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A THERMODYNAMIC ASSESSMENT OF THE NUTRIENT STATUS OF MALAYAN SOILS: QUANTITY-INTENSITY MEASUREMENTS FOR POTASSIUM USING CALCIUM CHLORIDE EQUILIBRIATION

by

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SUMMARY

Quantity/Intensity (Q/I) relationships for potassium status of soils were determined in nine acid soils of Malaya which are known to have widely differing K-status and on which rubber is commonly grown, by the calcium chloride equilibriation procedure of BECKETT. Quantity, Intensity and Buffer Capacity values derived from these Q/I relationships did not give better relation with the status of soil, as indicated by greenhouse cropping by Pueraria, than the conventional acid-extractable value. The best assessment parameter appeared to be a Buffer Capacity value (B.C. cropping), obtained from greenhouse cropping data and the laboratory measured intensity, although intensity, when taken alone is the poorest indicator of soil K status as assessed by greenhouse cropping by Pueraria.

INTRODUCTION

Methods of assessing nutrient availability in soils for uptake by plants are generally based on extraction procedures mostly using acids of different strengths or salt solutions. These methods, calibrated by laborious field trials, have met with some success. Since SCHOFIELD (1947) introduced his Ratio Law applicable to the equilibrium between the exchangeable cations and those in the soil solution, attempts have been made to place nutrient assessment in soils on a thermodynamic basis. SCHOFIELD's Ratio Law states that "when cations in solution are in equilibrium with a larger number of exchangeable cations, a change in the activity of the solution will not disturb the equilibrium if the activities of all monovalent ions are changed in one ratio, those of all the divalent ions in the square of that ratio and those of all trivalent ions in the cube of that ratio". This Law holds as long as the outside solution concentration is low enough for a diffuse double layer to form. K and Ca, for example, will therefore be in a fixed ratio on the soil for a given $K/\sqrt{Ca}$ activity ratio in solution. This activity ratio is called the Intensity (I) of the soil potassium and is a measure of the strength with which an ion is attached to the electro-chemical system of the soil. The concept of intensity led to the concepts of Quantity (Q) and Buffer-Capacity (B.C.). Quantity is the amount of the ion which is present at a definite potential or held at a definite strength in the soil at a particular time. The relationship between the quantity and intensity is termed the Q/I relationship for a nutrient ion in a soil and is therefore an inherent property of the soil which shows the variation of the quantity of the nutrient held at a particular strength, as well as in the strength itself with which the nutrient is held. Buffer Capacity is the rate of change of quantity with intensity (dQ/dI) and is a measure of the capacity of the soil to maintain the intensity against depletion.

Several methods of measuring the thermodynamic parameters of Q, I and B.C. have been proposed using notations as free energies of exchange (WOODRUFF, 1955), the expression $pK - \frac{1}{2}p(Ca + Mg)$ (TAYLOR, 1958; MOSS and HODNETT 1963) and cation activity ratios $K/\sqrt{(Ca+Mg)}$ (MATTHEWS and BECKETT, 1964a). Attempts have been made to relate these laboratory measurements to greenhouse cropping or field responses to manuring (WOODRUFF, 1955; ARNOLD, 1962; TINKER, 1964; MOSS and COULTER, 1964; MCCONAGHY and SMILLIE, 1965; ACQUAYE et. al., 1967). Nearly all of these measurements have however been with soils whose exchange complex is dominantly saturated with Ca ions. Since Mg behaves similar to Ca in ion-exchange, Ca and Mg are often considered together for convenience. The intensity index for potassium has therefore been expressed with reference to the Ca and Mg ions and expressions as $K/\sqrt{(Ca+Mg)}$ and $RT \ln K/\sqrt{(Ca+Mg)}$ have been widely used. TINKER (1964) showed that with acid soils of Nigeria, an index such as $K/\sqrt{(Ca+Mg)}$ based on calcium and magnesium only, was not related to potassium yield response of oil palm in field experiments and suggested that an activity ratio including aluminium ions also, of the type $K/\{\sqrt{(Ca+Mg)} + P\,{}^{3}\!\sqrt{Al}\}$; P being an arbitrary constant, is more appropriate. The purpose of this work was to examine whether Q/I relationships using the activity ratio $K/\sqrt{(Ca+Mg)}$ were applicable to the rubber-growing acid soils of Malaya.

