Potassium Dynamics in Soils

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Potassium (K) is a macronutrient required by plants in larger amounts such as nitrogen, however, different from all macronutrients because of its specific retention in the soils. It is a structural part of most of the soil minerals and its availability to plants is not directly proportional to the total amount of K in the soils. Potassium availability can be understood only by understanding the K content in soil, forms of K, soil mineralogy, and weathering status of the soils.

2.1 Potassium Content in Soil

Currently, the world's most important potash deposits are located in (1) the Elk Point, Maritimes, Paradox, and Salado Basins in North America; (2) the Zechstein, Pripyat, Solikamsk, and Pricaspian Basins in Europe; (3) the Danakil and Lower Congo Basins in Africa; (4) the Dead Sea, Khorat, Sakon Nakon, Qaidam, and Central Asia Basins in Asia; and (5) the Amazonas, Sergipe, and Neuquén Basins in South America (Fig. 2.1). Major potash producer countries are Canada, followed by Russian Federation, Belarus, Germany, Israel, Jordan, China, USA, Brazil, Chile, Spain, and UK (Jasinski 2011). In cultivated areas, K concentration may vary from 0.01% to 4%, with an average calculated value of 1.36% (Jakovljević et al. 2003). In mineral soils, the average concentration of K is ~1.4%, with a broad range of 0.01% to 3.7%. The total soil K contents frequently exceed 20,000 mg kg⁻¹ in most soils (Rehm and Schmitt 2002). In rocks and several soils, K is a major constituent of the primary rock-forming minerals, for instance, alkali feldspar group, namely microcline and orthoclase. Mica group, specifically biotite and muscovite and secondary minerals such as illite are also a rich source of K (Jakovljević et al. 2003).

The concentration of soil available K varies with the degree of weathering and the soil parent material which has direct impact on its supply (Table 2.1). In soils, K exists in four major forms, namely structural K, exchangeable (readily available), non-exchangeable or fixed (slowly available), and readily available solution K

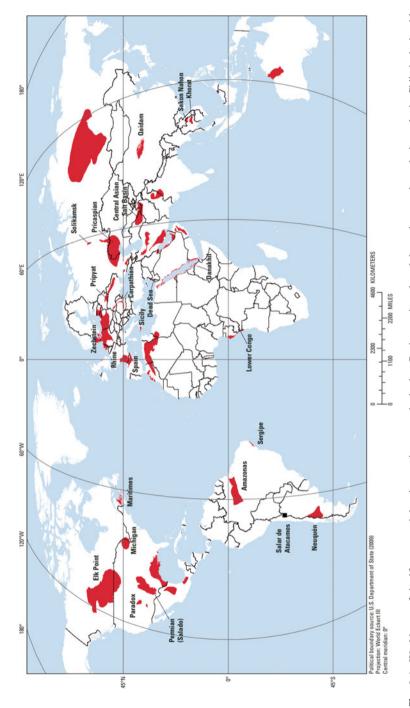


Fig. 2.1 World map of significant potash-bearing marine evaporite basins. Basins are in red, and the major potash-producing salar in Chile is depicted by a black square (adapted from Cocker et al. 2016). For more detail, interactive geographic information system-based maps and data are available at: https://pubs. usgs.gov/sir/2010/5090/s/pdf/sir2010-5090-S.pdf

Table 2.1 Total potassium concentration in some soil orders

Soil order	K concentration (mg g ⁻¹ soil)
Entisols	26.3 ± 0.6
Spodosols	24.4 ± 0.5
Alfisol	11.7 ± 0.6
Mollisol	11.7 ± 0.6

Source: Helmke PA (2000). In Sumner ME (ed), Handbook of soil

science. CRC Press, London, p B3-B24

(Rehm and Schmitt 2002). It has been revealed that more than 90% of soil K is present in the form of primary minerals, while the amount of plant available K in the soil solution is only about 0.2%, and it is the principle source of K for plant uptake (Fig. 2.3). The fixed form of K is called as structural, mineral, native, matrix or inert K. In many soils, the total K or the bulk of it is structural K is not directly available to plants. It has been found that nearby 90–98% K in the soil is in the unavailable form depending on soil type. This K is released through the weathering process, nevertheless this process is so slow that it cannot meet crop requirements. However, fixed K contents influence the concentration of soluble K in soil solution (Jakovljević et al. 2003).

