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9. ABSTRACT

Eleven Hawaiian soils, collected from areas varying in rainfall, were studied in relation to labile pool K obtained by K^{40} exchange and the K^{39} obtained by calcium exchange equilibria. The activity ratio (AR^K), buffering capacity and the K available to sweet corn grown in these soils also was studied. Unweathered volcanic soils of the island of Hawaii had labile pool K values as high as 4.71 meq./100g. and produced sweet corn plants containing 3.7% K. The weathered soils had pool values of only .09 to .07 meq./100g. and produced plants containing .10 to .48% K. A large labile pool indicated high availability of potassium to corn as shown by concentration of K in the plant tissue (coefficient of correlation .98). The correlation of the activity ratio AR^K with plant concentration gave a coefficient of .94. With the exception of the 2:1 layer Mg. clay, potassium extracted with ammonium acetate correlated with plant potassium. Small labile pools of potassium were found for soils subjected to high rainfall and intense leaching. The coefficient of correlation between pool size and rainfall was -.91. Along with increasing pool potassium, inside K concentration, measured after the soil was equilibrated with .05 M $CaCl_2$, also increased with decreasing rainfall. This indicates that soils from high rainfall areas have a higher positive charge than do less highly weathered soils. A study of the soil potassium in terms of inside-outside concentrations, labile pool size, activity ratio (AR^K), and buffer curve show characteristics of tropical soils which are of interest to students of soil development as well as to the agronomist. The activity ratios obtained were low compared with data obtained for some temperate zone soils. This probably results from high relative calcium activity associated with colloids of low negative charge of the more highly weathered Hawaiian soils.

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TROPICAL SOIL POTASSIUM AS RELATED TO LABILE POOL AND CALCIUM EXCHANGE EQUILIBRIA

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Measurements of soil potassium by cation replacement, isotopic exchange and the activity ratio of potassium to calcium have given useful data for predicting the potassium supply (both available and reserve) for plant growth. Most studies (2, 3) on soil potassium have been made on soils which contained illite or hydrous mica clays and soils which contain potassium bearing minerals in the sand and silt fractions. Typically, these soils have contained quartz, weatherable reserve minerals and small amounts of clays which are characterized by a high permanent negative charge resulting in high bonding for calcium and low bonding for potassium.

The purpose of this study was to investigate some soils of the tropics with regard to the following: (a) the amount of potassium in the labile pool; (b) potassium exchange equilibria in .05 *M* $CaCl_2$; (c) the relation of soil development to the potassium level; and (d) the correlation of the above measurements with plant uptake of potassium.

MATERIALS AND EXPERIMENTAL METHODS

The soils were selected to show differences due to the age of the parent material and the variations in weathering and leaching associated with different amounts of rainfall. Soil samples were collected from the islands of Oahu and Hawaii to include areas ranging in rainfall from 7 to 225 inches per year. One alluvial soil was dominated by Mg-montmorillonite. The parent materials (basaltic lava and ash) from which the other soils were derived are relatively uniform in chemical composition. These soils are dominated by kaolin and gibbsite and clay particles having amorphous coatings of variable composition[2]. Many of the high rainfall areas contain mica (6).

Most of the soils included in this study were agriculturally important. Many of the areas from which samples were collected have received applications of lime and fertilizers in the past. The soils are characterized by a high clay content (more than 60 per cent) and with the exception of the alluvial soil, by stable aggregates which resist dispersion in water. The samples were composites of the 0-6 inch layer. Some characteristics of the soils are presented in table 1.

Potassium Measurements

Isotopically exchangeable potassium was determined as follows: moist soil, equivalent to one gram of oven dry soil (70°C), was placed in a screw cap bottle and 4 ml. of .05 *M* $CaCl_2$ solution containing enriched radioactive K^{40} (activity = 200 d./m./sample) was added. Enough .05 *M* $CaCl_2$ was added to bring the final volume to 25 ml. The samples were shaken on an end-over-end shaker for 15 minutes. Shaking was repeated four times at weekly intervals. After equilibration the samples were centrifuged, 4 ml. of the supernatent solution was mixed with 5.5 ml. of Trition X-100 and 11 ml. of toluene containing PPO (4 g./liter) and POPOP (.1 g./liter) and counted with a Packard 3,000 series liquid scintillation counter. Corrections were applied for radioactivity due to soil potassium in the supernatent which amounted to 2 c./min. of K^{40} per mgm. of K^{39}-K^{41}. The counting efficiency as determined with 5 mgms. of non-enriched potassium per 4 ml. of .05 *M* $CaCl_2$ for this mixture and counter was found to be 82 per cent. A control sample without soil was counted to de-

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[2] Jones, R. C. Gel hulls on mineral surfaces. Science (Manuscript submitted 1970).