EXPERIMENTAL

Materials

Nine soils were sampled from 0-6" depth in unmanured plots of or adjacent to, current manurial trials, air-dried and sieved (< 2 mm). Mechanical analysis, pH, exchangeable cations and "total" (concentrated acid-extractable) cations are given in Table 1.

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Methods

10 g samples were brought to a moisture content of 50% of soil and left overnight. 25 ml of .012$\underline{M}$ $CaCl_2$ solutions containing varying amounts of potassium from 0 to 3 m.moles/litre. were added to the samples and shaken for 24 hours. After centrifuging at 9000 rpm for 30 minutes (in a refrigerated centrifuge). the supernatant solution was filtered and analysed for potassium. calcium and magnesium on a Unicam SP900A atomic absorption/emission flame spectrophotometer. potassium and calcium being determined by flame emission and magnesium by atomic absorption methods. The amount of soil potassium adsorbed (ΔK positive) or desorped (ΔK negative) by the equilibriation was plotted against the intensity (I) given by $K/\sqrt{(Ca+Mg)}$. where K. Ca and Mg are concentrations in the equilibrium solution. Concentrations are used instead of "activities" as the solutions are considered dilute enough to permit this approximation.

I_O. the "true" intensity of K in the soil was obtained from the no potassium exchange position ($\Delta K = 0$) of the Q/I curve: Q_O. the quantity in equilibrium with this intensity was obtained by interpolation of the linear part of the Q/I curve.* "B.C. (laboratory)" was determined as the slope of the linear portion of the Q/I curve.

Exchangeable cations were determined on a NH_4Cl extract (MOHINDER SINGH and RATNASINGAM. 1968). Potassium. calcium and magnesium were determined by atomic absorption/emission spectrophotometry. and Al by the "aluminon" method (CHENERY. 1948).

RESULTS AND DISCUSSION

Q/I curves are given in Figure 1. The shapes of the curves are similar to those reported by BECKETT (1964a). although the exchange complex of these soils is not dominantly saturated with Ca ions. Exchangeable Ca plus Mg of these soils are below 30% of the cation-exchange capacity for Rengam. Serdang and Selangor Series soils. 32 to 38% for Batu Anam. Ulu Tiram and Chemor. 43% for Malacca and above 50%. only for Segamat (58%) and Kuantan (62%) Series soils. The concentration of calcium in the equilibrium solution was between 0.63 x $10^{-2}\underline{M}$ (Selangor soil) to 0.93 x $10^{-2}\underline{M}$ (Chemor) while Ca plus Mg. which are normally considered together because of their similar exchange behaviour. was between 0.81 x $10^{-2}\underline{M}$ (Selangor) to 0.94 x $10^{-2}\underline{M}$ (Chemor). These figures represent a nett increase of 0.36 and 1.14 me/100g in the initial exchangeable Ca + Mg contents of the Chemor and Selangor soils respectively due to adsorption of calcium and desorption of magnesium from the equilibriating solutions. The initial exchangeable Ca + Mg status of the 9 soils studied were increased by 35 to 40% in the case of Selangor and Batu Anam soils. 40 to 50% with Kuantan. Malacca and Chemor. 60-70% with Ulu Tiram and Segamat. and 85-90% with Serdang and Rengam. that is. appreciable and variable quantities of calcium was adsorbed by soils from the equilibriating solutions. For comparison. the "Lower Greensand" soil used by BECKETT (1964a) in his Q/I studies. had 6.88 me/100g exchangeable calcium and 0.70 me/100g exchangeable magnesium. which together accounted for 93% of the exchange capacity. With 0.02$\underline{M}$ calcium chloride equilibriating solution. the equilibrium solution had a Ca + Mg concentration of 0.0194 $\underline{M}$. This represents a nett change (increase) of only 16% in the initial Ca + Mg status of the soil.

