Mathematical Models of Potassium Release Kinetics for Sonoran Desert Soils of Arizona

A. Galadima and J. C. Silvertooth

Abstract

The objective of this study was to determine the potassium (K) release kinetics of clay samples from 10 agricultural representative soils of Arizona by successive extraction using Ca-saturated cation resin. A 1993 physical and chemical characterization of the soils revealed that all soils contain smectite-mica K bearing minerals. Four mathematical models (power function, Elovich, parabolic diffusion and first-order) were used to describe the nonexchangeable K release reaction involving 700-hr cumulative reaction time. Comparison of the models using the coefficient of determination ($r^2$) and the standard error of the estimate (SE) indicated that the Elovich and the power function equations overall displayed the best fit. The first-order rate and for the most part, the parabolic diffusion equation did not describe the K release very well. The constants $a$ and $b$ for the Elovich and the power function equations, which represent the intercept and the release rate of the nonexchangeable K respectively, are at least in the order of magnitude as those found by others in several previous studies.

Introduction

The ability of the nonexchangeable K phase to release K to the labile phase has been successfully studied over the years using various techniques. Extensive and excellent literature capitulations of this subject are given in Beckett (1977), Havlin et al. (1985), Mengel and Kirby (1978), Rich (1985), Sparks and Jardine (1984), and Talibudeen et al. (1978). Several models and techniques have been employed in the study of K release kinetics. Both the miscible displacement and the batch techniques are popular and have been used with great success and are also known to yield similar results when similar time intervals are used (Brusseau et al., 1991c; Sparks, 1988). For its simplicity, the batch method has been used frequently and involves the placement of the adsorbent and the adsorptive in a centrifuge tube. The suspension is then agitated and centrifuged to separate a clear supernatant for analysis (Sparks, 1988). Using the batch method, it has been demonstrated that extraction using the Ca-resin best simulates K release from the nonexchangeable to the exchangeable phase; or more appropriately, the relationship between the interlayer K and plant roots (Feigenbaum et al., 1981; Havlin et al., 1985; Jardine and Sparks, 1984; Martin and Sparks, 1983). Plant roots take up the soil solution K creating a diffusion gradient as a result of keeping the solution K concentration very low; this is essential for further K release from the interlayer (Mengel, 1985). The efforts to describe K release kinetics has led to the successful use of several models which include; parabolic diffusion, first order rate, Elovich, and the power function equations (Feigenbaum et al., 1981; Havlin and Westfall, 1983; Havlin et al., 1985; Martin and Sparks, 1983; Sparks and Jardine, 1981; and Talibudeen et al., 1978).

However, most of the K kinetics studies in the literature have been reported for highly weathered, relatively acidic, and K responsive soils of moderate to high rainfall climates. Kinetic studies that involve relatively unweathered, calcareous or alkaline semi-arid to arid region soils are still minimal. In fact, information describing K kinetics of arid soils of the Sonoran Desert agricultural soils, where responses to K fertilizer are not usually observed due to high native labile K levels, is very limited. The previous studies (McGeorge, 1933; Hendricks, 1985; Silvertooth et al., 1992; Unruh et al., 1993 & 1994; and Galadima et al., 1995 and 1996) were focused on the immediate concentration levels of the labile K in the soils, and its (labile K) ability to support crop production. The purpose of this investigation was to determine the K release kinetics of ten agricultural soils of the Sonoran Desert soils of Arizona by the batch technique using the aforementioned mathematical models (Havlin et al., 1985; Mengel and Uhlenbecker, 1993; Talibudeen et al., 1978).
Materials and Methods

The ten soil samples used for the potassium (K) release studies were collected from ten sites across Southern Arizona that are representative of the common agricultural soils of the Sonoran Desert (Unruh, Silvertooth, and Hendricks, 1994). Soil were sampled from the Ap horizon and air-dried before being fractionated using the ultrasonic dispersion of the whole sample in 1M NaOAc (pH 8.3). NaOAc was used to disperse the soil as well as to remove the exchangeable K (Jackson, 1950). Prior to the use of NaOAc, coarse sand size particles were separated from the whole sample by wet sieving. Clay fraction was separated by the pipette method which is based on Stoke's law for sedimentation of particles in fluid (Hillel, 1992). Using Stoke's law \( t = \frac{18h}{d^2g(p_s - p_f)} \), the time \( t \) for a given particle size \( d \) to sediment or drop by height \( h \) in an aqueous solution (at a given temperature) is calculated. The clay in the in the suspension was pipetted from the sedimented sand and silt particles after time \( t \) had elapsed. Six repetitive settlings and pipetting of the resulting suspension was a requisite to the effective separation of the clay from the sample. The separated clay fractions were subsequently air dried after repeated decantation of the supernatant.

