

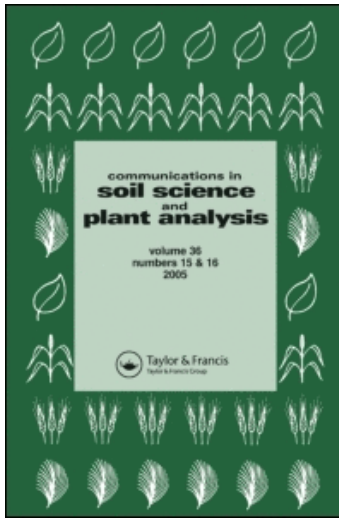
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On the behavior of nonexchangeable potassium in soils

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ON THE BEHAVIOR OF NONEXCHANGEABLE POTASSIUM IN SOILS¹

KEY WORDS: Chemistry of Soil K, K kinetics

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ABSTRACT

A comprehensive review on the chemistry and mineralogy of nonexchangeable potassium is presented. Forms of soil K, the effect of mineralogy on release of nonexchangeable K, methods of determining nonexchangeable K, and the kinetics of non-exchangeable K release are fully discussed.

INTRODUCTION

Equilibrium reactions existing between the solution and nonexchangeable phases of soil potassium (K) profoundly influence K chemistry. The rate and direction of these reactions determines whether applied K will be leached into lower horizons, taken up by plants, converted into unavailable forms or released into available forms. A knowledge of the rapidity of the reactions between solution and nonexchangeable phases of soil K is necessary to predict the rate of added K fertilizers in soils, and to properly make K fertilizer recommendations.

A voluminous amount of research has appeared in the literature on the chemistry and mineralogy of nonexchangeable K, but these data are widely scattered in numerous scientific

journals. The purpose of this paper is to synthesize the above data into a comprehensive review article.

Forms of Soil K

Soil contains an average of 1.7% K (3). The forms of K in the order of their availability to plants and microbes are soil solution, exchangeable, nonexchangeable and mineral. All of these forms are quantified as shown in Table 1. The equilibrium relationships between them are shown in Fig. (1).

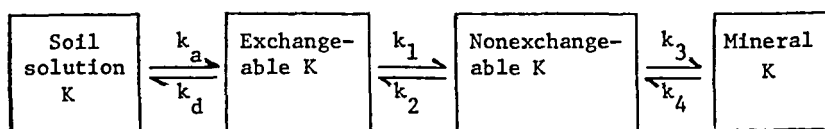
Soil solution K is the form taken up directly by plants and microbes (4), and is also subject to leaching (5). It is usually found in low quantities. The concentration of K in the soil solution is enigmatic. It fluctuates greatly and is difficult to measure. Because the soil solution is polyionic and is often fairly concentrated, the thermodynamic activity rather than just molar or molal concentration of K should be determined if a picture of what the plant root "sees" is desired (6). Levels of soil solution K are determined by the equilibria and kinetic reactions between the other forms of soil K, soil moisture content, and divalent ion content in solution and on the exchanger phase (6,7).

Exchangeable K is held by the negative charges of organic matter and clay minerals. It is easily exchanged with other cations and is readily available to plants (8). The release of exchangeable K to the soil solution is called desorption while the reverse reaction is termed adsorption.

Nonexchangeable K is distinct from mineral K in that it is not bonded covalently within the crystal structures of soil mineral particles. Rather, it is held between adjacent tetrahedral layers of dioctahedral and trioctahedral micas, vermiculites, and intergrade clay minerals (3,5,9,10,11,12,13,14). If nonexchangeable K is equated to "fixed" K, then it can also occur in random gaps in the structure of x-ray amorphous clay-sized minerals (15). Nonexchangeable K^+ ions held in these interlayers and gaps are bound coulombically to the negatively charged interlayer surface sites. This binding force exceeds

Table 1. Forms of soil K and extraction methods that are commonly used in K analysis of clays and soils (adapted from Sparks (3)).

