

Effect of Long-term Lime and Potassium Applications on Quantity-Intensity (Q/I) Relationships in Sandy Soil¹

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ABSTRACT

The effects of long-term lime and K applications on quantity-intensity (Q/I) relationships were investigated on the Ap and B2t horizons of a Kalmia soil (a fine-loamy over sandy or sandy-skeletal, siliceous thermic (Typic Hapludults) from the Delaware Coastal Plain. The predominant mineral suite of the <2 μ m clay fraction was mica, vermiculite, and chloritized vermiculite. Soil pH and exchangeable bases increased with depth and with lime additions. The equilibrium potassium activity ratio (AR^k) decreased with profile depth due to greater K fixation by specific sites for K in the B2t horizon. The AR^k decreased in the Ap horizon and increased in the B2t horizon with lime additions. The magnitude of AR^k [> 0.01 (moles/liter)^{1/2}] suggests that K adsorption in the Ap horizon occurred on planar positions while adsorption at specific sites was predominant in the B2t horizon [> 0.006 (moles/liter)^{1/2}]. The parameter ΔK° , which measures labile K, became more negative with increased lime and K additions, indicating a greater K release into soil solution. While the quantity of K extracted by NH₄OAc compared favorably to ΔK° in the Ap horizon, it exceeded ΔK° in the B2t horizon, suggesting K exchange involving specific sites in the B2t horizon. The number of specific sites (K_z) increased with K fertilization and with soil depth. The decreased K_z with increased lime additions could

be ascribed to increased neutralization of hydroxyaluminum interlayer material, resulting in an increase in interlayer "islands." The potential buffer capacity (PBC^k) parameter increased with lime additions due to increased pH-dependent cation exchange capacity (CEC).

Additional Index Words: K exchange, Coastal Plain soils, Debye-Hückel theory, specific K sites, activity ratios.

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FOR A GREATER understanding of the fertility status of agricultural soils, it is important to study K-(Ca-Mg) equilibria relationships. While researchers have noted a lack of crop response to K additions on Atlantic Coastal Plain soils (Liebhardt et al., 1976; Yuan et al., 1976; Sparks, 1980; Sparks et al., 1980; Woodruff and Parks, 1980), little is known of the quantity-intensity (Q/I) relationships of these soils. The latter (Beckett 1964a) relates the change in exchangeable K (quantity) to the ratio of $[a_K] / [a_{Ca} + a_{Mg}]^{1/2}$ (intensity). With Q/I information, sounder predictions could be made concerning the K supplying power of Atlantic Coastal Plain soils and how lime additions affect K availability in these soils.

Several indices of K availability in soils have been proposed. The quantity

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$$RT \ln a_K / a_{Ca}^{1/2}$$

may be presented as a measure of the free energy of exchange of K in the soil by Ca and hence as a measure of the availability of K (Woodruff, 1955). Beckett (1964a) introduced the Q/I concept to aid in predicting the K status of soils.

Theory of Q/I Determinations

A typical Q/I curve is shown in Fig. 1 with these parameters:

- ΔK = quantity by which the soil gains or loses K in reaching equilibrium or the Quantity (Q) factor,
- AR^k = activity ratio for K or the intensity (I) factor,
- ΔK^o = labile or exchangeable K,
- AR_e^k = equilibrium activity ratio for K,
- K_x = specific K sites, and
- PBC^k = potential buffering capacity.

The potassium intensity factor (AR^k) is computed from the measured concentrations of Ca, Mg, K, and Na corrected to the appropriate activities by application of extended Debye-Hückel theory as follows from Eq. 1 through Eq. 3 (Moore, 1972):

$$\log \sigma_{\pm} = \frac{-az^+z^- \sqrt{I}}{1 + \alpha\beta \sqrt{I}}, \quad [1]$$

where

- σ_{\pm} = the mean activity coefficient of the electrolyte,
- a = constant (0.5042),
- z^+ = valency of cation,
- z^- = valency of anion,
- $\alpha\beta$ = assumed to be 1, and
- I = ionic strength,

where

$$I = \frac{1}{2} \sum_i C_i z_i^2 \quad \text{and} \quad [2]$$

where

- C_i = concentration of ion i and
- z_i = valency of ion i .