The resin used for the reaction was Dowex-50 (HCR-W2) X8, dry mesh 16-40, strongly acidic cation exchanger (hydrogen ionic form). Prior to being used for the exchange reaction, the resin was transformed to the calcium (Ca) form. This form used in the K release reaction is believed to closely simulate the natural soil K release reaction (Havlin and Westfall, 1985). The moist resin was air dried overnight under the fume hood before being passed over a 20-mesh sieve. This enabled the particle size \( >850 \mu \text{m} \) to be retained and transformed to the Ca form. The process of transformation was as described in Havlin et al., 1985, and Talibudeen et al., 1978. This process involved a series of washings of the resin with a deionized water, followed by a titration with 1M NaOH until the pH stabilized between 6.5-7.0 for two days. The resin was then slowly leached with 1M CaCl\(_2\) until sodium (Na\(^+\)) level in the leachate was less than 1 µg/ml. The now Ca saturated resin was washed by 0.01M CaCl\(_2\) followed by another wash with deionized water until the leachate contained less than 2 µg/ml Ca\(^2+\). The resin was then stored under deionized water for subsequent use. Subsequently, the used resin was regenerated for further use by following the treatments described above. The transformation of the resin from the hydrogen to the calcium form may be summarized as follows:

\[
\begin{align*}
R_2\text{SO}_3\text{H} + \text{NaOH} &= R_2\text{SO}_3\text{Na} + \text{H}_2\text{O} \quad \text{(titration step)} \\
2R_2\text{SO}_3\text{Na} + \text{CaCl}_2 &= (R_2\text{SO}_3)\text{Ca} + 2\text{NaCl} \quad \text{(leaching step)} \\
(R_2\text{SO}_3)\text{Ca} + 2\text{NaCl} &= (R_2\text{SO}_3)\text{Ca} \quad \text{(a final washing step)}
\end{align*}
\]

Prior to being used for the K release reaction the stored resin \((R_2\text{SO}_3)\text{Ca}\) was scooped into a porcelain funnel (whose false bottom was covered with a filter paper) and leveled off. This charge of wet resin was then connected to a vacuum line and evacuated for two minutes so that a 10g weight of resin was reproducible to approximately ±0.02g.

The K release reaction involved weighing out the air-dried clay \((1.00 \text{g}, <2 \mu \text{m})\) samples into a plastic centrifuge tubes. An aliquot of 0.5 ml deionized water was then added to each tube and allowed to equilibrate overnight. Two grams of the evacuated Ca-resin together with 10ml of deionized water were added. The mixture of soil, resin, and water was then gently and continuously agitated at intervals representing the K release reaction periods. The reaction temperature was 22° ± 2°C. At the end of each reaction period, the resin was quickly separated in less than 5 minutes from the soil on a 48-mesh sieve with 25 ml deionized water. The resulting soil suspension was centrifuged at 12,000 rpm for 10 minutes; 25ml of the supernatant was then decanted, and its K concentration was determined on an atomic absorption spectrophotometer (AAS). A fresh charge of Ca-resin was again added to the centrifuged soil to initiate the next reaction period. The separated resin was leached at the rate of about 10-11 ml/hr with 150ml of 0.01M CaCl\(_2\) and the leachate was analyzed for K concentration by AAS.

The set-up for leaching the separated resin involved inserting the needle a 60-cc syringe needle into the piston of a 3-cc syringe tube. The 60-cc tube served as a reservoir for the 0.01M CaCl\(_2\) leaching solution. The 3-cc tube, to which a stop valve was attached held the separated resin. The stop valve enabled the flow rate to be adjusted so that a flow rate of about 10 -11 ml/hr was achieved. The needle attached to the stop valve enhanced the effective control of the flow rate and directed the leachate to the collecting flask. Two grams of Ca-resin in each duplicate were weighed out and leached the same way to determine their K content, if any, which was used to correct the measured K concentration of the soil-reacted resin. The total K released during a reaction period was the sum of the K concentration from the leached resin and the supernatant decanted after the centrifuging process.
Results and Discussion

A complete physical and chemical characterization of selected properties of ten agriculturally productive representative soils was undertaken prior to the K kinetic release study (Table 1) Unruh et al., 1994). The X-ray diffraction analysis of the clay mineralogy revealed a mixed mineral composition of smectite, mica, kaolinite, palygorskite, calcite and small amounts of quartz. The chemical analysis indicate none of the soils in the study contained less than 150 mg/kg exchangeable K, except the Superstition sand which contained less than 150 mg/kg. The important features to note in Table 1 is that all soils contain K bearing mica, and none contain vermiculite, which is known to possess a high capacity to fix K between layers within mineral, therefore, rendering it unavailable to plants. The CEC of the soils ranged from 25 cmol/kg to 4 cmol/kg, where the Gadsden and Indio soils showed the highest CEC levels and the Superstition soil, the lowest Southwest Desert soils generally possess low to moderate CEC, yet demonstrate a strong capacity for base saturation. This may be an attribute of soils still in relatively early stages of development with parent materials rich in basic cations.

