# CATION EXCHANGES IN CLAY LOAM FROM BOGOR, WEST JAVA

***(Pertukaran Kation pada Tanah Liat asal Bogor, Jawa Barat)***

**Ishak S. Erari**
*Laboratory of Physics, Papua State University*
*Jl. Gunung Salju Amban Manokwari*
*Email: ishakerari@yahoo.com*

## ABSTRAK

Kapasitas tukar kation dan koefisien selektivitas merupakan parameter penting yang mempengaruhi distribusi kation antara fase larutan dan fase padatan, dan mobilitasnya di dalam tanah. Studi tentang pertukaran kation melalui koefisien selektivitas pada tanah clay loam Bogor, Jawa barat yang ditanami sawi (Brassica juncea) telah dilakukan. Kation-kation utama yang dipelajari adalah Ca, Mg, K dan Na. Kompleks adsorpsi di dalam tanah tersebut didominasi oleh Ca dan Mg. K dan Na sangat sedikit diadsorpsi. Koefisien selektivitas antara ion adalah $K_{Ca,Mg}$, $K_{K,Ca}$, $K_{Na,Ca}$, $K_{K,Mg}$, $K_{Na,Mg}$ dan $K_{Na,K}$ adalah 0.67, 0.57, 0.37, 0.25, 0.32, dan 1.36. Koefisien selektivitas yang diperoleh didalam studi berada pada kisaran dari hasil studi lainnya. Didalam studi ini akan ditunjukkan penggunaan koefisien selektivitas untuk persiapan digunakan di dalam persamaan-persamaan *transport* kation.

***Kata kunci****: Selectivity coefficient, cation exchange capacity, cation absorption*

## INTRODUCTION

The transport and retention behavior of dissolved chemicals applied to soils is influenced by several physical, chemical, and biology process. The ability to predict the fate of dissolved chemicals is dependent upon our understanding of the processes that govern their fate in the soil environment. Several types of retention reactions influence the movement of dissolved chemicals in soils, e.g., precipitation, adsorption, and ion exchange (Robbins et al., 1980; Thabet et al., 1996; Vogeler et al., 1997). Reaction rate may be sufficiently fast and reversible so that equilibrium can be assumed. Alternatively, retention reaction when incorporated into a transport model may be described using a kinetic approach.

Prerequisite data for describing the transport of cation in soils are their cation exchange capacity (CEC) and the affinity is often expressed by selectivity coefficients.

In this paper will present binary cation exchange properties and selectivity coefficients in clay loam of top soil from Bogor, West Java to incorporate to equilibrium exchange model of Robbins et al., (1980) to prepare used in the transport equations. In this paper also will be discussed using selectivity coefficients to manage soil solutions.

## THEORY

Cation exchange reactions can be described by one of two conventions. TheVanselow convention designates the anion exchange charge as –1 and the reacting cations are designed in molar quantities. The exchange reaction is represented as:

$$nMX_m + mN^{n+} = nM^{m+} + mNX_n \qquad (1)$$

Where M and N are cations with charges of $m^+$ and $n^+$, respectively. The Gapon convention represents the cation reacting as equivalents and takes the form

$$X_{1/mM} + 1/nN^{n+} = X_{1/nN} + 1/mM^{m+} \qquad (2)$$

Still maintaining a-1 charge on X. It should be recognized that on a molecular scale $1/mM^{m+}$ or $1/nN^{n+}$ (for m>1 and n>1) does not exist, however, on a macro scale this form is thermodynamically equivalent and better lends itself to modeling multication systems.

Equation (2) can be evaluated as the equilibrium relationship

$$K = \frac{X_{1/nN}\left(M^{m+}\right)^{1/m}}{X_{1/mM}\left(N^{n+}\right)^{1/n}} \quad (3)$$

Where K is the selectivity coefficient.

Dutt et al., (1972) substituted exchange cation similar to Eq. (3) for Ca-Mg and Ca-Na equilibrium, expressed in terms of $X_{Mg}$ and $X_{Na}$, into the equation

$$CEC = X_{Na} + X_{Mg} + X_{Ca} \quad (4)$$

And then by rearranging they obtained the expression

$$X_{Ca} = CEC \div \left[\frac{(Mg)K_1}{(Ca)} + \frac{(Ca)^{1/2}K_2}{(Na)} + 1\right] \quad (5)$$

where $K_1$ and $K_2$ are the selectivity coefficients for the Ca-Mg and Na-Ca exchange relationships, respectively, and CEC is the cation exchange capacity. The terms (Na), (Ca), and (Mg) represent sodium, calcium, and magnesium activities in solution.

