CATION ACTIVITY RATIOS IN EQUILIBRIUM SOIL SOLUTION AND UPTAKE OF K, Ca, AND Mg BY LAWN GRASS

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ABSTRACT

K intensity decreased with cropping at all pH levels, reflecting that K in soil solution was absorbed by grass grown on the soils. Uptake of Ca and Mg increased progressively with increased rate of Ca and Mg application. The increase in uptake of Ca and Mg was associated with decrease in K uptake. Linear relationship existed between K and $aK/\sqrt{aCa+Mg}$ indicating that K uptake was largely regulated by equilibrium activity ratio of K. The uptake of Ca and Mg was linearly related to $\sqrt{aCa}/\sqrt{aCa+Mg}$ and $\sqrt{aMg}/\sqrt{aCa+Mg}$, respectively concluding that uptake of Ca and Mg was controlled by the square of the respective activity ratios. The linear relationship between the Ca uptake and $\sqrt{aCa}/\sqrt{aCa+Mg+B.aK}$ and Mg uptake and $\sqrt{aMg}/\sqrt{aCa+Mg+B.aK}$ demonstrated the existence of ion antagonism in soil.

INTRODUCTION

Though there is as yet no generally recognised view of the mechanism of ion uptake by roots which would allow a definite soil function to be identified as the quantity controlling the uptake, the concepts of chemical potential and activity have been much used in this regard during the recent times (14). The 'total activity'(7) and electrochemical potential(15) of an ion throughout the soil solution system is dependent upon the total concentration of the solution (2, 3). Although the chemical potential of the ion on the solid phase is taken to be constant yet, it cannot be measured. Hence, the adoption of activity ratios as a measure of the difference between the chemical potentials of two different ions in the soil is suggested(2). In earlier works, the ratio $aK/\sqrt{aCa+Mg}$ in soil solution was related to crop response from K dressing(18), or to K uptake(1). The ratio $^{90}[Sr]/[Ca]$ was also correlated with the corresponding ratio in plants (11). $\sqrt{aMg}/\sqrt{aK}$ was found to be poorly correlated with Mg in crops(6). The Mg concentration in grass was found to be linearly related to $\sqrt{aMg}/\sqrt{aCa+Mg+B.aK}$ on cropping a range of soils with different exchangeable K, Ca, Mg and soil pH(12). However, no such relationship was tried between Ca and other cations.

Green house and laboratory experiments were carried out to study the relationships bewteen (i) $aK/\sqrt{aCa+Mg}$ in soil solution and K uptake ; (ii) $\sqrt{aMg}/\sqrt{aCa+Mg}$

in soil solution and Mg uptake; (iii) $\sqrt{aCa}/\sqrt{aCa+Mg}$ in soil solution and Ca uptake ; (iv) $\sqrt{aMg}/\sqrt{aCa+Mg+B.aK}$ in soil solution and Mg uptake and (v) $\sqrt{aCa}/\sqrt{aCa+Mg+B.aK}$ in soil solution and Ca uptake by lawn grass.

EXPERIMENTAL

Materials and Methods : Two soils (0-15cm from surface) representing the Tejgaon and Karail series were collected from two rice growing areas of Bangladesh. Some of their physical and chemical properties are presented in Table I.

TABLE I

SOIL CHARACTERISTICS

Soils	*USDA taxonomy*	*pH*	*Texture*	*O.M.* (%)	*Exchangeable cations (meq/100g)*		
					K	*Ca*	*Mg*
Tejgaon	Typic paleudalts	4.0	Clay	0.542	5.12	65.20	24.24
Karail	Fluvaquentic haplaquept	4.5	Clay	3.923	6.12	137.60	26.40

Green house experiment : 350 gms of air dry soil were taken in five inches diameter plastic pots arranged in a completely randomized design in triplicate. As the soils were acidic in reaction, they were limed with a set amount of CO_3^{--} using different portions of $CaCO_3$ and $MgCO_3$ to obtain seven exchangeable Mg:Ca ratios from 2 to 40(Table II). 60 mgms of P and 57 mgms of N in the form of diammonium