Q_O values for all the nine soils (see Table 2) are lower than conventionally measured exchangeable K values. This is in line with BECKETT's information (BECKETT. 1964b) that the exchangeable K may be considered as being composed of (a) a "immediate" labile pool which equilibriates rapidly and is the one measured here as Q_O. and (b) a "slow" or "less readily" exchangeable pool which represents K held on "specific" sites. This potassium held on "specific" adsorption sites accounts for the lower curvilinear part of the Q/I curve.

Several indices of soil potassium status were correlated with the potassium uptake by Pueraria in greenhouse. These indices were the thermodynamic values of Q_O. I_O and B.C. (laboratory). obtained from the Q/I relationships. and the conventional indices of exchangeable K and acid-extractable K. obtained by common empirical extraction methods. Two other thermodynamic indices of buffer capacity. namely. "buffer capacity (cropping)" and "buffer capacity (exchangeable)". have also been calculated using the formula B.C. = dQ/dI. Buffer capacity (cropping) was calculated with dQ as the total uptake by Pueraria during greenhouse cropping and buffer capacity (exchangeable) was with dQ as the exchangeable value measured by a conventional laboratory method. In both cases I_O - 0.5 x 10^{-3}. where I_O is the initial intensity of the soil for potassium obtained from the Q/I relationship curve. was used for dI. The value 0.5 x 10^{-3} is the lower limit of the intensity of soil depleted by ryegrass cropping in Rothamsted greenhouse experiments (TALIBUDEEN and DEY. 1968). Ideally. this value at which cropping ceases or is terminated should have been measured on the depleted soils after cropping with Pueraria; in the absence of such a figure. the value of 0.5 x 10^{-3} obtained at Rothamsted. was taken as the intensity of the depleted soils for calculating B.C. (cropping) and B.C. (exchangeable). Further. a linear relationship between Q and I values is assumed in the cropping.

All the above-mentioned indices have been examined with respect to Pueraria K-cropping values. correlation coefficients of which are given in Table 3. The correlations are also shown graphically in Figure 2.

TABLE 3 RELATIONSHIP OF SOIL K INDICES WITH GREENHOUSE CROPPING BY PUERARIA

Soil Index	Correlation coefficient	
	All soils	Excl. Selangor Series soil.
Q_O	0.719*	0.026 NS
Exchangeable	0.832**	0.228 NS
Acid Extractable	0.951***	0.959***
B.C. (laboratory)	0.807**	0.363 NS
B.C. (cropping)	0.959***	0.957***
B.C. (exchangeable)	0.895**	0.568 NS
I_O	-0.215 NS	-0.314 NS

***: $P< 0.001$ **: $P< 0.01$ *: $P< 0.05$ NS : Not Significant

As one soil (Selangor Series) gave an exceptionally high cropping value, correlation coefficients were also calculated without this value (see Table 3). Taking all the 9 values (9 soils) into consideration, I_O is found not to relate at all (r = -0.215) to soil K status by Pueraria cropping. Acid-extractable and B.C. (cropping) values give correlations significant at the 0.1% level, r being 0.951 and 0.959 respectively. B.C. (exch.), B.C. (lab.) and exch. K values give correlations significant at the 1% level (r = 0.807 - 0.895) while Q_O only gives at the 5% level (r = 0.719). When the extreme value for the Selangor soil is excluded from the correlations, significant correlations are obtained only with B.C. (cropping) and acid-extractable indices, both still retaining their significance at the 0.1% level. An examination of the graphical plots of K-uptake by Pueraria against soil indices (see Figure 2) reveals that though the acid-extractable index gives a good fit, the soils are divided mainly into two distinct categories - soils with high and low potassium status. The index B.C. (cropping), on the other hand, gives a better spread of the index with Pueraria cropping status of soils, and therefore proves to be a more sensitive index.

