

COMPARISON OF KINETIC EQUATIONS TO DESCRIBE POTASSIUM-CALCIUM EXCHANGE IN PURE AND IN MIXED SYSTEMS

D. L. SPARKS AND P. M. JARDINE

Plant Science Department, University of Delaware, Newark, Delaware 19711

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ABSTRACT

We used first-order, Elovich, parabolic diffusion, and zero-order equations to describe the kinetics of K-Ca exchange in kaolinite, montmorillonite, vermiculite and soils of the Atlantic Coastal Plain Region. The first-order equation was the best of the various kinetic equations studied to describe the reaction rate of K adsorption in the clay minerals and soils, as evidenced by the highest simple correlation coefficients (r) and the lowest values of the standard error of the estimate (SE). The parabolic diffusion law described K adsorption best on vermiculite and soils dominated by vermiculitic clay minerals. The parabolic diffusion law did not describe K adsorption well on kaolinite and soils high in kaolinite. These differences were related to the kinds of binding sites present in the pure and mixed systems. The Elovich and zero-order equations did not satisfactorily describe K adsorption in the soils and clays. Apparent potassium adsorption rate coefficients (k_a') were 0.23, 0.58, and 2.65 h⁻¹ for vermiculite, montmorillonite, and kaolinite, respectively. The k_a' values for the soils ranged from 0.84 to 1.86 h⁻¹, and their magnitude was related to the type and quantity of clay minerals present.

INTRODUCTION

A number of equations have been used to describe the kinetics of K exchange in clays and in soils (Keay and Wild 1961; Burns and Barber 1961; Klobe and Gast 1967; Quirk and Chute 1968; Malcom and Kennedy 1969; Sparks et al. 1980a,b). However, little has appeared in the literature comparing these different equations for K exchange.

The Elovich equation was first developed to describe the kinetics of chemisorption of gases on solid surfaces (Low 1960). Parravano and Boudant (1955) criticized using the Elovich equation to describe one unique mechanism, because they found that it described a number of different processes, such as bulk or surface diffusion and activation and deactivation of catalytic surfaces. Recent theoretical studies with adsorption and desorption in oxide-aqueous solution systems showed that the applicability and method of fitting kinetic data to the Elovich equation require accurate data at short reaction times (Allen and Scaife 1966; Aharoni and Ungarish 1976, 1977). The Elovich equation described the kinetics of heterogeneous isotopic exchange reactions from goethite and gibbsite

surfaces (Atkinson et al. 1970; Atkinson et al. 1972; Kyle et al. 1975). More recently, a modified form of the Elovich equation was used by Chien and Clayton (1980) to describe simultaneous first-order kinetics data for phosphate sorption and release in soils.

The Elovich equation may reveal irregularities in data ordinarily overlooked by other equations (Low 1960). It has been suggested that if χ is characteristic of the nature of the sites involved in the adsorption process, then any "breaks" in the Elovich plot could indicate a changeover from one type of binding site to another (Low 1960; Atkinson et al. 1970; Chien and Clayton 1980). Such "breaks" may not be artifacts of kinetic treatments (Low 1960), but the nonlinear Elovich plots may indicate a differing reactivity of sites for the adsorption of ions on an irregular surface (Atkinson et al. 1970). Hingston (1981) notes that the Elovich equation may be quite applicable to adsorption in soils and sediments where there is wide variation in activation energies because the mixture of adsorption surfaces is so complex.

The parabolic diffusion law has been used successfully in describing K release in clays (Barshad 1954; Chute and Quirk 1967), but it

does not always describe kinetics of exchange in soils adequately (Sivasubramaniam and Talibudeen 1972; Evans and Jurinak 1976; Sparks et al. 1980a,b). The problem in using the parabolic equation for soil systems may be ascribed to the nebulous interpretation of the slope parameter. Sivasubramaniam and Talibudeen (1972) obtained parabolic plots that had two slopes. They suggested this could be indicative of two simultaneous diffusion-controlled reactions. Sparks et al. (1980b) noted a nonlinearity with the parabolic diffusion equation for the initial minutes of K desorption in soils. They attributed this deviation to film diffusion-controlled exchange in the early minutes of K exchange.

