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Cation Exchange Capacity of Roots and its Relationships with the Mineral Nutrition of Plants

by

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Introduction: Voluminous literature on ion uptake by plants has been reported, but mostly it is interpreted in terms of soil factors, the contribution of plant root characteristics, if any, is neglected. Since Devaux (1916) reported cation exchange properties in plant roots and suggested that it may play an important role in explaining the uptake of cations from soil colloids or nutrient solutions, voluminous work on different aspects of cation exchange capacity (CEC) of roots has been reported. Significance of ion exchange properties of roots has been emphasised by Mattson *et al.* (1948, 1949) while others (Epstein, 1956; Epstein and Lagget, 1954; Laties, 1959) do not consider cation exchange capacity of much significance in formulating ion uptake theories. Some of these points have been reviewed and discussed from time to time (Epstein, 1955; Heintze, 1961; Frejat *et al.* 1967). The objective of the present paper is to evaluate and discuss the literature available on the origin, methods of determination, variation due to different crops or their varieties, fertilizer application and absorption of nutrients in relation to CEC of plant roots.

Origin of charge: Cation exchange capacity of plant roots has been reported primarily due to free carboxylic groups of pectin (Keller and Deuel, 1957; Heintze, 1961) which is a non-nitrogenous homosaccharidic polymer of D-galacturonic acid. It has been shown to bear a linear relationship with cation exchange capacity of roots (Crooke, 1958; Crooke *et al.* 1960; Knight, *et al.* 1961; Crooke, 1964) with different proportionality factor. Keller and Deuel (1957) reported CEC and pectin in the proportion of 1:1 while Crooke (1964) found it as 1:2 and argued on the basis that the method used for the decarboxylation of uronic acid includes some groups of esterified pectin which do not take part in the process of ion exchange. Besides this, it includes the carbon-dioxide also that evolved from substances other than uronic acid (Tracey, 1948). Pectin content extracted by ammonium oxalate from roots indicated the presence of galacturonic acid and various other neutral sugars. Mattson *et al.* (1949) pointed out that these pectic substances are located near the root tip.

Ion exchange properties of plant roots: Generally all the ion exchange properties as found in soil colloids, are observed in root surfaces differing only in the cause of origin of charge on the exchange complex. Williams and Coleman (1950) observed 'suspension effect' with plant roots which indicated the presence of double layer at the root surface. Plant roots show amphoteric behaviour to a greater extent (Hartce, 1957). Previously ion exchange property in plant root was considered to be related with the metabolic activity of the plant (Smith and Wallace, 1956; Helmy and Elgabaly, 1958 and Zvara, 1964) but it has been shown that active and dried roots possess the same CEC as fresh one indicating thereby that CEC is unaffected by metabolic activity. Like soil, plant root system also possesses differential cationic affinity and adsorption behaviour and follow lyotropic series $H > Ba > Ca > Mg > Cu > Rb > NH_4 > K > Na$. Such a series was not observed by Keller and Deuel (1958) on the roots of wheat, maize, bean and tomato killed in ether as observed by other ion exchangers. There was a more selective uptake of divalent cations than H by the roots of dicots as compared to graminaceous plants. Such a difference in cation selectivity of plant roots seems to be associated with the structure and chemical composition of the roots.

Methods of determination of CEC: Various methods of determining CEC of plant roots have been proposed in literature. These methods and their modification are according to the development made in the knowledge of complex nature of the plant root. Earlier methods involve the use of fresh roots (Mattson and Larsson, 1948; Drake *et al.* 1951) as CEC was considered to be related with the metabolic activity of the plant. But when it was established that dried roots also show the same CEC as fresh ones (Smith and Wallace, 1956; Helmy and Elgabaly, 1958), dry roots were used for the

determination of CEC employing several empirical methods. CEC has been found reproducible under a particular set of experimental conditions but varies significantly with the method used (Crooke, 1958; Helmy and Elgabaly, 1958; Heintze, 1961; Mitsui and Ueda, 1963). Not much data are available in which various methods are compared for the same plant material except that of Heintze (1961).