TABLE II

RATIOS OF Ca AND Mg AND CORRESPONDING pH OF SOIL

Treatment	*Mg : Ca ratio*	*Soil pH*			
		Before cropping		*After cropping*	
		Tejgaon	*Karail*	*Tejgaon*	*Karail*
1	0	4.0	4.5	3.6	4.0
2	2:40	4.5	5.0	4.1	4.4
3	1:20	5.0	5.8	4.7	5.1
4	1:10	5.6	6.0	5.1	5.5
5	1:5	6.0	6.5	5.4	5.7
6	1:2.5	6.5	6.9	5.6	6.0
7	1:1	7.0	7.3	5.8	6.2

hydrogen phosphate were added to each pot. The soils were brought to their field capacities and then allowed to settle for a week so that the soils attained differet pH. Lawn grass was grown at the rate of 0.3gms of seed per pot . The grasses were cut every month afterwards leaving a 2 cm stubble. NH_4NO_3 at the rate of 50mg N per pot was added after each cut. The harvested grasses were dried at 80°C for 16 hrs. The roots left in the pots were also analyzed.

Laboratory analyses : The soils were sampled to the full depth of each pot (four cores per pot) after each cut and equlibrium ratios were determined immediately using $CaCl_2$ equilibrium method of Talibudeen and Dey(13). pH of the suspensions was measured by a Pye glass electrode pH meter. The activity ratios of the soils were determined by following the method of Mathews and Beckett(8). The K in the supernatant solution was determined by a Unicam sp 900 flame photometer and Ca and Mg by titration with EDTA.

Exchangeable K,Ca and Mg were determined before and after cropping by leaching with NH_4OAc using tube method of Mattson(9). K, Ca and Mg in the extract were measured by a Unicam SP 900 flame photometer.

Mechanical analyses were done by Hydrometer method (10) and the textures were determined by the USDA(16) method. The pH of the soils was determined by a Pye glass electrode pH meter at a soil : water ratio of 1:2.5. Organic carbon was determined volumetrically by wet-oxidation method (17).

Plant and root analyses : Samples of plants and roots were wet digested with nitric acid and perchloric acid(10). K, Ca and Mg were measured by a Unicam SP 900 flame photometer.

RESULTS AND DISCUSSION

(i) ***The relationship between the*** $aK/\sqrt{aCa+Mg}$ ***of soils and uptake of K*****:** The effect of cropping on the equilibrium activity ratios and the uptake of K by lawn grass are presented in Tables III and IV. From the tables it is seen that both the equilibrium activity ratio of K and the concentration of K in the aerial vegetative portion and root of grass were affected during cropping. The K intensity ranged between 2.0 to $6.5\times10^3M^{\frac{1}{2}}$ and 4.5 to $8.95\times10^3M^{\frac{1}{2}}$ in the Tejgaon and Karail soils, respectively before cropping. These values were 1.47 to 3.63 and 0.74 to $1.88\times10^3M^{\frac{1}{2}}$ in the Tejgaon and 2.92 to 6.06 and 0.82 to $2.49\times10^3M^{\frac{1}{2}}$ in the Karail soils during the periods of cropping Table III Grass accumulated 4.32 to 7.6 and 4.49 to 6.78 mg of K per 100g of soil in the Tejgaon and Karail soils, respectively. The correlation co-efficients between equilibrium K activity ratios of soils and corresponding uptake by lawn grass showed that the relationships were significant at various levels. The possitive correlation co-efficients suggested that with the increase in ARK° values of the soils the uptake of K also increased. To further substantiate this, linear regression analyses were made. The distribution of observed K uptake by grass during the growing period of three months fell very close to the regression line drawn from the expected uptake of K and $aK/\sqrt{aCa+Mg}$ of the soils (Fig. Ia). It was, therefore, concluded that uptake of K by plants was regulated by the K activity of the soils.

(ii) ***The relationships between (a)*** $\sqrt{aMg}/\sqrt{aCa+Mg}$ ***of soils and Mg uptake and (b)*** $\sqrt{aCa}/\sqrt{aCa+Mg}$ ***of soils and Ca uptake*** : Recent works have shown that Mg concentration in grass was linearly related to $\sqrt{aMg}/\sqrt{aCa+Mg}$. Such relationship with Ca has not been tried elsewhere. To calculate these relationships the activity coefficients of Ca and Mg were needed. Unfortunately no such data could be found. An attempt was, therefore, made to calculate these coefficients.

