

## DISTRIBUTION OF NA-IONS IN CA SATURATED SOIL COLUMNS BY USING RADIOISOTOPE ASSESSMENT

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### Abstract

In the present work, model experiments are carried out to study the vertical distribution of Na-ions in Ca saturated soil columns equilibrated with percolating NaCl solution. The vertical distribution of sodium ions was studied using radio-isotope technique. The obtained results are discussed in the light of different theories and models applied in such cases.

### INTRODUCTION

Soil is a polydispersed system, having solid, liquid and gaseous phases. The main soil properties determining its fertility, are affected by the conditions of the solid phase as well as by the equilibrium between the ions in the soil solution and those adsorbed on the surface of the soil particles. Water soluble salts, especially sodium salts, are responsible for undesirable physical, chemical, biological soil properties as well as its fertility. Soil salinization and alkalization processes are always associated with the movement of different sodium compounds in the soil profile (Szabolcs and Darab 1960). The laws applied for ion-exchange in ionic separation processes by synthetic ion-exchange resins, can be used to study ion transport processes in soils. The model of De Vault and Kovda (1963) was applied by Ribbe and Davis (1965) for studying ion-exchange reaction in soil profiles. Hiester and Ver-

meulen (1979) and Richards (1954) proposed a theoretical model, based on the kinetic theory of the reversible second-order reactions for ion chromatography. This was used by Bower *et al.* (1954) for the description of ion-exchange processes in soil columns treated with electrolyte solutions. Several simplified analytical solutions of chromatographic models have been elaborated for calculating the amount of adsorbed sodium cations in the different depths of a column (Carlson and Keeney 1978 and Poelstra and Frissel 1965).

### MATERIALS AND METHODS

0.5 - 2 mm particle size fraction of calcium saturated chernozem soil was used in these model experiments. Fifteen cm high soil columns were prepared by uniform packing of known weights of air-dry soil sample into plastic tubes of width 2.2 cm internal diameter, and having an outlet tube with a stopcock to control the flow. A plastic screen covered by filter paper was placed at the bottom of the tube before filling.

The concentrations of equilibrating NaCl solutions spiked with 2 K Bq of  $\text{Na}^{22}$  were between  $5 \times 10^{-3}$  and  $1 \times 10^{-2}$  N. The flow rate was 0.4 cm /h. Three centimeters constant head height of solution was kept on the top of the column.

The percolation was carried out until reaching a dynamic equilibrium i.e. reaching the same  $\text{Na}^+$  concentration in the influent and effluent solutions. The distribution of Na-ions in the different depths of the columns was studied in two ways:

1. The activity of each centimeter of the column was measured outside, without destroying the column itself, using a heavily shielded detector (EKCO N 618 type). The activity of each layer is expressed as the percentage of the total activity added to the column.
2. After equilibration with radioactive NaCl solutions, the soil column were sectioned into 1 cm thick layers. The total and exchangeable amounts of  $\text{Na}^+$  and the total and exchangeable amounts of  $\text{Ca}^{+2}$  were determined in each section with the isotope dilution method (Darab and Redly 1979, 1980; Antipov and Mamaeva 1983). The moisture content was determined with the thermostat method. One

column was equilibrated with  $1 \times 10^{-2}$  N isotopic NaCl solution labelled with  $\text{Cl}^{36}$ . After sectioning the column, the activity in 1 cm thick was measured with liquid scintillation technique.

## RESULTS AND DISCUSSION

The vertical distribution of  $\text{Na}^{22}$  in column equilibrated with  $1 \times 10^{-2}$  N NaCl solution is demonstrated in Fig. 1. The highest relative value of  $\text{Na}^{22}$  activity (30-40 percent of the total activity) was found in the 2-3 cm thick top layer of the column. In the deep layers the activity was sharply decreased. The relative activity reached 0.5-2 % in 14-15 cm depth. The distribution pattern of  $\text{Cl}^{36}$  in the soil column equilibrated with  $1 \times 10^{-2}$  N NaCl solution was similar to that of the moisture (Fig.2) (Szabolca and Reply, 1974).

Comparing the vertical distribution of  $\text{Na}^{22}$  representing the total amount of sodium and the distribution of  $\text{Cl}^{36}$  representing the amount of sodium in the solution, it can be seen that maximum adsorbed sodium is found in the top of the column, being in direct connection with the solution.