As the roots are mostly surrounded by a swarm of hydrogen ions at the outer surface (Williams and Coleman, 1950) all methods involve the removal of all other cations and saturating it with hydrogen ion as a first step. This can be done either by electro dialysis or treating the roots with an acid. Some workers have measured this hydrogen ion concentration on the root surface directly by titrating with KOH (Mattson and Larsson, 1948; Mattson *et al.*, 1949; Blanc, 1955; Crooke, 1958; Helmy and Elgabaly, 1958; Liani, 1960; Heintze, 1961) while others replaced it by a suitable cation as calcium and measured it by further displacement (Schuffelen and Middelburg, 1954; Keller and Deuel, 1957; Jain, 1959; Nijensohn and Olmos, 1959; Paliwal and Subramanian, 1964) and also barium and K (Heintze, 1961). While washing of excess salts leaching should not be prolonged as there is probability of replacing Ca by H during this process (Nijensohn and Olmos, 1959). Electro dialysed fresh roots were titrated into N KCl solution by KOH upto pH 7 after drying by Mattson and Larsson (1948) while Drake *et al.* (1951) used fresh roots for titration purposes. CEC is increased both by electro dialysis and acid treatments even from a concentration of 0.006 to 0.1 N (Helmy and Elgabaly, 1958) but electro dialysis is more drastic in comparison to acid treatment. Though several low concentrations of hydrochloric acid have been used (Blanc, 1955; Schuffelen and Middelburg, 1954; Keller and Deuel 1957; Helmy and Elgabaly, 1958; Crooke, 1958; Heintze, 1961; Liani, 1960); Nijensohn and Olmos (1959) have recommended 0.5 N oxalic acid on the ground that hydrochloric acid may not completely convert the fresh roots into the hydrogen system. Using the process of titration of H-roots in N-KCl solution exchange between hydrogen and K takes place and KOH required to restore pH 7 determines the CEC of the root. But in the case of fresh roots an acid drift has been observed which may be due to metabolic activity and uptake of K and release of hydrogen. It may also be due to enzymatic break down of pectin to pectic acid and methanol (Heintze, 1961). Degree of acid drift is much less in dried roots. Radio active method using Zn^{65} has been used by Huffaker and Wallace (1959) and Ca^{45} by Heintze (1961) and Tarabrin (1961). As CEC value is affected by pretreatment of acid or electro dialysis, recently Bartlett (1964) proposed a new method using unbuffered NaCl as an adsorbent and replacing it by nitric acid which does not involve the pretreatment of acid and is also free from acid drift.

Pretreatment of acid or electro dialysis increases CEC value significantly by dissolving out some amino acids and other organic compounds. It would, therefore, be more appropriate if experimental conditions are properly described while reporting the results.

C.E.C. and Crop Species: CEC of roots is a characteristic property though in limited sense and considerable data have been reported in evidence of the fact that CEC value of plant root varies widely with the nature of plant species its variety, time of sampling, growth conditions and method of analysis. Dicotyledonous roots which are generally coarse, thick and gelatinous possess much higher CEC (30-90 me/100 g) than those of monocots (10-30 me/100 g) possessing fine and fibrous structure (Drake *et al.* 1951; Dunham *et al.* 1956; Inden *et al.* 1958; Tarabrin, 1961; Heintze, 1961; Paliwal and Subramanian, 1964). On the whole CEC of plant roots can be arranged in the order: legume > weeds > grass > cereals.

Effect of fertilizer and root environment: Some workers are of the opinion that exchange sites of plant roots are possibly of nitrogenous nature (Smith and Wallace, 1956 b) as evidenced by the fact that CEC as well as the N content of plant roots of various crops increase with the increase of available N in the growth medium (Mclean *et al.* 1956; Helmy and Elgabaly, 1958; Blanc, 1958; Huffaker and Wallace, 1959; Crooke *et al.* 1960; Morita and Aoki, 1961 a; Drake and White, 1961). This increase is caused much more by $\text{NO}_3\text{-N}$, than $\text{NH}_4\text{-N}$ form (Wander and Sites, 1956; Mclean *et al.* 1956; Huffaker and Wallace, 1959; Bartlett, 1964). Wander and Sites (1956) explained it on the basis of differences in the size of roots but Bell and Walker (1957) showed that root size has little effect on CEC. This point needs some more experimental work for clarification.

On the contrary there are evidences to show that CEC does not increase with increasing levels of available N. This has been shown by Cunningham and Nielsen (1963) for rye grass with 0-500 ppm of $\text{NO}_3\text{-N}$ and Asher and Ozanne (1961) for eighteen out of twenty plant species. Systematic work is needed to find out the nature of this N induced increase in CEC. However, Drake (1964) has suggested that higher level of N may increase CEC possibly by increasing cell division and decreasing the non-pectic carbohydrate in the cell walls of the roots. He has also indicated that increased production of root hairs and lateral development of root tip increased CEC of oats and barley.