The first-order equation has been utilized by many soil chemists to describe diffusion-controlled kinetics in clays and in soils (Mortland and Ellis 1959; Sawhney 1966; Sivasubramaniam and Talibudeen 1972; Sparks et al. 1980a,b). Sawhney (1966) described the adsorption of Cs on vermiculite as a pseudo-first-order reaction. Adsorption and desorption of K-exchange in soil systems followed first-order kinetics (Sivasubramaniam and Talibudeen 1972; Sparks et al. 1980a,b; Sparks and Jardine 1981; Sparks and Rechcigl 1982). In a study examining the effects of temperature and moisture on K release from soils, Burns and Barber (1961) also noted first-order kinetics.

The purpose of this study was to compare different kinetic equations for K adsorption in the A and B horizons of Upper Atlantic Coastal Plain Region soils and in standard clay minerals.

MATERIALS AND METHODS

Theoretical considerations

First-order equation

For a miscible displacement technique, a first-order kinetic equation for K adsorption can be derived as follows

$$d\left(\frac{K_t}{K_\infty}\right) = k(K_\infty - K_t) \quad (1)$$

where K_t = amount of K on the colloid at time t , and K_∞ = amount of K on the colloid at equilibrium.

Separating variables

$$\frac{d\left(\frac{K_t}{K_\infty}\right)}{\left(1 - \frac{K_t}{K_\infty}\right)} = kK_\infty dt \quad (2)$$

Integrating of the form $\int (dx/1+x) = \ln 1+x$

$$\log\left(1 - \frac{K_t}{K_\infty}\right) = kK_\infty t \quad (3)$$

Because K_∞ is a constant, one can call this product a constant k . Thus

$$\log\left(1 - \frac{K_t}{K_\infty}\right) = k_a't \quad (4)$$

where k_a' = apparent adsorption rate coefficient.

Elovich equation

The Elovich equation can be derived as follows (Low 1960)

$$\frac{dq}{dt} = ae^{-\alpha q} \quad (5)$$

where q = amount of material adsorbed at time t , and a and α = constants during any one experiment. Assuming $q = 0$ at $t = 0$, Eq. (5) becomes,

$$q = \frac{2.3}{\alpha} \log(1 + aat) \quad (6)$$

or

$$q = \frac{2.3}{\alpha} \log(t + t_0) - \frac{2.3}{\alpha} \log t_0 \quad (7)$$

where $t_0 = 1/a\alpha$.

If a volume of gas, q_0 is adsorbed instantaneously and before Eq. (5) begins to apply, the integrated form of the equation becomes

$$q = \frac{2.3}{\alpha} \log(t + k) - \frac{2.3}{\alpha} \log t_0 \quad (8)$$

where $k = t_0 \exp \alpha q_0$.

If k is negligible in comparison with t , Eq. (8) reduces to

$$q = \frac{2.3}{\alpha} \log t - \frac{2.3}{\alpha} \log t_0 \quad (9)$$

or

$$q = \frac{2.3}{\alpha} \log aat \quad (10)$$

Equation (10) results directly from Eq. (6) if $a\alpha t \gg 1$, as shown by Chien and Clayton (1980).

Thus, for K adsorption one could evaluate the Elovich equation (Sparks et al. 1980b), by plotting the amount of K adsorbed ($\mu\text{g K/g soil}$) versus $\log t$ (min).

Parabolic diffusion equation

For K exchange, a radial diffusion law can be expressed as (Crank 1976)

$$\frac{K_t}{K_\infty} = \frac{4}{\pi^{1/2}} \left(\frac{Dt}{a^2} \right)^{1/2} - \frac{Dt}{a^2} \quad (11)$$

where

- K_t = quantity of K adsorbed at time t
- K_∞ = amount of K adsorbed at equilibrium
- a = average radius of soil or clay particle
- D = diffusion coefficient and
- t = time

Equation (11) can also be written as

$$\frac{1}{t} \left(\frac{K_t}{K_\infty} \right) = \frac{4}{\pi^{1/2}} \left(\frac{D}{a^2} \right)^{1/2} \frac{1}{t^{1/2}} - \frac{D}{a^2} \quad (12)$$

The parabolic diffusion equation (Laidler 1965) for K exchange can be expressed as

$$\frac{K_t}{K_\infty} = Rt^{1/2} + \text{constant} \quad (13)$$

where R = the overall diffusion coefficient.

Characterization analyses

Soil samples from the A and B horizons of a Matapeake silt loam (Typic Hapludults), a Kennansville loamy sand (Arenic Hapludults), and a Downer sandy loam (Typic Hapludults) were taken, air-dried, and gently ground to pass a 2-mm sieve in preparation for laboratory analyses. These soils are prevalent in the Upper Atlantic Coastal Plain region.

