

POTASSIUM REACTIONS IN THE SOIL

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(Met opsomming in Afrikaans)

Abstract

The availability of potassium in soils is varied and related to the crystal chemistry and structure of clay minerals. An outline is given of the structure of mica and vermiculite clays which are mainly responsible for the release/fixation phenomena of K in soils.

Factors which affect the equilibrium between the various forms of K in the soil, such as, the CEC, clay mineral composition, presence of complimentary cations, moisture content, etc. are enumerated. Although the exchangeable K value, in general, gives an estimate of the amount of K that could be expected to be "available" to plants, it is emphasized that the supplying power for K of a given soil system is characterised by both the amount present and the energy level at which it is supplied.

Introduction

Soil mineral matter normally contains a relatively high content of potassium (up to 2%) as shown by a full chemical analysis. However, its availability to plants is varied and related in many ways to the crystal chemistry and structure of soil minerals.

In most soils only a very small part of the total K is readily exchangeable (labile) to other cations; the bulk occurs in fixed (or difficult to exchange) forms in K feldspars, micas and micaceous clays, all of which are potential sources of K for plants. The non-exchangeable K reserves in many soils may become available to plants as labile K is removed. However, soils containing similar amounts of total K can vary greatly in their ability to release non-exchangeable K. Some soils can provide amounts of K adequate for crop growth during many years, but the release from reserves in others is too slow to meet crop requirements. The nature of the K containing minerals and their amount are undoubtedly of great importance in attempting to relate mineralogical composition of soils to their ability to release K.

No simple relation can be expected between the overall K status of soils and the availability of K since the supplying power of a given soil system with regard to nutrients is characterised by both the total amount present and the energy level at which they are supplied. For example, of the essential elements, K is the metal used in largest amounts by plants; Ca however, is normally the dominant

exchangeable cation in most soils. For a better understanding of the K status of soils it is therefore important to be aware of the various factors affecting the K/Ca system of equilibria and adsorption characteristics of the soil material.

Mineralogy of soil potassium

Most of the K that is readily available to plants exist as exchangeable ions principally on clay mineral surfaces. The main soil clay minerals are the 2:1 type, mica, montmorillonite and vermiculite, and the 1:1 type, kaolinite and halloysite. As the exchangeable K is removed it may be replaced at various rates depending on the amount and characteristics of the K-bearing minerals (mica and feldspar) present in the soil.

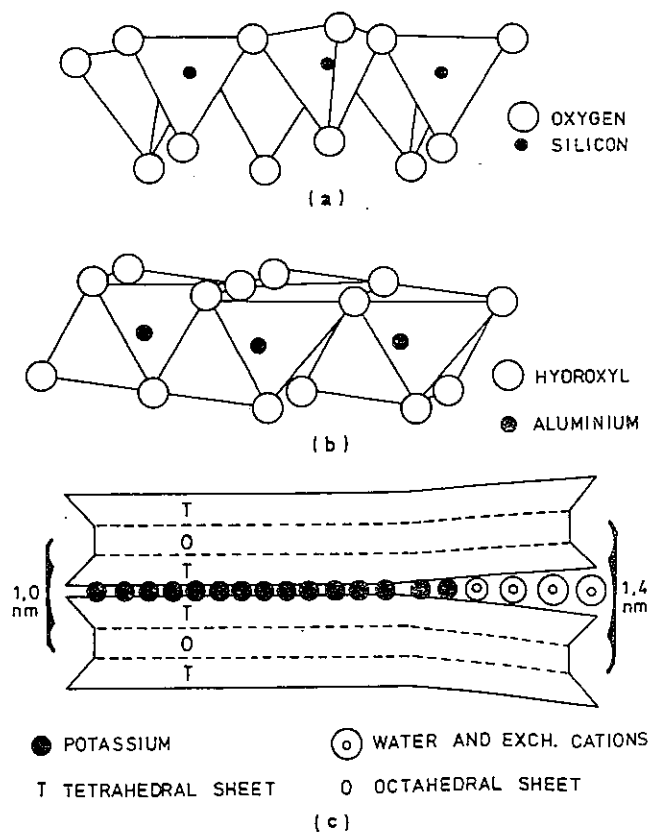


FIG 1 Diagrammatic representation of the structure of (a) a single tetrahedral sheet, (b) a single octahedral sheet, and (c) the 2:1 layer structure of mica (left) and vermiculite (right)