The second type of K present in the soil is the exchangeable K; which is present at the exchange sites of various soil colloid complexes. This K is held by different bond strengths at the non-specific adsorption sites. These sites may include the planer and edge positions of soil clay minerals or the negative charge sites which are developed by carboxylic and phenolic groups of humus colloids. The amount of K held at exchangeable sites of soil clay minerals depends upon the kinetic and thermodynamic factors (Parfitt 1992), for instance, the K concentration at exchangeable site in relation to other exchangeable cation, and the nature of the soil surface. Approximately 90% of available K is present in exchangeable K, whereas the proportion of exchangeable to total K is <2%. It is stated that exchangeable K has a strong link with CEC, pH, calcium carbonate, and organic carbon (Baruah et al. 1991). For example, aridisols and inceptisols have comparatively higher K rich mica (Srinivasarao et al. 2007), and K present in illite have less mobility as these minerals have narrow interlayer space which are K selective and ultimately decrease its desorption (Sparks and Huang 1985; Sparks 1987). Furthermore, sub-surface soils have less exchangeable K than surface soils and higher concentration of exchangeable K in the soil represent a good indication of ability of soil to supply K. Some exchangeable K may fix between layers of clay minerals and may be converted into slowly available K (Rehm and Schmitt 2002).

The third form of K is the non-exchangeable, fixed or slowly available, which is trapped between the clay mineral layers, and plants cannot use this K fraction during a single season. Nevertheless, this K can act as a reservoir for exchangeable K that is readily available (Rehm and Schmitt 2002). This form of K is held between the adjacent tetrahedral layers of di- and tri-octahedral vermiculites and micas or between the chloritized vermiculite (Sparks and Huang 1985; Sparks 1987). The fixation of K takes place due to the increase in the number of binding forces between

K and clay surfaces than the hydration forces which are present between the individual ions of K (Sparks 1987), making the release of K easy due to physical trapping. The conversion of non-exchangeable K into the exchangeable K occurs when the solution K and exchangeable K level are decreased due to K removal by crops, losses through leaching or through enhanced activates of soil microbes (Sparks 2000).

The non-exchangeable K is moderately to sparingly available to plants. The higher concentration of non-exchangeable K is noticed in sub-surface soils than surface soil. Furthermore, the soils enriched with illit clay minerals have high non-exchangeable K in the sub-surface because of the presence of clay and silt which have ability to fix K (Sharma et al. 2009). This K fixation depends on the amount of K released from clay minerals, particle size, and their distribution/quantity and type of clay minerals, because these properties have strong correlation with clay and silt proportion of soil. The quantity of K fixed in soil and type of clay minerals rich in K can influence the release of K to plants (Rao et al. 2001).

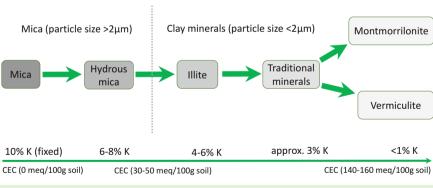
The fourth form of K is in the solution form which is readily available to plant. Readily available K may also be present at the exchangeable site of clay minerals which has been discussed earlier. The quantity of K in soil solution depends upon absorption through the plants and also involves the soil minerals from which K is released. When the plants dissolve K present in soil solution, the concentration of K in soil solution drops, which is balanced after the release of K from exchangeable sites of clay minerals. This form of K mostly faces a leaching problem in soil. In the soil solution, the amount of K is not constant and ranges from 3 to 30 mg kg⁻¹ for normal soils (Haby et al. 1990). The solution K level is mediated by kinetic reactions, soil moisture contents, and the equilibrium that occur between the forms of soil K, the concentrations of divalent cations in solution and on the exchanger phase (Sparks 2000). The amount of soil solution K is also affected by the buffering capacity of soil clay minerals. For example, well-buffered vermiculates and micas can hold the solution K level very firmly, while that of buffered allophonic clay mineral do not maintain the soil solution K level (Parfitt 1992). Additionally, slowly available K, exchangeable K, and water-soluble K are interconvertible (Fig. 2.3), and this conversion is mediated by various factors, for instance, K supply, soil moisture, soil temperature, and the removal of K via plant roots.