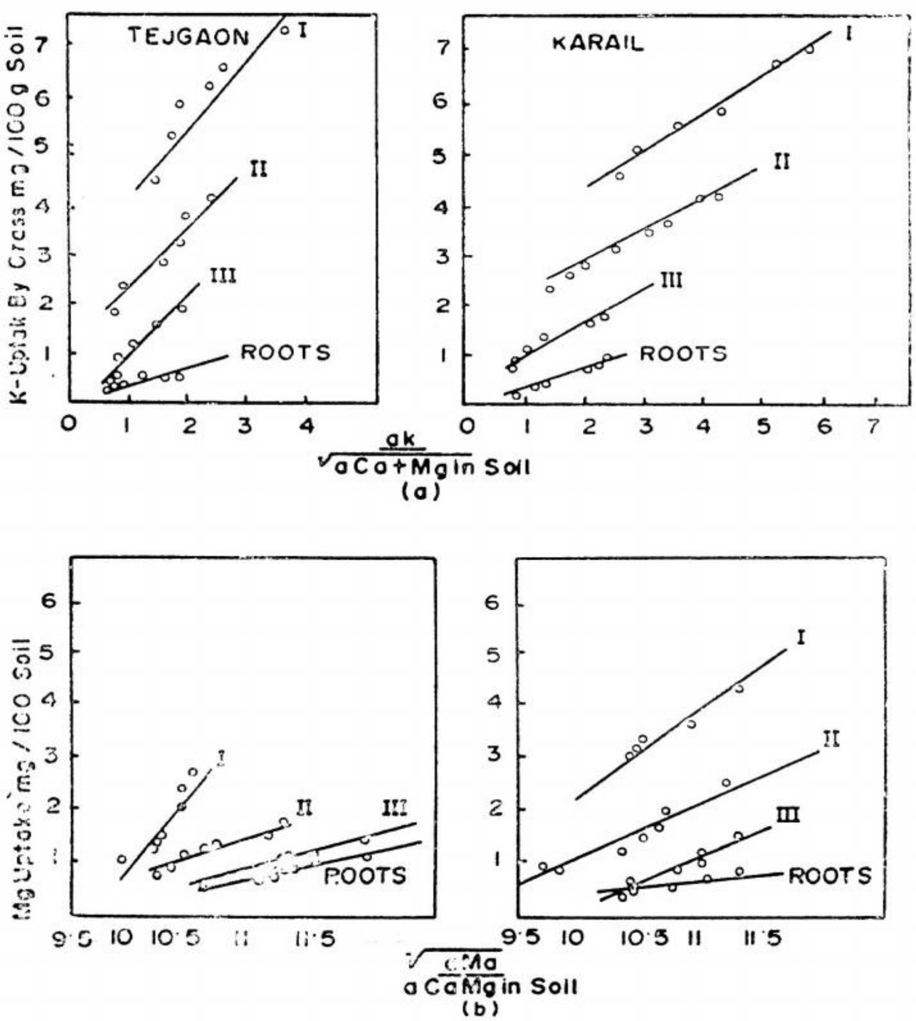

Fig. 1. Relationships between (a) K uptake and $aK/\sqrt{aCa+Mg}$; (b) Mg uptake and $\sqrt{aMg}/\sqrt{aCa+Mg}$; I, II and III indicate the regression lines for the different stages of cuttings.

TABLE III A

AVERAGE EQUILIBRIUM AR^k VALUES AT DIFFERENT CUTTINGS

Soils	*Tejgaon*						
Treatments	1	2	3	4	5	6	7
Before cropping	6.5	5.5	5.0	4.5	3.5	2.5	2.0
During Ist cut	3.6	2.7	2.4.	2.0	1.9	1.4	1.5
,, 2nd cut	2.6	2.2	1:9	1.5	1.0	0.9	0.8
,, 3rd cut	1.9	1.6	1.3	1.0	0.9	0.8	0.76

Soils	*Karail*						
Treatments	1	2	3	4	5	6	7
Before cropping	8.95	8.50	7.75	7.25	6.25	5.75	4.50
During 1st cut	6.06	5.42	4.91	4.61	3.98	3.26	2.92
,, 2nd cut	4.21	3.53	3.03	2.56	1.83	1.62	1.41
,, 3rd cut	2.49	2.36	2.07	1.36	1.06	0.94	0.82

Activity coefficient is calculated as follows[4],

$$\log fi = -a.Zi^2.I^{\frac{1}{2}}$$

Where, $a = 0.509$ at 25°C

Z = valency of ion i

$$I = \text{ionic strength of the solution} = \frac{1}{2}\sum_{ii}^{in} m_i Z_i^2$$

where, m_i = molality of ion i.