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Two basic units are involved in the crystal structure of phyllosilicate clay minerals (Figure 1). The tetrahedral unit consists of a silicon atom equidistant from 4 oxygens arranged in the form of a tetrahedron with a silicon atom at the centre. The silica tetrahedral groups are arranged to form a hexagonal network which is repeated indefinitely to form a sheet. The tetrahedra are arranged so that the tips of all of them point in the same direction and the bases are in the same plane. The structure can be considered as made of a perforated plane of oxygens which is the plane of the base of the tetrahedral groups, a plane of Si atoms with each Si in the cavity at the junction of 3 oxygen atoms and therefore forming a hexagonal network, and a plane of oxygen atoms with each oxygen directly above a Si atom. The tetrahedral unit is illustrated in Figure 1(a) and has the formula $(\text{Si}_2\text{O}_5^{2-})_n$.

The octahedral unit consists of two planes of closely packed hydroxyls in which Al, Fe or Mg atoms are embedded in octahedral co-ordination so that they are equidistant from 6 hydroxyls. When Al is present only $\frac{2}{3}$ of the possible positions are filled for balance, the structure being that of gibbsite $\text{Al}_2(\text{OH})_6$. When Mg is present all the positions are filled to balance the structure which is brucite $\text{Mg}_3(\text{OH})_6$.

The octahedral unit is illustrated in Figure 1(b). This structure is electrically neutral having 6 positive and 6 negative charges per unit cell, with the formula $(\text{Al}_2(\text{OH})_6)_n$.

Mica

The basic structural unit is a layer composed of 2 tetrahedral sheets with a central octahedral sheet. The tips of the tetrahedra point upwards towards the centre of the unit and are combined with the octahedral sheet in a single layer with a suitable replacement of hydroxyls for oxygens. Isomorphous substitution of Al for Si results in a charge deficiency which is balanced by K^+ ions. The K^+ occur between unit layers where they just fit into perforations in the surface of the oxygen layers (Figure 1c). Adjacent layers are stacked in such a way that each K^+ is equidistant from 12 oxygens, 6 in each layer.

Dioctahedral micas (high in Al — muscovite — $\text{KA1}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$) are much more abundant in soils than trioctahedral members (normally high in Fe and Mg — biotite — $\text{K}(\text{MgFe})_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$). This is mostly due to the greater weathering stability of the dioctahedral members. Mica exhibits a characteristic 10A (1,0nm) basal spacing (Figure 1c).

Grim introduced the term illite for all gradations between well crystallized muscovites and biotites on the one hand and montmorillonite on the other hand. He also suggested that typical illite has less substitution of Al^{3+} for Si^{4+} in the tetrahedral layer than mica and therefore require less K to satisfy the negative charge. Later workers de-

finied illite as a rock term which represents a random interstratification of muscovite and montmorillonite. It has also been reported that there may be mica layers that do not contain the theoretical amount of K for muscovite but contain, instead of some of the K, ions such as H_3O^+ , Na^+ , and Ca^{2+} . In practice, the clay minerals previously included under the name of "illite" apparently cover a wide range, and this term is no longer in general use.

Vermiculite and montmorillonite

Structurally, these two minerals are very similar to micas except that the unit mica layers are separated more and hydrated cations occupy the interlayer space (Figure 1c) rather than the nonhydrated ions (principally K). The possible distinction, structurally, between vermiculite and montmorillonite is that there is less randomness in the stacking of the vermiculite layers and the seat of the negative charge is essentially in the tetrahedral layer of vermiculite, whereas in montmorillonite it is in the octahedral layer. These minerals may be either trioctahedral or dioctahedral and they exhibit characteristic 14A (1,4nm) basal spacings. The outstanding feature of the montmorillonite structure is that water and other polar molecules can enter between unit layers causing them to expand.