The activity ratio (AR^k) was calculated as

$$AR^k = \frac{C_K (\sigma_{KCl})^2}{\sqrt{C_{Ca} + C_{Mg} (\sigma_{CaCl_2})^{3/2}}} \quad [3]$$

where

- C_{Ca}, C_K, C_{Mg} = equilibrium concentrations of Ca, K, and Mg,
- σ_{KCl} = activity coefficient of KCl, and
- σ_{CaCl_2} = activity coefficient of $CaCl_2$.

Interpretations and Applications of Q/I Parameters

Various interpretations have been made on the parameters that can be derived from a Q/I plot. The linear portion of the curve has been ascribed to non-specific sites for K (Beckett, 1964b), while the curved

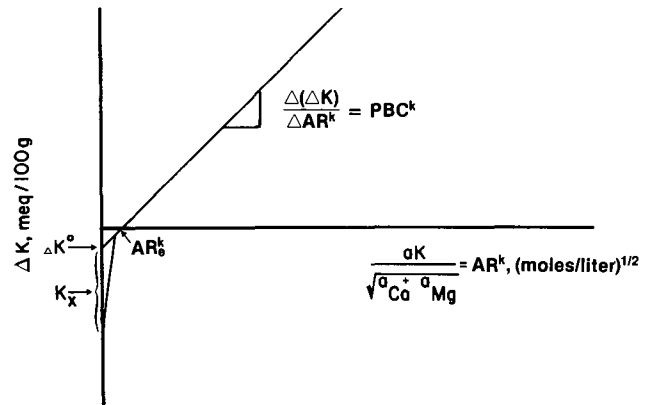


Fig. 1—A typical Quantity/Intensity (Q/I) plot.

portion has been attributed to specific sites with a high K affinity (Beckett, 1964b; Rich, 1964; Beckett and Nafady, 1967; LeRoux and Sumner, 1968). The nonspecific sites have been attributed to planar surfaces (Beckett, 1964b; Lee, 1973), while the specific sites have been ascribed to edges of clay crystals and to wedge sites of weathered micas (Rich, 1964; Beckett and Nafady, 1967).

The AR_e^k value is a measure of availability or intensity of labile K in soil. Beckett (1964b) and LeRoux and Sumner (1968) found that K fertilization increased AR_e^k values. San Valentin et al. (1973) investigated the effect of cropping on Q/I relations using a Red Bay soil from Florida. They found that before cropping, AR_e^k increased with added K and decreased with added lime. After cropping, AR_e^k was greater in limed than in the unlimed soils. Schouwenburg and Schuffelen (1963) theorized that if AR_e^k was <0.001 , the adsorbed K was at edge positions, and if >0.01 , K was adsorbed at planar positions.

LeRoux³ noted that ΔK^o was a better estimate of soil labile K than normal exchangeable K. He found that higher values of labile K ($-\Delta K^o$) indicated a greater K release into soil solution resulting in a larger pool of labile K. The labile K pool increased with K fertilization (LeRoux and Sumner, 1968; San Valentin et al., 1973). San Valentin et al. (1973) noted that labile K generally increased with lime additions on cropped soils.

The PBC^k value is a measure of the ability of the soil to maintain the intensity of K in the soil solution and is proportional to CEC (Lee, 1973). LeRoux³ noted that a high soil PBC^k value is indicative of good K availability while a low PBC^k soil would suggest a need for frequent fertilization. San Valentin et al. (1973) found that the PBC^k before and after cropping increased with lime additions as a result of the increase in pH-dependent CEC of a Florida soil.

This study was conducted to investigate the effect of long-term lime and K applications on the K supplying power of the Ap and B2lt horizons of a Kalmia soil from the Delaware Coastal Plain using Q/I analyses. Corn (*Zea mays* L.) and soybeans (*Glycine max* L.) grown on this soil have failed to show response to K fertilization over a nine-year period.

³ J. LeRoux. 1966. Studies on ionic equilibria in Natal soils. Unpublished Ph.D. Dissertation. Univ. of Natal, Republic of S. Africa.

Table 1—Selected chemical, mineralogical, and physical properties of Kalmia soil.