The above equation is applicable only up to ionic strengths of 0.01 or thereabouts i.e. approximately for soil solutions not more than 0.003M.

The activity coefficients for $CaCl_2$ and $MgCl_2$ differ very little up to $I = 0.1$ and by only 2% up to $I = 3$ [5]. Little error is likely to result if $fMg+Ca$ is calculated taking (Ca +Mg) as a single ionic species behaving like Ca.

Taking this fact into consideration, the activity coefficients for Mg was calculated and as the activity coefficients for Ca and Mg differ very little the values for Ca were also determined by taking the values for Mg. The results obtained are presented in Table V.

The square roots of activity of Mg and Ca for the Tejgaon and Karail soils corresponding to the 1st, 2nd and 3rd cuttings are presented in Table III. The values increased with the increased addition of Mg and Ca in the soils. The uptakes of Ca and Mg by lawn grass increased progressively with increasing rates of Ca and Mg application as well (Table V)

TABLE III B

VALUES OF THE SQUARES OF $\sqrt{aMg}/\sqrt{aCa+Mg}$; $\sqrt{aCa}/\sqrt{aCa+Mg}$; $\sqrt{aCa}/\sqrt{aCa+Mg+B.aK}$ AND $\sqrt{aMg}/\sqrt{aCa+Mg+B.aK}$ at DIFFERENT CUTTINGS

Soils		*Tojgaon*						
	Treatments	1	2	3	4	5	6	7
$\sqrt{aMg}/\sqrt{aCa+Mg}$ at different cut	1st cut	9.97	10.1	10.1	10.3	10.5	10.5	10.6
	2nd ,,	10.23	10.3	10.5	10.7	10.8	11.4	11.4
	3rd ,,	10.72	10.0	10.1	11.2	11.3	11.5	11.8
$\sqrt{aCa}/\sqrt{aCa+Mg}$ at different cut	1st cut	8.9	8.9	8.9	9.0	9.1	9.2	9.3
	2nd ,,	8.6	8.7	8.8	8.9	9.0	9.2	9.2
	3rd ,,	8.7	8.9	8.9	9.0	9.1	9.2	9.5
$\sqrt{aCa}/\sqrt{aCa+Mg+B.aK}$ at different cut	1st cut	2.9	3.3	3.7	4.1	4.7	5.4	5.8
	2nd ,,	2.9	3.4	4.1	4.7	5.5	6.2	6.6
	3rd ,,	3.7	4.6	5.4	6.2	7.2	7.9	8.4
$\sqrt{aMg}/\sqrt{aCa+Mg+B.aK}$ at different cut	1st cut	3.3	3.9	4.3	4.7	5.4	6.1	6.6
	2nd ,,	3.5	4.1	4.8	5.6	6.6	7.6	8.1
	3rd ,,	4.6	5.7	6.5	7.7	8.9	9.8	10.4

Soils		*Karail*						
Treatments		1	2	3	4	5	6	7
$\sqrt{aMg}/\sqrt{aCa+Mg}$ at different cut	1st cut	10.7	10.4	10.4	10.5	10.6	10.9	11.3
	2nd cut	9.9	9.7	10.4	10.6	10.6	10.7	11.2
	3rd cut	10.44	10.4	10.8	10.9	11.1	11.1	11.7
$\sqrt{aCa}/\sqrt{aCa+Mg}$ at different cut	1st cut	8.6	8.8	8.8	8.8	9.1	9.2	9.3
	2nd cut	8.4	8.4	8.8	9.1	9.2	9.3	9.5
	3rd cui	8.8	8.7	9.0	9.1	9.4	9.4	9.7
$\sqrt{aCa}/\sqrt{aCa+Mg+B.aK}$ at different cut	1st cut	3.8	4.6	4.8	5.1	5.5	6.3	6.5
	2nd cut	3.1	3.7	4.4	5.1	5.8	6.3	7.0
	3rd cut	3.7	4.2	4.7	5.9	6.6	7.1	8.0
$\sqrt{aMg}/\sqrt{aCa+Mg+B.aK}$ at different cut	1st cut	4.5	5.4	5.7	6.0	6.4	7.5	7.9
	2nd cut	3.7	4.2	5.2	6.0	6.7	7.3	8.3
	3rd cut	4.5	5.0	5.7	7.1	7.8	8.4	9.6