One of the outstanding advancements in the description of clay minerals was the discovery that individual unit layers of different clay minerals often are interstratified in a random or regular fashion, particularly those in the mica group. In a single profile, one often encounters many different proportions of two (or more) minerals regularly or randomly interstratified. Aside from random and regular interstratification of unit silicate layers of different minerals, there is also evidence for "islands" or incomplete layers of hydroxy — Al groups in the interlayer space of expanded three-layer minerals. The latter group is often called pedogenic Al-chlorite.

Weathering and charge characteristics

Dioctahedral micas (high in Al) are much more abundant in soils than trioctahedral members (normally high in Fe and Mg), due to the greater weathering stability of the former. The removal of K from micas yields vermiculite, which is fairly stable in the presence of Ca and Mg. In turn vermiculite gradually transforms to montmorillonite in the fine flay fraction. Generally, the weathering of micaceous clays yield a complex mosaic of vermiculite, chlorite, and possibly montmorillonite crystallites, mixed with mica cores or remnants as follows:

- (i) a decrease in the K content of the material,
- (ii) a decrease in intensity and a broadened angle of diffraction of X-rays, with the appearance of basal spacings intermediate between 10 and 14A°; as weathering and depotassication proceeds the 14A° peak is strengthened,

- (iii) an increase in internal surface area,
- (iv) an increase in OH content,
- (v) a lowering in charge.

The major part of the negative charge carried by clay minerals is due to substitution of Si and Al by other cations, of lower valence, resulting in an excess negative charge. This is referred to as isomorphous substitution, for example, Al^{3+} can substitute for Si^{4+} in the tetrahedral layer, or Mg^{2+} can substitute for Al^{3+} in the octahedral layer, and this results in an excess negative charge. In the case of mica the total interlayer negative charge of about 250 milli-equivalents per 100 gram (me%) is covered by K ions which fit into the interlayer space. Vermiculite carries a potential negative charge of about 150 me%, while that of montmorillonites and kaolinites are 80 – 100 me% and 10 – 20 me%, respectively.

The K fixing properties of vermiculite has been used as a model for soil clay vermiculite determination, i.e. assuming that the interlayer charge attributable to the vermiculite component is 154 me per 100 g clay. The vermiculite is determined on the basis of the part of the CEC, measured by Ca replaced by Mg, which is blocked by K fixation on oven drying the sample at 110°C and subsequently not exchanged by NH_4 . Mica determinations are based on the total K contents (HF – $HClO_4$ dissolution analysis) of the clay fraction based on the fact that dioctahedral micas contain 10% K_2O . Normally feldspar K should be deducted but it is normally only present in negligible quantities in the clay fraction of most soils.

Feldspar

The K bearing feldspars are framework silicates consisting of SiO_4 and AlO_4 tetrahedra linked in all directions through the oxygen of the tetrahedra. K is held in the interstices of the Si, Al–O framework. The formula for this feldspar is $KA1Si_3O_8$, showing that only one out of four of the tetrahedra contain Al. Feldspars are generally only present as primary minerals in the coarser fraction or slightly weathered soils and the K is unavailable or slowly available to plants.

Potassium equilibria in soils

Only a fraction of the total amount of K in most soils can be immediately utilized by plants. The various forms in which K exists in soil can be considered to be in equilibrium and this is illustrated diagrammatically in Figure 2. The K which is generally not available to plants occurs as part of the structure of unweathered mica. Slowly available K can gradually be taken up by plants on releases from weathered mica-vermiculite or K may be fixed by vermiculite if present in substantial quantities. Readily available K, the combination of soil solution and exchange-