Horizon	Particle size analyses			Textural class	Organic matter	CEC	Mineral suite of <2 μm clay fraction†				
	Sand	Silt	Clay				%	meq/100 g	VC ₁ ‡	VR ₁	MI ₁
Ap	72.3	17.8	9.9	Sandy loam	1.7	4.1	VC ₁ ‡	VR ₁	MI ₁	KK ₁	QZ ₁
B21t	68.0	17.0	15.0	Sandy loam	0.3	4.8	MI ₁	VR ₁	VC ₁	KK ₁	QZ ₁

† VC = chloritized vermiculite; VR = vermiculite; MI = mica; KK = kaolinite; QZ = quartz.

‡ Subscript 1 = most abundant; 5 = least abundant.

Table 2—Effect of long-term lime and K applications on pH and NH₄OAc-exchangeable K in Kalmia soil.†

Horizon	Potassium kg/ha	pH			NH ₄ OAc-Exchangeable K meq/100 g		
		1‡	2§	3¶	1	2	3
Ap	0	5.5	5.9	6.1	0.20	0.23	0.33
	67	5.2	5.4	6.2	0.23	0.25	0.30
	135	5.4	5.6	5.9	0.28	0.30	0.43
B21t	0	6.0	6.3	6.7	0.24	0.25	0.38
	67	5.9	6.2	6.8	0.28	0.29	0.46
	135	5.7	6.0	6.3	0.40	0.42	0.53

† Values reported represent the arithmetic mean of duplicate samples.

‡ Denotes 0.00 metric tons/ha lime.

§ Denotes 2.24 metric tons/ha lime.

¶ Denotes 8.96 metric tons/ha lime.

MATERIALS AND METHODS

This study was established in 1970 on a Kalmia silt loam soil (Typic Hapludults) at the University of Delaware Substation, Georgetown, Del. Lime (29% Ca-6% Mg) to give a 1:1 weight-to-weight mixture of dolomitic and calcitic lime was applied December of 1970 and October of 1973 at rates of 0.00, 2.24, and 8.96 metric tons/ha. Potassium at 0-, 67-, and 135-kg K/ha as KCl has been applied annually. Corn and soybeans have been grown on the soil since 1970. Bulk samples from the Ap and B21t horizons of selected plots of this study were taken in 1979, dried, and ground to pass through a 2-mm sieve.

Soil Characterization Analyses

Particle size analyses were determined by the hydrometer method (Day, 1965). Mineralogical analyses, consisting of x-ray diffraction, were performed on the <2 μm clay fraction. Prior to soil mineral fractionation, subsamples were treated with 30% H₂O₂ 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 (1934) method as modified by Allison (1965) and CEC by a MgCl₂

Table 3—Effect of long-term lime and K applications on Q/I parameters in Kalmia soil.†

Horizon	Potassium kg/ha	-ΔK°			K _x			AR _e ^k			PBC ^k		
		1‡	2§	3¶	1	2	3	1	2	3	1	2	3
Ap	0	0.28	0.29	0.29	0.30	0.22	0.16	0.050	0.043	0.020	3.98	4.23	5.29
	67	0.33	0.34	0.34	0.53	0.49	0.17	0.055	0.051	0.043	4.62	5.71	7.34
	135	0.39	0.41	0.46	0.60	0.62	0.76	0.058	0.053	0.052	5.75	6.00	7.02
B21t	0	0.06	0.08	0.08	0.60	0.50	0.45	0.006	0.006	0.006	5.46	6.58	12.92
	67	0.07	0.08	0.13	0.90	0.80	0.43	0.007	0.008	0.009	5.20	6.00	6.04
	135	0.09	0.10	0.11	1.35	1.30	0.87	0.009	0.010	0.010	5.98	7.02	9.14

† Values reported represent the arithmetic mean of duplicate samples.

‡ Denotes 0.00 metric tons/ha lime.

§ Denotes 2.24 metric tons/ha lime.

¶ Denotes 8.96 metric tons/ha lime.

saturation with subsequent displacement by CaCl₂ (Rich, 1962; Okazaki et al., 1963). Exchangeable Ca, K, and Mg were extracted with 1N NH₄OAc (Jackson, 1958) and analyzed by atomic absorption spectrophotometry. The pH measurements were obtained from a 1:1 soil-to-water mixture.