CONCLUSIONS

In comparing a number of analytical indices based on both thermodynamic principles and conventional extraction procedures for measuring availability of potassium in soil for plant-uptake, Buffer Capacity (cropping) and acid-extractable K values were found to relate well to greenhouse cropping by Pueraria. The former appeared more sensitive in the sense that it gave a better spread of results compared to the latter. The "immediate" labile pool (Q_O) and Buffer Capacity derived from the Q/I curve using calcium ion for equilibriation were found to be less sensitive. The poorer relations of the thermodynamic parameters derived from the Q/I curve may be a consequence of using calcium as the equilibriating ion with soils where aluminium appears to be the dominant ion occupying exchange sites. Improved relationships may be expected if aluminium (Al^{+++}) were used for equilibriation. Results of Q/I relationship studies using Al^{+++} as the reference ion are underway and will be the subject of a subsequent paper under preparation (MOHINDER SINGH AND TALIBUDEEN, 1968).

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TABLE 1 MECHANICAL AND CHEMICAL COMPOSITION OF TOP SOILS (0-6") USED IN EXHAUSTIVE CROPPING FOR POTASSIUM BY PUERARIA IN GREENHOUSE

	Mechanical Analysis[a] (% oven dry soil)				pH[b]		Exchangeable cations[c] me/100g						Acid extractable cations[e] me/100g		
Soil Series	C.S.	F.S.	Silt	Clay	$CaCl_2$	H_2O	K^+	Ca^{++}	Mg^{++}	Al^{+++}	% K in C.E.C.	% Ca + Mg C.E.C. (d)	K^+	Ca^{++}	Mg^{++}
1. Rengam	38	6	8	41	4.0	4.6	0.14	0.78	0.09	1.92	4.8	29.7	0.32	0.30	0 66
2. Serdang	29	30	10	26	3.8	4.6	0.10	0.63	0.08	5.08	1.7	12.1	2.95	0.23	4.50
3. Selangor	1	9	43	40	3.6	4.5	0.37	1.39	1.80	12.40	2.3	20.0	3.99	0.67	14.16
4. Kuantan	3	8	33	46	4.3	5.0	0.10	1.23	0.40	0.90	3.8	62.0	0.37	1.54	8.26
5. Malacca	48	12	5	29	4.0	4.6	0.09	1.00	0.13	1.43	3.4	43.0	0.20	0.34	0.42
6. Segamat	6	4	25	57	4.3	5.2	0.16	0.84	0.35	0.70	7.8	58.0	0.42	0.76	0.63
7. Batu Anam	1	8	34	51	3.8	5.0	0.12	1.20	0.33	3.10	2.5	32.2	2.76	0.77	1.44
8. Chemor	58	20	3	15	4.2	5.1	0.06	0.80	0.06	1.33	2.7	38.2	0.26	0.24	1.36
9. Ulu Tiram	62	10	7	20	4.2	5.2	0.06	0.78	0.07	1.60	2.4	33.9	0.40	0.24	0.77

(a) International scale
(b) 1:5 soil: solution, 30 min. shaking; strength of $CaCl_2$ used is 0.01 M
(c) to N - NH_4Cl, adjusted to pH 4.0
(d) C.E.C. is taken as K + Ca + Mg + Al
(e) 1 hr. boiling, 6N HCl (MOHINDER SINGH AND K. RATNASINGAM, 1966).