The standard clay minerals used in the study were Washington County, Texas, kaolinite; Gonzales County, Texas, montmorillonite; and Llano vermiculite. These were obtained from the University of Missouri Source Clay Minerals Depository. The clays were fractionated and prepared for laboratory analyses according to procedures outlined by Jackson (1976). The CEC of the clay minerals, as determined by Mg-Ca

exchange (Rich 1962), was 1.15, 70.21, and 207.00 meq/100 g for kaolinite, montmorillonite, and vermiculite, respectively.

Soil pH was determined using a 1:1 water-to-soil ratio, and organic matter was quantified using a modified Walkley-Black procedure (Allison 1965). Cation exchange capacity was measured by an MgCl_2 saturation with a subsequent displacement by CaCl_2 (Rich 1962; Okazaki et al. 1963). Particle size analysis was determined by the hydrometer method (Day 1965).

Before mineralogical analysis, samples were treated with NaOCl adjusted to pH 9.5 to remove organic matter (Anderson 1963). Iron oxides were removed using a Na-dithionite-citrate-bicarbonate procedure (Mehra and Jackson 1960). The clay and silt fractions were passed wet through a 300-mesh sieve and separated by centrifugation. Oriented mounts of the clay fraction were prepared by depositing ~ 250 mg of clay on a ceramic tile, saturating with K or Mg under suction, washing free of salts, and glycolating the Mg-saturated samples. X-ray diffraction patterns of Mg-glycerol-saturated samples at 25, 110, 300, and 550°C were obtained using a Diano XRD 8300 AD x-ray diffractometer equipped with a graphite monochromator, PDP-8 computer, and a printout. The samples were scanned at 2° (2θ) per min using $\text{CuK}\alpha$ radiation.

Prior to the kinetic studies, the soil horizons and clay minerals were made homoionic with respect to Ca by saturating with 0.5 M CaCl_2 . The excess salt was removed with deionized water until a negative test for Cl^- was obtained using AgNO_3 .

Kinetics of K adsorption using miscible displacement

The kinetics of K adsorption of the soils and clays was determined using a miscible displacement technique (Sparks et al. 1980b). Duplicate 1-g samples of the homoionic soils and duplicate 0.50-g samples of the clays were mixed with 50 ml of deionized water. The suspension was injected into a 47-mm Nucleopore filter column. The column was attached to a Fractomette Alpha fraction collector and a peristaltic pump. The pump delivered the K solution through the soils and clays at a uniform flow rate of 1.0 ml min^{-1} . Aliquots were collected at various time intervals until the concentration of the leachate equaled that of the initial K solution. The K

concentration was measured in each aliquot using atomic absorption spectrophotometry.

Mathematical equations, including the Elovich, parabolic diffusion, first-order, and zero-order, were tested by least-square regression analysis for K adsorption in the soils and clays 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

$$SE = [\Sigma(K_t - K_t^*)^2 / (n - 2)]^{1/2} \quad (14)$$

where K_t and K_t^* are the measured and calculated concentration of K adsorbed at time t , and n is the number of measurements.

RESULTS AND DISCUSSION

Selected chemical, mineralogical, and physical properties of the soils are given in Table 1. Of the three soils, the Matapeake contained the largest amount of clay. Clay content increased in all three soils with increasing depth. The <2- μ m clay fraction of the A horizons of the Matapeake and Kennansville soils were dominated by chloritized vermiculite, with lesser quantities of kaolinite, mica, and quartz. The A horizon of the Downer soil contained substantial quantities of vermiculite, with lesser amounts of chloritized vermiculite, mica, and kaolinite. The <2- μ m clay fraction of the B horizons of all three soils was dominated by kaolinite.

Kinetics of potassium adsorption

The kinetics of K adsorption in the clays and soils is shown in Figs. 1 and 2, respectively.