Quantity-Intensity (Q/I) Determinations

Soil samples (0.2 to 7.0 g) in duplicate were weighed out into a series of 100-ml polypropylene centrifuge tubes. To the samples was added 50 ml of solution, which was 0.002 1M CaCl₂ and from 0 to 0.002 1M KCl. The tubes were stoppered and equilibrated for 20 hours at 25°C in a reciprocating shaker with periodic agitation. The samples were centrifuged, and the filtered supernatant was analyzed for Ca, Mg, K, and Na by atomic absorption spectrophotometry. The K quantity factor (ΔK) was found by computing the difference in K concentration between the initial and equilibrium solutions. The K intensity factor (AR^k) was calculated as outlined in Eq. [3].

A plot of ΔK on the ordinate axis and AR^k on the abscissa axis was constructed for each soil sample from which values for AR^k, ΔK°, PBC^k, and K_x were determined as explained earlier.

RESULTS AND DISCUSSION

Soil Characterization

The Kalmia soil was very sandy in the Ap and B21t horizons with 72.3 and 68.0% sand, respectively (Table 1). With increasing depth, clay content and CEC increased and organic matter decreased. The predominant minerals of the <2 μm clay fraction were chloritized vermiculite, mica, and vermiculite, with lesser quantities of kaolinite and quartz (Table 1). The presence of mica and vermiculite in the soil would suggest specific sites for K adsorption (Rich, 1964; Rich and Black, 1964).

Soil pH and exchangeable K increased with depth and with lime additions (Table 2). Although not shown, exchangeable Ca and Mg followed a similar trend. These data suggest movement of lime into subsoil (Strasser et al., 1944). The observation that exchangeable K increased with lime additions could be ascribed to increased pH-dependent CEC (San Valentin et al., 1973).

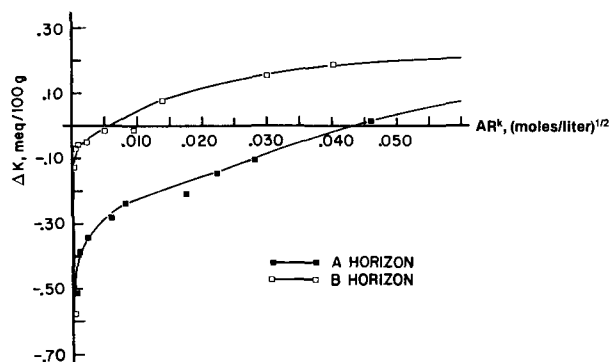


Fig. 2—Q/I relationships in Kalmia soil with 2.24 metric tons/ha lime and 0 kg/ha K.

Q/I Relationships

The AR^k_e values ranged from 0.020 to 0.058 and from 0.005 to 0.010 (moles/liter)^{1/2} in the Ap and B2t horizons of the Kalmia soil, respectively (Table 3). The values of AR^k_e in the Ap horizon of this soil were higher than those found in South African soils by LeRoux and Sumner (1968). With lime additions, AR^k_e decreased in the Ap horizon but increased slightly in the B2t horizon (Table 3, Figs. 2 through 4). The decrease in AR^k_e with depth for all lime and K treatments could be attributable to a greater number of specific K sites in the B2t horizon which could fix K. Increased levels of K fertilization increased AR^k_e , which conformed with findings of Beckett (1964b) and of LeRoux and Sumner (1968). It would appear that the adsorbed K in the Ap horizon was primarily held at planar positions since the AR^k_e was >0.01 (Schouwenburg and Schuffelen, 1963). In the B2t horizon, it can be theorized that K was preferentially held at edge positions since the AR^k_e values ranged from 0.006 to 0.01 (Schouwenburg and Schuffelen, 1963).

In the Kalmia soil (Table 3, Figs. 2 through 4), ΔK^o generally became more negative with increased lime additions or there was a greater release of K into soil solution, resulting in a large pool of labile K (LeRoux³; San Valentin et al., 1973). Labile K tended to become less negative in the B2t horizon. This would indicate that the Kalmia subsoil had a strong ability to adsorb K (Rich, 1964). Additions of K generally increased labile K in the Ap and B2t horizons of the Kalmia soil as was found previously by LeRoux and Sumner (1968) and by San Valentin et al. (1973). LeRoux³ noted that ΔK^o is a better estimate of soil