TABLE 2 SOIL INDICES FOR POTASSIUM AND VALUES OF TOTAL UPTAKE BY *PUERARIA* IN GREENHOUSE CROPPING FROM TOP SOILS (0 - 6")

No.	Soil Series	Exch. K	Acid Extr. K	Q_O	$I_O \times 10^{-3}$ (moles/l)$^{\frac{1}{2}}$	Buffer Capacity			Uptake by *Pueraria* me/100 g
		me/100 g				B.C. "laboratory"	B.C. "cropping"	B.C. "Exch."	
1	Rengam	0.14	0.32	0.085	10.2	8.3	16.5	14.4	0.16
2	Serdang	0.10	2.95	0.060	5.9	10.2	77.8	18.5	0.42
3	Selangor	0.37	3.99	0.184	8.6	21.4	92.6	45.7	0.75
4	Kuantan	0.10	0.37	0.084	6.7	12.5	16.1	16.1	0.10
5	Malacca	0.09	0.20	0.076	16.0	4.8	7.7	5.8	0.12
6	Segamat	0.16	0.42	0.120	10.4	11.5	10.1	16.2	0.10
7	Batu Anam	0.12	2.76	0.092	8.1	11.4	43.4	15.8	0.33
8	Chemor	0.06	0.26	0.050	10.6	4.7	5.9	5.9	0.06
9	Ulu Tiram	0.06	0.40	0.044	5.2	8.5	14.9	12.8	0.07