<u>Form</u>	<u>Location</u>	<u>Extractants</u>
Water soluble	Soil Solution	Column displacement Pressure membrane Immiscible displacement and centrifugation
Exchangeable	Colloidal exchange sites - clay and organic matter	$\frac{N}{N}$ NH_4OAc $\frac{N}{N}$ NH_4Cl , Dilute H_2SO_4 and HCl , $\frac{N}{N}$ CaCl_2 or MgCl_2 Dilute CaCl_2 or MgCl_2 Electrodialysis Electroultrafiltration Silver thiourea
Nonexchangeable	Vermiculite Trioctahedral mica Diocahedral mica Hydrous mica (Illite) Chlorite-vermiculite intergrades Interstratified mica-smectites X-ray amorphous minerals	Exhaustive cropping Exhaustive leaching with 0.01N HCl Equilibration with 0.5N HCl Strong HCl at 373K Boiling 23% HCl Exhaustive leaching with 0.1N NaCl Sodium Cobaltinitrate Hot MgCl_2 Successive moist incubations and salt leachings Equilibration with sodium-tetraphenylboron (NaBPh_4) Serial extractions with NaBPh_4 Boiling HNO_3 Electrodialysis Electroultrafiltration Serial extractions with Ca - saturated cation exchange resin Equilibration with H - saturated cation exchange resin
Mineral	Trioctahedral mica Diocahedral mica Orthoclase(K-feldspar)	Selective dissolution with Na-pyrosulfate fusion
Total	-----	HF digestion



- k_a = Adsorption rate coefficient
 k_d = Desorption rate coefficient
 k_1 = Fixation rate coefficient
 k_2 = Release rate coefficient
 k_3 = Weathering and dissolution rate coefficient
 k_4 = Crystallization rate coefficient

FIG. 1. Equilibrium and kinetic relationships between the various forms of K.

the hydration forces between individual K^+ ions resulting in a partial collapse of the crystal structure. Thus, the K^+ ions are physically trapped to varying degrees making diffusion the rate-limiting step. Barshad (16) attributes the good fit of K^+ ions in interlayers to holes in adjacent oxygen layers of the tetrahedral sheet of 2:1 clay minerals.

Nonexchangeable K can also be found in "wedge zones" of weathered micas and vermiculites (10,11). These "wedge zones" are too narrow for exchanging Ca^{2+} or Mg^{2+} ions to enter; however, NH_4^+ and H_3O^+ ions, due to their similar hydrated radii, can enter these zones (10,16,17,18).

Nonexchangeable K is moderately to difficulty available to plants, depending on various soil parameters (5,8,9,12,19,20,21). Release of nonexchangeable K to the exchangeable form occurs when levels of exchangeable and soil solution K are decreased (5,22) by crop removal and/or leaching (9,14,20) and perhaps by large increases in microbial activity.

As much as 94% or more of the total K in soil is in the mineral form (14,23,24). Mineral K is only very slowly available to plants (5,8,9,12,24). Common soil K bearing minerals in the order of availability of their K to plants are biotite (trioctahedral mica), muscovite (dioctahedral mica), orthoclase (K-feldspar) and microcline (25,26,27,28,29). Small amounts of mineral K are released by weathering during a growing season (9,20) but over long periods K release could be substantial. This is particularly true where erosion is important (30) or where rapid soil genesis is taking place and unweathered material is abundant. The release of mineral K to more available forms is referred to as weathering or in severe cases, dissolution. The reverse of this reaction is immobilization or precipitation.

Effect of Mineralogy on Release of Nonexchangeable K

The release of nonexchangeable K is not thought to be the result of dissolution of primary K bearing minerals but actually a diffusion controlled exchange reaction. This exchange is too slow to be measured with normal methods of determining exchangeable K. When this slow exchange occurs in the interlayers of clay minerals such as mica, the replacing ion without its hydration shell must first enter the unexpanded interlayer. Then (31) or simultaneously (32), the interlayer will expand upon hydration of these ions (31), allowing fixed or trapped K^+ ions to hydrate and slowly diffuse to exchange sites on outer parts of the clay particle. Evidence also exists for very slow solid state diffusion of unhydrated nonexchangeable K^+ ions out of these interlayers and inward diffusion of exchanging cations. This diffusion occurs in 1.0 nm areas of interlayers that are near expanded 1.4 nm areas (32).

