considerable depth, down to 4 m when sampling the rhizosphere of eucalypt trees in Brazil. They observed an increase of exchangeable K in the rhizosphere, possibly related to weathering of K-bearing minerals, as speculated by these authors. Even those that have endeavored to account for changes in the amount of available K in different profile layers have found it difficult to precisely identify the K pool acting as the predominant source or sink for K. This relates to the limitations of existing soil test methods, discussed in Chap. 8, which are effectively limited to identifying changes in exchangeable and nonexchangeable K. Both measures will access different K pools in soils with different mineralogy, making extrapolation to other soil types and cropping systems challenging.

7.15 Prognosis

A better understanding of the allocation of K bioavailability to plants among different functional pools in agricultural soils will allow the development of more defensible and economically justifiable fertilizer recommendations. This will particularly apply to soils where there are significant amounts of nonexchangeable K in either (or both of) three-dimensional framework or layer silicate minerals. The development of such an understanding will require the use of a combination of diagnostic soil K tests, including those that will provide an assessment of the likely availability of applied K fertilizer. While this will increase the costs of soil testing, the greater certainty provided around understanding the K status of the particular field under management will add considerable confidence to fertilizer decisions. Further research is clearly required on this topic, as is research on soil sampling protocols that allow quantification of K status in the soil layers from which the crop acquires significant quantities of K.

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