The removal of K by the plant is facilitated by K concentration in soil solution, K availability index, organic matter, clay minerology, cation exchange capacity, calcium carbonate, and other properties. The knowledge regarding the variation in K adsorption, differences among various soil types and the equilibration between K intensity and the phases of the quantity is valuable for precise and site-specific potash recommendation. Furthermore, the K contents in the soil may increase and decrease depending on environmental and soil conditions. The indigenous soil K contents are depleting with time owing to intensive cultivation of crops with less potash fertilization and other crop management practices, particularly the removal of crop residues from the field.

2.2 Soil Mineralogy and Potassium Dynamics

Soil clay mineralogy has great consequence in soil nutrient supplying capacity and overall nutritional status of a particular soil. It is exposed that the mineralogical composition of the soil may largely impact the K dynamics within the soil (Surapaneni et al. 2002), and this relationship between the K forms and clay mineralogy can be used to predict soil K fertility, and ultimately the potash fertilizer recommendation. Clay mineralogy in the soil influences the fixed K which is not readily available fraction of K in the soil. For instance, when the soil becomes dry, montmorillonite clays fix K because K is trapped in clay mineral layers. When the soil becomes wet, this trapped K release. In contrast, illite dominant soils, the K is fixed between the layers of clay minerals when the soil is dry, but releases only small amount of K when soil becomes wet. Furthermore, clay minerals such as smectite and kaolinite easily release all of their adsorbed K than do illite and vermiculite (Mengel and Uhlenbecker 1993). Therefore, the age of soil developed from these clay minerals determines the extent of weathering are responsible to regulate the soil K dynamics (Fig. 2.2).

The major share of K exists in micas and feldspars clay minerals which contain 6–9% and 3.5–12% of the total soil K and such 2:1 type of clay mineral revealed as major sources of non-exchangeable K (Moritsuka et al. 2004). However, the plants are unable to use this crystalline-insoluble K present in these minerals. Weathering of these rocks result in the release of K; some of this K moves towards the readily available pool and some towards slowly available pool. Thus, this K fixation in illite clays without release causes serious problems for management of potash fertilizer for crop production (Rehm and Schmitt 2002). The other clay minerals which bear K are primary aluminosilicates such as micas-muscovite, biotite and secondary



As a result of weathering process soil hydration, specific surface area, and CEC are increasing with reducing particle size, meanwhile indigenous soil K contents are decreasing

Fig. 2.2 Schematic diagram of the soil weathering process in relation to potash availability. With the passage of weathering process; soil surface area expands having smaller particle size, whereas indigenous K content reduces

K fraction	Kaolinitic ($n = 26$)	2:1 type clay ($n = 23$)	Mixture $(n = 53)$
Exchangeable	45	183	224
Water-soluble	2	4	5
Total	3340	15,780	8920

Table 2.2 Representative K concentrations (mg kg^{-1} soil) in soil fractions related to dominating clay types

Source: From Brady NC, Weil RR (1999) The nature and properties of soils. 12th edition. Prentice-Hall, Englewood Cliffs, NJ

aluminosilicates, namely phyllosilicates. The formation of these phyllosilicates occurs through the weathering of primary minerals or from the secondary silicates after adequate rainfall (Essington 2004). The K availability to plants is very easy from phyllosilicates and its associated clay minerals. A majority of clay particles in soil have particle size of <0.002 mm, and are made from the secondary clay minerals.

The exchangeable K may bind on non-specific adsorption sites of clay minerals, at the carboxylic and phenolic groups of soil and also on soil organic matter. The absorption of the K⁺ takes place non-specifically in hydrated form. These non-specific adsorption sites are present on the edge "e" and planar "p" position of clay minerals, and aluminum hydroxides and amorphous iron (Sparks 2003). The lattice or structural K is covalently bonded with the crystalline structure of K enriched primary silicate minerals such as feldspars, namely microcline, orthoclase showing framework structure and micas, namely muscovite biotite showing layered structure. The micas consist of ~8% of soil K. These types of clay minerals are present in the coarser fractions of soils (e.g. sand and silt) and the contained K in these minerals is release through the long-term weathering process. However, this K is not practically available to plants. The typical process of weathering proceeds in following order: (1) muscovite, (2) hydro muscovite, (3) illite, (4) mixed clay minerals, e.g. kaolinite-illit or illit-montmorillonite (Fig. 2.2). In this weathering process, the K ion is substituted by hydroksyanion H₃O⁺, and thus the next product contains less K (Pracz 2003).