Much work has been done on the release of interlayer K from trioctahedral micas (33,34,35,36,37,38,39,40,41,42,43). It is convenient to work with trioctahedral micas since their interlayer K is more easily removed than the interlayer K in dioctahedral micas (38). The trioctahedral micas are also much more

subject to acid dissolution than their dioctahedral counterparts (41). The more unstable trioctahedral mica - ferruginous biotite, can be completely broken down by H-saturated resin in about 10 days, releasing all of its K (36). This explains the much higher rate coefficients for K release from these micas than has been observed for dioctahedral micas (37). Bassett (37) attributes this difference to the angle of the O-H bond in the tetrahedral layer of the micas. In trioctahedral micas, this angle is perpendicular to the tetrahedral sheet whereas in the dioctahedral micas, it is oblique to the plane. The oblique angle allows a closer approach by a K^+ ion to the negatively charged oxygen, resulting in a stronger electrostatic attraction. Because of their instability, trioctahedral micas generally occur only in soils where little weathering has taken place and thus such soils contain large quantities of nonexchangeable K (44). Highly weathered soils of temperate, subtropical and tropical regions usually contain none of these minerals and are even very low or lacking in dioctahedral micas. This is why most mineralogical studies of nonexchangeable K release in the literature are of limited applicability to these weathered soils.

Little is known about how nonexchangeable K is held and released by the intergrade clays and x-ray amorphous minerals that occur in such soils. Fields (45) asserts that there is no possible mechanism for K fixation by allophanes. Schuffelen and van der Marel (46), Martini and Suarez (47), and Barber (15) however, present evidence for such fixation. Martini and Suarez (47) attribute this fixation to changes in the degree of crystallinity and hydration of these minerals, especially when subject to wetting and drying cycles.

Many Atlantic Coastal Plain soils of the United States do contain some hydrous mica and weathered vermiculite (10,24,48, 49,50,51). Hydrous mica can fix K (52,53) as can vermiculite (54). Coastal Plain and tropical soils, especially Ultisols and Oxisols, tend to be high in kaolinite, which while releasing exchangeable K quite rapidly (8,55), do not fix K (56,57,58).

With all these minerals, it is logical to assume that if fixation takes place, nonexchangeable K release also occurs.

The nonexchangeable K status of chloritized vermiculite, an intergrade clay, has not been reported on to any extent, but this mineral has been identified in soils by Cook and Hutcheson (59), Garaudeau and Quemener (60); Sparks et al., (49); and by Martin and Sparks (24). It is common in Southeastern U.S. soils (48,49, 50,61).

Methods of Determining Nonexchangeable K

The various methods used to extract nonexchangeable K include exhaustive cropping of soil in the greenhouse, boiling HNO_3 , hot HCl, leaching with dilute HCl, electroultrafiltration, Na^+ -tetrphenylboron (NaBPh_4) with EDTA, and H-saturated and Ca-saturated exchange resins. Exhaustive cropping techniques are quite useful in evaluating the availability and plant uptake of nonexchangeable K. However, to assess accurately the kinds and quantities of nonexchangeable K, soil chemical and mineralogical techniques must be applied since cropping entails too many uncontrollable variables. Accordingly, extractions with salts, acids, electric current, and ion exchange resins are manually employed.

Exhaustive cropping to determine nonexchangeable K availability to plants and to characterize the K supplying power of soils has been used by numerous workers (60,62,63,64, 65,66,67,68,69,70,71,72,73,74,76,77,78,79,80,81,82,83,84,85,86, 87,88,89). Soils are cropped in the greenhouse to plants that are clipped repeatedly for many months or until the plants die. Total plant top and root uptake is measured along with exchangeable soil K levels before and after the cropping. Simple equations for determining nonexchangeable K release by this method have been described by Reitemeier et al., (72), Pratt (90) and Addiscott and Johnston (87). This method has helped to define the K supplying power of soils and the K depleting abilities and depletion tolerances of various crop species of regional interest. A variation on this technique used by Burns

and Barber (76) involved exhaustively cropping the soil, then incubating it in a moist condition at high temperatures for various periods of time. They extracted exchangeable K with \underline{N} NH_4OAc after each incubation and called this K nonexchangeable.