TABLE IV

UPTAKE OF K, Ca AND Mg AT DIFFERENT CUTTINGS

Soils		*Tejgaon*						
	Treatments	1	2	3	4	5	6	7
K uptake, mg/100g of soil at different cuttings	1st cut	7.6	6.6	6.2	5.8	5.4	4.6	4.3
	2nd ,,	3.9	3.6	3.1.	2.7	2.2	2.0	1.8
	3rd ,,	1.6	1.4	1.7	0.8	0.6	0.5	0.4
	Root	0.5	0.5	0.4	0.3	0.2	0.2	0.1
Ca uptake, mg/100g of soil at different cuttings	1st cut	2.4	2.6	2.9	3.2	3.6	4.0	4.5
	2nd ,,	1.3	1.5	1.8	1.9	2.3	2.7	2.9
	3rd ,,	0.7	0.9	0.97	0.99	1.3	1.7	1.98
	Root	0.7	0.74	0.74	0.85	0.94	0.98	0.85
Mg uptake, mg/100g of soil at different cuttings	1st cut	1.2	1.3	1.5	1.6	2.2	2.4	2.8
	2nd ,,	0.75	0.82	0.85	1.1	1.2	1.4	1.5
	3rd ,,	0.52	0.62	0.83	0.91	0.91	0.98	1.09
	Root	0.51	0.53	0.56	0.61	0.64	0.75	0.72
Soils			*Karail*					
	Treatments	1	2	3	4	5	6	7
K uptake, mg/100g of soil at different cuttings	1st cut	6.7	6.3	5.9	5.6	5.2	4.9	4.5
	2nd ,,	4.1	3.8	3.5	3.2	2.8	2.6	2.3
	3rd ,,	2.0	1.9	1.7	1.4	1.2	1.0	0.85
	Koot	1.2	0.8	0.6	0.4	0.3	0.3	0.24
Ca uptake, mg/100g of soil at different cuttings	1st cut	3.3	3.9	4.0	4.3	4.6	5.0	5.2
	2nd ,,	1.7	1.9	2.3	2.8	3.2	3.4	3.5
	3rd ,,	0.94	0.97	0.98	1.2	1.6	1.7	2.1
	Root	0.73	0.77	0.78	0.84	0.89	0.94	0.97
Mg uptake, mg/100g of soil at different cuttings	1st cut	2.1	2.8	2.9	3.0	3.2	3.6	4.2
	2nd ,,	0.75	0.97	1.08	1.3	1.6	1.9	2.6
	3rd ,,	0.56	0.74	0.87	0.98	1.13	1.14	1.8
	Root	0.63	0.65	0.65	0.73	0.78	0.84	0.93

The values for Ca ranged between 5.14 and 10.19mg per 100g and 6.66 and 11.83 mg per 100g in the Tejgaon and Karail soils, respectively. The corresponding values for Mg were 2.96 to 6.17mg per 100g and 4.05 to 9.59mg per 100g, respectively. The uptake of both Ca and Mg was higher in the Karail soil. This was related to the higher amount of native exchangeable Ca and Mg in this soil. The uptakes of Ca and Mg by harvested grass grown on the soils declined steadily with the numbers of harvests at all the treatments. Correlation co-efficients between the activity ratios of the ions and their uptake at different stages were calculated. The 'r' for Mg uptake with the square root of its activity ranged between 0.91 and 0.99 in the Tejgaon soil and 0.82 and 0.96 in the Karail soil. Lesser values were found for Ca in the Tejgaon soil. The values for the Karail soil was as before. Linear analyses also showed similar trends (Figs. 1b and 1c). It was, therefore, concluded that uptake of Mg was greatly and that of Ca was generally regulated by the corresponding square roots of their activity ratios.