Initial K adsorption by the soils and clays was rapid and then leveled off with increasing time. For the clays, the quantity of adsorbed K increased in the order montmorillonite > vermiculite > kaolinite. Although vermiculite had a higher CEC than montmorillonite, the quantity of K adsorbed by vermiculite was less, be-

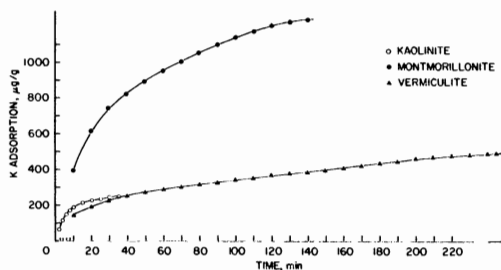


FIG. 1. Potassium adsorption versus time in pure systems.

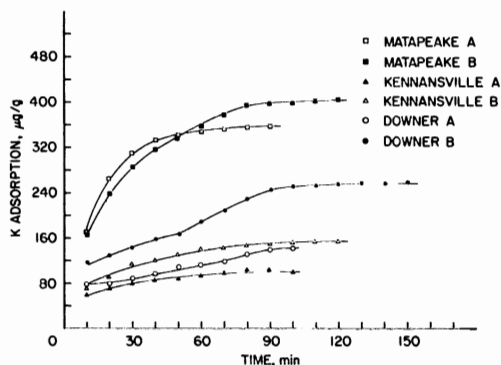


FIG. 2. Potassium adsorption versus time in mixed systems.

TABLE 1

Selected chemical, mineralogical, and physical properties of soils studied

Horizon	Particle size analysis			Organic matter	CEC, meq/100 g	pH	Mineralogy of <2- μ m clay fraction ^a
	Sand	Silt %	Clay				
Matapeake silt loam							
A	14.5	70.0	15.5	2.3	8.9	6.3	Cv ₁ , Ka ₂ , Mi ₃ , Q ₄
B	7.0	75.0	18.0	1.9	10.5	6.0	Ka ₁ , Cv ₂ , Vr ₃ , Q ₄
Kennansville loamy sand							
A	81.6	15.0	3.4	1.2	5.8	5.7	Cv ₁ , Ka ₂ , Q ₃ , Mi ₄
B	71.9	19.1	9.0	0.2	3.4	5.5	Ka ₁ , Cv ₂ , Mi ₃ , Ka ₄ , Gi ₅
Downer sandy loam							
A	76.5	15.0	8.5	1.3	5.9	5.9	Vr ₁ , Cv ₂ , Mi ₃ , Ka ₄
B	70.0	16.0	14.0	0.5	6.2	5.6	Ka ₁ , Vr ₂ , Cv ₃ , Mi ₄ , Q ₅

^a Cv = chloritized vermiculite, Ka = kaolinite, Mi = mica, Q = quartz, Vr = vermiculite, Gi = gibbsite. 1 = most abundant, 5 = least abundant.

cause the interlayer space of this mineral undergoes partial collapse upon K adsorption. The rate of K exchange on kaolinite was rapid, an apparent equilibrium being reached in 35 min. X-ray diffraction of the kaolinite we used in this study revealed only 7.12-Å material, total analysis of the clay (Bernas 1968) showed only small amounts of K, and the CEC was 0.012 meq g⁻¹. Thus, the kaolinite was relatively pure. The rapid K adsorption on the kaolinite is due to exchange taking place only from planar external surface sites. The apparent equilibrium of K exchange on montmorillonite was attained in ~140 min. As would be expected, the rate of K adsorption was considerably slower on vermiculite than on kaolinite and montmorillonite, with apparent equilibrium being reached in ~250 min. The slow rate of K exchange on vermiculite was also observed by others (Keay and Wild 1961; Malcom and Kennedy 1969). Malcom and Kennedy (1969) found that 50 and 97% of Ba-K exchange reactions were complete after 10 and 720 s, respectively, using a batch equilibrium technique. With a miscible displacement technique like ours, the rate of K exchange would be considerably lower (Sparks and Rechcigl 1982). The low rate of K exchange on vermiculite is due to intraparticle transport and to tortuous exchange reactions (Barshad 1954; Sparks et al. 1980b).

More K was adsorbed in the B horizons of the soils than in the A horizons due to a higher percentage of clay and the type of clay found in the former horizons (Table 1, Fig. 2). The <2-

µm clay fraction of the B horizons was predominantly 1:1 layer silicates, which do not have collapsible interlayer spaces. The larger quantity of this type of clay would afford more sites for K exchange. The Matapeake soil adsorbed the largest quantity of K, and the Kennansville soil adsorbed the least. This also conforms to the clay contents in the soils. Equilibrium in K adsorption averaged 105, 110, and 125 min in the two horizons of the Matapeake, Kennansville, and Downer soils, respectively. The longer equilibrium time in the Downer soil relative to the other soils is probably related to the higher amounts of vermiculite (Table 1).