The quickest and easiest way of measuring the amount of nonexchangeable K in soil is with boiling HNO_3 (47,54,77,81,91,92,93,94,95,96,97,98,99). Most workers boil the soil in $\underline{1N}$ HNO_3 for 10 minutes over a flame, transfer the slurry to a filter, leach the soil with dilute HNO_3 , and then, determine the K content of the extract. This method has been described by Pratt (100). Huang et al., (29) did not boil the slurry but rather allowed it to stand at 301 and 311K for various periods of time. McLean (77) used overnight soaking in $0.\underline{1N}$ HNO_3 and repeated boiling, extracting more K than the regular procedure would. One of the problems with boiling only 10 minutes over flame (100) is that it is difficult to be precise about the correct boiling time, the time it takes for boiling to occur, and the vigor of boiling. To avoid this problem, Pratt and Morse (94), Pratt (100), and Conyers and McLean (81) have used a 386K oil bath for 25 minutes including heating time. This releases the same amount of K as with a flame but is more precise and easier when large numbers of samples must be handled. The main problem with boiling HNO_3 and other strong acids for soils is their potential for dissolution of mineral forms of K (19,24).

Other researchers have used continuous leaching with dilute acids (36) such as $0.01\underline{N}$ HCl (77,101), or with electrolyte solutions such as $0.\underline{1N}$ NaCl (102), repeated extractions with 3, 0.3 and $0.03\underline{N}$ NaCl (40), strontium salts (41), hot MgCl_2 (103), and sodium cobaltinitrate (103).

The use of cation exchange resins to simulate the uptake of nonexchangeable K by plants was suggested by Wiklander (104). Hydrogen-saturated resins have been used for this purpose by Pratt (90), Schmitz and Pratt (93), Salomon and Smith (105), Arnold (35), Stahlberg (106), Scott et al., (107), MacLean (77),

Barber and Mathews (19), Haagsma and Miller (108), Feigenbaum et al., (43), and Martin and Sparks (24). These resins have very high cation exchange capacities, far exceeding those of soils. When saturated with an appropriate cation and mixed with soil and with a dilute solution of some sort, they will adsorb and hold all of the K released from the soil.

Calcium- and Na-saturated resins have been tried and found unsatisfactory by Arnold (35), Stahlberg (106), Haagsma and Miller (108) and Feigenbaum et al., (43) when used with any soil minerals more stable than trioctahedral micas. However, Talibudeen et al., (109) argued that H-saturated resin may be destructive to soil minerals and consequently used Ca-saturated resin. After ~ 100 hours of equilibration the resin could not absorb further K and K release stopped. Talibudeen et al., (109) ameliorated this problem by separating the resin and the soil before further K release stopped and then adding a new charge of resin. The separation process however seemed to have caused some exfoliation of clay particles during dispersion in deionized water.

The question of the role of H_3O^+ ions in nonexchangeable K release and soil mineral weathering is surely important. Arnold (35) found muscovite and hydrous mica to be comparatively resistant to H-resin attack. The replacement of interlayer K has been shown to be unaffected by pH changes in the range of 4.6 to 9.2 (110), 4 to 8 (111), 3 to 6.8 (112), and 3 and above (41). Haagsma (113) found that little acid decomposition of soil minerals took place above pH 2.5 in a soil-resin mixture. Wells and Norrish (41) showed that the H_3O^+ ion behaves like a metal cation with regard to K replacement. Norrish (114) further states that in very weak acid concentrations ($10^{-3}N$), the H_3O^+ ion behaves as any other cation in replacing interlayer-K and that only with higher concentrations of acid is the octahedral sheet attacked and its structure destroyed. Martin and Sparks (24) found that H-saturated resin did not cause release of mineral K from two Atlantic Coastal Plain soils. Huang et al.,

(29) justify mild acid treatment for measuring K release on the basis of Keller's (115) statement that the rhizosphere ionic atmosphere is dominated by H_3O^+ . The generally accepted notion that the rhizosphere pH is lower than that in the bulk soil has been seriously challenged by Nye (116). He provides evidence for the rhizosphere pH being 1-2 units higher than the bulk soil. This issue remains unresolved.