TABLE V

ACTIVITY COEFFICIENT RATIO FOR Ca OR Mg (fCa OR Mg/fCa+Mg) IN 0.01M $CaCl_2$ SOLUTION

Concentration of Ca or Mg me/L	*Values of fCa or Mg/fCa+Mg*
0.5	1.7024
1.0	1.7048
3.0	1.7144
4.0	1.7192
5.0	1.7230
10.0	1.7460
50.0	1.9300

Similar results were obtained by Salmon([12]) with Mg, but for Ca this was probably a new relationship. The uptake of Mg depends on the exchangeable K, Ca and NH_4 contents and on soil pH as well as the exchangeable Mg ([12]). Hovland and Caldwell ([6]) found that $\sqrt{aMg}/\sqrt{aK}$ in soil solution was poorly correlated with Mg in crops. However, they did not account for the variation in other cation activities.

(iii) *The relationship between the uptake of (a) Mg and* $\sqrt{aMg}/\sqrt{aCa+Mg}+B.aK$ *and (b) Ca and* $\sqrt{aCa}/\sqrt{aCa+Mg}+B.aK$ *in soil solution* : The relationship between the Mg or Ca content of the lawn grass grown on the soils that varied in their Ca and Mg levels, and the function of the ion activities in equilibrium soil solution were calculated by following Salmon's([12]) technique (Table III). The correlation co-efficients calculated between Mg in grass and $\sqrt{aMg}/\sqrt{aCa+Mg}+B.aK$ in soil solution were 0.84 to 0.99. From the regression analyses it was found that the Mg concentration in the plant was proportional to $\sqrt{aMg}/\sqrt{aCa+Mg}+B$. aK or per cent Mg $\alpha \sqrt{aMg}/\sqrt{aCa+Mg}(I/I+B.aK/\sqrt{aCa+Mg})$, where, aMg, aCa+Mg and aK are the initial ion activities calculated from the composition of the equilibrium soil solution and B is proportionality factor which is, in part, determined by the properties of the particular plant. The value for proportionality factor B is given by

$$B=\left[\frac{K}{Ca+Mg}\right]_{plant} /(aK/\sqrt{aCa+Mg})_{solution}$$

and it expresses the relative ability of K to compete with Ca and Mg — assumed to be the dominant soil cation-uptake process.

The regression analyses (Fig. Id) showed that introducing the K-activity function in the denominator accounted almost quantitatively for the effects of varying soil K. The results showed that the K-Mg antagonism was the result of ionic competition in the soil solution. The expression,

$$\underset{X}{\sqrt{aMg/aCa+Mg}}\ (I/I+B.\ \underset{Y}{aK}/\sqrt{aCa+Mg})$$

that described Mg availability as the product of the two component terms which Salmon[12] referred to as X and Y. The term X was largely dependent upon the exchangeable Mg content of a soil and a measure of the intensity with which Mg was available in relation to the predominant soil cations. Although $\sqrt{aMg}/\sqrt{aCa+Mg}$ was almost directly proportional to the exchangeable Mg content of a soil, the Mg concentration in grass was proportional to the square root of the solution ratio. So, to double the Mg in grass the exchangeable Mg must, in theory, be quadrupled. The term I deals with the effect of 'antagonistic' cations which may be only a small proportion of the total soil cations, but still compete effectively with Mg in the uptake process. The competitive abilities of ions (in this case potassium) could be taken into account by appropriate proportionality factors, determined for a given set of growing conditions $(K/\sqrt{Ca+Mg})$ in plant/$(aK/\sqrt{aCa+Mg})$ in solution. Term Y was independent of term X, but its effect on Mg uptake depended on the exchangeable Mg content, because increasing the value of X also increased the differences between X and XY. This explained why K decreased the Mg content of grass more when much Mg was present.

Correlation co-efficients calculated between Ca uptake and $\sqrt{aCa}/\sqrt{aCa+Mg}$ $+B.$ aK in soil solution ranged between 0.91 and 0.99 except for the root in the Tejgaon soil indicating that the Ca content in grass was closely related to $\sqrt{aCa}/\sqrt{aCa+Mg}+B.aK$. Linear regression analyses clearly demonstrated that there was a straight line relationship between them suggesting ionic antagonism between Ca and other cations (Fig. Ie).