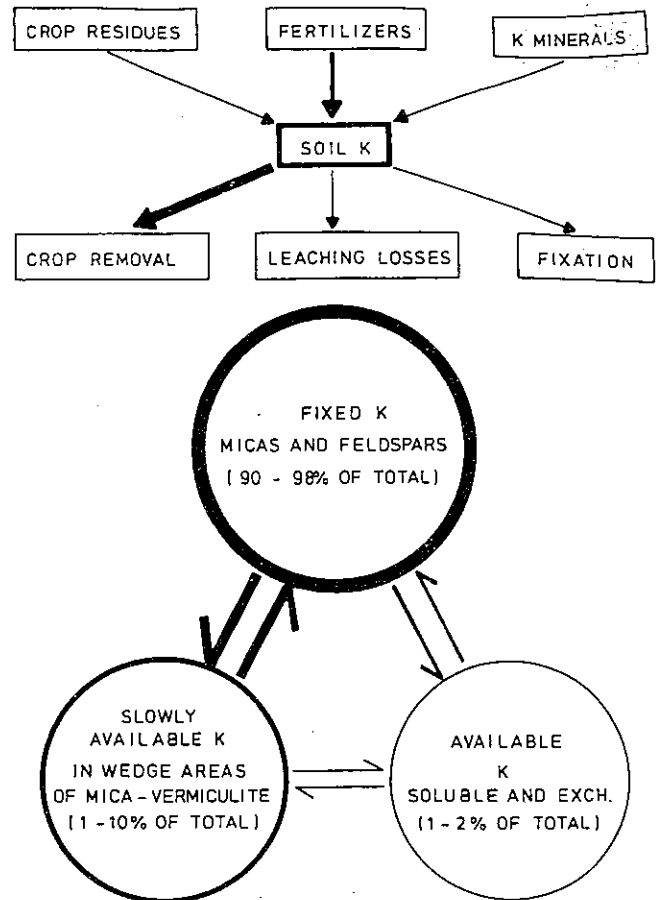


FIG 2 Illustration of the various forms of potassium in the soil

able K, can easily be absorbed by growing plants. These divisions serve in a general way to define the types of K in the soil and the relative availability to plants. Of the total soil K, 90 – 98% is considered to be unavailable for annual crops, 1 – 10% is slowly available and 0,1 to 2% is readily available.

The distribution of K between negatively-charged sites on the soil colloids and the soil solution is a function of the kinds and amounts of complementary cations. Exchangeable Ca and Mg, because of their bivalent nature, are held with considerable energy by soils. However, because of their high degree of hydration are easily exchanged from interlayer positions, and fixation of these cations do not occur in 2:1 layer silicates. Their abundance in the soil solution may inhibit the uptake of K ions.

For these reasons K/Ca equilibria in soils have been studied most often. Empirical extraction techniques, although useful for routine advisory services, generally only give an estimate of the "available" soil K. However, in order to understand the supplying power of a soil for K, both the amount and degree of availability of K needs to be known. It has been proposed that the activity ration $[K] \sqrt{[Ca + Mg]}$ in a solution in equilibrium with a soil gives a satisfactory measure of the potential or availability or intensity (I) of

labile K in the soil. This is not a measure of the capacity of the soil to release K to the plant as different soils having similar equilibrium activity ratios do not necessarily contain the same amount of labile K. Therefore the K status of a soil may be fully described if both the current K potential in the labile pool and the way in which this potential depends on the quantity (Q) of labile K, are known. This relationship is given by the quantity-intensity (Q/I) curve.

Studies using the Q/I technique have been conducted on a variety of soils and has led to a better understanding of K availability. In general, a high value for Q/I suggests the quantity of K is adequate with the reverse being the case at low Q/I values. However, in soils with a high CEC and hence high Q/I values (e.g. montmorillonite soils) it has been found that although the supply of labile K (Q) is very high, the value of $[K] / \sqrt{[Ca+Mg]}$ (I) is too low to support optimum plant growth. Conversely, in soils with low Q/I values and low CEC (sandy soils and highly weathered soils) the amount of labile K can rapidly be exhausted by crop demand.

In general, there is a good relationship between exchangeable K and soil solution K. On the other hand the total K that can diffuse through the soil solution is dependent on the proportion of K which is in the soil solution at any given time. For this reason, the "intensity" of K in the

equilibrium soil solution is of great significance in plant nutrition.

Factors affecting K equilibria

In intensive agriculture considerable K is required to fulfil the needs of crops. The K released from slowly available forms under such conditions is generally inadequate compared with that released under low yield conditions. As mentioned earlier, plant available K is greatly influenced by the soil colloids present, the CEC of the soil, soil texture, the kinds and amounts of complimentary cations, as well as wetting and drying cycles in soils, soil pH, etc.