In order for electrolyte solutions and cation exchange resins to be effective, the K concentration in the solution phase must be kept very low, or K release is inhibited (32,41,43,110,117,118,119,120). The critical concentration above which release is inhibited has been reported as 4 $\mu\text{g/ml}$ (110) for soils in general, 2.3 to 16.8 $\mu\text{g/ml}$ for trioctahedral micas in dilute solution, and as low as $<0.1 \mu\text{g/ml}$ for muscovite and illite. Maintenance of a low enough concentration of K can be accomplished with continuous flow of extracting or exchanging solution (32,41), cation exchange resins (35,43,90) or with Na-tetraphenylboron (121).

The NaBPh_4 method was developed by Scott et al., (121) and has been used also by Scott and Reed (39), Reed and Scott (38), Scott (122), Conyers and McLean (81) and Ross (123). The BPh_4^- anion combines with released K in solution and precipitates, while the Na^+ acts as an exchanger for interlayer K.

Some of these methods have been compared on the same soil samples. Pratt (90) found that H-resin extracted K correlated better ($r=0.96$) than boiling HNO_3 extracted K ($r=0.913$) with alfalfa (Medicago sativa L.) uptake of nonexchangeable K. Schmitz and Pratt (93) found exhaustive cropping released 1.2 times as much K as H-resin while HNO_3 released 2.3 times as much; however, both H-resin and HNO_3 extractions correlated equally well with cropping. Conyers and McLean (81) found that NaBPh_4 sometimes removed more K than HNO_3 , sometimes less. Reed and Scott (38) found NaBPh_4 a better way of evaluating nonexchangeable K than the 0.1N NaCl leaching method of Mortland (36). MacLean (77) reported "r" values for various methods of extracting nonexchangeable K.

Schmitz and Pratt (93) found that while 47% of crop yield variation could be attributed to exchangeable K levels, 88% of yield variation was attributed to HNO_3 extractable K [including exchangeable and nonexchangeable K]. Pratt (90) incorporated K released to Dowex 50 resin into a multiple regression equation for predicting crop removal by alfalfa on Iowa soils. Barber and Mathews (19) included exchangeable K and H-resin extractable nonexchangeable K into simple linear correlation, multiple linear correlation, and multiple quadratic regression equations to predict field response of corn (Zea mays L.), wheat (Triticum durum Def.), oats (Avena sativa L.), and potatoes (Solanum tuberosum L.) to K. These three equations accounted for 27, 37, and 56 percent, respectively, of the yield variation in the four crops. Their precision was quite low however from year to year and within each crop. The highest correlation of nonexchangeable K with yield was for silt loam soils, while the lowest correlation was for sandy loams.

Another technique that has been used for nonexchangeable K analysis is electro dialysis. It has been used by Peech and Bradfield (124), Gilligan (125), Ayres et al. (126), Ayres (70), and Reitemeier et al. (3). A soil slurry is subjected to a current, usually 110V, for various lengths of time, causing various forms of K to be released into solution. More recently, electro dialysis equipment has become more sophisticated (127). Electro dialysis and a new technique, electroultrafiltration (EUF) have been used extensively for soil analysis in Germany and Austria and has been used in Malaysia (128) and in the Philippines (129). Its use in English speaking countries has been very limited. Barber and Mathews (19) warned that electro dialysis may break down K minerals excessively; but whether the same is possible for EUF has not been determined.

Kinetics of Nonexchangeable Potassium Release

The rate of release of nonexchangeable K from the inter-layers of mica (9,38,43,88,122,130) and vermiculite (102) is a diffusion controlled process. A diffusion controlled process

is characterized by a linear relationship between the percent of total K released versus $\sqrt{\text{time}}$ (24,43,50,51,131,132). The difference in concentration between newly mobile (just released) K and that in the external solution supplies the driving force for this diffusion (111).