Values for $X_{Na}$ were then calculated using Eq. (3) for (Na) and (Ca). Exchangeable Mg was then calculated as the different between the CEC and exchangeable Ca plus Na.

Ion activity was definite

$$a_i = f_i \, x c_i$$

Where $a_i$ was activity of ion i, fi was activity coefficient of ion i, and $c_i$ was molar concentration of ion I.

Activity coefficient was calculated of Davis Relationship

$$Log\ fi = -0.509\ x\ v^2\ x\left\{I^{0.5}/\left(I^{0.5}+1\right) - 0.3xI\right\} \quad (6)$$

Where I was ionic strength of solution defined as

$$I = 0.5\sum c_i\ x v_i^2 \quad (7)$$

With VI was valence of ion i.

Robbins et al., (1980) developed notation as developed in Eq. (3) and assumes that the CEC is a constant for a given soil, independent of pH, ion type and concentration, that the soil solution is a "true solution ", in that cation activities are not affected by the presence of charged surfaces and that cation exchanges reversible process. The CEC was assumed as sum of exchangeable cations

$$CEC = X_{1/2Ca} + X_{1/2Mg} + X_{Na} + X_K \quad (8)$$

where $X_{1/2Ca}$, $X_{1/2Mg}$, $X_{Na}$ and $X_K$ are the exchangeable cations (meq/100g).

The selectivity coefficient $K_1$ through $K_6$ for the equilibrium between the cations in solution and the exchangeable cation are defined as:

$$\frac{[Ca]^{1/2}\ X_{Mg}}{[Mg]^{1/2}\ X_{Ca}} = K_1, \quad (9)$$

$$\frac{[K]\ \ X_{Ca}}{[Ca]^{1/2}\ X_K} = K_2, \quad (10)$$

$$\frac{[Na]\ \ X_{Ca}}{[Ca]^{1/2}\ X_{Na}} = K_3 \quad (11)$$

$$\frac{[K]\ \ X_{Mg}}{[Mg]^{1/2}\ X_K} = K_4, \quad (12)$$

$$\frac{[Na]\ \ X_{Mg}}{[Mg]^{1/2}\ X_{Na}} = K_5 \quad (13)$$

$$\frac{[Na]\ X_K}{[K]\ X_{Na}} = K_6 \quad (14)$$

Cation activities used in the above equations are corrected for ionic strength effect (Robbins et al., 1980).

The equation for calculating developed by rewriting Eq. (9-11) in terms of $X_{1/2Mg}$, $X_{Na}$ and $X_K$, and substituting them into Eq.(4), $X_{1/2Ca}$ is factored from each right hand term and the resulting equation is then rearranged to give

$$X_{Ca} = CEC \div \left[\frac{(Mg)^{1/2}K_1}{(Ca)^{1/2}} + \frac{(K)}{(Ca)^{1/2}K_2} + \frac{(Na)}{(Ca)^{1/2}K_3} + 1\right] \quad (15)$$

Following this same procedure for Mg, Na, and K gave equivalent equations for calculating $X_{1/2Mg}$, XNa and XK.

## METHODS

Selectivity coefficient calculation data were obtained from field soil samples where mustard greens were growing. Application of K into soil at the age of the crop was four days whereas Ca, Mg and Na were in the soil naturally. The soil samples from the field were taken at the age of the crop was fifteen days. The soil samples were taken at depth of 0-5 cm, 5-10 cm, 10-15 cm and 15-20 cm. Three samples were taken at 0-5 cm and 5-10 cm, respectively, and two samples were taken at 10-15 cm and 15-20 cm, respectively. To determine exchangeable Ca, Mg, K and Na in the adsorption complex was used ammonium acetate 1M at pH 7.0. Extract of the cations was measured by AAS for Ca and Mg, and flame photometer for K and Na. To determine nation concentration in the solution phase was used the 1:5 water extract method. Each sample was measured in duplicate.

## RESULT AND DISCUSSION

Table 1. Shows the composition of the adsorption complex and the solution phase for the samples of the soil used to grow mustard greens. The adsorbed amount and the amount in the solution phase are both given per 100 d dry soil. Average CEC computed of total adsorbed cations is 5.9 which range of 5.5 to 6.4. Magnitude of the CEC is same as found in loam but it is smaller than silty clay loam found from data for XCHANG subroutine. For all samples, Ca was the major component adsorbed by the soil followed by Mg. Only small amount of K and Na were adsorbed. The amount of Ca adsorbed was 18 to 32 times higher than the amount present in the solution phase. For Mg this ratio ranged from 9 to 12. For K ranged 16 to 38 whereas for Na was relatively same between adsorbed phase and solution phase.

