0038-075X/82/1331-0010$02.00/0
SOIL SCIENCE

January 1982
Vol. 133, No. 1
Printed in U.S.A.

TEMPERATURE EFFECTS ON POTASSIUM EXCHANGE AND SELECTIVITY IN DELAWARE SOILS[1]

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Received for publication 31 October 1980; revised 14 April 1981

ABSTRACT

We investigated the effect of temperature on K availability using quantity-intensity (Q/I) analyses and on K selectivity on the Ap and B21t horizons of a Kalmia sandy loam (Tppic Hapludults), an Evesboro loamy sand (Typic Quartipsamments), and a Matapeake silt loam (Typic Hapludults) from the Delaware Coastal Plain. The predominant mineral suite of the <2-μm clay fraction consisted of vermiculite, mica, and chloritized vermiculite, with lesser quantities of kaolinite and quartz. Quantity-intensity analyses revealed that as temperature increased from 0 to 40°C, the amount of K adsorbed by the soils decreased. For similar initial electrolyte concentrations, ΔK (K concentration difference between initial and equilibrium solutions) decreased, while the activity ratio of K^+ to $(Ca^{2+} + Mg^{2+})^{1/2}$, or AR^k, increased. Thus, to maintain an equal amount of K on the soil as temperature increased, a higher ratio of K^+ to $(Ca^{2+} + Mg^{2+})^{1/2}$ in solution was needed. The equilibrium potassium activity ratio (AR_e^k), which is a measure of available K, increased in the soil horizons as temperature increased. The labile K parameter, (ΔK^0), changed little with temperature, though the potential buffering capacity (PBC^k), which is related to the CEC of the soil, decreased with increased temperature. Potassium selectivity coefficients (k_K), based on the Gapon equation, decreased with increased temperature, indicating decreased K sorption relative to Ca^{2+} and Mg^{2+}, with increased temperature. As temperature increased from 0 to 40°C, the quantity of K in the equilibrium solution increased from an average of 19.3 to 20.9 moles/liter and from 14.0 to 17.0 × 10^{-4} moles/liter in the Ap and B21t horizons, respectively, of the three soils. The amounts of Ca and Mg in solution, however, decreased as temperature increased.

INTRODUCTION

A recent study observed that soil test K levels using the dilute-double acid extractant (0.05 *N* HCl and 0.25 *N* H_2SO_4), varied considerably during the year in a Kalmia soil from Delaware (Liebhardt and Teel 1977). Soil samples taken on a monthly basis from 0 kg K/ha plots of a field study (Liebhardt et al. 1976) with corn (*Zea mays* L.) were highest in K in late May. The soil test K levels decreased while the corn was growing, which was attributed to crop uptake. Soil test K levels remained close to the August sampling level during the winter months, and then they increased dramatically by the May sampling.

The fluctuations in soil test K levels could be ascribed to the dynamic K equilibria reactions that exist among the various phases of soil K (Sparks 1980; Sparks et al., 1980; Sparks and Liebhardt 1981). As the K concentration in the solution and exchangeable K forms decreased, due to crop uptake or to leaching of K into lower horizons, K could be slowly released from nonexchangeable and mineral phases (Cook and Hutcheson 1960; Rich 1972; Sparks 1980). This seems plausible in the Kalmia soil, because it contains feldspars and micas (Liebhardt et al. 1976; Sparks and Liebhardt 1981).

Liebhardt and Teel (1977) did not investigate the effect of temperature on soil test K levels. Although temperature may play an important role in K reactions in soils, little has appeared in the literature on the effect of temperature on K exchange and particularly on K selectivity in soil systems. In pure solutions, where homovalent

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[1] Published with approval of the director of the Delaware Agricultural Experiment Station as Miscellaneous Paper No. 924. Contribution No. 124 of the Plant Science Department.

ions are involved, increased temperature results in decreased selectivity, whereas increased temperature results in increased selectivity in systems where heterovalent species predominate (Coleman 1952; Boner and Pruett 1959 *a* and *b*; Loven and Thomas 1965).

Vanselow (1932) investigated Ca-NH_4^+ exchange on a bentonite clay at 25 and 75°C. He found that the quantity of NH_4^+ in the equilibrium solution was greater while the exchangeable NH_4^+ levels were lower at the higher temperatures.

