

POTASSIUM RELATIONSHIPS OF THREE OHIO SOILS¹

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Abstract. Three Ohio soils, Hoytville clay, Brookston silty clay loam, and Wooster silt loam located at various branches of the Ohio Agricultural Research and Development Center, were studied. Bulk samples from each horizon were tested for exchangeable basic cations, pH, sulfuric acid extractable potassium (K^+), and particle-size distribution. The surface horizons of each soil were characterized by measurement of cation exchange capacity, quantity-intensity adsorption isotherms for K^+ and x-ray diffraction of the clay ($<2 \mu$) fraction. The Hoytville soil was highest in exchangeable and sulfuric acid extractable K^+ ; Wooster was lowest; and Brookston was intermediate but closer to Wooster than to Hoytville. Hoytville and Brookston had high quantity-intensity labile buffer capacities for K^+ , the values being 2–2½ times greater than that for Wooster. Hoytville clay was predominantly illitic while the Brookston and Wooster clays were of a more mixed mineralogical nature. The potassium content and crystallinity of the illite in the Hoytville clay is lower than those of the Brookston and Wooster clays.

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Potassium (K^+) is considered a macro-nutrient for plants and, although Ohio soils contain 1–2% K^+ by weight, much of this K^+ exists in unavailable forms in the soil. Since Ohioans spend millions of dollars annually on K^+ fertilizer, studies on soil K^+ and its availability to plants are of economic significance as well as academic interest.

Plant roots absorb K^+ from the soil solution. The forms of K^+ in the soil can be grouped into 3 categories: readily available K^+ , that dissolved in the soil solution or existing as an exchangeable cation adsorbed on soil colloids; intermediate, i.e., slowly available K^+ , and unavailable mineral K^+ found in minerals such as K-feldspars and micas and released only as the minerals are chemically weathered in the soil (Tisdale and Nelson 1975). Most soil testing laboratories in the North Central United States measure available K^+ by extracting air dried soil with 1 N ammonium acetate at a pH of 7.0 (Carson 1975). Hunter and Pratt (1957) developed a strong H_2SO_4 acid extraction K^+ procedure which removes both the readily available and slowly

available fractions. The correlation between H_2SO_4 -extractable K^+ and K^+ uptake was very good ($r=0.946$ for corn on 16 soils and 0.990 for alfalfa on 9 soils). H_2SO_4 -extractable K was found to predict K^+ uptake better than exchangeable K alone.

Woodruff (1955) presented the concept that availability of K^+ to plants is related to the energy of exchange of K^+ for Ca^{2+} on soil colloids or plant root surfaces. In midwestern soils with a neutral pH, Ca^{2+} is usually the predominant exchangeable cation. The energy of exchange (ΔG) is calculated as:

$$1) \quad \Delta G = RT \log_e \frac{a_{K^+}}{\sqrt{a_{Ca^{2+}}}}$$

where R is the gas constant, T the absolute temperature and a_{K^+} and $a_{Ca^{2+}}$ the chemical activities of K^+ and Ca^{2+} respectively. ΔG 's of –3500 to –4000 calories per equivalent of K^+ were associated with K^+ deficiency in test crops while ΔG 's more positive than –2000 calories per equivalent represented an excess of K^+ in proportion to Ca^{2+} in the soil.

Beckett, in Great Britain, has extended Woodruff's concept of energy of exchange of K^+ for Ca^{2+} to 2 indexes of a

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soil's K⁺ supplying power to plants. (Beckett and Craig 1964, Beckett 1972). The first of these indexes of K supplying power is the activity ratio of K⁺ remaining in solution relative to the divalent cations, Ca²⁺ and Mg²⁺, after equilibration with the soil cation exchange sites. This activity ratio (K⁺[AR_K]) is found as follows:

$$2) \quad AR_K = {}^aK^+ / \sqrt{{}^aCa^{2+} + {}^aMg^{2+}}$$

It is an intensity factor relating the activity and plant availability of K⁺ to activities of the 2 most abundant cations in near-neutral soils. The second index of K supplying power is the soil's ability to buffer or maintain nearly constant the activity of K in the soil solution (AR_K) when K⁺ is added as a fertilizer or removed by crop uptake or leaching. This property is called the labile buffer capacity for K⁺ (LBC), and is related to the amount and kind of soil colloids. A soil with a high LBC for K⁺ does not increase rapidly in the activity ratio AR_K when K⁺ is added to the soil nor does it drop rapidly in AR_K if K⁺ is removed from the soil. AR_K is an intensity factor relating the availability of K⁺ to the chemical activities of Ca²⁺ and Mg²⁺ in the soil and LBC is a measure of the soil's ability to sustain a relatively constant AR_K in the face of K⁺ additions or removals from the soil.