Cation activities as defined by Eq. (5) and selectivity coefficients as defined by Eq. (3) were calculated for all samples are presented in table 2. Na activities was the highest followed by Ca, Mg and K. Na activities are 0.1 to 1.2, Ca ranged 0.6 to 1.4, Mg ranged 0.43 to 0.55 and K ranged 0.12 to 0.49. These values were lower than that of loam and silty clay loam found by Robbins et al (1980). For Ca-Mg exchange the average selectivity coefficients was 0.67, which means that Ca is preferred over Mg by a factor of 1.5. This value is same as found loam and silty clay loam (Robbins et al., 1991) and several mineral soils as reported in table 3. Mg is preferred over K by a factor 4. K is preferred over Na by a factor of 1.36 which is smaller than the average factor of 17 found for mineral soil (Robbins et al., 1980) but same found for peat (Otten, 1994). In the top soil frequently contains high organic matter.

Adsorption of cations is an important mechanism which influences the concentration of cation in the solution plant roots. The concentration of Ca and Mg in the solution phase is buffer to against factors that might change the composition of the solution, e.g. plant uptake or fertilization.

Exchange reactions and selectivity coefficients of all cation are revealed in table 4. This chemical reaction will be used to simulate cation transport in clay loam from Bogor West Java.

Table 1. Amount of Ca, Mg, K and Mg divided between adsorbed and liquid phase (meq/100g) to calculate the selectivity coefficients of clay loam from Bogor, West Java

| **Depth** | **Solution cation concentrations** | | | | **Exchangeable captions** | | | | **CEC** |
|---|---|---|---|---|---|---|---|---|---|
| **(cm)** | **Ca** | **Mg** | **K** | **Na** | **Ca** | **Mg** | **K** | **Na** | |
| 0-5 | 0.10 | 0.07 | 0.03 | 0.12 | 3.25 | 1.18 | 0.98 | 0.14 | 5.55 |
| 0-5 | 0.14 | 0.07 | 0.03 | 0.09 | 3.37 | 1.17 | 0.87 | 0.14 | 5.55 |
| 0-5 | 0.22 | 0.09 | 0.04 | 0.08 | 3.72 | 1.18 | 1.06 | 0.11 | 6.07 |
| 5-10 | 0.18 | 0.08 | 0.01 | 0.12 | 4.28 | 1.02 | 0.38 | 0.13 | 5.81 |
| 5-10 | 0.15 | 0.06 | 0.03 | 0.10 | 3.55 | 1.01 | 0.55 | 0.15 | 5.26 |
| 5-10 | 0.23 | 0.08 | 0.05 | 0.11 | 4.12 | 1.11 | 0.69 | 0.12 | 6.04 |
| 10-15 | 0.18 | 0.08 | 0.06 | 0.09 | 3.72 | 1.21 | 0.85 | 0.14 | 5.92 |
| 10-15 | 0.20 | 0.07 | 0.06 | 0.13 | 4.10 | 1.20 | 0.98 | 0.13 | 6.41 |
| 15-20 | 0.21 | 0.07 | 0.05 | 0.08 | 3.98 | 1.08 | 1.02 | 0.12 | 6.20 |
| 15-20 | 0.19 | 0.09 | 0.05 | 0.09 | 4.02 | 1.31 | 0.89 | 0.16 | 6.38 |

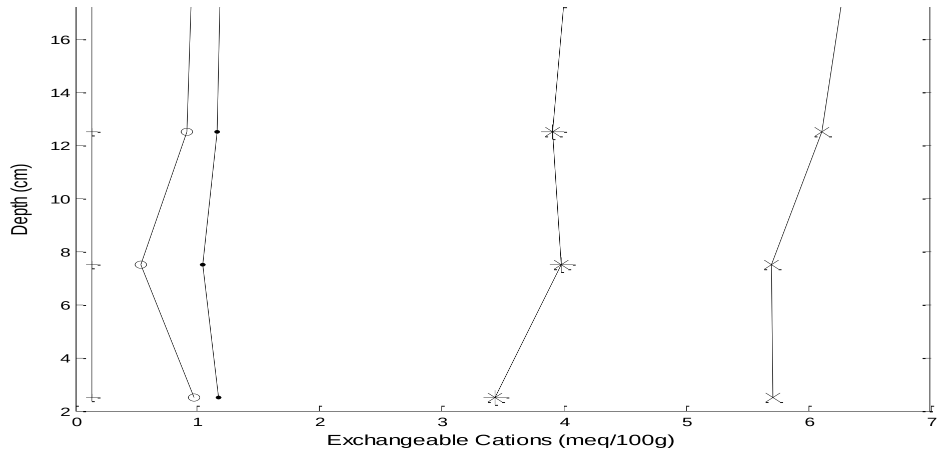


Figure 1. Distribution of Measured exchangeable Ca (-*), Mg (-.), K (-o) and Na (-+) concentration and CEC (-x) obtained by sum of the exchange cations in top soil of clay loam Bogor, West Java.