Burns and Barber (1961) studied the effect of temperature on release of K from nonexchangeable to exchangeable forms. They found that, as temperature increased, the amount and rate of release of nonexchangeable K increased.

Soil temperature is known to affect plant uptake of K. As soil temperature was increased, K uptake was increased in wheat seedlings (Miller and Davey 1967) and in soybeans (Wallace 1957). Recently, Ching and Barber (1979) reported that corn root length was eight times greater and shoot K concentration was $\simeq$ 2.2 times greater when root temperature increased from 15 to 29°C. Walker (1969) noted that, as K uptake increased, there was a concomitant decrease in Ca uptake by maize seedlings as temperature increased. The seedlings showed Ca deficiency at high temperatures.

Temperature affects many chemical parameters. Activity coefficients (γ) decrease with increasing temperature in weak electrolyte solutions and increase to a maximum and then decrease with increasing temperature in strong electrolyte solutions (Harned and Owen 1958). Deist and Talibudeen (1967) found that the γ of adsorbed K and Ca decreased with increased temperature. Hydrolysis of Al salts in aqueous solutions is enhanced by increased temperature (Thorne and Roberts 1948; Matijevic and Tezak 1953). Freshly prepared solutions, or those with added acid, contained only trivalent ions, whereas aging or heating the solution resulted in dimer formation (Matijevic and Tezak 1953). Turner and Ross (1970) found that an $AlCl_3$ solution converted to gibbsite when heated from 10 to 40°C. Rich (1960) found that hydrolysis was retarded by dry heating an Al-saturated vermiculite, but, when an Al-vermiculite suspension was boiled, hydrolysis occurred, as evidenced by reduced NH_4^+ fixation and CEC.

The objectives of this study were to determine the effects of temperature on K exchange using Q/I analyses and on K selectivity in three major soil types from Delaware.

MATERIALS AND METHODS

Bulk samples were taken form the Ap and B21t horizons of an Evesboro loamy sand (Typic Quartipsamments), a Kalmia sandy loam (Typic Hapludults), and a Matapeake silt loam (Typic Hapludults) from Delaware. These soils represent three of the major soil types in the state, and the Evesboro and Matapeake soils constitute major acreages in the Atlantic Coastal Plain region. The soils were air-dried and ground to pass a 2-mm sieve in preparation for laboratory analyses.

Soil characterization analyses

Particle size analysis was determined by the hydrometer method (Day 1965). Mineralogical analysis, by x-ray diffraction, was performed on the <2-μm clay fraction. Prior to soil mineral particle size fractionation, subsamples were treated with 30% H_2O_2 to remove organic matter (Kunze 1965) and with Na-dithionite-citrate-bicarbonate to remove Fe oxides (Mehra and Jackson 1960). Sand was separated from silt and clay by wet-sieving, and clay was separated from silt by centrifugation and decantation. X-ray diffractograms were obtained with a Diano XRD 8300 AD instrument, employing a CuKα radiation source and a graphite monochromator, from oriented clay slides prepared according to the procedures of Rich and Barnhisel (1977).

Organic matter was determined by the Walkley-Black method as modified by Allison (1965), and cation exchange capacity by an $MgCl_2$ saturation with subsequent displacement by $CaCl_2$ (Rich 1962; Okazaki et al. 1963). Exchangeable Ca, K, and Mg were extracted with 1 *N* NH_4OAc (Jackson 1958) and analyzed by atomic absorption spectrophotometry. The pH measurements were obtained from a 1:1 soil:water mixture.

Quantity-intensity (Q/I) determinations

Soil samples (0.2 to 7.0 g) in duplicate were weighed out into a series of 80-ml polypropylene centrifuge tubes. To the samples was added 50 ml of solution, which was 0.002 *M* $CaCl_2$ and from 0 to 0.002 *M* KCl. The tubes were stoppered and equilibrated in a reciprocating shaker for 20 h at 0, 25, and 40°C. Temperature was kept to within 0.3° in temperature-controlled growth chambers. The samples were centrifuged, and the filtered supernatant was analyzed for Ca, K, and Mg by atomic absorption spectrophotometry.