The general equation for the diffusion of K from clay interlayers (111) is:

$$\left(\frac{K_t}{K_o}\right) = \left(\frac{4}{\pi^{1/2}}\right) \left(\frac{Dt}{a^2}\right)^{1/2} - \left(\frac{Dt}{a^2}\right) \quad [1]$$

where K_t = K released at time t

K_o = K released at equilibrium

D = diffusion coefficient

a = cylindrical radius of the area through which the K diffuses

Dividing through by t yields

$$\left(\frac{1}{t}\right) \left(\frac{K_t}{K_o}\right) = \left(\frac{4}{\pi^{1/2}}\right) \left(\frac{D}{a^2 t}\right)^{1/2} - \left(\frac{D}{a^2}\right) \quad [2]$$

The D value can be calculated if the value of "a" is known. In pure systems, "a" can be determined from mean particle size diameter by means of N_2 adsorption surface area measurements while a width to thickness ratio of the particles must be assumed (40). In particle size controlled pure mica systems two or three different diffusion coefficients have been found (32,133). Each diffusion coefficient corresponded to a different release mechanism. Rausell-Colom et al. (32) and Scott (122) speculate that the small coefficient represents the slow diffusion of unhydrated ions toward the outer edge of 1.0 nm interlayers, while the next highest coefficient represents diffusion of partially or fully hydrated ions out from interlayers 1.4 nm or thicker. A third D value was found by Talibudeen et al. (109) and Goulding and Talibudeen (21). According to Crank (133), the linear relationship of ion release with the square root of time is not degraded by the presence of more than one value of D. Crank (133) and Rausell-

Colom et al. (32) have also found that not only release, but also the movement of observed release-exchange weathering fronts is linearly related to $\sqrt{\text{time}}$.

In a heterogeneous soil with numerous types of clay of varying particle sizes, a realistic value for "a" is usually not measurable; thus, D cannot be measured either (134). For this reason, Eq. [2] must be arbitrarily simplified to:

$$\left(\frac{K_t}{K_0}\right) = \left(k'_2\right) \left(t^{\frac{1}{2}}\right) \quad [3]$$

where k'_2 is an apparent diffusion rate coefficient. Difficulties in accurately determining the value of K_0 are caused by an initial fast release of K which did not obey the parabolic diffusion equation (40,50), and perhaps the problems inherent in distinguishing between mineral K and slowly released nonexchangeable K.

Using H-resin, Feigenbaum et al. (43) found k'_2 values for muscovite of 0.44 hour^{-1} for 5-20 μm particles and 0.38 hour^{-1} for 20-50 μm particles. The authors used the total K content of the mica as the K_0 value. Corresponding values for trioctahedral micas were 7 to 18 times as high, phlogopite releasing K more slowly than biotite.

There is a paucity of classical kinetic analyses of nonexchangeable K release in the literature. Mortland (36) used leaching of biotite with 0.1N NaCl to calculate release rates. He found the appearance of K in solution as a function of time could be described as:

$$K = k \ln t + c \quad [4]$$

where $K = \text{mg K/g biotite released at time } t$

$k = \text{rate constant}$

$c = \text{integration constant}$

During depletion of the first 75% of the K in a miscible displacement system, the rate did not change viz.,

$$\frac{dR}{dt} = 0 \quad [5]$$

where $R =$ the release rate

or

$$\frac{dK}{dt} = -k \quad [6]$$

and the release was thus zero order. In an equilibrium experiment, R did change with time, viz.,

$$\frac{dK}{dt} = -kt^{-2} \quad [7]$$

indicating a first order process. Differentiating Eq. [4]

$$\frac{dK}{dt} = \frac{k}{t} \quad [8]$$

and since $\frac{dK}{dt} = R$ [9]

then

$$R = \frac{k}{t} \quad [10]$$

Equation [10] indicates that the rate of K release is a function of the reciprocal of time under equilibrium conditions.

Mortland and Ellis (102) found the release of fixed K from vermiculite to be first order when they used the 0.1N NaCl leaching technique. Using an exhaustive cropping and hot incubation technique to extract nonexchangeable K , Burns and Barber (76) found release to be first order initially and then release was zero order. They reported a first order rate constant from a Cherokee clay at 382K of $5.83 \times 10^{-3} \text{ hour}^{-1}$.

Using HNO_3 extraction at 301 and 311K, Huang et al. (29) found release to be first order for biotite, muscovite, and microcline. Where M was the percent of residual mineral K at time t , they showed that release obeyed the equation:

$$\log M = \frac{k}{2.303} t + \text{constant} \quad [11]$$

The k value for muscovite was $1.39 \times 10^{-4} \text{ hour}^{-1}$ at 301K. As would be expected the rate constants for microcline were a bit lower than for muscovite, while those for phlogopite were almost one order of magnitude higher and for biotite, two orders of magnitude higher than for muscovite. The authors, however, did not remove K from solution as it was released.