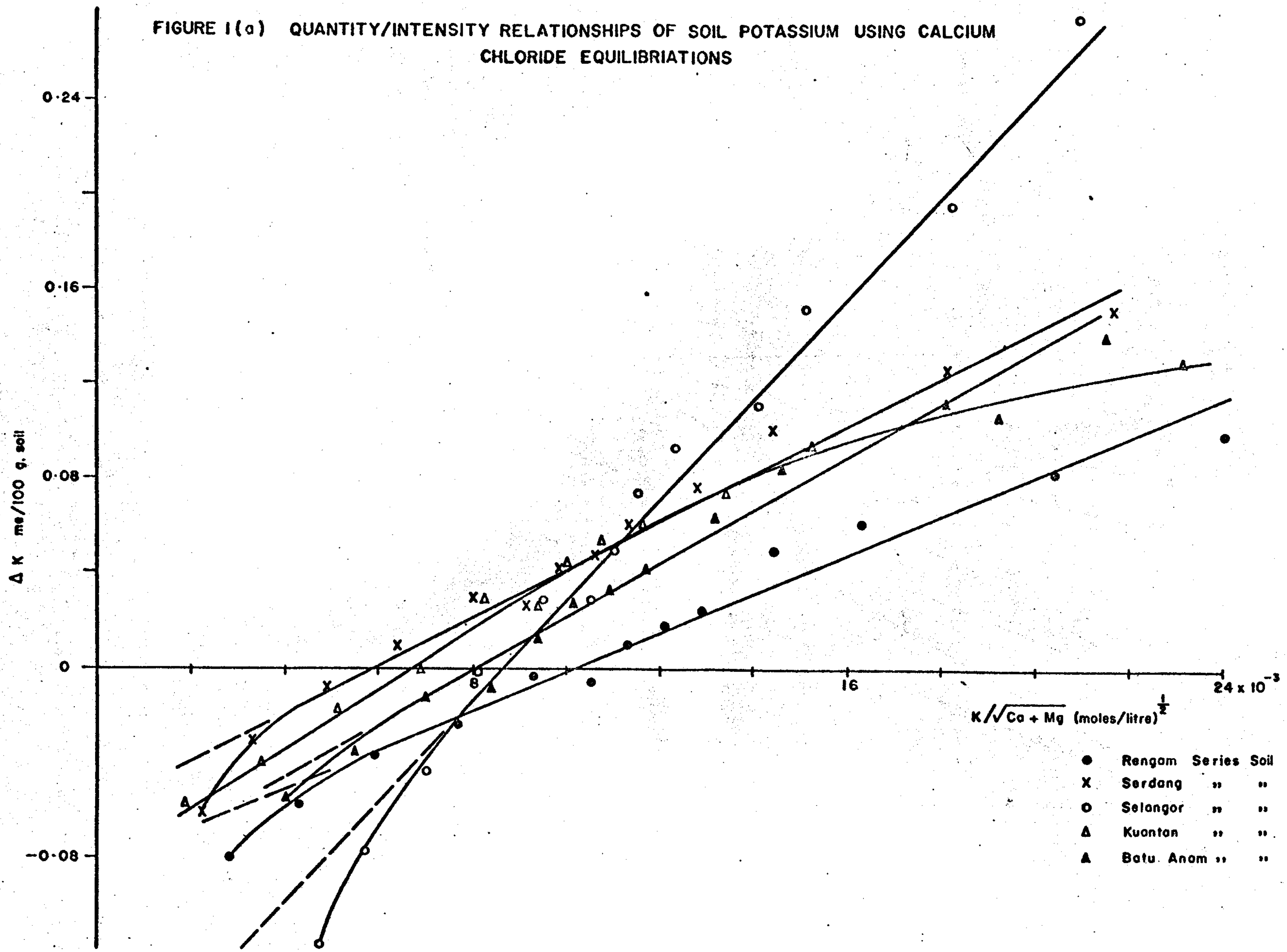


FIGURE I(a) QUANTITY/INTENSITY RELATIONSHIPS OF SOIL POTASSIUM USING CALCIUM CHLORIDE EQUILIBRIATIONS