TABLE 1

*Characteristics of the experimental soils**

Great Soil Group	Soil Series	Rainfall *In./year*	pH H_2O	pH Salt†	% K_2O	Am. Acetate *meq. K/100 g.*	Dominant Clay Mineral	Parent Material
Reddish Prairie	Waimea	25	6.8	6.2	—	3.90	Amorphous Sesquioxides	Ash
Red Desert	Kawaihae	7	6.5	6.4	.51	1.54	Kaolin Amorphous Sesquioxides	Ash
Low Humic Latosol	Molokai	22	6.9	6.3	.59	.74	Kaolin, Sesquioxides	Basalt
Dark Mg-Clay	Lualualei	20	7.9	7.5	.23	.36	Montmorillonite	Alluvial
Low Humic Latosol	Wahiawa	50	6.2	5.8	1.46	.45	Kaolin, Sesquioxides	Basalt
Low Humic Latosol	Waipahu	30	6.6	6.1	—	.21	Kaolin	Alluvial
Humic Latosol	Ookala	88	5.2	4.8	.68	.20	Amorphous Sesquioxides	Ash
Humic Latosol	Paaloa	80	4.8	4.4	1.66	.09	Geothite, Illite, Hollaysite, Gibbsite	Basalt
Latosolic Brown Forest	Maile	95	6.0	5.4	—	.22	Amorphous, Geothite, Gibbsite	Ash
Humic Ferrugenous Latosolic	Kapaa	90	5.3	4.5	.28	.09	Gibbsite, Geothite, Kaolin	Basalt
Hydrol Humic Latosol	Akaka	180	6.1	5.8**	.21	.08	Amorphous Sesquioxides	Ash

* Clay mineral data supplied by Staff, Department of Agronomy and Soil Science, University of Hawaii.

† Determined in .01 *N* $CaCl_2$ 1 to 2 ratio.

** This area has received applications of lime.

termine the total radioactivity added to each soil sample.

Quadruplicate samples of each of the soils were equilibrated with $CaCl_2$ in the same manner as for the radioactive samples. The concentration of K^{39}–K^{41} in the outside (supernatent) solution was determined, using the flame photometer. To improve the accuracy of the radioactive counting, all of the supernatent was counted; therefore additional samples were equilibrated for the flame determination of K^{39}.

After the activity had been determined by liquid scintillation the concentration of stable potassium in solution was established. The concentration of the inside exchanger was calculated (3). The sum of potassium retained by the solid phase (inside) and that in the supernatent solution (outside) still is referred to as the potassium labile pool (ΔK^0) and is expressed as meq./100 grams of soil. This term and symbol have been used by Beckett (2), Zandstra and MacKenzie (7) and Le Roux and Sumner (5). These workers have estimated the potassium labile pool by extrapolation of the straight portion of the curve; in this study the labile pool was directly determined by isotopic exchange.

Concentrations of K and Ca in solution after equilibration were used to calculate activities for the activity ratio determination. For the determination of the activity ratio potassium

$$(AR^K = A_K/\sqrt{A_{Ca+Mg}}),$$

as suggested by Beckett (2), a series of duplicate 1 gm. soil samples in 25 ml. of .05 *M* $CaCl_2$ was set up with KCl added equivalent to 1 meq./100 g. dry soil.

Ammonium acetate extractable K was determined by the following method: 25 g. soil (dry basis) was equilibrated in 400 ml. 1 *N* neutral ammonium acetate over-night. The soil was then

filtered and washed with four lots of 100 ml. ammonium acetate solution. The extracted potassium was determined with the flame photometer.

Plant Available Potassium

To determine the potassium available to plants in each soil, the following experiment was conducted.

Five replicates of 1500 ml. each of the several field-moist soils were measured. Lime equal to 2,000 ppm. was added to those soils with a pH of less than 5.2. Phosphorus was added as $Ca(H_2PO_4)_2$ to all soils. Soils from low rainfall regions received 50 ppm. P; soils from moderate rainfall regions received 100 ppm. P; soils from high rainfall regions received 400 ppm. P; and soils from very high rainfall regions received 500 ppm. P. All soils were treated with $MgSO_4$: 100 ppm. for soils from low rainfall areas and 250 ppm. for soils of high rainfall areas. Nitrogen as NH_4NO_3 was added to all soil at the rate of 100 ppm N. Zinc, as $ZnSO_4$, was added to all soils at the rate of 10 ppm. Zn (4). The soils were adjusted to field moisture capacity, covered with polyethelene bags and allowed to equilibrate for one month.

After the equilibration period the soils were planted with four seeds of a Hawaiian single cross hydrid corn (H-38). After germination the plants were thinned to two per pot and grown for four weeks. The plants were then harvested, dried, weighed and analyzed for their potassium content by flame photometery. Quantities of potassium harvested by the plants and concentration of potassium in the plants were determined and the means subjected to statistical analysis using Duncan's multiple range test.

