

Calcium-Ammonium Selectivity of Two Benchmark Soils from Botswana as Assessed by Competing Semi-empirical Ion Exchange Equations

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The effectiveness of lime-ammonium-nitrate (LAN) as a nitrogen (N) fertilizer in weathered soils depends on the respective selectivity for ammonium (NH₄) and calcium (Ca) by the soils. The study assessed Ca²⁺/NH₄⁺ exchange selectivity of two benchmark soils from Botswana and examined the soil fertility management implications. Surface horizons (0–20 cm) of Pellustert and Haplustalf were equilibrated with 50 ml stock solution containing variable concentrations of Ca²⁺ and NH₄⁺. The Ca²⁺/NH₄⁺ exchange data were fitted into the Vanselow (K_V), Gaines and Thomas (K_{GT}), Davies (K_D), and the regular solution (K_{RS}) equations. The selectivity coefficients for the Ca²⁺/NH₄⁺ exchange reactions varied widely with the soil exchanger composition except for the relatively stable K_{RS}. The selectivity coefficients indicated strong preference for NH₄⁺ to Ca²⁺. The thermodynamic exchange constant, K_{ex}, was 5.75 ± 1.24 in the Pellustert, indicating preferential adsorption of NH₄⁺, but not in the Haplustalf with K_{ex} = 0.92 ± 0.27. The free energy for Ca²⁺/NH₄⁺ exchange (ΔG°_{ex}) was negative (−4.26 ± 0.59 kJ mol^{−1}) in the Pellustert but slightly positive in the Haplustalf (0.34 ± 0.87 kJ mol^{−1}). In conclusion, the soil-NH₄ complex was more stable than soil-Ca complex in the Pellustert, indicating LAN as a N fertilizer would have greater potential effectiveness in the Pellustert than in the Haplustalf.

Keywords Change in free energy of exchange (ΔG°_{ex}), equilibrium exchange constant (K_{ex}), ion exchange, regular solution model coefficient (K_{RS}), selectivity coefficients

Introduction

Sub-Saharan Africa is caught in the paradox of rapidly expanding population and declining food production, and hence it is rapidly expanding its fertilizer use to alleviate soil fertility constraints and increase food production capacity and security (Dreschel et al. 2001; Heerink 2004). Regretfully, however, the impact of increasing fertilizer use on food production has been minimal because of nutrient losses caused by inappropriate application rates and methods, predicated solely on empirical field response trials with little or no information on the chemical interactions between nutrient elements in soils. In most cases, fertilizer

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recommendations are extrapolated from one soil to the other regardless of differences in soil chemistry. To maximize the benefits of chemical fertilizers, data on ion exchange equilibria of soils are required to predict the composition of soil aqueous phase and ionic nutrient/pollutant mobility in the soil environment (Gatson and Selim 1991; Verbug and Baveye 1994).

A review by Verbug and Baveye (1994) showed that some other studies have examined calcium and ammonium (Ca-NH_4) exchange in soil colloids starting from Vanselow (Vanselow 1932). However, approximately 90% of these studies have been conducted with specimen clay minerals and temperate soils characterized by the preponderance of 2:1 layer silicates (Laudelout et al. 1967; Hulbert 1987; Chung and Zasoski 1994; Evangelou and Lumbanraja 2002; DeSutter, Pierzynski, and Baker 2006). Studies of cation exchange of specimen clays are predicated on the assumption that a particular clay mineral largely determines selectivity in whole soil, an assumption that is now questionable, especially in weathered tropical soils dominated by low-activity clays, iron and aluminum oxides, low cation exchange acidity and organic matter, strong to moderate acidity, and variable charge characteristics (Agbenin and Yakubu 2006). For instance, Gaston and Selim (1991) reported that selectivity coefficients determined for specimen kaolinitic clay could not predict cationic composition of a kaolinitic soil.

Cation exchange has been widely indexed with several selectivity coefficients to determine the preferential adsorption by soil colloids and soil solution composition (Essington 2004; Sposito 2008). Whereas some of them are strictly empirical with no thermodynamic basis, others are semi-empirical with some thermodynamic significance. Several ion exchange equations, especially those proposed by Vanselow (1932), Gaines and Thomas (1953), and Davies (1950), have been widely used to index binary cation exchange isotherms based on the law of mass action. However, less used in soil literature is the regular solution model (Elprince, Vanselow, and Sposito 1980; Essington 2004; Sposito 2008) even though its mechanistic basis is consistent with thermodynamic equilibrium exchange constant. The Vanselow equation and Gaines and Thomas equation including the Davies equation all assumed that the activity of solid-phase cations can be approximated either by molar fractions or equivalent fractions (Vanselow 1932; Gaines and Thomas 1953), and hence geochemical models use either or both of these approximations in modeling exercises (Pankhurst and Appelo 1999).

The $\text{Ca} \rightarrow \text{NH}_4$ exchange reaction of weathered soils is an important heterovalent ion exchange study, particularly for tropical savanna soils, whose exchange sites are dominated by Ca^{2+} ions (Jones and Wild 1975) coupled with the widespread application of ammonium salts as fertilizers. In Botswana, the study of $\text{Ca} \rightarrow \text{NH}_4$ is highly imperative because lime-ammonium nitrate (LAN) is widely applied to arable fields to alleviate nitrogen (N) deficiency and moderate soil acidity. Therefore, the objectives of this study were to (i) describe $\text{Ca}^{2+}/\text{NH}_4^+$ exchange in two benchmark soils from Botswana and determine the appropriateness of the regular solution model for indexing ion exchange in the soils and (ii) assess the consistency of regular solution selectivity coefficient with the thermodynamic equilibrium exchange constant.