Comparison of kinetic equations to describe K adsorption

The first-order equation was the best of the various kinetic equations studied to describe the reaction rate of K adsorption in the clay minerals, as evidenced by the overall highest value of *r* and the lowest value of SE (Table 2). That K adsorption in clays was described well by first-order kinetics is also shown in Fig. 3. This observation conforms to findings of others (Keay and Wild 1961; Klobe and Gast 1967). The slope of the first-order plots was highest for kaolinite, indicating the highest rate of K adsorption; the lowest rate of K adsorption occurred in vermiculite.

The parabolic diffusion law described K adsorption best in vermiculite, as characterized by the highest *r* value and lowest SE (Table 2, Fig. 4). This observation shows intraparticle diffu-

TABLE 2

Correlation coefficient (r) and standard error of estimate (SE) of various kinetic equations for potassium adsorption in pure systems

Equation	Kaolinite		Montmorillonite		Vermiculite	
	SE ^a	<i>r</i>	SE	<i>r</i>	SE	<i>r</i>
1. Elovich: $K_t = a + b \ln t$	7.27	0.990	11.50	0.999	24.79	0.985
2. Parabolic diffusion law: $\frac{K_t}{K_\infty} = a + bt^{1/2}$	8.40	0.942	3.10	0.988	2.36	0.997
3. First-order: $\log \left(1 - \frac{K_t}{K_\infty} \right) = a - bt$	1.19	-0.997	1.25	-0.994	1.08	-0.992
4. Zero-order: $\left(1 - \frac{K_t}{K_\infty} \right) = a - bt$	15.40	-0.882	10.85	-0.962	12.14	0.977

^a SE is in micrograms per gram.

sion-controlled exchange in vermiculite. This was also found by others (Barshad 1954; Mortland and Ellis 1959; Mortland 1961; Reed and

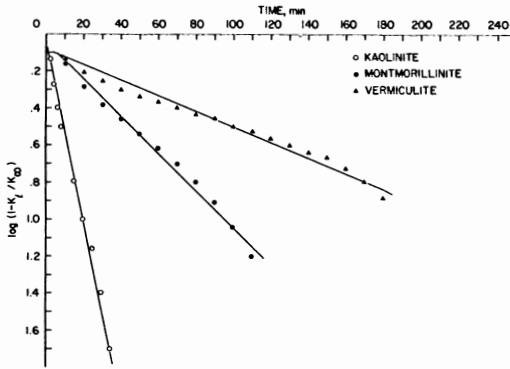


FIG. 3. First-order plots of K adsorption in pure systems.

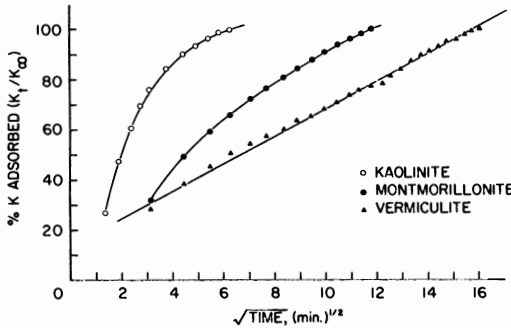


FIG. 4. Parabolic diffusion plots for K adsorption in pure systems.

Scott 1962; Chute and Quirk 1967; Feigenbaum et al. 1981). The parabolic diffusion law did not describe K adsorption well in kaolinite, as evidenced by the relatively low r value and high SE value (Table 2, Fig. 4). Relatively pure kaolinite, which we worked with, should have only external planar surface sites exposed for K exchange, and thus only film diffusion-controlled exchange should occur. This type of exchange is usually not described well by the parabolic diffusion law (Chute and Quirk 1967; Sparks et al. 1980b), because the latter best describes intraparticle transport (Boyd et al. 1947).

The Elovich equation is not suitable to describe K adsorption in pure clays, as can be seen from the large values of SE, even though the r values are quite high. The zero-order equation also did not describe K adsorption well, as shown by the larger SE values and lower r values than for the other equations (Table 2).