The concentrations of Ca and K were corrected to their chemical activities. The mean activity coefficients were calculated from the extended Debye-Hückel equation (Moore 1972)

$$\log \phi\pm = \frac{-az^+ z^- I^{1/2}}{1 + \alpha\beta I^{1/2}} \quad (1)$$

where

$\phi\pm$ = mean activity coefficient of the electrolyte

z^+ = valency of cation

z^- = valency of anion

$$a = \frac{\epsilon^3}{2.303\,(DkT)^{3/2}} \cdot \frac{2\,\pi N^{1/2}}{1000} \quad (2)$$

I = ionic strength of the solution = ½ $\sum_i C_i Z_i^2$ (3)

where

C_i = concentration of ion i

Z_i = valency ion i

$$\alpha = \frac{.008\,\pi\epsilon^2 N^{1/2}}{DkT} \quad (4)$$

β = distance of closest approach

where

N = Avogadro's number = 6.024×10^{23} molecules mole^{-1}

ϵ = electronic charge = 4.802×10^{-10} esu

D = dielectric constant of the medium (80 for water)

k = Boltzmann's constant = 1.380×10^{-16} ergs mole^{-1} and

T = absolute temperature

The a and α values are temperature-dependent (Harned and Owen 1958), and values used at the three temperatures were: 0°C ($a = 0.4883$; $\alpha = 0.3241 \times 10^{-8}$), 20°C ($a = 0.5042$; $a = 0.3276 \times 10^{-8}$), 40°C ($a = 0.524$; $\alpha = 0.3315 \times 10^{-8}$). The β values for K and for Ca were taken as 3×10^{-8} and 6×10^{-8} cm, respectively, for the three temperatures (Klotz 1964).

The activity ratio (AR^k) was calculated as follows (Beckett 1964)

$$AR^k = \frac{C_K\,(\phi\,\text{KCl})^2}{(C_{Ca} + C_{Mg})^{1/2}\,(\phi\,\text{CaCl}_2)^{3/2}} \quad (5)$$

where C_{Ca}, C_K, C_{Mg} = equilibrium concentrations of Ca, K, and Mg; ϕ KCl = activity coefficient of KCl; and ϕ $CaCl_2$ = activity coefficient of $CaCl_2$.

From plots of ΔK (K concentration difference between initial and equilibrium solutions, or the quantity factor) on the ordinate and of AR^k (activity ratio for K, or the intensity factor) on the abscissa, AR_e^k was determined at the AR^k value when ΔK = 0. The parameter ΔK^0 was the ΔK value obtained when the linear portion of the Q/I plot was extended to intersect the ordinate. The PBC^k value was the slope value of the linear portion of the plot.

K *selectivity coefficient*

The K selectivity coefficient, based on the Gapon equation (Kelley 1948), was determined by the method outlined by Rich and Black (1964).

The K selectivity coefficient $k_K{}^+/Ca^{2+}, Mg^{2+}$, was calculated as follows

$$k_K{}^+/Ca^{2+}, Mg^{2+} = \frac{K^+\ (\text{sorbed})}{Ca^{++} + Mg^{++}\ (\text{sorbed})} \cdot \frac{K^+\ (\text{solution})}{(Ca^{2+} + Mg^{2+})^{1/2}\ (\text{solution})} \quad (6)$$

Sorbed cation concentration were expressed as meq/100 g of soil, and the cations in solution as moles/liter.

RESULTS AND DISCUSSION

The Kalmia and Evesboro soils contained an average of 70 and 74% sand in the Ap and B21t horizons, respectively (Table 1). The Matapeake soil contained larger quantities of silt and clay than the other two soils. With increasing depth, clay content and CEC increased, and organic matter decreased in the three soils. The predominant mineral suite of the <2-μm clay fraction of the three soils was chloritized vermiculite, mica, and vermiculite, with lesser quantities of kaolinite and quartz (Table 1). The presence of mica and vermiculite would indicate possible specific sites for K (Rich and Black 1964; Sparks and Liebhardt 1981).