Materials and Methods

The surface horizons (0–20 cm) of Pellustert and Haplustalf from Botswana were used for this study. The Pellustert was a dark-cracking Vertisol from Pandamatenga with clay mineralogy consisting of 2:1 layer silicates ($\text{Si/Al} = 2$), principally smectite (Pardo et al. 2003), which can be represented by the general formula $\text{M}_x[\text{Si}_8]\text{Al}_{3,2}\text{Fe}_{0,2}\text{Mg}_{0,6}\text{O}_{20}(\text{OH})_4$, where M_x represents monovalent interlayer cation, and $[\]$ indicates a tetrahedral coordination. The Haplustalf is a

soil characterized by textural B horizon with high base saturation and mineralogy dominated by 1:1 layer silicate mineral ($\text{Si/Al} = 1$) and can also be represented by the general formula $[\text{Si}_4]\text{Al}_4\text{O}_{10}(\text{OH})_8 \cdot n\text{H}_2\text{O}$, where $n = 0$ for kaolinite and $n = 4$ for halloysite (Sposito 2008).

Routine Analysis

The particle-size analysis of the soils was determined by the standard hydrometer method after dispersing the soil particles with sodium hexametaphosphate solution (Gee and Bauder 1986). The pH of the soils was measured in 1:1 soil–0.01 M potassium chloride (KCl) solution ratio; the soil organic carbon was determined by dichromate oxidation (Nelson and Sommers 1982), while soil exchange acidity was displaced with 1.0 M KCl solution and titrated with 0.1 N sodium hydroxide (NaOH) (Agbenin 1995). Exchange bases were displaced with neutral 1.0 N ammonium acetate (NH_4OAc) solution buffered at pH 7.0 (Rhoades 1982). Potassium, Ca, Mg, and Na in the soil filtrates were determined using inductively coupled plasma–atomic emission spectroscopy (ICP-AES). The cation exchange capacity of the soils was determined by summing exchange bases and exchange acidity. Some properties of the soils are given in Table 1 and also described elsewhere (Agbenin and Modisaemang 2014, 2015).

$\text{Ca}^{2+}/\text{NH}_4^+$ Exchange Procedure

Ten grams of < 2-mm sieved soil were weighed into centrifuge tube in duplicate and 50 ml of solution containing variable amounts of $\text{Ca}^{2+}/\text{NH}_4^+$ were added to the soil with 4–5 drops of acetone to inhibit microbial mineralization of organic nitrogen (N) in soil organic matter (OM) to ammonium ($\text{NH}_4\text{-N}$) and shaken for 30 min. The solution containing variable amounts of $\text{Ca}^{2+}/\text{NH}_4^+$ consisted of a constant chloride concentration (0.1 M). The initial NH_4 equivalent of the $\text{Ca}^{2+}/\text{NH}_4^+$ mixture increased from 0 to 1 while the Ca equivalent was decreased from 1 to 0. The soil suspension was centrifuged and the supernatant solution discarded. The soil was resuspended twice with the variable $\text{Ca}^{2+}/\text{NH}_4^+$ solution and centrifuged, but the last supernatant solution was saved to determine the equilibrium concentration of Ca, NH_4 , and other

Table 1
Sampling location and selected properties of the experimental soils

Property	Soil	
	Pellustert	Haplustalf
Textural class	Sand clay loam (SCL)	Loamy sand (LS)
pH ^a	7.0	5.7
Sand (%)	59.0	78.5
Silt (%)	9.0	13.0
Clay (%)	32.0	8.5
Organic carbon (g/kg)	6.6	8.7
Exchange acidity (cmol _c /kg)	0.35	0.60
Effective CEC (mmol _c /kg)	14.0	3.2
Base saturation (%)	97.5	81.3

^aMeasured in 0.01 M CaCl_2 solution.

cations. Thereafter, the soil was repeatedly washed with ethanol solution until free of chloride (Cl⁻) ions, tested by adding few drops of 0.1 M silver nitrate (AgNO₃) solution to the supernatant. Lack of white precipitate indicated that the soil was free of Cl⁻. The concentrations of NH₄ and Ca sorbed by the soils were successively displaced with 50 mL of 0.5 N lithium chloride (LiCl) solution three times, and all supernatant solution was saved for the determination of Ca, NH₄, and other cations. The concentrations of potassium, calcium, magnesium, and sodium (K, Ca, Mg, and Na) in the supernatant solution were determined in ICP-AES, while the concentration of NH₄ in the solution was determined by the Kjeldahl method (Bremner and Mulvaney 1982).

Data Handling and Analysis

Adsorption Isotherms. The Ca²⁺/NH₄⁺ adsorption isotherms were plotted as the equivalent fractions in the exchanger phase (E) versus charge fractions of the cations in the aqueous solution phase (É) in relation to the thermodynamic nonpreference isotherms (TNI) of Ca²⁺ and NH₄⁺. The nonpreference isotherms were determined for adsorbed NH₄⁺ and Ca²⁺ with Eqs. (1) and (2), respectively (Sposito 2008; Essington 2004):

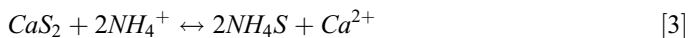
$$E_{\text{NH}_4} = \left[1 + \frac{2}{\Gamma N_T} \left(\frac{1}{\dot{E}_{\text{NH}_4}^2} - \frac{1}{\dot{E}_{\text{NH}_4}} \right) \right]^{-\frac{1}{2}} \quad [1]$$

$$E_{\text{Ca}} = 1 - \left[\frac{A(1 - \dot{E}_{\text{Ca}})^2}{\dot{E}_{\text{Ca}} + (1 - \dot{E}_{\text{Ca}})^2} \right]^{\frac{1}{2}} \quad [2]$$

where Γ is defined as $\frac{\gamma_{\text{NH}_4}^2}{\gamma_{\text{Ca}}}$, A is given as $M \frac{\gamma_{\text{NH}_4}^2}{\gamma_{\text{Ca}}}$, M is the molar concentration of Ca²⁺ and NH₄⁺ in the soil solution, and N_T is the total normality of the equilibrium soil solution of the cations calculated as $2(\text{Ca}^{2+}) + (\text{NH}_4^+)$.