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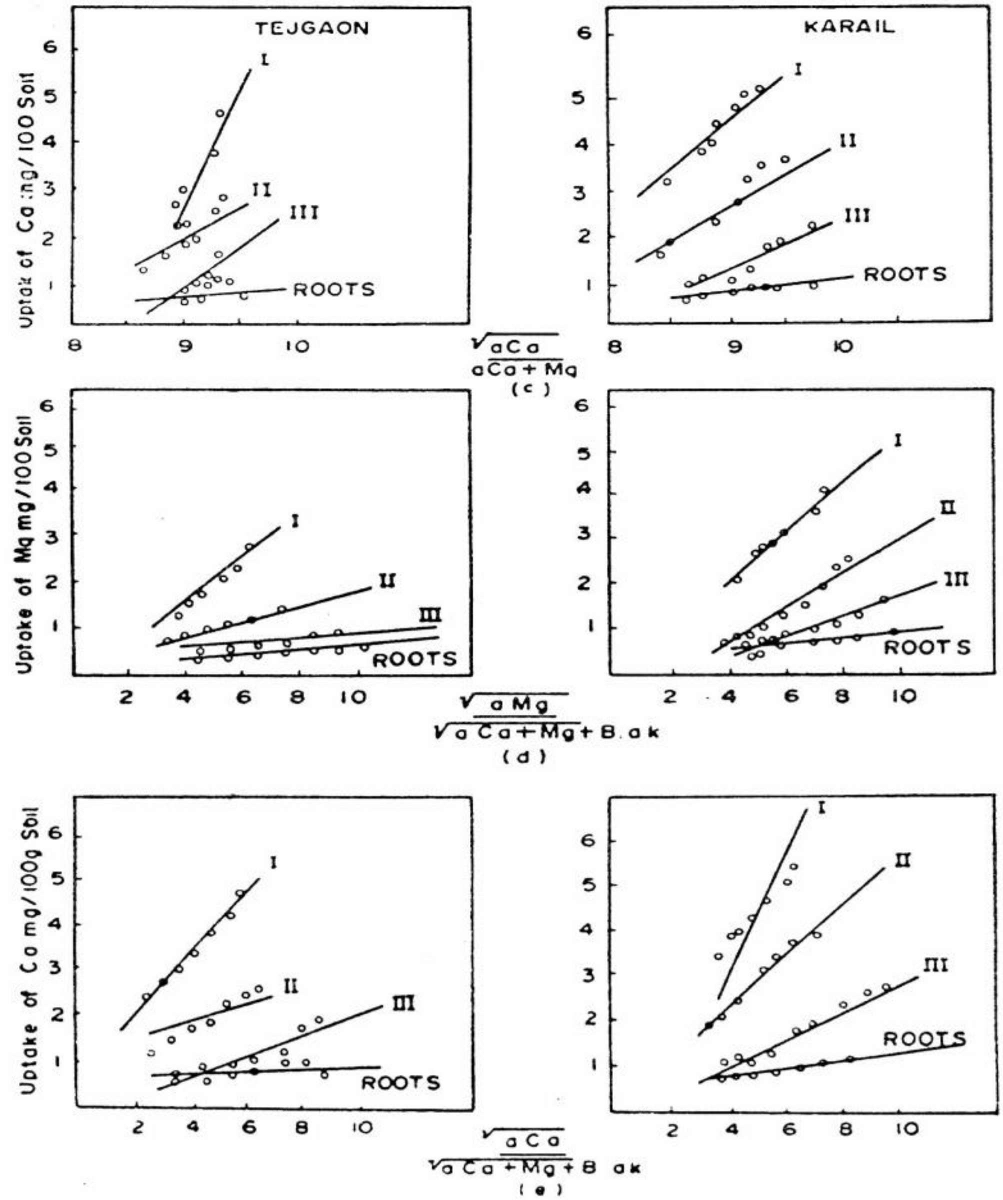

Fig. 1. (c) Ca uptake and $\sqrt{aCa}/\sqrt{aCa+Mg}$; (d) Mg uptake and $\sqrt{aMg}/\sqrt{a\ Ca+Mg}+B.\ aK$; (c) Ca uptake and $\sqrt{aMg}/\sqrt{^{a}Ca+Mg+}$ B.aK I, II and III as in Fig. 1 (a) and (b).

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