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Ionic Exchange in Soils: I. Measurement of the Exchange Reaction by Means of an Ion Exchange

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IONIC EXCHANGE IN SOILS:

I. MEASUREMENT OF THE EXCHANGE REACTION BY MEANS OF ION EXCHANGE MEMBRANES

(Preliminary Report)

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Investigations designed to elucidate the uptake of nutrients by plants from the soil have been beset by many problems. Such problems have been clarified considerably in the light of recent knowledge of how nutrient uptake by plants is affected by (a) the exchange characteristics of the clay mineral, (b) the percentage saturation of the clay mineral by cations, and (c) the surface exchange properties of the plant root. Despite our increased knowledge of the exchange characteristics of the clay minerals (4, 6, 7, 8, 9, 11, 12), we are still not always able to relate nutrient uptake by plants to the nutrient status of the soil. This failure is due primarily to the limited knowledge of the ionic interactions which occur between the plant root and the soil colloid. Metabolic effects make these interactions even more complicated. From this point of view it has been advisable to divide nutrient uptake into two distinct steps, (a) the exchange of nutrient cations from the clay colloid to the plant root surface, and (b) the subsequent absorption of these cations into the plant due to metabolism (1, 2). By such a technique it should be possible to reproduce the first step of nutrient uptake independently of plant metabolism.

The purpose of this experiment was to explore the possibilities of simulating the first step of nutrient uptake, *i.e.*, the exchange of nutrient ions from the soil colloid to the plant root, by the use of ion exchange membranes and plant roots.

Experimental Procedure. The basic concept of utilizing a cation exchange material was proposed by Brown (2). In this original work, hydrogen colloidal clay was used to simulate the surface exchange properties of the plant root. Soil enclosed in a collodion tube was immersed in a suspension of hydrogen clay and the exchange of hydrogen ions for the cations of the soil allowed to proceed (2). This investigation advances this basic concept to the point of utilizing porous ion exchange membrane sheets to reproduce the surface exchange properties of plant roots. Furthermore, it was designed to compare the exchange properties of plant roots with those of the membrane.

Preparation of Membranes and Plant Roots. Cation exchange membranes 1 inch by 4 inches in size, and having an exchange capacity of 2.5 milliequivalents, were washed with 4 N HCl to make certain that the entire exchange capacity was satisfied by the hydrogen ion. The unadsorbed HCl was washed from the membrane by the use of distilled water.

For measuring the cation exchange from the soil colloid to the plant root the following technique was used: Soybeans (Ogden variety) were grown for 30 days in a gravel culture where the nutrients were supplied by Hoagland's nutrient solution. The tops of these plants were cut away so as to leave one inch of the stem attached to the roots. Eight plant roots were tied together for use as a single group. The roots were washed in successive aliquots of 0.1 N HCl until no further evidence of calcium was found in the washings. Subsequent rinses in distilled water removed the unadsorbed HCl.

Measuring the Exchange Capacity of Membrane and Roots. Following preparation, membranes and roots were washed with three consecutive aliquots of $CaCl_2$. The strength of the $CaCl_2$ used was 4 N for the membranes and 0.1 N for the roots. These washings were titrated for exchangeable hydrogen as exchanged from the root or the membrane and reported as the milliequivalents of exchange capacity.

Preparation of Soils. Six representative soils of Arkansas were chosen for this investigation, including the Lakeland, Ruston, Richland, Crowley, Sharkey, and Houston series. Aliquots (100 grams) of each of these soils were moistened

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by means of a water atomizer to bring the soil to optimum moisture content. Each aliquot then was placed in a metal pan (1½ inches by 3 inches by 4½ inches) and covered until ready for use.

Measurement of the Exchange Reaction. Each membrane was buried in an aliquot (100 grams) of soil. A glass cover was sealed on top in order to prevent moisture loss. After the chosen equilibrium period, the membrane was removed from the soil. After removing all adhering soil particles with carbon-dioxide free distilled water, the membrane was washed with four 50 ml aliquots of 4 N HCl. The washings were composited and taken to dryness on a hot plate. The residue was taken up in 10 ml of 4 N HCl, taken to 100 ml volume with distilled water, and filtered. Determinations of calcium, potassium, and sodium were carried out by means of the Beckman flame spectrophotometer, using the oxygen-acetylene burner.

Exchange studies with soybean roots were carried out by placing the hydrogen-saturated roots between two thin sheets of cellophane. The roots were then buried in the soil and the exchange of the hydrogen ions for the cations of the soil was allowed to proceed. The equilibrium time for the roots, as well for the membranes, used for direct comparison of cation exchange was 24 hours. The cations exchanged to the roots were removed by four washings with 50 ml aliquots of 0.1 N HCl. The determinations of the calcium and potassium exchanged to the roots were carried out as previously described.

Discussions of Results. The exchange data as obtained by the use of ion exchange membranes are summarized in Table 1. The total cations exchanged increased from 0.229 for the Ruston silt loam (3 m.e./100 grams exchange capacity) to 2.132 for Sharkey clay (41 m.e./100 grams exchange capacity).