Clay mineralogical investigations are useful in determining soil K⁺ relationships. Page and Bayer (1939) first explained K⁺ fixation (the immobilization of applied fertilizer K⁺ into non-exchangeable forms unavailable to plants) as the entrapment of K⁺ between the layers of 2:1 silicate clays. Release of K⁺ from illite (clay mica) has also been extensively studied and quantified by x-ray diffraction of oriented clay specimens given selected pre-treatments (Wilding *et al* 1971).

The present study reports soil K⁺ characterizations for 3 Ohio soils that are found over large acreages in Ohio. The study sites were located on land held by the Ohio Agricultural Research and Development Center (OARDC) where many K⁺ fertility studies have been and will be conducted.

METHODS AND MATERIALS

The profiles of 3 Ohio soils were studied in 1973 and bulk samples taken from each horizon.

1. Hoytville clay (Mollic Ochraquall) at the N.W. Branch of OARDC in Wood County.
2. Brookston (Typic Argiaquoll) at the Western Branch of OARDC in Clark County.
3. Wooster silt loam (Typic Fragiudalf) from the Snyder Farm, OARDC, in Wayne County.

These soils are found in glacial deposits of Wisconsin Age and the profiles are described in detail by Munn (1974). Hoytville soils are very poorly drained soils formed in calcareous, fine textured glacial till in level broad areas of Northwest Ohio known as the Lake Plain. Wooster soils are well drained soils formed in low lime loamy tills on nearly level positions to steep slopes in Northcentral-Northeastern Ohio. Brookston soils are very poorly drained soils formed in level landscape positions on calcareous loamy till in Western Ohio.

Soil samples were air dried then crushed and screened with a 2 mm sieve to remove coarse fragments. Soil particle sizes were determined by the pipette method (Steele and Bradfield 1934), exchangeable ("available") K⁺ by the method of Carson (1975), sulfuric acid extractable ("potentially available") K⁺ by the method of Hunter and Pratt (1957), and cation exchange capacity by the sum of exchangeable Ca²⁺, Mg²⁺, and K⁺, plus exchangeable acidic cations. Soil pH was determined in a 5 g soil/5 ml distilled water suspension. Clay mineralogical analyses were done by the methods of Smeck *et al* (1968) with a General Electric x-ray diffractometer under the following conditions: a power source of 45 Kv and 15 milliamps, divergence slit angular aperture of 3° and a receiving slit width of 0.0254 cm. Clay minerals were quantitatively estimated by procedures of Wilding *et al* (1971). The quantity-intensity relationships were done by the procedure of Beckett and Craig (1964) with modifications described by Munn and McLean (1975), temperature was 25 °C ± 2 °C.

The 2 indexes of soil K (AR_K and LBC) were measured by equilibrating soil samples with 0.01 molar solutions of CaCl₂ containing increasing amounts of K⁺. After an equilibration period of 30-60 minutes the solution was separated from the soil and analyzed for K⁺, Ca²⁺, and Mg²⁺, and changes in exchangeable K⁺ (ΔK) and values of AR_K computed. The quantity of K⁺ adsorbed or desorbed by the soil (ΔK) was plotted versus the AR_K values. The shape of this quantity-intensity (Q/I) curve was evidence of a unique soil property, and the slope of the curve at the equilibrium AR_K, at the point where K was zero, was the LBC. A tangent to the Q/I curve was estimated and extended to the vertical axis (ΔK axis). The value of the intercept (ΔK⁰) was a measure of the K⁺ held on readily accessible cation exchange sites of the soil colloids.

Soil samples from 0-15 cm depth were collected in June 1973 from fertility plots which had been treated with K fertilizer at 5 different

rates (range 42 to 457 mg K⁺/kg soil) during 1970, 71, and 72 and cropped with corn during each of those years. The plots were replicated 2 or 3 times at each site, all plots were sampled and ammonium acetate exchangeable K⁺ and H₂SO₄-extractable non-exchangeable K⁺ were determined on each sample.