The kinetics of K adsorption in the soils was also best described by the first-order equation (Table 3, Fig. 5), as shown by relatively high r values and low SE values. The parabolic diffusion equation also described the kinetics of K adsorption well, although conformity was better in the A than in the B horizons (Table 3). This can probably be related to clay mineralogical differences in the two horizons of the three soils. Kaolinite predominated in the B horizons of all three soils (Table 1), and vermiculitic clay minerals were most prevalent in the A horizons. It was previously shown (Table 2, Fig. 4) that the

TABLE 3
Correlation coefficient (r) and standard error of estimate (SE) of various kinetic equations for potassium adsorption in mixed systems

Equation	Horizon	Matapeake silt loam		Kennansville loamy sand		Downer sandy loam	
		SE ^a	r	SE	r	SE	r
1. Elovich: $K_t = a + b \ln t$	A	18.93	0.958	2.09	0.993	8.27	0.954
	B	11.30	0.989	4.15	0.989	15.68	0.958
2. Parabolic diffusion law: $\frac{K_t}{K_\infty} = a + bt^{1/2}$	A	1.29	0.989	1.29	0.997	2.40	0.996
	B	1.79	0.973	1.79	0.971	4.89	0.986
3. First-order: $\log \left(1 - \frac{K_t}{K_\infty} \right) = a - bt$	A	1.17	-0.995	1.41	-0.989	1.33	-0.990
	B	1.35	-0.988	1.42	-0.990	2.18	-0.989
4. Zero-order: $\left(1 - \frac{K_t}{K_\infty} \right) = a - bt$	A	15.80	-0.852	12.50	-0.926	16.50	-0.965
	B	14.32	-0.926	14.60	-0.903	15.42	-0.952

^a SE is in micrograms per gram.

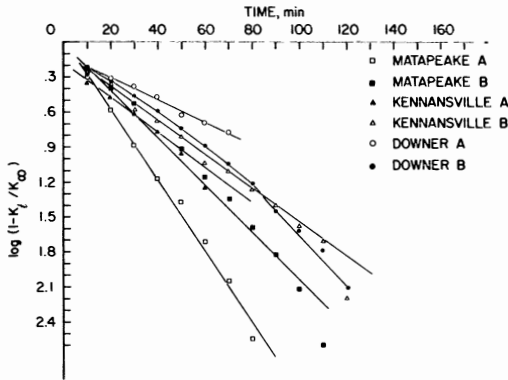


FIG. 5. First-order plots of K adsorption in mixed systems.

TABLE 4

Apparent potassium adsorption rate coefficient (k_a') and apparent half-times ($t_{1/2}'$) in pure and mixed systems

System	Horizon	k_a' , h ⁻¹	$t_{1/2}'$, h
Matapeake silt loam	A	1.86	0.37
	B	1.38	0.50
Kennansville loamy sand	A	1.50	0.46
	B	0.96	0.72
Downer sandy loam	A	0.96	0.72
	B	0.84	0.83
Kaolinite		2.65	0.26
Montmorillonite		0.58	1.20
Vermiculite		0.23	3.01

^a k_a' values were calculated from the first-order equation.

^b $t_{1/2}'$ values were calculated from relationship $t_{1/2}' = (0.693/k_a')$.

parabolic diffusion law did not describe K adsorption well on kaolinite, though it did on vermiculite. As was observed for the clay minerals, the Elovich and zero-order equations did not describe K adsorption kinetics well in the soils, producing lower r values and higher SE values than were found with first-order and parabolic diffusion equations.

Apparent adsorption rate coefficients (k_a')

Apparent K adsorption rate coefficients (k_a') and apparent half-times ($t_{1/2}'$) were calculated for the clays and soils, using first-order kinetics (Table 4). For the clay minerals the k_a' values were in the order kaolinite > montmorillonite > vermiculite, and $t_{1/2}'$ values were in the order vermiculite > montmorillonite > kaolinite.

The k_a' values were higher and the $t_{1/2}'$ values were lower in the A horizons of the three soils than in the B horizons. Even though the A horizons had more chloritized vermiculite relative to the B horizons, the A horizons contained a much larger percentage of organic matter, causing the k_a' and $t_{1/2}'$ values of these horizons to be higher and lower, respectively. The Matapeake and Kennansville soils had average k_a' values for the two horizons, which were similar, as would be expected, due to similar mineral suites in the two soils (Table 1). However, the k_a' values of the Downer soil were lower than for the other two soils. This can be ascribed to the large amount of vermiculite in the Downer soil (Table 4).

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