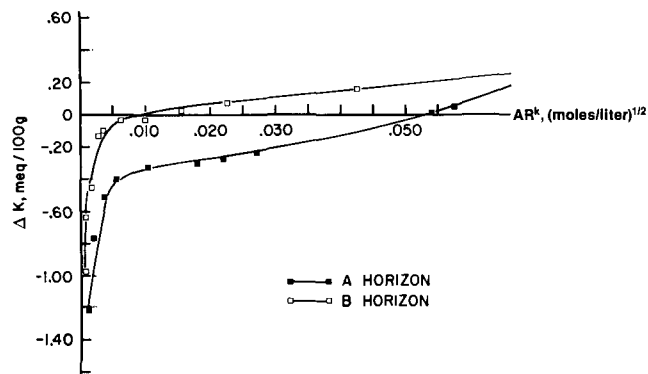


Fig. 4—Q/I relationships in Kalmia soil with 8.96 metric tons/ha lime and 135 kg/ha K.

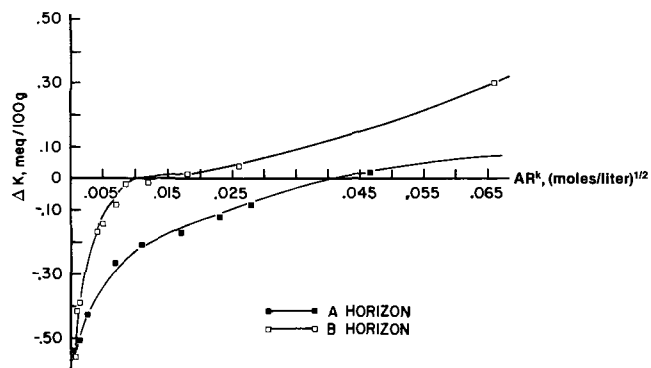


Fig. 3—Q/I relationships in Kalmia soil with 8.96 metric tons/ha lime and 67 kg/ha K.

labile K than normal exchangeable K. The values of ΔK^o compared favorably with NH_4OAc -extractable K in the Ap horizon of the Kalmia soil (Tables 2 and 3). However, in the subsoil, NH_4OAc -exchangeable K values were always considerably higher than ΔK^o values (Tables 2 and 3). This strongly suggests that there were more specific sites for K in the B2t horizon of this soil. This hypothesis seems plausible since there was more clay in the B2t horizon, the number of specific sites as measured by K_x was generally larger in the B2t horizon (Table 3), and the clay mineralogy was dominated by mica and vermiculite (Table 1). The latter minerals have been shown to contain "wedge zones" or specific sites for K adsorption (Rich, 1964). Ammonium, with a crystalline radius of 1.43Å (Rich, 1968), could displace K^+ with a crystalline radius of 1.33Å (Rich, 1968) from these specific sites, resulting in the higher exchangeable or labile K with NH_4OAc (Rich, 1964; Rich and Black, 1964). In soils of this type, NH_4OAc would tend to over-predict exchangeable K.

The K_x in the Kalmia soil tended to increase with increasing K fertilization and with liming (Table 3, Fig. 2 through 4). This soil contained 14Å-intergrade minerals (chloritized vermiculite) with hydroxyaluminum interlayer material (Table 1). With increased liming, increased neutralization of the hydroxyaluminum material would occur and the size or total number of interlayer "islands" could increase. Thus, depending on steric factors and on the cation distribution, K_x could either increase or decrease with lime additions.

In the Kalmia soil, PBC^k generally was not drastically different in the two horizons (Table 3, Figs. 2 through 4). This would be expected because both CEC and clay content were similar in the two horizons (Table 1). Liming generally increased PBC^k which was probably due to an increase in pH-dependent CEC (San Valentin et al., 1973). Additions of K also had little effect upon the PBC^k values, which were low, particularly where no lime additions had been made (Table 3). The PBC^k values are indicative of the low CEC of this soil, due to the high sand and low organic matter contents (Table 1).

Despite a low PBC^k , which LeRoux³ equated with a need for frequent K fertilization, and low ΔK^o and AR^k_e values, crops grown on this soil have not responded to applied K (Liebhardt et al., 1976). This lack of response can be ascribed to the large quantity of K-bearing minerals (Tables 1 and 3). With time,

these minerals could release K to exchangeable and to solution forms (Sparks, 1980; Sparks et al., 1980). The latter would be readily available for plant uptake.

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