As already pointed out the K contained in the soil solution and that on the exchange complex are in dynamic equilibrium. The release/fixation phenomena of K reaches its maximum in soils high in 2:1 clays, especially those containing substantial quantities of mica-vermiculite and montmorillonite. The openings in the oxygen network of the silica sheets in mica structures are of a size similar to that of the K ion and it is firmly held by electrostatic forces. In this connection the NH_4^+ ion has a similar ionic radius to the K^+ ion and can be fixed in the same way by vermiculitic clays. Hydrated cations such as Ca^{++} and Mg^{++} have a larger ionic radii and are not subject to entrapment by expanding-type clays.

TABLE 1 Selected physical and chemical properties of several Natal topsoils and the effects of drying on exchangeable K

Soil Series	% Mica	% Vermiculite	% Clay	K Content, moist (me %)	%K Release air dry	%K Release, oven dry
Balmoral	4,39	3,35	49	0,54	20	— 2
Farningham	0,50	1,77	18	0,21	20	0
Griffin	2,06	1,36	23	0,54	23	— 7
Farmhill	1,17	7,61	47	0,97	8	27
Clovelly	3,99	5,52	36	0,44	2	10
Glendale	2,58	1,06	29	0,47	7	13
Shortlands	1,20	1,93	39	0,08	106	40
Mispah	2,71	0,53	13	0,57	2	— 12
Leksand	1,30	0,68	11	0,19	5	10
Avalon	0,75	0,89	11	0,58	35	45
Bergville	4,12	4,80	52	0,18	16	80
Rensburg	2,31	2,27	40	0,31	17	97
Rydlevale	1,60	1,89	41	0,35	13	4
Arcadia	1,74	1,78	44	0,20	30	60

Several workers have shown that, depending on moisture conditions, various states of equilibrium may be attained among the different forms of K in soils. Relating the change in exchangeable K to plant availability, however, is complicated since diffusion rate, soil oxygen content, root growth and many other factors are also a function of soil moisture.

When field-moist soils are dried, there is usually an increase in measured exchangeable K, especially when the levels are medium to low. However, the reverse situation may occur when the levels are high. It appears that mica-like zones in the clay fraction of soils may be responsible for K release and vermiculite for K fixation.

To assess the significance of K release/fixation some Natal soils were analysed for K at several stages during the air-drying process and after oven drying (Table 1)*. Air drying resulted in some K release in all the soils examined while oven drying resulted in further release in eight of the soils examined. The fact that some of the soils exhibited both release and fixation suggests that both may occur simultaneously — the net affect depending on several independent factors. This and other data demonstrates that the release/fixation phenomena should receive closer attention in fertility evaluation studies designed to establish critical soil K levels.

Liming acid soils can also markedly affect the K equilibria. When an acid soil is limed the exchangeable A1 is precipitated and the resulting exchange sites is competed for by K and Ca. Therefore K leaching losses are a much less se-

rious problem in limed soils than in acid ones. The combination of these effects greatly increases the K held by the clay on exchange sites and may decrease the amount of K in the soil solution. However, the increased root vigour and volume in limed soils compared to soils in which A1 dominates, offsets the lime effect of K availability to crops.

Opsomming

KALIUMREAKSIES IN DIE GROND

Die beskikbaarheid van kalium in gronde is wisselend en na verwant aan die kristalstruktuur van die kleimineraal en hulle fisiese en chemiese eienskappe. In die verband is die 2:1 kleimineraal mika en vermikuliet veral belangrik aangesien die verskynsel van kalium vrystelling/vaslegging in gronde in nou verband staan met die teenwoordigheid van die twee minerale.

Die ewewig tussen die verskillende vorms waarin kalium in die grond voorkom word deur verskeie faktore beheer, naamlik, die katoonuitruilingskapasiteit, tipe en hoeveelheid klei, uitruilbare katione, grondreaksie, grondvog, ens. Alhoewel uitruilbare kalium in die algemeen 'n redelike maatstaaf is van die hoeveelheid K wat verwag kan word om "beskikbaar" te wees vir gewasse, moet dit egter beklemtoon word dat die K-status van gronde beter beskryf word deur die verhouding tussen die beskikbaarheid of intensiteit van K in die labiele pool en die hoeveelheid of kwantiteit teenwoordig.

*Farina, M.P.W. and J. le Roux, Fertilizer Society of South Africa Journ. 1, 1974, pp. 39-42.