Martin and Sparks (24) determined first-order rate coefficients for nonexchangeable K release from whole soils at 298K using a H-saturated resin.

First-order kinetics in the soils were described as:

$$\frac{dK_t}{dt} = k_2 (K_o - K_t) \quad [12]$$

where K_t = nonexchangeable K released at time t

K_o = nonexchangeable K released at equilibrium

$(K_o - K_t)$ = the amount of nonexchangeable K remaining at time t

k_2 = first order nonexchangeable K release rate coefficient

Integrating

$$\ln (K_o - K_t) = \ln K_o - k_2 t \quad [13]$$

Martin and Sparks (24) found that the k_2 values ranged from 1.1 to 2.2 X 10⁻³ hour⁻¹ (Table 2). The low k_2 values indicated slow rates of K release. The authors found that the parabolic diffusion law also explained the data well with apparent diffusion rate coefficients (k_2') ranging from 1.7 to 2.6 X 10⁻² hour^{-1/2}. Thus, diffusion appeared to be the major rate limiting step in the rate of K release.

Martin and Sparks (24) used the Elovich, parabolic diffusion, first-order diffusion, and zero-order kinetic equations to describe nonexchangeable K release (Table 3). Least square regression analysis was employed to determine which equation best described the data. The correlation coefficient (r) and the standard error of the estimate (SE) were calculated for each equation. The first-order diffusion equation was the best of the various kinetic equations studied to describe the reaction rates of K release from the two soils, as evidenced by the highest value of r and the lowest value of SE (Table 3). The parabolic diffusion law also described the data satisfactorily indicating diffusion-controlled exchange. This was also found in pure minerals by others (38,43,102,122,

Table 2. First-order nonexchangeable K release rate coefficients (k_2) of Kalmia and Kennansville soils (Martin and Sparks (24)).

Depth	$k_2 \times 10^{-3}$
m	h^{-1}
<u>Kalmia sandy loam</u>	
0 - 0.15	1.9
0.15 - 0.30	1.9
0.30 - 0.45	2.1
0.45 - 0.60	1.5
0.60 - 0.75	1.8
0.75 - 0.90	2.2
<u>Kennansville loamy sand</u>	
0 - 0.15	1.8
0.15 - 0.30	1.6
0.30 - 0.45	1.7
0.45 - 0.60	2.3
0.60 - 0.75	2.9
0.75 - 0.90	2.5

130). The relationship showing the good fit of the data for the 0.45-0.60 m depth of the two soils to the first-order equation is shown in Fig. 2. The zero-order equation was not suitable to describe the kinetic data as could be seen from the large values of SE, despite the fact that the values of r were quite high (Table 3). The Elovich equation satisfactorily described the rate of K exchange between solution and exchangeable phases in soils (50) and the kinetics of P release and sorption in soils (135). However, it did not satisfactorily describe the kinetics of nonexchangeable K

Table 3. Correlation coefficients (r) and standard error of estimate (SE) of various kinetic equations for nonexchangeable potassium release from Kalmia and Kennansville soils[†] (Martin and Sparks (24)).

Equation	Kalmia sandy loam		Kennansville loamy sand	
	SE [‡] x 10 ⁻⁴	r	SE [‡] x 10 ⁻⁴	r
1. Elovich: $K_t = a + blnt$	3.30	0.812	2.30	0.871
2. Parabolic diffusion law: $\left(\frac{K_t}{K_o}\right) = a + bt^{\frac{1}{2}}$	5.49	0.980	1.26	0.984
3. First-order diffusion: $\ln(K_o - K_t) = a - bt$	1.35	-0.990	1.40	-0.986
4. Zero-order: $(K_o - K_t) = a - bt$	9.71	-0.985	6.63	-0.977

+ The r and SE values represent an average for the six depths of each soil.

‡ SE is in mol kg⁻¹.

release from the soils studied by Martin and Sparks (24) as evidenced by the low r values and high SE values (Table 3).