Although K is found in large quantities in world soil, the immediate plant available K is non-sufficient to meet the requirement of a specific crop. Beside this, the added K fertilizer may adsorb on soil colloids, may fix in clay minerals, or can leach to the underground water, especially in sandy soils. It has been found that ~57% of the applied K can be adsorbed by soil colloid depending on the type and amount of soil clay minerals (Pal et al. 1999), for example, illite and vermiculite have higher K adsorption specificity. In contrast, some studies have quantified that the rate of K adsorption on illite and vermiculite clay minerals is slower than that recorded on kaolinite and montmorillonite. The particle size and chemical composition of the clay minerals affects considerably the release of K from clay minerals (Huang 2005) (Table 2.2). Furthermore, the fixation process of K is relatively fast, whereas the release of fixed K is very slow due to the strong binding force between K

and clay minerals (Öborn et al. 2005). Whether a soil fixes or releases K highly depends on the K concentration in the soil solution (Schneider et al. 2013).

2.3 Nature of Minerals in Pakistani Soils

The soils of Pakistan are composed of the various types of clay minerals such as muscovite, biotite, mica, smectite and vermiculite, feldspar, quarts, chlorite, montmorillonite, kaolinite, and illite. Among these clay minerals, both mica and illite are dominent in the soils of Pakistan, and it determines the chemistry of soil solution, and thus the fertilizer behavior (Fig. 2.3). The silt and sand fractions of these soils consist of primary clay minerals such as mica, feldspar, and quarts; mica and feldspar present in large fractions and are ores of K. The clay fractions consist of secondary clay minerals, namely vermiculite, chlorite, montmorillonite, kaolinite, illite, montmorillonite, and kaolinite being most abundant. Although the soils of Pakistan also have chlorite and kaolinite clay minerals which contain K, but their significance as potash nutrition is low due to their low nutrient retention ability. Indeed, the poor drainage and semi-arid environmental conditions may cause the further weathering of these both clay minerals to saponitic smectites.

The alluvial soils of Pakistan have both clay minerals, namely mica and illite; crucial source of K nutrient. Mica is most dominate K bearing clay mineral in Pakistan which is formed by slow weathering of Himalayan rocks. The K contents of mica in clay, silt, and sand are 97%, 93%, and 70%, respectively (Ali et al. 2006). During weathering, mica releases the K ions into soil solution. If the process of weathering proceeds enough, mica is converted into expandable illite, also known as hydrated mica, after the entry of water in interlayer. The hydrous mica in Pakistani soils is of two types namely biotite mica and muscovite. Among both these types, the biotite mica is more important form fertility point of view as it releases the K, 100 times more than muscovite in soil solution (Ali et al. 2006).

Like other clay minerals, smectite and vermiculite are found in very low quantity in most of the soils in Pakistan, but these clay minerals play a crucial role in the fixation and release of K fertilizers due to their shrinking and swelling properties and higher nutrient exchange capacity. The formation of vermiculite clay minerals takes place after intensive weathering of illite, accomplished with the release of K. In soils, where the vermiculite is a dominant clay mineral, the phenomenon of fixation may occur due to high nutrient exchange capacity and high adsorption selectivity of vermiculites for ammonium and K than other nutrients, which may reduce the fertilizer use efficiency. However, the vermiculite clay minerals are rarely developed in the Pakistani soil except in Murree, Wazirabad, Gujranwala, and Satgarh soil series (Ali et al. 2006).