Recently Crooke, *et al.* (1960) measured CEC of different sections of leak roots and found that it was highest near the apex and decreased with the increase of distance from it. N content was directly related to CEC. It is not yet established whether decrease in CEC is due to development of cell wall

and concentration of pectin and carbohydrates into the inner layers, which are less accessible to exchange reactions or due to some other mechanism.

Not only the effect of nitrogenous fertilizers on variation of CEC but also of various levels of P, K, Ca and micronutrients has been studied. CEC values of wheat, tobacco, maize and mung grown under varying levels of Ca/K ratio (1:5 to 39) in sand culture and also at different levels of P showed no significant variation (Paliwal and Subramanian, 1964). But Wiersum and Bakema (1959) found fluctuation in CEC with the availability of nutrients. CEC was raised in regions where competition for cations was high and lowered where only anions were available. Variation in CEC of the roots of tomato, pea, bean, sunflower and oats suffering from heavy metal toxicity were noted by Crooke (1958). It was increased by Ni, Co, Zn and decreased by Mn, while Cu increased CEC of oats and sunflower and reduced those of tomato, pea and bean. Whatever may be the nature of ion exchange spots the CEC of some plant species is affected by fertility level especially of N. This increase may be due to increased number of exchange spots and partly from protein amino group and also increased root hairs and root tip development (Drake, 1964).

CEC of roots generally decreases with increase of age of the plant (Helmy and Elgabaly, 1958; Morita and Aoki, 1961; Heintze, 1961). It has also been observed that CEC value is independent of soil type and has been shown by other plant organs like leaves and stems (Crooke, 1964). It also decreases in presence of growth inhibitors such as NaCN, and Na_2SO_4 , even in low concentration as 0.001N (Helmy and Elgabaly, 1958).

Mineral Nutrition of Plants: Plants absorb nutrients primarily through roots but how much is it related with the charge density of the roots has been the point of investigation since the time of Deavaux (1916).

Root colloids by virtue of their charged nature adsorb cations and anions selectively and a sort of chemical attraction is necessary between the soil and plant colloids for the absorption and accumulation of ions. This causes an active competition for the cations between the soil and root colloids. Mattson and coworkers (1948, 1949) developed a theory relating CEC of plant roots and differential uptake of mono and divalent cations for different plant species on the basis of Donnon equilibria. According to this concept plant roots of high CEC would adsorb relatively more divalent cations than those of monovalent ones and in species of low CEC monovalents would be preferably adsorbed over the divalents. This is simply the application of 'Valence effect' generally noticed in soil colloids of varying charge density to root colloids and this relationship of CEC with cation uptake is fully supported (Elgabaly and Wiklander, 1949a; 1949b; Wiklander and Elgabaly, 1955; Nagai and Matagio, 1959; Helmy *et al.* 1963).

Uptake of Ca, Mg & K. Quantitatively the relationship between the uptake of Ca, Mg and K and CEC of roots for two different plant species can be expressed by the equations below :

$$\frac{CEC_1}{CEC_2} \times \frac{K_2}{K_1} \dots\dots\dots(1)$$

$$\frac{CEC_1}{CEC_2} \times \frac{(Ca+Mg)_1^{\frac{1}{2}}}{(Ca+Mg)_2^{\frac{1}{2}}} \dots\dots\dots(2)$$

$$\frac{CEC_1}{CEC_2} \times \frac{K_2}{(Ca+Mg)_2^{\frac{1}{2}}} / \frac{K_1}{(Ca+Mg)_1^{\frac{1}{2}}} \dots\dots\dots(3)$$

Where subscript 1 and 2 refer to different plant species. These relations were found to hold good for a large number of citrus, maize and soya bean plants by Huffaker and Wallace (1958). In spite of such significant correlations they are of opinion that the relations appear to be far from simple and in some cases it did not hold good. Satisfactory relationship between uptake of mono and divalent cations and CEC of roots have been found by Fox and Kacar (1964, 1965) for legumes and grasses, Asher and Ozanne (1961) for twenty plant species, Drake and White (1961) for tomato, wheat and oats, Heintze (1961) for legumes, clover and rye grass, Morita and Aoki (1961) for five fruit species, Nagai and Matagio (1959; 1961) and Novat (1960) for rice varieties. Uptake of chlorine and sulphate is also related with CEC of roots (Elgabaly, 1962). While reviewing the literature on mineral composition of plants Crooke and Knight (1962) concluded that CEC is positively correlated with total cations, the excess base, total trace elements and total protein content and negatively with crude fibre. On the other hand CEC of roots showed no relationship with uptake of cations for rye grass (Cunningham and Nielson, 1963), fruit plants (Dunham *et al.* 1956) and maize, wheat, tobacco and mung (Paliwal, 1967).