Importance of Nonexchangeable K in Soil-Plant Relationships

The importance of nonexchangeable K in soil-plant relationships has long been recognized. When exchangeable soil K levels are low, plants take up more K than was initially exchangeable (136). The equilibrium between exchangeable and nonexchangeable K must be better understood if K fertilizer use efficiency and economic plant yields are maximized. Exchangeable K levels correlate well in many soils with plant uptake and with the release of nonexchangeable K during cropping

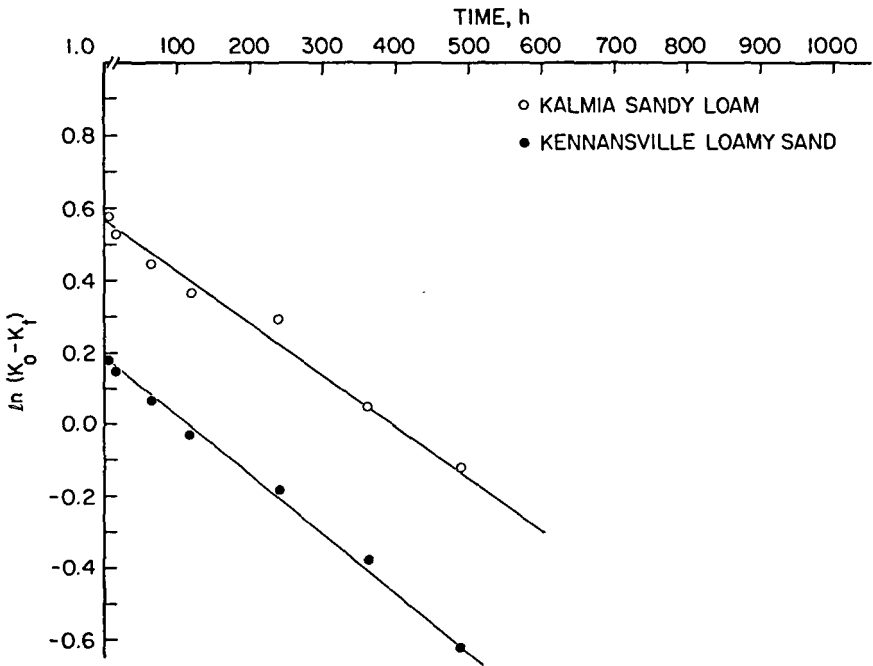


FIG. 2. First-order kinetics of nonexchangeable K release from the 0.45- to 0.60-m depth of Kalmia and Kennansville soils (from Martin and Sparks (24)).

(62,63,70). For other soils, this correlation is poor (66,92, 137). Nonexchangeable K release can proceed locally in the root zone even though the exchangeable K level in the soil outside the root zone is too high for such release (86). The extent to which root zone K depletion occurs is a function not only of the soil's K status, but of the plant's ability to draw down the available K (86). Pratt (90) found that in soils that are not highly weathered, exchangeable K correlated well with plant uptake. In highly weathered soils, the reverse was true. Abel and Magistad (66) showed, however, that once the exchangeable K had been depleted, less weathered Hawaiian soils generally release more nonexchangeable K than highly weathered soils.

SUMMARY

In this paper we have reviewed the chemistry and mineralogy of nonexchangeable K in soils. This phase of soil K, along with the mineral form, comprises the bulk of total K in most soils. Its importance in supplying K to plant roots cannot be over-emphasized.

Perhaps the most important aspect of nonexchangeable soil K is the rate at which it is released to exchangeable and solution forms which are readily available for plant uptake. The rate and magnitude of release is dependent on a number of factors. The level of K in the soil solution greatly affects the release of nonexchangeable K. If the level is low, more release will occur from the nonexchangeable form. This is due to the dynamic equilibrium reactions that exist between the phases of soil K. If the soil solution K level is high, release from the nonexchangeable K phase will be less. A second factor controlling the magnitude of K release from the nonexchangeable form is the type of clay minerals present. Soils that are high in kaolinite and low charge montmorillonite contain very small quantities of nonexchangeable K, while soils containing vermiculitic and micaceous minerals contain copious quantities of nonexchangeable and mineral K.

Regrettably, there are few reports in the literature on the kinetics of nonexchangeable K release from soils. This information is imperative in predicting the K supplying power of soils.

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