Table 2. Cation activities and selectivity coefficients calculated from data in Table1.

| **Depth (cm)** | **Cation activities (mmol/l)** | | | | **Selectivity coefficients** | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | **Ca** | **Mg** | **K** | **Na** | $K_{Ca,Mg}$ | $K_{K,Ca}$ | $K_{Na,Ca}$ | $K_{K,Mg}$ | $K_{Na,Mg}$ | $K_{Na,K}$ |
| 0-5 | 0.60 | 0.45 | 0.24 | 1.20 | 0.48 | 0.37 | 0.92 | 0.15 | 0.38 | 2.44 |
| 0-5 | 0.80 | 0.43 | 0.24 | 0.90 | 0.67 | 0.37 | 0.60 | 0.18 | 0.29 | 1.62 |
| 0-5 | 1.30 | 0.54 | 0.37 | 0.80 | 0.77 | 0.42 | 0.61 | 0.20 | 0.30 | 1.45 |
| 5-10 | 1.10 | 0.47 | 0.12 | 1.20 | 0.53 | 0.49 | 0.98 | 0.17 | 0.35 | 1.99 |
| 5-10 | 0.90 | 0.40 | 0.23 | 0.10 | 0.62 | 0.56 | 0.64 | 0.24 | 0.27 | 1.13 |
| 5-10 | 1.40 | 0.52 | 0.45 | 1.10 | 0.71 | 0.86 | 0.83 | 0.37 | 0.36 | 0.96 |
| 10-15 | 1.10 | 0.49 | 0.49 | 0.90 | 0.71 | 0.76 | 0.59 | 0.37 | 0.28 | 0.77 |
| 10-15 | 1.20 | 0.44 | 0.49 | 1.30 | 0.79 | 0.70 | 0.96 | 0.33 | 0.46 | 1.38 |
| 15-20 | 1.30 | 0.44 | 0.46 | 0.80 | 0.77 | 0.59 | 0.61 | 0.27 | 0.27 | 1.02 |
| 15-20 | 1.10 | 0.55 | 0.39 | 0.90 | 0.67 | 0.62 | 0.54 | 0.29 | 0.25 | 0.88 |
| **Selectivity coefficients means** | | | | | **0.67** | **0.57** | **0.73** | **0.25** | **0.32** | **1.36** |
| **Standard deviations** | | | | | **0.09** | **0.15** | **0.16** | **0.07** | **0.06** | **0.50** |

Table 3. Selectivity coefficient values obtained in this study and found in the literature

| **Sample** | $K_{Ca,Mg}$ | $K_{K,Ca}$ | $K_{Na,Ca}$ | $K_{K,Mg}$ | $K_{Na,Mg}$ | $K_{Na,K}$ |
|---|---|---|---|---|---|---|
| Penoyer loam (Robbins, 1980) | 0.69 | 0.36 | 6.4 | 0.24 | 4.30 | 18.0 |
| Hunting silty clay loam (Robbins, 1980) | 0.58 | 0.37 | 6.1 | 0.22 | 3.50 | 16.2 |
| Oakley soil (Paul et al., 1966) | 0.64 | - | 5.5 | - | - | - |
| Hanford soil (Robbins et al., 1980) | 0.54 | - | 7.0 | - | - | - |
| Arbuckley soil (Robbins et al., 1980) | 0.59 | - | 5.6 | - | - | - |
| Yolo soil (Robbins et al., 1980) | 0.67 | - | 7.1 | - | - | - |
| Kaolinite (Udo, 1978) | 0.64 | 0.27 | | | | |
| Manalu fine sandy loam (Vogeler et al., 1997) | 0.70 | - | - | - | - | - |
| Peat (Otten, 1994) | 0.52 | 0.59 | 0.79 | 0.31 | 0.42 | 1.33 |
| Perlite (Otten, 1994) | 0.50 | - | 0.01 | - | 0.013 | - |
| **This study** | **0.67** | **0.57** | **0.73** | **0.25** | **0.32** | **1.36** |