Calculation of Selectivity Coefficients

Calcium–ammonium (Ca²⁺/NH₄⁺) exchange reactions of the two soils were represented by the following reactions:



where S designated the charged soil surface. Four competing selectivity coefficients based on the Vanselow (K_V), Gaines and Thomas (K_{GT}), and Davies (K_D) equations and regular solution model (K_{RS}) were calculated for the exchange reactions as follows:

$$\text{Vanselow } (K_V) = \frac{N_{\text{NH}_4}^2 (\text{Ca}^{2+})}{N_{\text{Ca}} (\text{NH}_4^+)^2} \quad [4]$$

$$\text{Gaines and Thomas } (K_{GT}) = \frac{E_{\text{NH}_4}^2 (\text{Ca}^{2+})}{E_{\text{Ca}} (\text{NH}_4^+)^2} \quad [5]$$

$$\text{Davies (K}_D) = \frac{N_{\text{NH}_4}^2 (N_{\text{Ca}} + \frac{2(n-1)N_{\text{NH}_4}^2}{n}) (\text{Ca}^{2+})}{N_{\text{Ca}} (\text{NH}_4^+)^2} \quad [6]$$

$$\text{Regular Solution model(K}_{RS}) = \frac{[\exp(qN_{\text{Ca}}^2)] N_{\text{NH}_4}^2 (\text{Ca}^{2+})}{[\exp(qN_{\text{NH}_4}^2)]^2 N_{\text{Ca}} (\text{NH}_4^+)^2} \quad [7]$$

where N_{NH_4} and N_{Ca} were the molar fractions of adsorbed NH_4 (S- NH_4) and Ca (S-Ca) by the soil surface, respectively, while E_{NH_4} and E_{Ca} were the equivalent fractions of S- NH_4 and S-Ca, respectively. The ion exchange data were fitted to the ion exchange equations described in Eqs. [4]–[7] to calculate the selectivity coefficients. However, in fitting the Davies equation to the experimental data, we assumed $n = 4$, meaning that adsorbed Ca^{2+} or NH_4^+ was surrounded by a square configuration of surface charges (Essington 2004). The regular solution model coefficient (K_{RS}) for the $\text{Ca}^{2+}/\text{NH}_4^+$ exchange was calculated by reducing Eq. [7] to Eq. [8]:

$$K_{RS} = \frac{[\exp(qN_{\text{Ca}}^2)]}{[\exp(qN_{\text{NH}_4}^2)]^2} K_V \quad [8]$$

since an inspection of Eq. [7] shows a close relationship with Vanselow selectivity coefficient, where qN_{Ca} and qN_{NH_4} are defined by the rational activity coefficients of adsorbed Ca^{2+} and NH_4^+ . By the regular solution model, rational activity coefficients (f) of an adsorbed ion can be estimated by the quadratic truncation of the Margules power equation, which, for $\text{Ca}^{2+}/\text{NH}_4^+$ exchange (see Eq. [3]), can be written as

$$\ln f_{\text{Ca}} = a_2 N_{\text{NH}_4}^2 + a_3 N_{\text{NH}_4}^3 \quad [9]$$

$$\ln f_{\text{NH}_4} = (a_2 \frac{3}{2} a_3) N_{\text{Ca}}^2 + a_3 N_{\text{Ca}}^3 \quad [10]$$

where the coefficients a_2 and a_3 are defined by Eqs. [11] and [12] (Essington 2004)

$$a_2 = 2q_{\text{NH}_4} - q_{\text{Ca}} \quad [11]$$

$$a_3 = 2(q_{\text{Ca}} - q_{\text{NH}_4}) \quad [12]$$

where q_{NH_4} and q_{Ca} were set by the limit of f_{NH_4} and f_{Ca} as N_{NH_4} and N_{Ca} approached zero, respectively. Thus, when $q_{\text{Ca}} = q_{\text{NH}_4}$, then $a_2 = q_{\text{Ca}} = q_{\text{NH}_4}$ and $a_3 = 0$, substitutions into Eqs. [9] and [10] yielded estimates of the rational activity coefficients of Ca^{2+} and NH_4^+ in the exchange reaction as

$$\ln f_{\text{Ca}} = qN_{\text{NH}_4}^2 \quad [13]$$

$$\ln f_{\text{NH}_4} = qN_{\text{Ca}}^2 \quad [14]$$

In fitting the experimental data to the regular solution model, Eq. [8] was linearized by taking the natural logarithm and substituting $1 - N_{Ca}$ for N_{NH4} to yield the expression (Essington 2004)

$$\ln K_v = \ln K_{RS} + q[N_{NH4}(N_{NH4}+2)-1] \quad [15]$$

A plot of $\ln K_v$ as a function of $[N_{NH4}(N_{NH4} + 2) - 1]$ would be linear whereby the intercept of the regression line is equal to $\ln K_{RS}$ and the slope equivalent to q . The appropriate estimate of q was inserted into Eq. [7] or [8] to calculate K_{RS} as a function of the exchanger phase composition.