FIGURE I(b) QUANTITY/INTENSITY RELATIONSHIPS OF SOIL POTASSIUM USING CALCIUM CHLORIDE EQUILIBRIATIONS

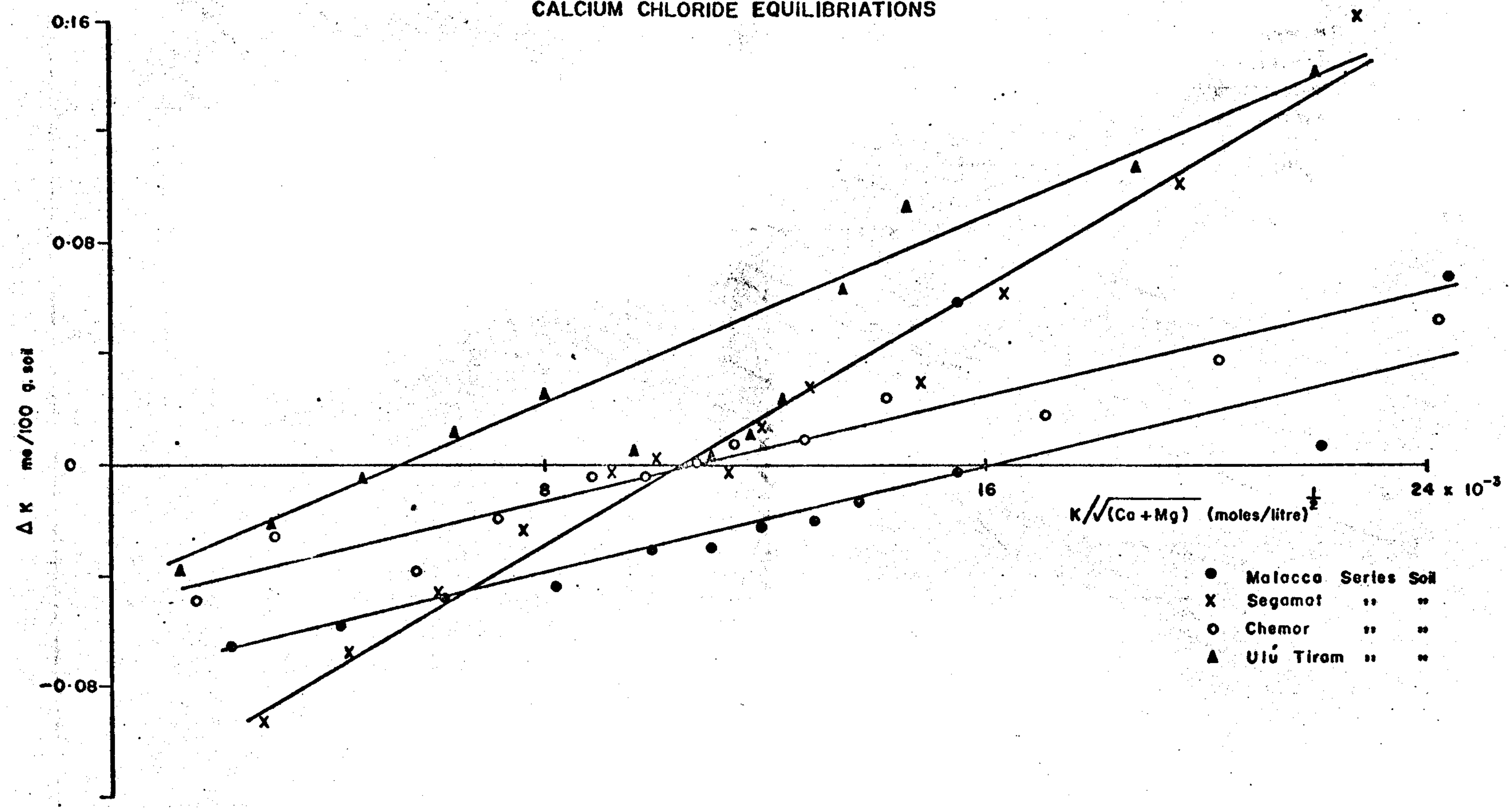
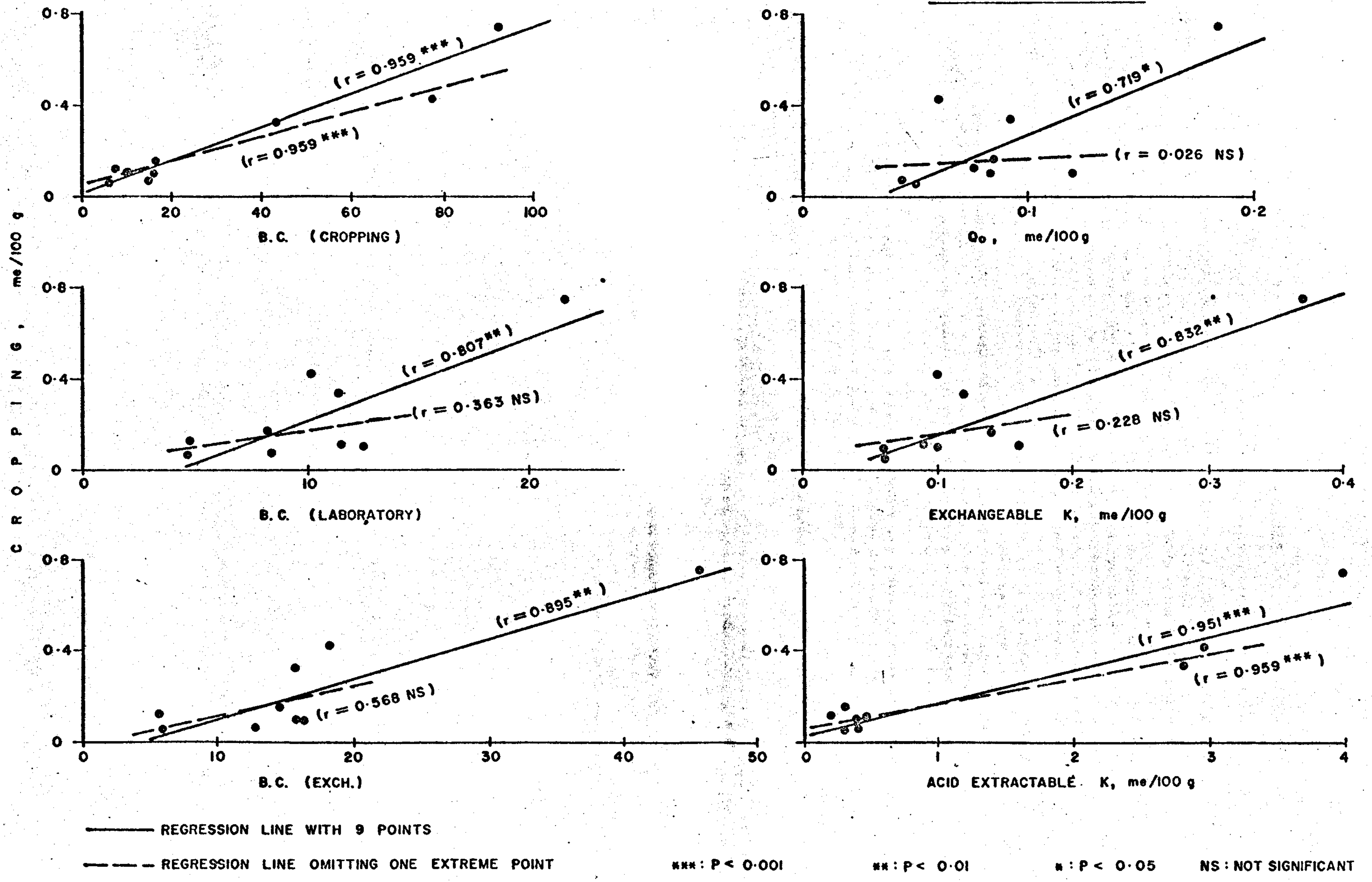