Table 4. Cation exchange reactions and selectivity coefficients dari Ca, Mg, K and Na in clay loam Bogor West Jawa

| Reactions | Selectivity coefficients |
|---|---|
| Ca-ads + $Mg^{2+}$ ⟷ Mg-ads + $Ca^{2+}$ | 0.67 |
| 2K-ads + $Ca^{2+}$ ⟷ Ca-ads + $2K^{+}$ | 0.57 |
| 2Na-ads + $Ca^{2+}$ ⟷ Ca-ads + $2Na^{+}$ | 0.73 |
| 2Na-ads + $Mg^{2+}$ ⟷ Mg-ads + $2Na^{+}$ | 0.32 |
| Na-ads + $K^{+}$ ⟷ K-ads + $Na^{+}$ | 1.36 |
| 2K-ads + $Mg^{2+}$ ⟷ Mg-ads + $2K^{+}$ | 0.25 |

Thabet et al., (1996) and Vogeler et al., (1997) incorporated cation exchanges of Ca, Mg and K by the selectivity coefficients into the cation transport equations. Cation exchange not only retards movement, it also changes the shape of the breakthrough curve. Cation exchange model used in their works is model proposed by Robbins et al., (1980) l which incorporated all selectivity coefficients of competition captions into transport equations. Calculations to find fractions (Eq. 15) of the four cations with incorporating selectivity coefficient are

$$X_{Ca} = CEC \div \left[ \frac{(Mg)^{1/2} K_1}{(Ca)^{1/2}} + \frac{(K)}{(Ca)^{1/2} K_2} + \frac{(Na)}{(Ca)^{1/2} K_3} + 1 \right]$$

$$X_{Mg} = CEC \div \left[ \frac{(Ca)^{1/2}}{(Mg)^{1/2} K_1} + \frac{(Na)}{(Mg)^{1/2} K_5} + \frac{(K)}{(Mg)^{1/2} K_4} + 1 \right]$$

$$X_{Na} = CEC \div \left[ \frac{(Ca)^{1/2} K_3}{(Na)} + \frac{(Mg)^{1/2} K_5}{(Na)} + \frac{(K)\, K_6}{(Na)} + 1 \right]$$

$$X_{K} = CEC \div \left[ \frac{(Ca)^{1/2} K_2}{(K)} + \frac{(Mg)^{1/2} K_4}{(K)} + \frac{(Na)}{(K) K_6} + 1 \right]$$

Where $K_1$ = 0.67 K2 = 0.57, K3 = 0.73, $K_4$ = 0.25, $K_5$ = 0.32, $K_6$ = 1.36.

The resulting four equations are the basis of the cation exchange subroutine which equilibrates solution activities with exchangeable cation concentrations. Initial exchangeable cation concentrations are calculated from the soil CEC, the solution cation activities, and the selectivity coefficients for the appropriate exchange reactions.

To use the model in transport equations still needed input parameters as bulk density, CEC, volumetric water content, solute concentrations and amount of adsorbed cation.

## CONCLUSIONS

This study shows that a considerable amount of cations in the soil is adsorbed by solid phase. Average CEC computed of total adsorbed cations was 5.9. Under normal growing conditions, Ca and Mg occupy more than 80% of the adsorption sites, with Ca favoured over Mg by a factor 1.5. K is preferred over Na with a factor of 1.36.

This study described equilibrium cation exchange equation of Robbins et al., (1980) to find the four exchangeable cations.

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## REFERENCES

Otten, W. 1994. Dynamics of water and nutriens for potted plants induced by flooded bench fertigation: experiments and simulation. Thesis. Wageningen Agricultural University. Wageningen, the Netherlands.

Paul, J.L., K.K. Tanji, and W.D. Anderson. !966. Estimating soil and saturation extract composition by a computer method. Soil Sci. Soc. Am. Proc. 30:15-17.

Robbins., C.W, J.J. Jurinak, and R.J. Wagenet. 1980. Calculating cation exchange in a salt transport model. Soil Sci. Soc. Am. J. 44:1195-1199.

Robbins, C.W. 1991. Solute transport and reactions in salt-affected soils. Modeling plant and soil systems. Agron. No.31.

Salmon, R.C. 1964. Cation exchange reactions. J. Soil Sci. 15:273:283.

Thabet, A.G., and H.M. Selim. 1996. Determination of cation selectivity coefficients of soils: A thin disk flow method. Soil Sci. Soc. Am. J. 161:405-410.

Vogeler, D.R., D.R. Scotter, B.E. Clothier and R.W. Tillman. 1997. Cation transport during unsaturated flow through two intact soils. European Journal of Soil Science. 48:401-410.