The activities of NH_4^+ and Ca^{2+} in the equilibrium soil solution were determined by multiplying the concentrations with their respective activity coefficient (γ). The activity coefficient was determined by the Davies equation (Sposito 2008):

$$\log \gamma \equiv -0.512Z^2 \left(\frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.3\mu \right) \quad [16]$$

where Z is the valence of the ion and μ is the ionic strength of the equilibrium soil solution estimated from the electrical conductivity (EC_e) of the equilibrium soil solution. The μ of the soil solution was determined by the Marion-Babcock equation that relates EC_e to μ , given as Eq. [17]:

$$\log \mu \equiv 1.159 + 1.009 \log EC_e \quad [17]$$

Thermodynamic Equilibrium Constant (K_{ex})

The thermodynamic equilibrium exchange constant for Ca^{2+}/NH_4^+ exchange described in Eq. [3] as a function of the exchanger phase composition was determined according to Eq. [18]:

$$K_{ex} = \frac{f_{NH4}^2 N_{NH4}^2 (Ca^{2+})}{f_{Ca} N_{Ca} (NH_4^+)^2} \quad [18]$$

where f_{NH4} and f_{Ca} are the rational activity coefficients of adsorbed NH_4^+ and Ca^{2+} . Since Eq. [18] is intrinsically related to Eq. [4], it was simplified and rewritten as

$$K_{ex} = \frac{f_{NH4}^2}{f_{Ca}} K_v \quad [19]$$

where K_v is the Vanselow selectivity coefficient. The rational activity coefficients of adsorbed NH_4 and Ca were evaluated by a simplified method described elsewhere (Essington 2004; Agbenin and Yakubu 2006). An overall K_{ex} for the exchange reaction was calculated by integrating $\ln K_v$ over the exchanger phase composition as follows:

$$\ln K_{ex} = \int_0^1 \ln K_v dE_{NH4} \quad [20]$$

The change in free energy of the exchange reaction (ΔG_{ex}) was estimated from the equation:

$$\Delta G_{\text{ex}} = -RT \ln K_{\text{ex}} \quad [21]$$

Results and Discussion

Adsorbed Metal Charge

The adsorbed metal charge (Q_i), which is the summation of the surface excesses of Ca^{2+} and NH_4^+ (S-Ca + S- NH_4), increased with increasing NH_4^+ saturation in the Pellustert but remained nearly constant in the Haplustalf (Table 2). Compared to the cation exchange capacity (CEC) of the soils (Table 1), Q_i in the Pellustert was lower than its CEC, whereas there was little or no difference between Q_i and CEC in the Haplustalf. The apparent inconsistency between Q_i and CEC in the Pellustert whose mineralogy contains, albeit in small amounts, some 2:1 layer silicates is generally attributed to dehydration or interlayer collapse due to cation adsorption (Evangelou and Lumbanraja 2002). A careful perusal of the data in Table 2 would indicate that high S-Ca was associated with low Q_i , leading us to conclude that flocculation of layer silicate clays by adsorbed Ca^{2+} was probably responsible for decreasing Q_i . Flocculation of colloids minimizes the surface area available for exchange reaction. Furthermore, the inability of NH_4^+ or Ca^{2+} to displace specifically adsorbed H^+ from soil colloids could also cause difference between Q_i and CEC in the Pellustert.

Table 2.

Equilibrium concentration of Ca and NH_4 in soil solution and the concentration of Ca and NH_4 adsorbed by the soil exchanger phase

Equilibrium concentration (mmol/L)		Exchange concentration (mmol _e /kg)		
Ca	NH_4	S-Ca	S- NH_4	Q_i
Pellustert				
37.3 ±2.44	0.86 ±0.09	83.4 ±4.74	4.30 ±0.42	87.7 ± 4.74
33.1 ±4.02	13.0 ±2.72	58.8 ±11.7	58.8 ±11.7	91.4 ± 11.4
27.4 ±1.59	22.3 ±5.55	48.0 ±2.48	42.8 ±5.09	90.8 ± 4.35
19.9 ±2.57	32.3 ±1.67	43.8 ±2.72	59.0 ± 6.85	102.8 ± 9.46
8.50 ±0.40	42.3 ± 10.5	35.8 ±2.70	70.2 ±6.92	106.0 ± 6.18
1.30 ± 0.34	57.8 ± 6.50	18.3 ±1.99	89.6 ± 4.48	107.9 ± 2.79
Haplustalf				
44.5 ±0.72	0.91 ±0.07	33.5 ±0.29	1.08 ±0.04	34.4 ± 0.06
43.8 ±1.23	14.8 ±0.95	27.5 ±1.90	7.83 ±0.38	35.3 ± 1.53
28.3 ±0.60	24.0 ±1.00	22.7 ±0.85	11.2 ±0.33	33.9 ± 1.21
18.5 ±0.03	40.8 ±5.25	19.7 ±0.02	15.8 ± 0.02	35.5 ± 0.11
11.0 ±0.83	46.9 ± 3.00	17.2 ±0.99	17.8 ±0.40	35.0 ± 0.59
1.33 ± 0.32	66.7 ± 4.24	10.6 ±0.77	26.1 ± 1.36	36.6 ± 1.59