Regardless the concentration of the equilibrating solution,  $\text{Na}^+$  was not removed from the columns by treatment with distilled water. Water did not penetrate into the 2-3 cm top layer. But after leveling the columns with different volumes of  $\text{CaCl}_2$  solution the maximum value of sodium became less and moved towards the deep layers. That was clear when the concentration of the leaching solution was lower than that of the equilibrating one (Fig. 1). Also, the higher the concentration or volume of  $\text{CaCl}_2$  solution, the deeper the sodium moved downward. In the vertical distribution of total and exchangeable amounts of sodium, a sharp maximum was recorded in the top layer of the column, similar to the radiochromatographic distribution pattern (Filep, 1975). The data of the exchangeable and soluble in the solution in each 1 cm thick layer of the columns determined with the  $\text{Na}^{22}$  isotopes dilution method were compared with those calculated with the chromatographic equation used by Filep (1975).



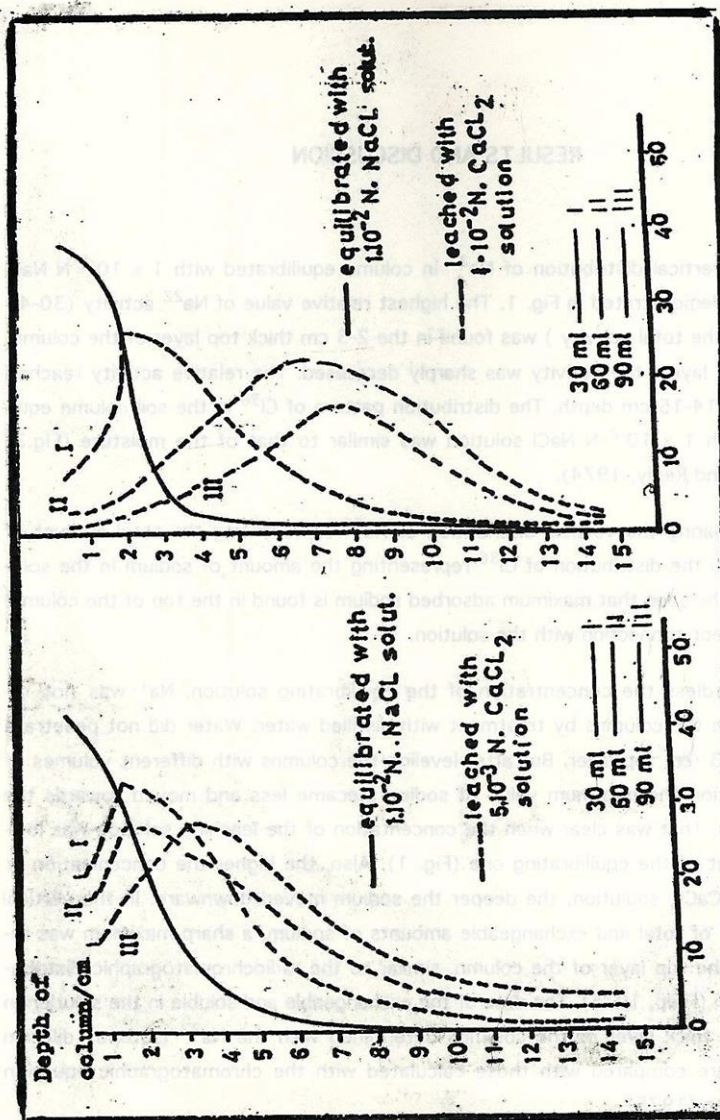


Fig 1. Distribution of  $\text{Na}^{22}$  in soil column equilibrated with  $1 \times 10^{-2}$  N. NaCl solutions and leached with  $\text{CaCl}_2$ .

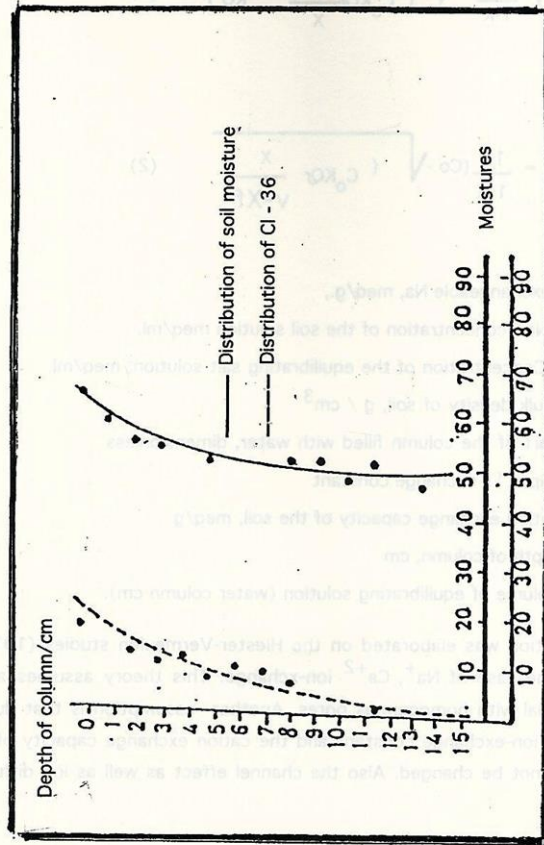


Fig 2. The Cl-36 activity of each 1 cm layer as a percentage of the total activity added to the column.