Temperature effects on Q/I parameters

Excellent relationships existed between ΔK and AR^k at each of the temperatures and for each of the soils with simple correlation coefficients ranging from 0.983 to 0.990 (Table 3, Figs. 1,2). As temperature increased, the amount of K adsorbed by the Kalmia soil decreased (Figs. 1 and 2). Although not shown, the same trends were noted for the Evesboro and for the Mata-

TABLE 1

Selected chemical, mineralogical, and physical properties of soils used

Horizon	Particle size analyses, %			Organic matter, %	CEC mg/100 g	Mineral suite of <2 μm clay fraction[a]
	Sand	Silt	Clay			
Kalmia sandy loam						
Ap	72.3	17.8	9.9	1.7	4.1	VC_1[b], VR_2, MI_3, KK_4, QZ_5
B21t	68.0	17.0	15.0	0.3	4.8	MI_1, VR_2, VC_3, KK_4, QZ_5
Evesboro sandy loam						
Ap	76.5	15.0	8.5	1.5	4.0	VC_1, MI_2, CL_3, KK_4, QZ_5
B21t	72.2	14.4	13.4	0.6	4.2	VC_1, MI_2, VR_3, KK_4, CL_5, QZ_6
Metapeake silt loam						
Ap	14.5	70.0	15.5	2.3	8.9	VC_1, VR_2, MI_3, QZ_4
B21t	7.0	71.0	22.0	1.9	10.5	VR_1, VC_2, MI_3, QZ_4

[a] VC = chloritized vermiculite; VR = vermiculite; MI = mica; KK = kaolinite; CL = chlorite; QZ = quartz.

[b] Subscript 1 = most abundant; 6 = least abundant.

TABLE 2

Effect of temperature on Q/I parameters in Delaware soils

Horizon	Temperature, °C	ΔK°, meq/100 g	AR^k_e, moles/l$^{1/2}$	PBC^k, meq/100 g
Kalmia sandy loam				
Ap	0	−0.31	0.036	8.86
	25	−0.35	0.043	8.79
	40	−0.39	0.047	8.20
B21t	0	−0.02	0.001	6.82
	25	−0.05	0.007	6.10
	40	−0.08	0.011	5.49
Evesboro sandy loam				
Ap	0	−0.20	0.021	5.62
	25	−0.23	0.025	4.84
	40	−0.25	0.028	4.20
B21t	0	−0.02	0.001	4.80
	25	−0.04	0.003	4.30
	40	−0.05	0.007	3.90
Metapeake silt loam				
Ap	0	−0.40	0.058	9.20
	25	−0.42	0.063	9.10
	40	−0.46	0.065	8.98
B21t	0	−0.09	0.003	8.91
	25	−0.10	0.004	8.54
	40	−0.12	0.005	8.42

peake soils. For similar initial electrolyte concentrations, ΔK decreased while AR^k increased, as temperature increased from 0 to 40°C. Thus, to maintain an equal amount of K on the soil as temperature increased, a higher ratio of K to $(Ca + Mg)^{1/2}$ in solution was needed.

The K adsorption process in these three soils would appear to be exothermic (ΔH is negative), because the extent of K adsorption decreased with increasing temperature (Figs. 1 and 2). That K adsorption is exothermic would concur with findings of others (Deist and Talibudeen 1967; Filep and Khargitan 1977).

The AR_e^k parameter, which is a measure of available K, increased in the Ap and B21t horizons of the three soils as temperature increased. The lower AR_e^k in the B21t horizons was probably due to greater K fixation of the subsoil, for there was more clay in this horizon (Sparks and Liebhardt 1981) that contained vermiculite and

TABLE 3

Simple correlation coefficients and prediction equations of ΔK versus AR^k as a function of temperature in the Ap and B21t Horizons of Delaware soils

Horizon	Temperature, °C	r Value[a]	Prediction equation
Kalmia sandy loam			
Ap	0	0.992	$\Delta K = 8.86\,AR^k - 0.31$
	25	0.990	$\Delta K = 8.79\,AR^k - 0.35$
	40	0.990	$\Delta K = 8.20\,AR^k - 0.39$
B21t	0	0.986	$\Delta K = 6.82\,AR^k - 0.02$
	25	0.997	$\Delta K = 6.10\,AR^k - 0.05$
	40	0.980	$\Delta K = 5.49\,AR^k - 0.08$
Evesboro sandy loam			
Ap	0	0.994	$\Delta K = 5.62\,AR^k - 0.20$
	25	0.987	$\Delta K = 4.84\,AR^k - 0.23$
	40	0.996	$\Delta K = 4.20\,AR^k - 0.25$
B21t	0	0.995	$\Delta K = 4.80\,AR^k - 0.02$
	25	0.998	$\Delta K = 4.30\,AR^k - 0.04$
	40	0.996	$\Delta K = 3.90\,AR^k - 0.05$
Matapeake silt loam			
Ap	0	0.990	$\Delta K = 9.20\,AR^k - 0.40$
	25	0.989	$\Delta K = 9.10\,AR^k - 0.42$
	40	0.991	$\Delta K = 8.98\,AR^k - 0.46$
B21t	0	0.980	$\Delta K = 8.91\,AR^k - 0.09$
	25	0.983	$\Delta K = 8.54\,AR^k - 0.10$
	40	0.984	$\Delta K = 8.42\,AR^k - 0.12$