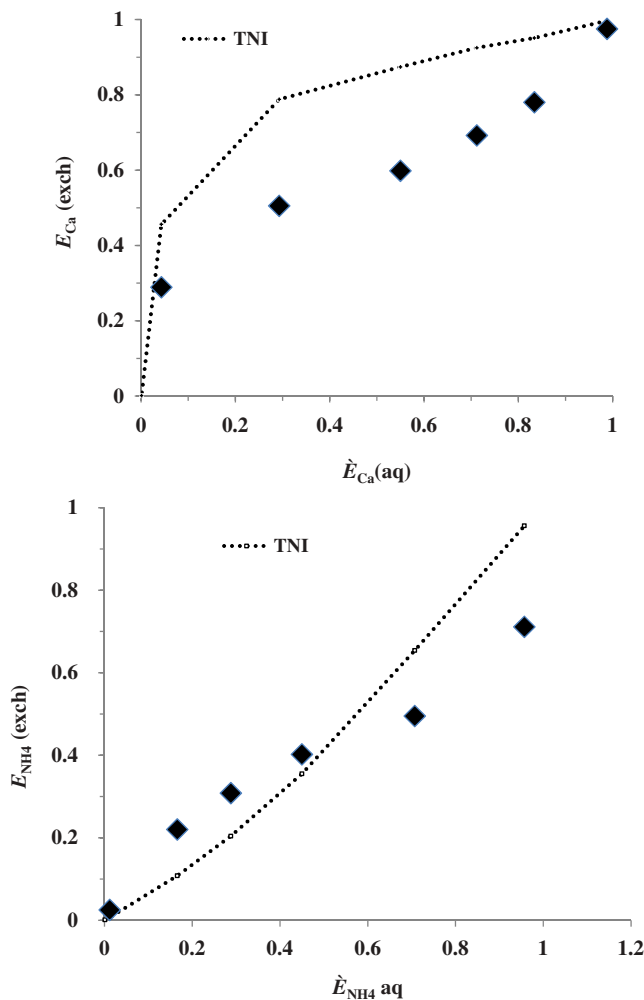


Figure 1. The NH_4 (top) and Ca (bottom) adsorption isotherms in the Vertisol plotted as the equivalent fractions of the adsorbed ions (E_{NH_4} and E_{Ca}) versus the charged fractions in soil solution (\dot{E}_{NH_4} and \dot{E}_{Ca}). The dashed line is the thermodynamic non-preference isotherm (TNI).

Cation Adsorption Isotherms

As can be seen in Figures 1 and 2, the E_{Ca} data points were clearly below the thermodynamic nonpreference isotherm line of Ca^{2+} while E_{NH_4} data points were above the nonpreference isotherm line across a wide range of the exchanger phase composition of the Pellustert but not in the Haplustalf. Whereas the Pellustert had preferential retention of NH_4^+ to Ca^{2+} , the Haplustalf had equal preference for both cations over a great range of the exchanger phase composition except at $\dot{E}_{\text{NH}_4^+} > 0.60$ (Figure 1). The apparent selectivity of NH_4^+ by the Pellustert is in agreement with some other reports (Okamura and Wada 1984; Wada and Masaki 1990; Chappell and Evangelou 2002) but inconsistent with lyotropic selection series of cations by soil colloids based on valence and ionic size considerations.

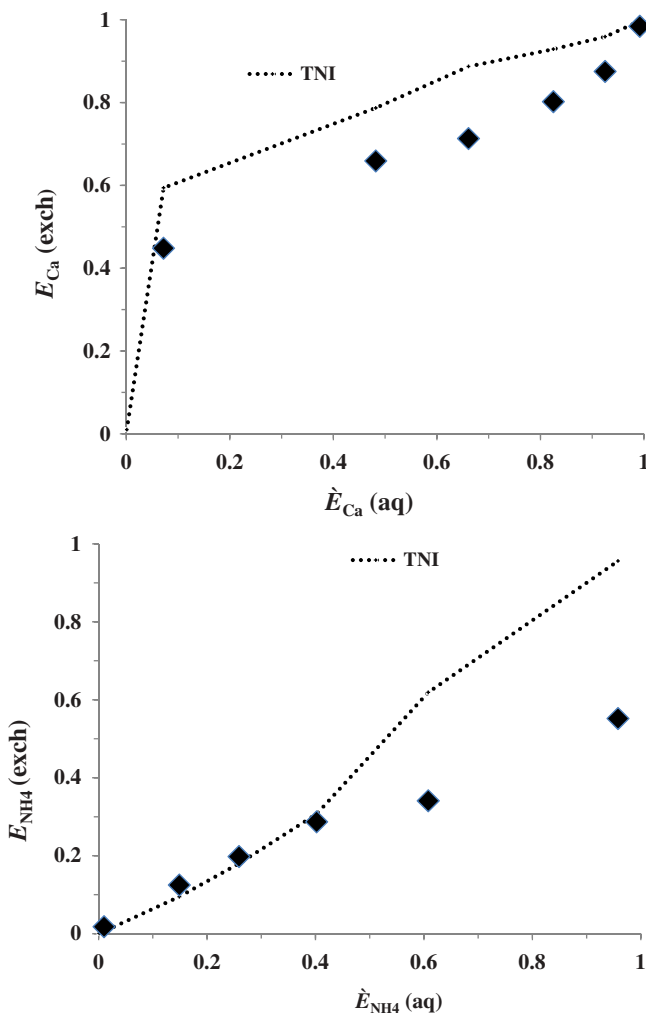


Figure 2. The NH_4 (top) and Ca (bottom) adsorption isotherms in the Alfisol plotted as the equivalent fractions of the adsorbed ions (E_{NH_4} and E_{Ca}) versus the charged fractions in soil solution (\hat{E}_{NH_4} and \hat{E}_{Ca}). The dashed line is the thermodynamic non-preference isotherm (TNI).

Selectivity Coefficients

The selectivity coefficients for CaS- NH_4S as a function of the soil exchanger phase composition are shown in Table 3. Values of K_V , K_{GT} , K_D , and K_{RS} less than one or unity are indicative of preferential adsorption of Ca^{2+} by the soils whereas values greater than one indicated preferential NH_4^+ adsorption to Ca^{2+} . The different selectivity coefficients derived from the different ion exchange equations led to the same conclusions about $\text{Ca}^{2+}/\text{NH}_4^+$ exchange reactions of the soils.