$$Na_x = \frac{1}{1-K} \sqrt{\left( C_o K Q r \frac{v-Xf}{X} - K Q \right)} \quad (1)$$

$$Ca_{Na} = \frac{1}{1-K} \left( C_o - \sqrt{\left( C_o K Q r \frac{X}{v-Xf} \right)} \right) \quad (2)$$

- Where  $Na$  = exchangeable  $Na$ , meq/g.,  
 $C_{Na}$  =  $Na^+$  concentration of the soil solution meq/ml.  
 $C_o$  = Concentration of the equilibrating salt solution, meq/ml.  
 $r$  = bulk density of soil, g / cm<sup>3</sup>  
 $f$  = Part of the column filled with water, dimensionless  
 $k$  = Gapon 's exchange constant  
 $Q$  = Cation exchange capacity of the soil, meq/g  
 $X$  = Depth of column, cm  
 $V$  = Volume of equilibrating solution (water column cm).

The equation was elaborated on the Hiester-Vermeulen studies (1979), and simplified for the case of  $Na^+$ ,  $Ca^{+2}$  ion-xchange. This theory assumes a laminar flow in a material with homogenous pores. Another assumption is that during the experiment the ion-exchange constant and the cation exchange capacity of the adsorbent should not be changed. Also the channel effect as well as ion diffusion are negligible.

Comparing the measured and calculated data, a small deviation was shown only in the 0-2 cm top layer (Table 1) . That difference can be due to experimental error. The amount of exchangeable  $Na^+$  in the solution throughout the column. The ration of the two kinds of sodium ions is much higher on the top of the column than in the deep layers. Assuming an apparent equilibrium between the cation in the solution phase and that adsorbed, the Vanselow selectivity coefficient was calculated from the measured data of each layer using the following equation (Darab 1967).

Table 1. Vertical distribution of Na-ions in soil columns equilibrated with  $1.10^{-2}$  N NaCl solution and leached with  $\text{CaCl}_2$  solutions of different concentrations.

| Depth of column cm | Na <sup>+</sup> meq / 100 g soil |       |          |       | Ratio between exchangeable sodium and Na -22 in the solution | Na + meq / 100 g soil   |  | Total amount |
|--------------------|----------------------------------|-------|----------|-------|--|---|--|--------------|
|                    | Total amount                     |       | Adsorbed |       |  | In column leached with 60 ml 0.005 N CaCl <sub>2</sub> solution | In column leached with 60 ml 0.01 N CaCl <sub>2</sub> solution |              |
|                    | Meas.                            | Clac. | Meas.    | Clac. |  |   |  |              |
|                    |                                  |       |          |       |  |   |  |              |
| 0 - 1              | 4.65                             | 6.85  | 4.05     | 6.37  | 8.19   | 0.43  |  | 0.23         |
| 2 - 3              | 3.43                             | 3.93  | 3.00     | 3.54  | 7.04   | 1.94  |  | 1.88         |
| 4 - 5              | 2.84                             | 2.82  | 2.48     | 2.50  | 6.84   | 3.38  |  | 2.06         |
| 6 - 7              | 2.95                             | 2.53  | 2.20     | 2.18  | 5.55   | 2.16  |  | 2.81         |
| 8 - 9              | 2.42                             | 2.21  | 2.01     | 1.86  | 4.85   | 1.95  |  | 2.25         |
| 10 - 11            | 2.15                             | 1.96  | 1.96     | 1.65  | 5.05   | 1.94  |  | 2.03         |
| 12 - 13            | 1.18                             | 1.78  | 1.48     | 1.47  | 3.54   | 1.66  |  | 1.81         |
| 14 - 15            | 1.80                             | 1.73  | 1.42     | 1.38  | 3.62   | 1.75  |  | 1.73         |

\* Determined in 1 : 10 soil - water suspension with Na-22 isotope dilution method.