The percentage distribution of each cation in the total amount exchanged reveals some significant facts. For example, the suite of cations exchanged from the Ruston silt loam soil show 66.4 per cent calcium and 17.5 per cent potassium, whereas for the Houston clay the percentage is 99.2 and 0.4 for calcium and potassium, respectively. Similar differences between these soils are shown by the Ca/K ratios, increasing from 3.8 for the Ruston soil to 245 for the Houston clay. These differences can be accounted for (a) by differences in the exchange properties of the clay minerals composing these soils, and (b) by the ratio of cations held in the exchangeable form by the clay. They indicate that the ratio of calcium to potassium reaching the plant root may vary considerably as a result of these two factors. A straight line relationship is obtained between the Ca/K ratio of exchangeable cations in the soil and the percentage of calcium in the suite of cations exchanged. The Richland soil is the only one which fails to fall on this straight line. These data show quite clearly the importance of considering the type of clay mineral and the exchange capacity in attempting to relate nutrient uptake to the nutrient status of the soil.

TABLE 1. Cation Exchange Data as Measured by Means of Cation Exchange Membranes

Soil type	Sum of Ca, K, and Na[1]	*Suite of cations*[2] Ca	K	Na	Ca/K[3]	*Percentage exchange*[4] Ca	K
Lakeland Sandy Loam - - -	0.068	73.5	10.3	16.2	7.1	3.3	7.0
Ruston Silt Loam - - - -	.229	66.4	17.5	16.1	3.8	6.1	9.0
Crowley Silt Loam - - - -	.203	89.1	3.5	7.4	25.9	3.6	4.1
Richland Silt Loam - - -	.523	86.4	6.7	6.9	12.6	9.0	7.0
Sharkey Clay - - - - - -	2.132	98.4	0.5	0.1	209	8.4	1.6
Houston Clay - - - - - -	1.979	99.2	0.4	0.4	245	7.9	1.4

[1]Expressed as total m.e. of Ca, K, and Na exchanged.

[2]Expressed as percentage of sum of Ca + K + Na.

[3]m.e.Ca/m.e.K.

[4]Percentage of total exchangeable in soil.

A comparison between the calcium and potassium uptakes by membranes and roots is given in Table 2. The total quantity of cations exchanged to the membrane is much greater than the exchange to the plant root. However, a more critical evaluation is to be found in the Ca/K ratio. The ratio of Ca/K for the plant roots is approximately twice as high as that for the membranes. Although this might lead one to believe that this difference is too great to justify the use of membranes to reproduce the exchange of cations from the soil colloid to the plant root, there are other factors to consider. It has been found possible to vary the Ca/K ratio by altering the time interval for equilibrium; thus, for longer equilibrium periods, the Ca/K ratio increases significantly. By increasing the equilibrium period it should be possible to adjust the Ca/K ratio to that of plant roots. One other possibility exists, and that is the preparation of ionic exchange membranes which will more closely approach the acid strength exhibited by plant roots. Weakly-acid membranes may more nearly reproduce the exchange of cations from the soil to the plant root. The present status of this investigation indicates that by the use of this technique there are a great many possibilities of answering some of the complicated interactions occurring between the plant root and the soil colloid.

TABLE 2. Cation Exchange Data: Soybean Roots *vs.* Cation Exchange Membranes[1]

	Ca *m.e.*	K *m.e.*	Ca/K *ratio*
Membranes[2]			
1 - - - - - - - - - - - -	0.217	0.038	5.7
2 - - - - - - - - - - - -	.222	.040	5.6
3 - - - - - - - - - - - -	.292	.052	5.6
4 - - - - - - - - - - - -	.234	.039	6.0
Roots[3]			
1 - - - - - - - - - - - -	.069	.006	11.5
2 - - - - - - - - - - - -	.071	.006	11.8
3 - - - - - - - - - - - -	.072	.006	12.0
4 - - - - - - - - - - - -	.065	.006	10.8

[1]Soil used was Richland silt loam at 20 per cent moisture; time interval for exchange was 24 hours.

[2]Exchange capacity 2.30 m.e.

[3]Exchange capacity 0.278 m.e.

Summary. Cation exchange data, as obtained by the use of ionic exchange membranes and soybean roots, are reported. The suite of cations exchanged from soils having medium and low exchange capacities was found to be relatively less rich in calcium than those from soils with high exchange capacity; the range was 66 per cent to 99.2 per cent. Potassium was richer in the suite of cations exchanged from the medium and low exchange capacity soils. The range was 17.5 per cent to 0.4 per cent. This gave a range of 3.8 to 245 for the Ca/K ratio.

Comparisons of calcium and potassium uptake between membranes and soybean roots showed that the Ca/K ratio as obtained by use of plant roots was about twice that obtained by the use of membranes. Possible ways of decreasing the differences between these Ca/K ratios are enumerated.

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