Three of the selectivity coefficients (K_V , K_{GT} , and K_D) decreased with increasing NH_4^+ saturation of the exchanger surface due probably to differential adsorption energy as a result of heterogeneity of exchange sites (Figure 4). Decreasing selectivity coefficient with increasing surface saturation of soil exchange is indicative of heterogeneous adsorption or exchange

Table 3
Molar fractions and the selectivity coefficients of Ca→NH₄ exchange reaction in a Pellustert and a Haplustalf from Botswana

Molar fraction		Selectivity coefficients		
N_{Ca}	N_{NH_4}	K_V	K_{GT}	K_D
Pellustert				
0.951 ± 0.006	0.049 ± 0.006	102.8 ± 2.50	26.3 ± 0.58	98.1 ± 2.83
0.641 ± 0.052	0.359 ± 0.052	32.5 ± 6.20	9.97 ± 1.61	27.2 ± 5.13
0.530 ± 0.038	0.470 ± 0.038	20.0 ± 6.45	6.51 ± 1.95	17.2 ± 5.26
0.427 ± 0.014	0.573 ± 0.014	11.9 ± 0.88	4.15 ± 0.27	10.9 ± 0.69
0.338 ± 0.032	0.662 ± 0.032	5.33 ± 1.46	1.98 ± 0.51	5.28 ± 1.31
0.169 ± 0.022	0.831 ± 0.022	1.26 ± 0.21	0.54 ± 0.09	1.52 ± 0.22
Haplustalf				
0.969 ± 0.001	0.032 ± 0.001	45.6 ± 8.32	10.7 ± 2.41	40.7 ± 9.17
0.778 ± 0.020	0.222 ± 0.020	10.8 ± 1.62	2.78 ± 0.47	8.41 ± 1.34
0.669 ± 0.002	0.331 ± 0.002	8.07 ± 1.90	2.42 ± 0.57	6.72 ± 1.59
0.556 ± 0.002	0.444 ± 0.002	5.58 ± 0.27	1.79 ± 0.09	5.33 ± 0.78
0.491 ± 0.020	0.509 ± 0.020	2.15 ± 0.20	0.72 ± 0.06	1.89 ± 0.15
0.289 ± 0.018	0.711 ± 0.018	0.47 ± 0.05	0.18 ± 0.03	0.49 ± 0.06

Note. K_{GT} values were calculated from equivalent fractions

sites as also reported by other investigators (Goulding 1983; Evangelou and Lumbanraja 2002; Yakubu and Agbenin 2010). The K_V was remarkably similar to K_D ($n = 4$) in the soils, thus suggesting that the Davies equation is somewhat consistent with Vanselow equation despite the different assumptions about an adsorbed ion on the soil surface.

The result of fitting the regular solution model to the Ca²⁺/NH₄⁺ exchange data is given in Table 4. The test of the applicability of the regular solution model was performed by plotting $\ln K_V$ as a function of $q(N_{NH_4} / (N_{NH_4} + 2 - 1))$ to determine if any linear relations could be established (Figure 3). The plots were strongly linear in character with R² values of 0.995 and 0.990 for the Pellustert and Haplustalf, respectively. The K_{RS} did not exhibit any significant variability with exchanger phase composition when compared to K_V , K_D , and K_{GT} ; instead it remained fairly invariant or stable with increasing NH₄⁺ saturation of the soil exchanger phase (Figure 5). However, as compared to the thermodynamic exchange constant K_{ex} determined by Eq. [18] or [19] as a function of NH₄⁺ saturation of the exchange sites, there were some numerical differences (Table 4). The numerical differences between K_{RS} and K_{ex} can be partly attributed to the different approaches for determining the rational activity coefficients of adsorbed cations.

The rational activity coefficients measured by the Argesinger approach using equivalent fractions (Goulding 1983; Essington 2004) were not exactly equal to the regular solution model rational activity coefficients based on the Margules' power expansion (Figure 6). Because K_{RS} is also a pseudoequilibrium constant (Sposito 2008) it might not be numerically equal to K_{ex} but the relative stability of K_{RS} across the exchanger phase composition (Figure 5) is important when choosing a selectivity coefficient for predicting Ca→NH₄ exchange and solution phase composition, and possibly the fate of cationic movement within the experimental soils.

Table 4

Regular solution selectivity coefficients and the computed thermodynamic equilibrium constants in relation to the exchanger phase composition for $\text{Ca}^{2+}/\text{NH}_4^+$ exchange reaction in the two soils from Botswana

E_{Ca}	E_{NH_4}	K_{RS}	$\ln K_{\text{RS}}$	K_{ex}	$\ln K_{\text{ex}}$
Pellustert					
0.98 ± 0.00	0.02 ± 0.00	18.6 ± 1.7	2.92 ± 0.09	6.79 ± 2.57	1.87 ± 0.39
0.78 ± 0.04	0.22 ± 0.04	24.5 ± 4.1	3.13 ± 0.16	6.48 ± 2.20	1.83 ± 0.34
0.69 ± 0.03	0.31 ± 0.03	26.6 ± 3.2	3.28 ± 0.13	6.30 ± 0.86	1.83 ± 0.13
0.60 ± 0.01	0.40 ± 0.01	29.2 ± 1.9	3.37 ± 0.06	6.64 ± 0.58	1.89 ± 0.09
0.51 ± 0.04	0.49 ± 0.04	22.4 ± 4.2	3.10 ± 0.18	4.98 ± 0.60	1.60 ± 0.12
0.29 ± 0.03	0.71 ± 0.03	16.4 ± 2.3	2.79 ± 0.14	4.23 ± 0.66	1.43 ± 0.16
Haplustalf					
0.98 ± 0.00	0.02 ± 0.00	6.50 ± 1.54	1.90 ± 0.23	1.43 ± 0.27	0.35 ± 0.06
0.88 ± 0.01	0.12 ± 0.01	4.23 ± 0.05	1.44 ± 0.01	0.74 ± 0.09	-0.31 ± 0.12
0.80 ± 0.00	0.20 ± 0.00	5.11 ± 1.14	1.61 ± 0.24	0.93 ± 0.25	-0.07 ± 0.29
0.71 ± 0.00	0.29 ± 0.00	6.66 ± 0.36	1.89 ± 0.06	1.11 ± 0.04	0.15 ± 0.03
0.66 ± 0.02	0.34 ± 0.02	3.73 ± 0.17	1.32 ± 0.05	0.66 ± 0.18	-0.42 ± 0.08
0.45 ± 0.02	0.55 ± 0.02	2.99 ± 0.45	1.09 ± 0.15	0.65 ± 0.24	-0.48 ± 0.38