[a] These r values and prediction equations represent the relationship between ΔK versus AR^k for the linear part of the Q/I curve. The slope was used to calculate PBC^k.

mica as the predominant clay minerals (Table 1). The latter have been shown to be responsible for K fixation in soils (Rich and Black 1964; Sparks et al. 1979; Sparks 1980). These data would suggest that field soil temperatures could significantly affect the availability of K in these soils over a year.

The ΔK, or labile K parameter, changed little, and the PBC^k ($\Delta K/\Delta AR^k$), or potential buffering capacity parameter, which is related to the CEC of the soils, decreased with increased temperature (Table 2, Figs. 1 and 2). Deist and Talibudeen (1967) found that the CEC decreased with increased temperature on some British soils.

Temperature effects on K *selectivity and on cations in solution*

Potassium selectivity coefficients (k_K), based on the Gapon equation (Kelley 1948), decreased with increased temperature (Table 4). Thus, the k_K would indicate decreased K sorption by each of the soils with increased temperature (Rich and Black 1964). The quantity of K in the equilibrium solution as a function of temperature (Table 4) verified this conclusion. For example, in the Kalmia sandy loam, as temperature increased from 0 to 40°C, the quantity of K in the equilibrium solution increased from 19.5 to 21.2 and from 14.8 to 18.7 moles/liter × 10^{-4} in the Ap and B21t horizons, respectively. The amounts of Ca and Mg in solution however, were decreasing in both horizons as temperature increased.

At present, we can only speculate about the mechanism(s) to explain the decreased K selectivity with increased temperature in these soils. Further works need to be conducted. The presence of mica and vermiculite in these soils (Table 1) would suggest specific sites for K (Rich 1964; Rich and Black 1964). These sites, or "wedge-zones," would selectively screen out large hydrated cations such as Ca^{2+} and Mg^{2+} and would favor selection of smaller ions such as NH_4^+ and K^+. However, with increased temperature, the hydration of Ca^{2+} is decreased relative to that of K^+. Thus, size is not as important in K selectivity. These soils also contained chloritized vermiculite, which likely contained $Al(OH)_x$ interlayers (Rich 1960). The $Al(OH)_x$ "islands" serve

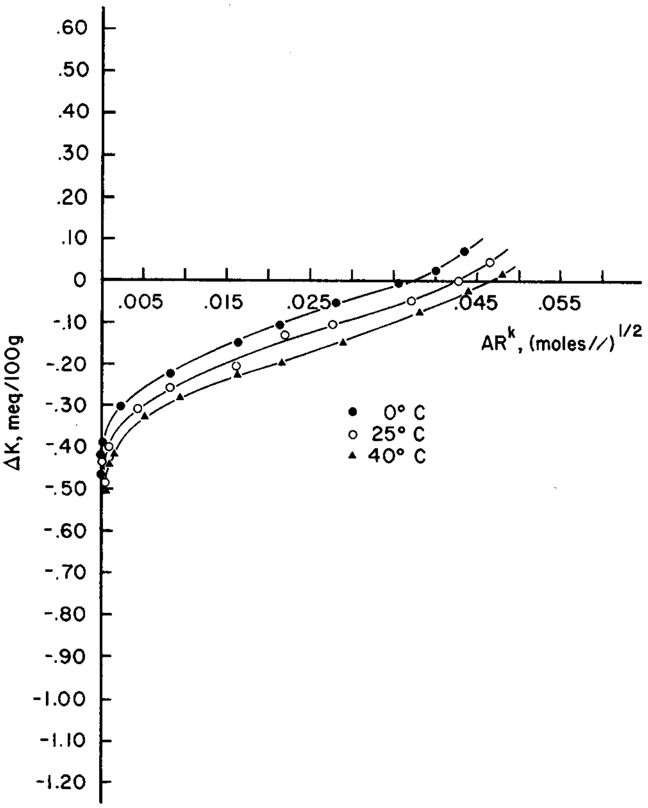

FIG. 1. Effect of temperature on Q/I parameters in the Ap horizon of Kalmia soil.