Cumulative K Release Curves

The total K released from the soil after each reaction period was the sum of the K in the resin and the K in the supernatant liquid of the resulting centrifugation of the separated soil suspension. The K content desorbed from the nonexchangeable phase of the clay samples were cumulatively added and plotted against the cumulative desorption time so that cumulative release curves were obtained as shown in Fig. 1. The amount of K desorbed (released) from the 10 clay samples were in the range of 6.48-116.3mg/kg. The cumulative curves displayed in Fig. 1 show two segments of the three that are typically associated to K release studies of more than 1000 hr cumulative desorption time. The first segment of the curves, which comprised about 35 hours represent the so-called "initial rate", and varies with the soil. This first segment is believed to represent the rapid K release from the mica fraction of the soil and to mass action exchange from the planar surface of the clay (Jardine and Sparks, 1984). The second segment following a transition stage is the immediate long-term release rate representing the first 1000 hrs of K release. This second segment is known to be crucial for the replenishment of the labile soil K. The third segment, which is the second long-term rate usually occur after 1000 h of release time and is lacking in this study since only 700 h cumulative time was attempted. Exchangeable K was removed during the particle separation procedure using the NaOAc, hence, the clay samples employed in the K release (desorption) study were saturated with Na prior to the release reaction with the Ca-resin. The initial K release rates (0-35 hrs) were higher than the rates observed after 35 h, with about 55% of the total K release occurring during the first 35 h (Fig. 1). The cumulative K release plot (Fig. 1) shows a pattern similar to that demonstrated by Talibudeen et al., 1978 and Mengel and Uhlenbecker, 1993. Out of the 10 soil series involved in the study, the Casa Grande sandy loam curve showed the highest K release rate as displayed.

K Release Kinetic Models

Four mathematical models were used to describe the kinetics of nonexchangeable K release in the 10 soil series representing important agricultural soils of Arizona. The power function equation applied to K release is expressed as:

\[ \ln y = \ln a + b \ln t \]

where \( y \) is the amount of K released at time \( t \), and \( a \) and \( b \) are constants. The constant \( a \) represents the initial rate and refers to the \( y \) intercept of the straight line plot of \( \ln y \) vs. \( \ln t \). The constant \( b \) is the slope of the plot, and is the rate constant of the reaction. The Elovich equation applied for the description of K release reaction is in the form expressed below:

\[ y = a + b \ln(t + t_0) \]

The form of the linear parabolic diffusion equation applied to the K desorption is expressed as

\[ y = a + b t^{1/2} \]

and the linear first order equation is of the form:

\[ \ln y = \ln a - bt \]

where the elements of the equations are as described for the power function equation above. According to Havlin and Westfall, (1985) this form of the Elovich equation is suitable for describing cumulative reaction time of below 1000 h. When cumulative time exceeded 1000 h, the equation may be applied as in the form shown below:

\[ y = a + b \ln(t + t_0) \]

The form of the linear parabolic diffusion equation applied to the K desorption is expressed as

\[ y = a + b t^{1/2} \]

and the linear first order equation is of the form:

\[ \ln y = \ln a - bt \]

where the elements of the equations are as described for the power function equation. Ploting the K+ released (y or ln y) versus the term of the duration of the extraction (lint, t or t1/2), straight lines were obtained (Fig. 2 - 4).

Results of the statistical analysis obtained by plots, which were fits between the models and the experimental data, are reflected by the Coefficients of Determination \( (r^2) \) and the Standard Errors of the estimates (SE) (Table 2). The best fit (highest \( r^2 \) and lowest SE) overall were obtained by the Elovich equation and the power function equation. This finding is
in good agreement with the results obtained by Mengel and Uhlenbecker (1993), Havlin and Westfall (1985), Sparks and Jardine (1984), Martin and Sparks (1983), and Sparks et al. (1980). The first order model consistently did not describe K release reactions of the nonexchangeable phase (Table 2), and displayed the poorest fit of all with the experimental data. This finding contrasts with those of Feigenbaum and Shainberg (1975), and Martin and Sparks (1983), but is in agreement with Havlin and Westfall (1985) and Mengel and Uhlenbecker (1993). The parabolic diffusion equation similar to the first order model did not adequately describe K release of the nonexchangeable phase of the samples employed in the study. In Table 2 however, exception can be made for the Casa Grande soil series where this model was only exceeded by the power function, which adequately described the K release process. In general, the finding associated with the parabolic diffusion equation is in contrast with Havlin et al. (1985). The low r² values, and particularly the relatively high values of the SE of the estimates of the parabolic diffusion model provide a strong case for its non-fit (Table 2).