TABLE 2

Potassium labile pool, activity ratio and PBC for soils of the tropics

Soil Series	K Outside* *meq./100g.*	Radio-activity % *Outside*	Labile Pool *meq./100g.*	AR^K	PBC†
Waimea	1.391	40	4.713	.0070	673
Kawaihae	.519	45	1.153	.0028	412
Molokai	.673	64	1.052	.0029	362
Lualualei	.288	38	.758	.0014	541
Wahiawa	.256	43	.595	.0014	425
Waipahu	.237	69	.343	.0013	264
Ookala	.141	68	.207	.0010	207
Paaloa	.122	72	.169	.0009	188
Maile	.109	69	.158	.0010	158
Kapaa	.064	73	.088	.0006	147
Akaka	.064	88	.073	.0007	104
Mean			.846	.0019	316

* Equilibrated in .05 *M* $CaCl_2$.
† meq./100 g. labile K/AR^K.

RESULTS AND DISCUSSION

Potassium labile pool values are presented in table 2. The mean value observed for the eleven Hawaiian soils of this study was 0.846 meq./100 g. The highest values were for soils from areas of low rainfall. Low values were observed for soil of high rainfall. The soils showing the highest and the lowest labile pool values were from the island of Hawaii and were developed from geologically recent volcanic ash. The degree of development of these soils has been greatly influenced by differences in rainfall.

A mean activity ratio AR^K as reported in table 2, was found to be .0019 with the values ranging from .0006 to .007. When compared with midwest U. S. and British soils, the observed activity ratio is low for the amount of labile potassium found. Probably this results from differences in the soil colloid, with a lower negative charge and a low relative attraction for calcium being found for tropical soils.

Equilibrium time for calcium exchange was determined by finding the time required for steady state potassium concentration. Equilibrium was reached in four weeks. Such slow equilibrium might be explained as the time required for K to diffuse into stable clay aggregates which are commonly found in suspensions of tropical soils or in coatings of amorphous materials which coat all surfaces in some soils at least.

Soils showing low activity ratios also were low in the amount of K in the labile pool, as would be expected from the general equation for ion exchange. The activity ratios increased per unit of pool K as K in the outside solution increased. The amount of potassium in the outside solution, as shown in table 2, increased with increasing soil development. Soils Waimea, Kawaihae, Molokai, Lualualei and Wahiawa have large pools, low relative potassium activity and low outside solution concentration of potassium. The remaining soils of the study contain small labile pool K (.343 to .073 meq./100 g.), a higher relative potassium activity and a larger percentage of K in the outside solution. This indicates that the negative charge of the over-all colloid is

higher on the less developed, less leached, high K pool soils.

The PBC values shown in table 2 were a function of pool potassium and not clay content, as usually found in Midwest and British soils. Soils Waimea, Kawaihae, Molokai, Lualualei and Wahiawa, which have large amounts of pool potassium and somewhat lower amounts of K in the outside supernatent, have high PBC values appearing to be like high clay content soils. The others lower in pool potassium behave like sands; yet they have very high clay contents.

The results of the study on plant uptake of potassium are presented in table 3. Plant K, as per cent dry weight, ranged from 4.03 to .48 per cent. A statistical analysis of the plant data shows that the soils can be divided into four categories. Four soils supplied very high amounts of available K, two soils were very low, and four supplied intermediate amounts.

The correlation coefficients for the mean K content of the corn plants and soil characteristics are shown in table 4. The correlation coefficient between the labile pool and per cent of plant potassium was .98. Correlation coefficients between the other measurements of soil K and plant K were lower but were all highly significant.

It has been observed that weathering of volcanic ash soils may proceed at a rapid rate under the influence of biotic and chemical processes (1). This is demonstrated here by a comparison of K by labile pool measurements and ammonium acetate extracts of the Kawaihae soil. Rainfall of the area where this soil occurs is only 7 inches per year. Yet the primary volcanic glass is completely weathered. Neutral 1 *N* ammonium acetate extracted 1.54 meq./100 g. for the labile pool. In most observations, K extracted by ammonium acetate has been found to be the same, or much lower, than amounts of K in the labile pool and would only exceed the labile pool when the soil contains potassium minerals which are extremely unstable. This unusual solubility of K in ammonium acetate solution indicates that this soil contains easily weatherable K. The more usual situation is demonstrated by the Lualualei soil which is an Mg-clay appearing like Bentonite. The labile pool for this soil was .76 meq./100 g. and only .36 meq./100 g. for the ammonium acetate extract. Only 38 per cent of the pool potassium was in the outside solution when equilibrated with .05 *M* $CaCl_2$, indicating that there is surface-held potassium which is plant-available, and which exchanges with the isotope K^{40} and is not extractable with ammonium acetate. The Lualualei soil was air dried. It was sampled from a low rainfall region. It differs from the other soils in that the clay minerals present are of the expanding lattice type.