FIGURE 2. RELATIONSHIP OF SOIL INDICES WITH GREENHOUSE CROPPING BY <u>PUERARIA PHASEOLOIDES</u>



Discussion

Chui: What force gives rise to the *intensity*, mainly electrostatic force?

For different samples the electrostatic forces involved would be different.

Singh: The main force would be the electrostatic force but this is not the only force.

It is difficult to explain this without going into the nature of how the cations are held in the soil, this brings us to colloid science because the soil is a colloid, the cations are distributed accordingly to known, definite, physical chemistry laws and they are not simply distributed. They form a diffuse double layer and as long as the colloid system does not break up (which it will do as the solution becomes too concentrated, as is for instance the case with the acid - sulphate soils in which the sulphate concentration is very high) the double layer will exist and this will control the exchange reaction. One has to go into this double layer to learn exactly how these cations are held.

Ashworth: Would this method not be too laborious and therefore uneconomic for routine use?

Singh: Initially the method was laborious because we tried to understand in detail the reactions that occur. This will not be done in routine work. The measurement of total acid extractable cations is much more laborious than the one presented here. The former may take about a week while the present method would take not more than half a day when routined.

Intensity is being measured on a routine basis in other places as in England, although not for routine advisory purposes yet, and in Rothamsted a method has been developed where intensity can be obtained very successfully by a rapid successive equilibration method. More details on this will be given in a second paper on this subject. I do think this method is applicable to routine analysis.

Ashworth: Is it right to correlate your method with exhaustive cropping? Can it then be used for recommendations for one single year cropping?

Singh: The ideal correlation would be with field results but this will take many years with *Hevea*. The relatively rapid method of exhaustive cropping is accepted as a good indicator of soil status although it is removed from many variables in the field. The method once successfully developed will however be ultimately tested in the field.

Chui: Comment. Once a new method is developed, encouragement should be given instead of discouragement. It is realised that more research is needed but it is too early to say that it is not suitable.

Ashworth: This was not my intention.