The K_{RS} values indicated a preferential adsorption of NH_4^+ to Ca^{2+} by the two soils, with the Pellustert exhibiting greater affinity for NH_4^+ than the Haplustalf as can be deduced from the magnitude of K_{RS} values. According to Talibudeen (1981), soils with significant amounts of layer silicates have preferential adsorption of NH_4^+ because of the strong NH-O bond formed in the hexagonal cavity of S-O tetrahedral structure on the one hand and the O.H-N-H.O bond formed with the oxygen plane in the interlayer space (Van Bladel 1967).

Overall K_{ex} and Free Energy ($\Delta G^\circ_{\text{ex}}$) of Exchange

The overall K_{ex} for the exchange reactions estimated by means of Eq. [20] and $\Delta G^\circ_{\text{ex}}$ (Table 5) are consistent with the notion that NH_4^+ had greater affinity for the Pellustert than the Haplustalf, probably because of the presence of 2:1 layer silicates in this Pellustert than the Haplustalf (Pardo et al. 2003). The Haplustalf, largely dominated by kaolinite, really showed no clear-cut preference for either Ca^{2+} or NH_4^+ (Table 4), in contrast to the report by Okamura and Wada (1984), who found preferential retention of NH_4^+ to Ca^{2+} in halloysitic soils even although kaolinite is structurally similar to halloysite except for hydration water in the latter (Sposito 2008). Where a low-activity clay soil preferentially adsorbs NH_4^+ to Ca^{2+} there is probably the existence of steric features of the cation exchange sites that tend to favor NH_4^+ adsorption (Okamura and Wada 1998), which was not the case in the Haplustalf studied in this report. This result is somewhat in agreement with that of Chung and Zasoski (1994), who reported preferential adsorption of Ca^{2+} to NH_4^+ by some soils.

Generally, extensive studies of ion exchange reactions of weathered tropical soils are still lacking to enable and facilitate data comparison and extrapolation. In some other weathered soils, however, the results of $\text{Ca}^{2+}/\text{NH}_4^+$ exchange have been mixed. Whereas

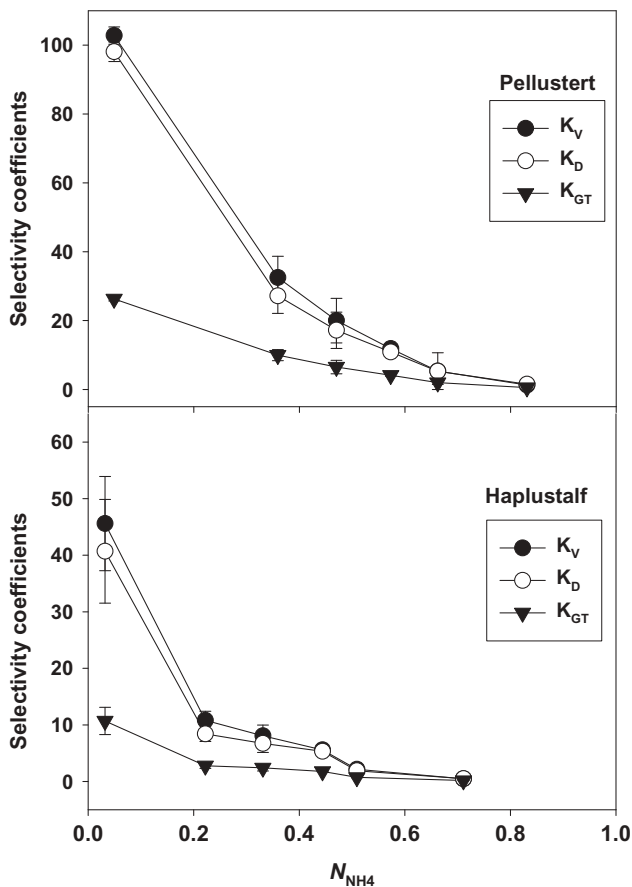


Figure 3. The variation in the selectivity coefficients (K_V , K_D and K_{GT}) as a function of NH_4^+ saturation of the exchange sites expressed either as mole fraction of NH_4^+ ($N_{\text{NH}_4^+}$) or equivalent fraction of NH_4^+ .

Talibudeen (1981) and Wada and Masaki (1990) concluded that NH_4^+ might be generally preferred to Ca^{2+} by soils depending on the level of organic matter (OM), Chung and Zasoski (1994) reported preferential adsorption of Ca^{2+} to NH_4^+ by soils following OM addition. Thus, OM levels in soils might complicate the extrapolation of $\text{Ca}^{2+}/\text{NH}_4^+$ exchange from one soil to the other.

There is little information about the $\Delta G^\circ_{\text{ex}}$ for $\text{Ca}^{2+}/\text{NH}_4^+$ exchange in whole soils, but $\Delta G^\circ_{\text{ex}} = -4.26 \text{ kJ mol}^{-1}$ for the Pellustert (Table 5) is almost twice lower than $\Delta G^\circ_{\text{ex}} = -8.34 \text{ kJ mol}^{-1}$ reported for $\text{Ca}^{2+}/\text{NH}_4^+$ exchange in montmorillonite by Laudelout and Van Bladel (1967) because of the high selectivity of 2:1 layer silicate minerals for NH_4^+ (Elprince, Vanselow, and Sposito 1980; Talibudeen 1981; Evangelou and Lumbanraja 2002; Weatherly and Milaclinovic 2004). The slight positive $\Delta G^\circ_{\text{ex}}$ for $\text{Ca}^{2+}/\text{NH}_4^+$ in the Haplustalf (Table 5) is consistent with the lack of distinct preference for either Ca^{2+} or NH_4^+ .