RESULTS AND DISCUSSION

The particle size analyses for the soil profiles by horizon and depth increment showed that the Hoytville soil was highest in clay, followed by Brookston, and then Wooster (table 1). The mineralogy

either Wooster or Hoytville clay, and more interstratified clay than did the Wooster. The Wooster soil clay was the highest in kaolinite by a considerable margin. Appreciable amounts of chlorite and quartz were found in the clay fraction from all 3 soils (Munn 1974).

The 10Å/5Å peak ratios were 4.4, 1.9 and 1.6 for the Hoytville, Brookston, and Wooster soils, respectively. According to Weaver (1965) and White (1961) this suggests that the Hoytville 10Å (illite)

TABLE 1
Particle size analyses, levels of extractable K⁺, and pH of the soil profiles.

Soil Series	Soil Horizon	Depth (cm)	Sand*	Silt*	Clay*	Exch. K ⁺ (µgK/g)	H ₂ SO ₄ -nonexch. K ⁺ (µgK/g)	Soil pH
Hoytville	Ap	0-20	19	38	43	340	1100	6.2
	B1t	20-30	18	37	45	271	780	6.8
	B2lgt	30-53	18	36	45	251	930	7.2
	B22gt	53-76+	19	35	46	241	780	7.2
Brookston	Ap	0-18	11	61	28	150	250	5.8
	A1	18-30	11	58	30	120	305	5.9
	B&A	30-43	10	55	34	170	217	6.0
	B2gt	43-74	24	44	32	110	240	6.9
	B3	74-81+	26	57	18	80	282	8.0
Wooster	Ap	0-18	22	65	14	135	290	6.6
	B1	18-30	18	65	18	86	214	6.5
	B2lt	30-46	20	57	23	86	201	5.3
	II B22	46-58	23	49	29	110	240	5.0
	II B23	58-66	20	50	30	110	377	5.0
	II B24X	66-74+	23	47	31	90	397	5.0

*Percent of sand, silt or clay in sample.

of clay fraction from the soil Ap horizon is presented in table 2. The Hoytville clay fraction was very high in illite (~60%) with some vermiculite, expanding clay (smectite), interstratified clays, chlorite, quartz and traces of kaolinite. The Brookston and Wooster soil clays were comparable in illite and vermiculite content, but the Brookston clay had much more expanding clay in it than

clay is less crystalline and lower in K than the 10Å clays from the Brookston and Wooster soils. This lower crystallinity than for clays from other Ohio soils was also reported for Paulding soil developed from similar parent material (Munn 1974).

The exchangeable K⁺ and sulfuric acid extractable non-exchangeable K⁺, as well as soil pH for each horizon are presented

TABLE 2
Relative amounts of various Ap horizon clay minerals with less than 2 micron particle size.

Soil*	Ill.	Ver.	Mon.	Int.	Kao.	Cl.	Q.
Hoytville	++++**	++	++	+++	+	++	++
Brookston	+++	++	+++	++	++	++	++
Wooster	+++	++	+	+++	++	++	+++

*Ill=Illite, Ver=Vermiculite, Mon=Montmorillonite, Int=Interstratified, Kao=Kaolinite, Cl=Chlorite, Q=Quartz.

** (4+) = >40%, (3+) = 15-40%, (2+) = 5-15%, (+) = <5%.

in table 1. The order of both exchangeable and sulfuric acid extractable non-exchangeable K⁺ in the profiles was Hoytville > Brookston > Wooster. Hoytville and Brookston soils have neutral to mildly alkaline subsoils, while the Wooster subsoil is acid. Surface horizon pH depends greatly upon recent agricultural practices such as liming or nitrogen fertilization. The cation exchange capacities of the 3 soils were 25.0, 26.8, and 13.5 meq/100g for the Hoytville, Brookston and Wooster Ap horizons, respectively.