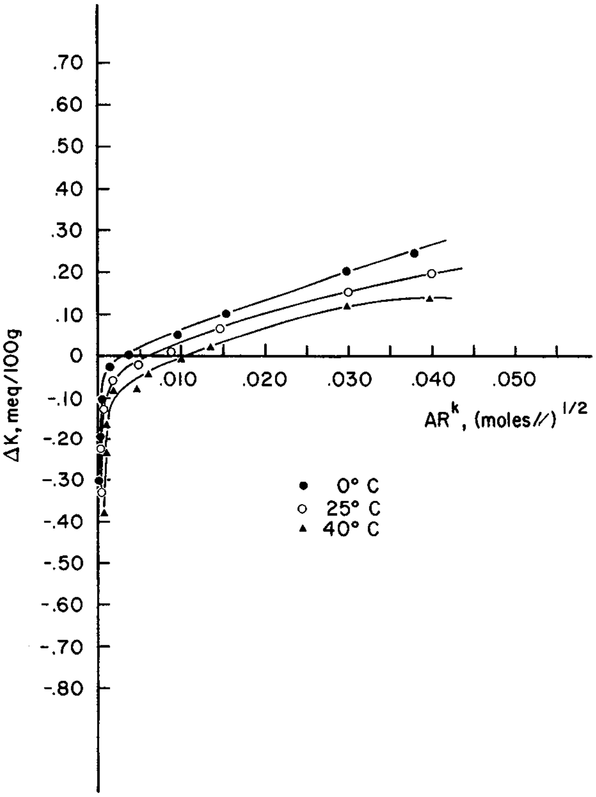

FIG. 2. Effect of temperature on Q/I parameters in the B21t horizon of Kalmia soil.

TABLE 4

Effect of temperature on K *selectivity coefficients* (k_K) *and on quantities of* Ca, Mg, *and* K *in equilibrium solutions of Delaware soils*

Horizon	Temperature, °C	k_K, liter/mole$^{1/2}$	moles/l × 10^{-4}		
			Ca	Mg	K
Kalmia sandy loam					
Ap	0	0.72	30.5	3.21	19.5
	25	0.12	28.5	1.73	20.0
	40	0.03	19.1	0.99	21.2
B21t	0	5.72	41.6	2.80	14.8
	25	4.60	34.0	1.64	15.4
	40	4.17	19.1	1.36	18.7
Evesboro sandy loam					
Ap	0	0.65	26.8	3.40	20.3
	25	0.08	22.4	1.91	21.2
	40	0.02	16.5	1.20	22.2
B21t	0	4.71	37.2	3.00	15.2
	25	4.20	31.0	1.81	16.3
	40	4.11	20.0	1.54	17.1
Matapeake silt loam					
Ap	0	0.97	39.7	2.50	18.2
	25	0.24	30.2	2.20	19.1
	40	0.12	24.3	2.00	19.4
B21t	0	7.21	50.7	2.21	12.1
	25	6.65	40.2	2.10	13.4
	40	5.80	29.6	1.98	15.2

as props to enhance K selectivity. However, with increased temperature, hydrolysis of the $Al(OH)_x$ material should increase (Rich 1960), which would result in a larger polymer. This could cause collapse of the interlayer and thus decrease K selectivity.

The k_K values were lower in the Ap than in the B21t horizons of all three soils (Table 4). This would be expected, for there was more clay in the B21t horizon that could afford more sites for K sorption. The higher K selectivity in this horizon could also be ascribed to the generally higher subsoil mica and vermiculite contents present (Table 1). The latter generally have high k_K values (Rich and Black 1964). Because the k_K values were higher in the B21t horizon than in the Ap horizon, more K was sorbed and less K occurred in the B21t horizon equilibrium solution (Table 4). Additionally, a higher amount of Ca and Mg in solution occurred in the B21t than in the Ap horizon for any temperature. The k_K values tended to be higher in the Matapeake silt loam soil than in the other two soils. This is probably reflective of the considerably higher clay contents in this soil, which were high in vermiculite and mica (Table 1).

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