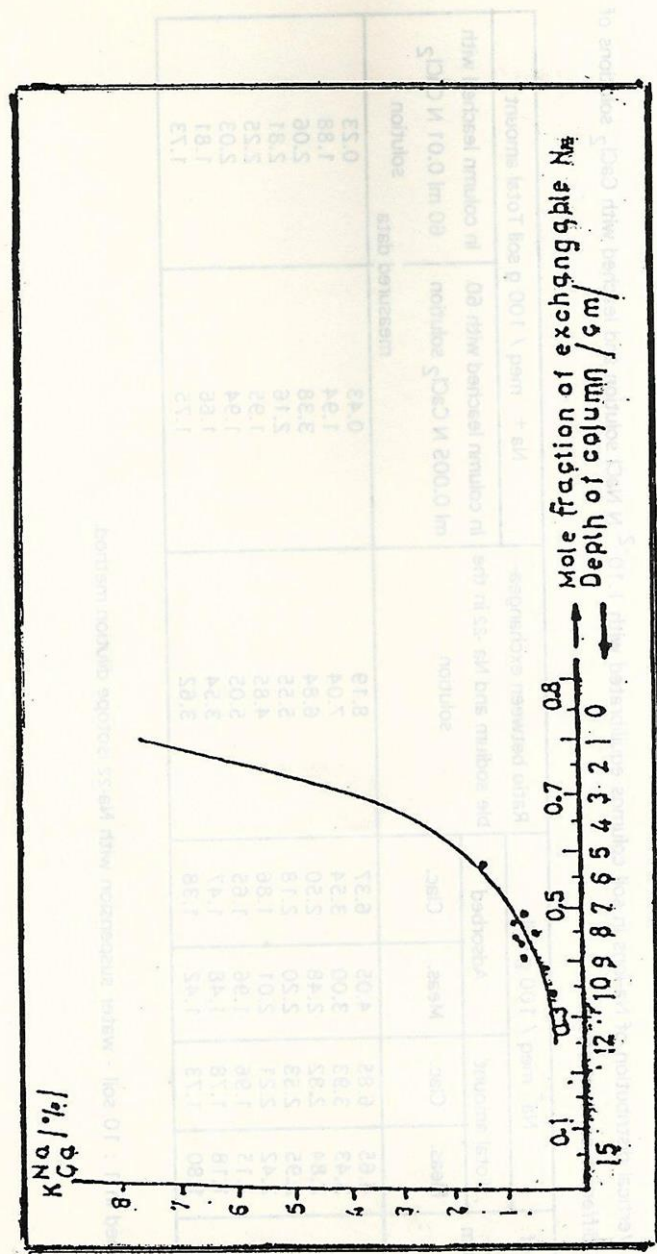


Fig. 3. Vanselow selectivity co-efficient as a function of the exchangeable  $Na^+$  ions mole fraction on soil column equilibrated with  $5 \times 10^{-3}$  N NaCl solution.



the measured data of each layer using the following equation (Darab 1967):

$$K_{Na} = \frac{(N_{Na} C_{Ca} f^3 (CaCl_2))}{C_{Na} \frac{N_{Ca} C_{Na} f^4 (NaCl)}{Na}}$$

Where :

$K_{Ca}$  = Vanselow selectivity co-efficient

$N_{Na}, N_{Ca}$  = The mole fraction of the exchangeable Na<sup>+</sup> and exchangeable Ca<sup>2+</sup>, respectively.

$C_{Na}, C_{Ca}$  = Na<sup>+</sup> and Ca<sup>2+</sup> concentration in the equilibrium solution mole/l.

$f^4 NaCl, f^3 CaCl_2$  = Activity coefficients of the salt in the solution.

Data related to the soil column equilibrated with  $5 \times 10^{-3}$  N NaCl solution are plotted in Fig. 3. In the deep layers, where the mole fraction of exchangeable Na<sup>+</sup> was less than 0.5, the selectivity of the adsorbent for sodium changed slightly. In the five cm depth where the mole fraction of the exchangeable Na is higher than 0.5, a deep increase was found in the value of the moderating selectivity co-efficient was increased showing an increase in the sodium saturation of the upper layers of the column concomitant with certain changes in colloidal properties of the adsorbent (Redly and Darab 1982).

Generally, the value of the Vanselow selectivity coefficient increases with the decrease of ionic strength in the solution. Leaching the columns with CaCl<sub>2</sub> solution, the total amount of Na<sup>+</sup> considerably decreased and its maximum was found in the deep layers of the column (Table 1).

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## دراسة رأسية لتوزيع أيونات الصوديوم في أعمدة التربة المشبعة بالكالسيوم باستخدام الصوديوم المشع

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تمت دراسة معملية لأيون الصوديوم ومدى توزيعه في التربة باستخدام الصوديوم المشع في أعمدة من التربة المشبعة بأيون الكالسيوم .

وقد نوقشت النتائج المتحصل عليها في ضوء النظريات والنماذج المختلفة المستخدمة في مثل هذه الحالات .