Linear regression analysis of extractable K⁺ from the fertility plots upon the rate of K⁺ fertilizer addition showed a significant ($P < 0.01$) increase in exchangeable K⁺ for all soils and an increase in H₂SO₄-nonexchangeable K⁺ for the Hoytville soil (table 3). The accumulation of exchangeable K⁺ (high versus low fertilization rates) was greatest in Wooster (240 μgK⁺/g increase), intermediate for Brookston (192 μgK⁺/g increase) and lowest for Hoytville (118 μgK⁺/g). The increase in nonexchange-

TABLE 3
Effect of annual K⁺ fertilization in 1970-72 on levels of extractable soil K⁺ in 1973.*

Soil	Ann. rate, K ⁺ Appl.	Exch. K ⁺ **	H ₂ SO ₄ -nonexch. K ⁺ **
Hoytville	42	236 ± 35	745 ± 43
	76	278 ± 9	720 ± 96
	138	258 ± 18	732 ± 145
	251	351 ± 19	799 ± 50
	457	354 ± 24	1011 ± 2
Brookston	42	190 ± 42	384 ± 29
	76	157 ± 53	392 ± 123
	138	195 ± 0	410 ± 115
	251	233 ± 39	460 ± 30
	457	383 ± 94	510 ± 84
Wooster	42	164 ± 8	256 ± 25
	76	154 ± 22	253 ± 24
	138	178 ± 54	221 ± 44
	251	329 ± 36	195 ± 76
	457	406 ± 101	277 ± 101

*Values expressed in μgK⁺/g soil.

**Values are shown ± standard deviation.

able H₂SO₄-extractable K⁺ was greatest in Hoytville (266 μgK⁺/g), intermediate in Brookston (127 μgK⁺/g) and lowest in Wooster (23 μgK⁺/g). Crop yield and

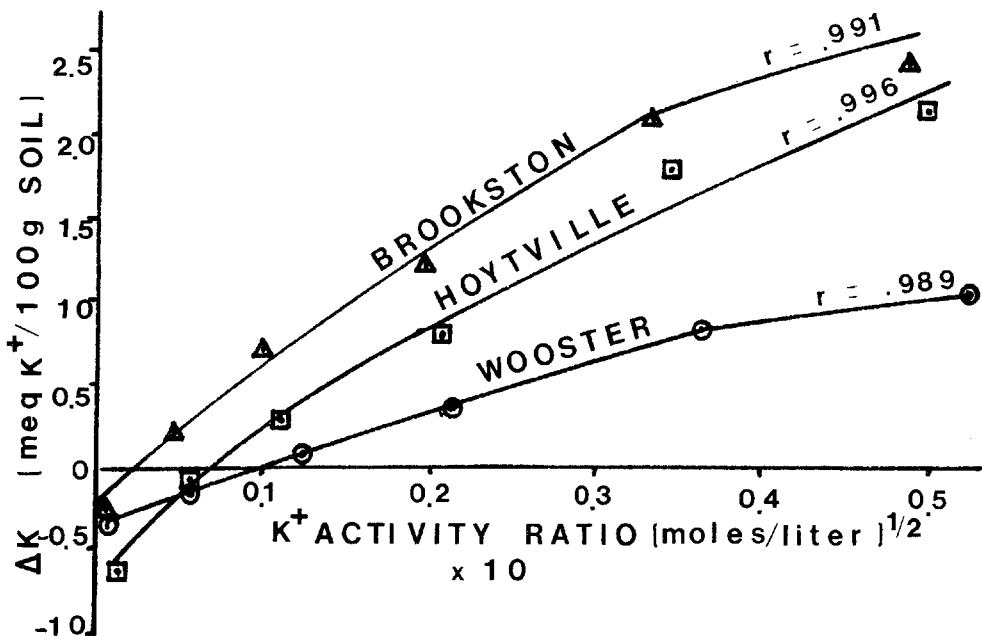


FIGURE 1. Quantity-intensity relationships of the soil Ap horizons with ΔK (K⁺ adsorbed or released by the soil) plotted versus the K⁺ activity ratio. The data points are treatment means (6 levels of K⁺ with 3 replications) and the smooth curves are the second degree polynomial $SK = b_0 + b_1AR_K + b_2(AP_K)^2$, fitted to the experimental data by a least squares statistical procedure.

K⁺ uptake data were not available. The trends in the soil test results suggest that added K⁺ in Wooster (lower in clay fraction and illite) accumulates in the exchangeable form to a great extent, and in the "fixed" form to only a small degree. Hoytville soil, on the other hand, with its high concentration of clay fraction and illite clay content, is a soil where substantial amounts of added potassium fertilizer are converted to "fixed" nonexchangeable K⁺ and where the buildup in exchangeable K⁺ is smaller. The Brookston soil was intermediate in these tendencies, falling between the other 2 soils.