TABLE 3

Potassium content and potassium harvested by corn plants

Soil Series	K Content *Mean Percentage Dry Weight*	K *Harvested Mean Percentages mgms. K Per Culture*
Waimea	3.68 ef	148 f
Kawaihae	4.03 f	67 c
Molokai	3.58 ef	124 e
Lualualei	3.30 e	147 f
Wahiawa	2.18 d	65 c
Waipahu	3.25	101 d
Ookala	1.86 cd	60 c
Paaloa	1.49 bc	19 b
Maile	1.01 b	21 b
Kapaa	.60 a	6 a
Akaka	.48 a	5 a

Means with the same letter are not significantly different at the 5% level (Duncan's Multiple Range Test).

TABLE 4

Coefficient of correlation for mean K content harvested potassium by corn plants measurable soil characteristics and soil characteristics

	ΔK^0 (r)	AR^K (r)	PBC (r)	NH_4O-Ac (r)	Plant K (r)	Harvested K (r)
ΔK^0	1.00	.97	.93	.94	.98	.91
AR^K	.97	1.00	.90	.95	.94	.93
PBC	.93	.90	1.00	.86	.87	.91
NH_4OAc	.94	.95	.86	1.00	.90	.84
Plant *K*	.98	.94	.87	.90	1.00	.89
Harvested *K*	.91	.93	.91	.84	.39	1.00

SUMMARY AND CONCLUSIONS

Eleven Hawaiian soils, collected from areas varying in rainfall from 7 to 180 inches per year, were studied in relation to labile pool K obtained by K^{40} exchange and the K^{89} obtained by calcium exchange equilibria. The activity ratio (AR^K), buffering capacity and the K available

to sweet corn grown in these soils was also studied.

Unweathered volcanic soils of the island of Hawaii had labile pool K values as high as 4.71 meq./100 g. and produced sweet corn plants containing 3.7 per cent K. The weathered soils had pool values of only .09 to .07 meq./100 g. and produced plants containing .60 to .48 per cent K.

A large labile pool indicated high availability of potassium to corn as is shown by concentration of K in the plant tissue (coefficient of correlation .98). The correlation of the activity ratio AR^K with plant concentration gave a coefficient of .94. With the exception of the 2:1 layer Mg-clay, potassium extracted with ammonium acetate correlated with plant potassium.

Small labile pools of potassium were found for soils subjected to high rainfall and intense leaching. The coefficient of correlation between pool size and rainfall was −.91. Along with increasing pool potassium, inside K concentration, measured after the soil was equilibrated with .05 *M* $CaCl_2$, also increased with decreasing rainfall. This indicates that soils from high rainfall areas have a higher positive charge than do highly weathered soils.

A study of the soil potassium in terms of inside-outside concentrations, labile pool size, activity ratio (AR^K) and buffer curve show characteristics of tropical soils which are of interest to students of soil development as well as to the agronomist. The activity ratios obtained were low compared with data obtained for some temperate zone soils. This probably results from high relative calcium activity associated with colloids of low negative charge of the more highly weathered Hawaii soils.

REFERENCES

(1) Ayres, A. S. 1949. "Release of Non-Exchangeable Potassium in Hawaiian Sugar Cane Soils." University of Hawaii Agricultural Experiment Station Tech. Bul. No. 9.

(2) Beckett, P. H. T. 1964. Potassium-calcium exchange equilibria in soils: specific absorption sites for potassium. Soil Sci. 97: 376–383.

(3) Graham, E. R., Kampbell, D. H. 1968. Soil potassium and reserve as related to the isotopic pool and calcium exchange equilibria. Soil Sci. 106: 101–106.

(4) Kanehiro, Y., and Sherman, G. D. 1967. Distribution of total and .1 normal hydrochloric acid-extractable zinc in Hawaiian soil profiles. Soil Sci. Soc. Am. Proc. 31: 394–399.

(5) Le Roux, J., Sumner, M. E. 1968. Labile potassium in soils: 1. Soil Sci. 106: 35–41.

(6) Swindale, L. D. and Uehara, G. 1966. Ionic relationships in the pedogenesis of Hawaiian soils. Soil Sci. Soc. Am. Proc. 32: 76–79.

(7) Zandstra, H. G., MacKenzie, A. F. 1968. Potassium exchange equilibria and yield response of oats, barley, and corn on selected Quebec soils. Soil Sci. Soc. Am. Proc. 32: 76–79.