For the limited application of Mattson's valence effect quantitatively, various probable reasons have been suggested from time to time. These may be summarised as that 'Valence effect' is most suitable in very dilute solutions while soil solution of fertile soil or nutrient solution is fairly concentrated and Donnan's unequal distribution of cations is evened out. Also at higher levels of Ca or K or both luxury consumption and ion antagonism influence relative uptake of cations. Besides these factors plant roots might have adsorbed cations according to the Donnan equilibria but their proportionate absorption into plant leaves may not take place due to translocation of ions at different

parts of the plant. The other source of error may be due to the complex nature of the internal part of the root which partly contributes in CEC. It is also not known whether all the apparent CEC of the root takes part in adsorption and subsequent absorption of cations or only a fraction of it. The integrated effect seems responsible for a poor and limited applicability of the relation between CEC of roots and cationic uptake.

N uptake: Some workers are of the opinion that availability of N is related with the CEC of the plant roots and that it can be increased by increasing CEC of roots. Mclean *et al.* (1956) reported 10 to 40% increase in CEC as well as in N% in the roots and leaves of oats, corn, buckwheat, cotton vetch and soybean grown in solution. Similar conclusion was drawn by Smith and Wallace (1956) for valencia oranges and Drake and White (1961) for buckwheat, tomato and oats grown in soil poor in exchangeable Ca and in the later case total Ca uptake was doubled in tomato and tripled in buckwheat. It seems that higher CEC increased release of Ca from insoluble CaCO_3 by virtue of the increased surface area per unit weight and fibrous nature of roots (Blanc, 1958).

P uptake: Evidences in favour of higher uptake of P by plant species possessing higher CEC values are reported in literature (Asher and Ozanne, 1961; Fox and Kacar, 1964, Graham, 1955). While comparing legumes and grasses for P uptake, Fox and Kacar (1964) reported that P solubility in calcareous soils and rock phosphate has increased by legumes possessing higher CEC values. Both uptake of Ca and P increased in legumes and were positively correlated with CEC of roots. These results are in conformity with those of Graham (1955) and Drake and Steckel (1955) who reported that higher solubility of P from rock phosphate should increase with the increase of CEC of plant root which should act as a chelating agent and dissolve out the rock phosphate crystal. Resseter and Ozanne (1955) who found clover (CEC 27) much superior than capeweed (CEC 19) in the ability to dissolve and absorb P from the rock phosphate.

Evidences both in favour and against are available regarding the role of CEC in the uptake of nutrients, but the question, whether CEC is any how related with the uptake of nutrients or not, still remains unsolved. While reviewing the various theories of mechanisms of ion uptake Epstein (1956) and Latic (1959) do not regard CEC solely responsible for the uptake mechanisms. Black (1957) also denies the significance of CEC of roots in ion uptake on the ground that exchange sites of roots are distinct from those of active transport and ion can reach there by free diffusion without being attached to exchange site.

It may also be pointed out that so far various models to explain ion uptake mechanism have been put forward but none of them is capable of explaining all the complicated facets of plant nutrition.

It is certain that ions are not absorbed in the proportion they exist in soil root environment as their uptake depends upon the nature of the plant species, its variety, relative CEC of root and soil colloids, relative affinity and concentration of the ions in growth medium, selectivity of ion absorption and translocation characteristics. Keeping these points in view, though there may not be a simple and quantitative relationship between nutrient uptake and CEC yet mineral nutrition of plants is somehow related with root surface properties (Novat, 1960) and the presence of electrically charged root surfaces affect the free diffusion of ions.

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Response of Rice to Fertilizer Application in Cultivators' Fields in Tamil Nadu

by

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Introduction: Indian soils are known to be deficient particularly in N, but believed to contain large reserves of P and K. This belief was based on the results of numerous trials conducted at the Research Stations where negligible responses to phosphate and potash applications were obtained. The Research Stations, however, are likely to be not quite representative of the tract not merely because of their small number but because of the continued manuring and better managerial practices over a number of years which is not a feature of an average cultivator's field. The need for trials on cultivators' fields has been increasingly felt on the recognition that recommendations based on the results of such trials alone could be reliably passed on for adoption by cultivators in a given tract. A series of simple fertilizer trials were therefore, laid out in cultivators' fields since 1951. From the results

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