In Pakistani soils, the smectite clay mineral can be divided into beidellite and montmorillonite. Under wet conditions, both of these clay minerals expand, while both shrink on drying. Regarding the K fixation, the behavior of beidellite clay mineral is similar to vermiculite, while the K fixation capacity of montmorillonite is 50 times less than beidellite. Thus, in Pakistani soils, the occurrence of beidellite and

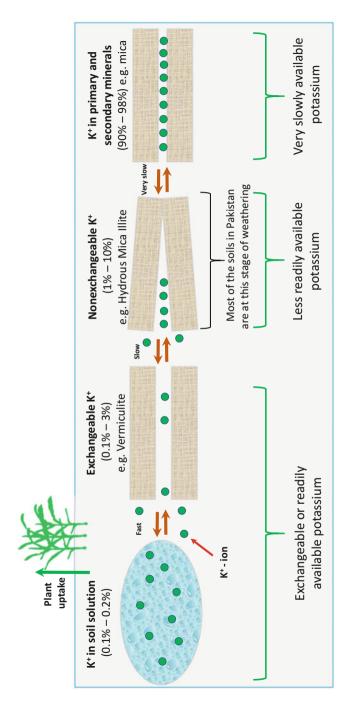


Fig. 2.3 The major fraction of potassium in soils is in the fixed form which is not readily available for plants. Most dominant clay minerals in agricultural soils of Pakistan are illite/hydrous mica; however, vermiculite has also been reported in small areas

vermiculite is highly related to K deficiency, while the occurrence of illite and montmorillonite to optimum K supply status. A soil can be regarded as best which contain montmorillonite and both illite/mica, because the K released from both these clay minerals can be held as an exchangeable nutrient by montmorillonite clay mineral with less fixation but more easy availability to crop roots (Ali et al. 2006).

2.4 Plant Available Potassium

The amount of K present in the soil is evaluated by a number of soil factors such as its uptake by plant, degree of weathering such as the amount and type of clay, the addition of fertilizer, leaching losses, and the fixation process/K release that occur in the soil. As mentioned earlier, the plants are unable to take up most of the soil indigenous K because it is present in structural or fixed form. Plants can take up only those fractions of the K which are present in the dissolved form (<100 mg kg⁻¹) or exchangeable form (Rehm and Schmitt 2002). Furthermore, the supply of K to plant is directly controlled by the K concentration in soil solution. Additionally, some soils with low plant available K can maintain the high levels of solution K which fulfill the crop requirements and hence the outer K input did not impact crop growth as the needs are fulfilled by K already in soil.

In Pakistan, K content in soils has traditionally been considered adequate for normal plant growth as they are developed from mica type of clay minerals; but in most soils, most of this K is not necessarily available to plants to complete their life cycle. In such soils, K is bound to the clay mineral which do not release the K at the rates which are required for optimum crop harvest. In an early study, it was reported that most of soils in Pakistan have less than 150 mg kg⁻¹ of exchangeable K (Bajwa and Rehman 1996), and it is considered deficient to fulfill the requirements of most of the crops. Furthermore, the extensive cropping with high yielding cultivars accomplished with no potash fertilizer in Pakistani soils have seriously dropped soil indigenous K level. More than 30% of soils in Pakistan require potash fertilizer because these soils are K deficient (Akhtar and Dixon 2009). However, the application rate is also very low and according to the most recent report only 16% farmers in cotton growing areas of Pakistan use potash containing fertilizers while 44% soils are revealed K deficient (Wakeel and Ishfaq 2016).

In intention to assess the changing pattern of soil K levels in Pakistan, data from soil samples analyzed for advisory purpose to farmers from two particular years, namely 1990 and 2005 were compared (Table 2.3). The Punjab province of Pakistan was categorized into four agroecological zones, namely Rainfed Zone comprises of northern parts of the province; Rice Zone consists of irrigated north-eastern parts of the province; Central Zone comprises of central irrigated districts of the province and cotton Zone falls in southern parts of the province. It was observed that within 15 years; soil available K declined 7–49% in different agroecological zones of Punjab province. Such dramatic depletion of K is alarming, and soils are prone to additional K deficiency if potash fertilizers will not be oriented in farmer input practices.

	1990		2005						
Zone	No. of samples	Mean value	No. of samples	Mean value	Percent decrease				
Rainfed	1500	114	1550	106	7				
Rice	1400	176	1645	132	33				
Central	2670	295	3200	198	49				
Cotton	1658	210	2280	165	27				

Table 2.3 Soil potassium level (mg kg⁻¹) in various crop zones of Punjab–Pakistan by 1990 to 2005 (analyzed by Soil Fertility Research Institute, Punjab)

Source: Ahmad and Mian (2009)

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