Potassium Release Constants (a and b)
The constants a and b of each model represent the intercept and the slope of the linear curves resulting from plotting the released K⁺ vs. time (Table 3). The constant b mirrors the release rate of the nonexchangeable K. The b values are known to correlate well with crop K released from the nonexchangeable K phase (Havlin and Westfall, 1985; and Mengel and Uhlenbecker, 1993). When plant uptake does not positively correlate with the b value, this may represent the soil’s inability to meet the K demand by the crop. On the other hand, a high positive correlation can be an indication of adequate K release from the nonexchangeable K to meet the crop K needs. Out of the four models used to describe K release in the 10 samples in the study, the Elovich equation which demonstrated the best fit (r² and SE) and displayed the highest b values (Table 3). The b values (also referred to as rate constant, k) of the Elovich equation are at least two orders of magnitude greater than those shown by Havlin et al., 1985. This may present a strong indication that the clay fraction in Arizona soils has a high capacity to release K to compensate for crop uptake. It is also evident from Table 3 that the power function equation which displayed the second highest fit, also showed a rate constant (k) for its model indicative of a healthy K release rate typical for non-fixing clays. Figures 2-4 illustrates the fit between the models and the K release data. The similarities of these plots (r² and SE) particularly, Fig. 2-4 attest to the fact that the K release kinetic reaction is diffusion controlled, particularly between Fig. 2 and 4. The Elovich equation (y = a + b ln t) generally had the best fit of all the models which is in agreement with Havlin et al. (1985) and Mengel and Uhlenbecker (1993).

Conclusions
The results provide a basis for these important observations:
1) None of the soils contain K fixing minerals but rather K bearing minerals.
2) The Elovich and the power function equations adequately described the K release kinetics of the soils tested.
3) The K release rates (b in Table 3) are at least in the order of magnitude in comparison to those obtained elsewhere.

Future Research
A thorough study could be conducted to evaluate K potential (K buffering capacity) using Quantity and Intensity (Q/I) factors, and hence, rank the soils on the basis of their K supplying power to maintain cotton production.

Havlin et al. (1985) found that clay contribution to total K release to Ca-resin ranged from 65.1 – 79.7 percent and that of silt from 20.3 - 34.7. It would seem appropriate that since both clay and silt fractions contribute to total K release, a study of the contribution of the silt fraction would be valuable for determining the percent contribution of each fraction.

Acknowledgment
The authors would like to thank Dr. W. T. Molin and Dr. D. M. Hendricks for their technical support. The invaluable assistance rendered by Eric Norton is also greatly appreciated.
References


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<th>Soil Classification</th>
<th>Depth (cm)</th>
<th>NH₄Oac K (mg/Kg)</th>
<th>CEC (cmol/Kg)</th>
<th>Clay (%)</th>
<th>Textural Class</th>
<th>Clay minerology†</th>
<th>Mineralogy</th>
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<td>Cl</td>
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† S-smectite; M1-mica; K-kaolinite; Q-quartz; CA-calcite; PG-palygorskite
Table 2. Coefficient of Determination ($r^2$)* and Standard Error of the Estimate (SE)* of various kinetic models for K release in ten Arizona soils.

<table>
<thead>
<tr>
<th>Models</th>
<th>Pima</th>
<th>Casa Grande</th>
<th>Mohall</th>
<th>Gilman</th>
<th>Indio</th>
<th>Gadsden</th>
<th>Glenbar</th>
<th>Antho</th>
<th>Grabe</th>
<th>Superstition</th>
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<td>0.972</td>
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<td>0.964</td>
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<td>0.964</td>
<td>0.974</td>
<td>0.962</td>
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<tr>
<td>Lny = Ina + b lnt</td>
<td>SE</td>
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<td>0.112</td>
<td>0.109</td>
<td>0.082</td>
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<td>Parabolic Diffus.</td>
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<td>0.861</td>
<td>0.850</td>
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<td>0.873</td>
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<td>$y = a + bt^{1/2}$</td>
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* significant at $\alpha = 0.05$ level
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* significant at $\alpha = 0.05$ level
Fig. 1. Cumulative K released to calcium resin by ten representative soils.
Fig. 2 Relationship between observed and predicted nonexchangeable K release over time as described by the Elovich \( y = a + b \ln t \) equation.
Fig. 3 Relationship between observed and predicted nonexchangeable K release over time as described by the power function ($\ln y = \ln a + b \ln t$) equation.
Fig. 4 Relationship between observed and predicted nonexchangeable K release over time as described by the Parabolic Diffusion (y = a + bt^{1/2}) equation.