The quantity-intensity relationships were best fitted by a second degree polynomial relating the amount of K⁺ released (-ΔK) or adsorbed (+ΔK) by the soil to the equilibrating solution final activity ratio (equation 2). The quantity-intensity isotherm for each type of soil (fig. 1) represents 18 points, i.e., 6 levels of K with 3 replications. Parameters of interest from the Q/I isotherms are presented in table 4. The Brookston and

the equilibrium AR_K was 5 x 10⁻⁴ (mole, liter)^{1/2} at the point of K⁺ exhaustion (zero K⁺ uptake) with 4 test crops. Fergus *et al* (1972) have suggested that an equilibrium AR_K of 2 x 10⁻³ (mole, liter)^{1/2} gave a satisfactory K⁺ content (1% K⁺) to achieve 90% of the maximum observed yield with millet (*Setaria sp-celata* cv. Nandi).

The Brookston soil as sampled had a lower equilibrium activity ratio (AR_o) and ΔK^o than the Wooster and Hoytville soils. The values of AR_o and ΔK^o are affected by fertilizer K⁺ additions, leaching, and crop removal. The ΔG values are calculated by: ΔG = RT ln (AR_K) where R = 1.99, cal/K/mole, T = 298K, ln = log_e. According to Woodruff (1955) these ΔG's would indicate a satisfaction balance of K⁺ and divalent cations with the Brookston soil approaching low K⁺ status.

The Hoytville soil has throughout the root zone a high clay content and high levels of both available and potentially available potassium as measured by am-

TABLE 4
Quantity-intensity parameters and curve fitting regression coefficients for the soil Ap horizons.

Soil Series	Equilibrium* Activity Ratio (x 10 ³)	Δ K ^o (meq K ⁺ /100 g)	Exch. Energy (ΔG cal./equiv. of K ⁺)	LBC**	Regression Coefficient†		
					b ₀	b ₁	b ₂
Hoytville	8.1	0.70	-2851	84	-.74	103	-942
Brookston	2.9	0.25	>3455	97	-.29	97	-726
Wooster	9.7	0.35	-2748	38	-.40	44	-296

* K⁺ / √^aCa²⁺ + ^aMg²⁺ at point where SK = 0.

** Slope of polynomial regression equation at equil. activity ratio (Labile Buffer Capacity).

† Regression equation Δ K = b₀ + b₁ (AR_K) + b₂ (AR_K)².

Hoytville soils had slopes (Labile Buffer Capacities, LBC), measured at the point where ΔK = 0, 2-2½ times greater than that of the Wooster soil. This means that these soils have the ability to sustain the activity ratio of K⁺ in the face of K⁺ removals to a much greater degree than the Wooster soil. However, it would conversely require 2-2½ times as much added K⁺ to increase AR_K in the Brookston and Hoytville soils as in the case of the Wooster soil. The polynomial equations relating ΔK to AR_K are given in table 4. Martin and Fergus (1973) reported that for several Australian soils

monium acetate and sulfuric acid extractants, respectively. The LBC is also high in the Ap horizon. Soils with high cation exchange capacities have been shown to have high LBC's and this was confirmed earlier with 7 Ohio soils (Munn and McLean 1975). The Wooster soil on the other hand represents a soil lower in clay throughout the profile with lower levels of available and potentially available potassium and a lower LBC. The Brookston soil proved to be intermediate, but much closer to Wooster than to Hoytville.

The soils in this study occupy large

acreages in Ohio. In fact, soils belonging to these 3 series represent over 0.6 million hectares (1.5 million acres) according to an Ohio Conservation Needs Inventory done by the USDA Soil Conservation Service in 1967. They have medium to high cation exchange capacities which can be regarded as nutrient holding reservoirs for K⁺ available to plants, and substantial amounts of both unavailable and slowly available potassium. Modern agronomic and horticultural practices prescribe high plant populations for crops with genetic potential for high yields. To sustain high yields with present cropping practices, farmers must supplement the soil's natural K⁺ supplying power with potassium fertilizers and, while not yet an exact science, soil test procedures provide the best guidelines to farmers for economically satisfactory potassium fertilizer use. Basic studies of this type involving soil K⁺ availability in the major soils of Ohio provide a basis for adjustment of soil testing techniques, where necessary, to keep pace with changing agricultural practices.

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