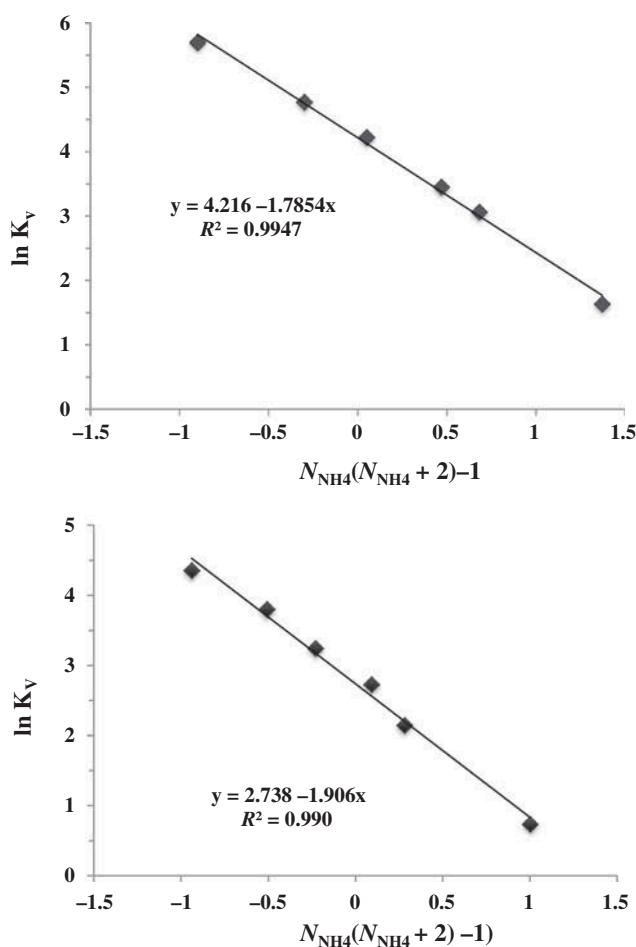


Figure 4. The linear plot of the regular solution model to Ca/NH_4 exchange of the two soils according to Eq. [21].

Managing Ca^{2+} and NH_4^+ Fertility of the Soils

The selectivity of NH_4^+ by the Pellustert has huge implications for the effectiveness of LAN as a fertilizer. As alluded to elsewhere (Agbenin and Modisaemang 2014), the greater stability of S- NH_4 complex than S-Ca in the Pellustert is quite advantageous for the soil N economy because of the increased residence time of NH_4^+ in the exchange complex. This will likely curtail the amount of NH_4^+ in soil solution available for oxidation to nitrate (NO_3^- -N) at any one time as NO_3^- -N is quite susceptible to leaching. These results would also suggest that the availability of Ca^{2+} from LAN application to the Pellustert is likely to be short-lived when Ca^{2+} and NH_4^+ are released from the congruent dissolution of this fertilizer. This means that Ca^{2+} will be rapidly leached from the soil solution if not taken up immediately by the plants. However, the slight or nearly equal preference of Ca^{2+} and NH_4^+ by the Haplustalf will have consequences for NH_4 -N and NO_3 -N availability similar to Ca^{2+} in the Pellustert.

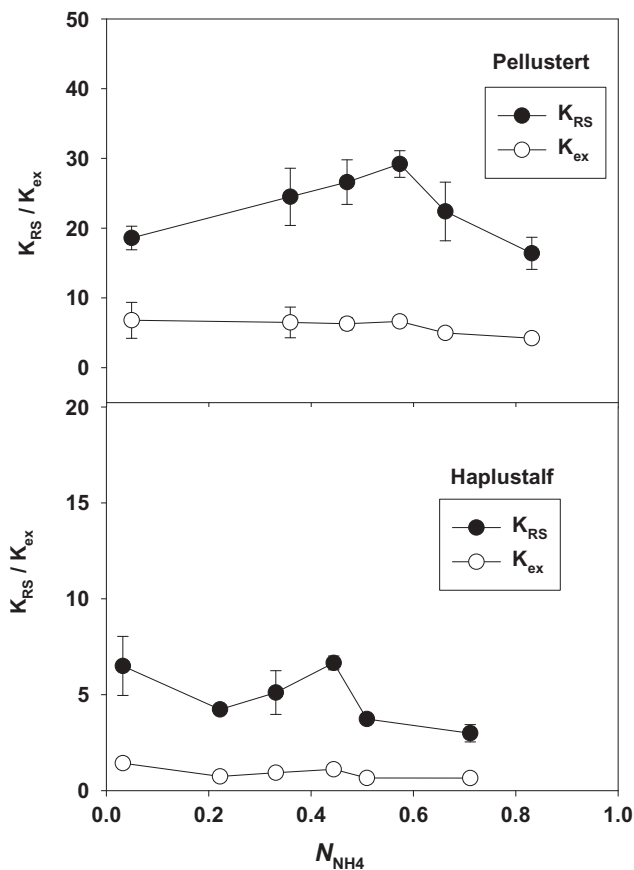


Figure 5. The variation in K_{RS} and K_{ex} as a function of NH_4^+ saturation of the exchange sites expressed either as mole fraction of NH_4^+ ($N_{NH_4^+}$) or equivalent fraction of NH_4^+ .

Conclusions

In conclusion, K_V , K_{GT} , K_D , and K_{RS} indicated preference for NH_4^+ to Ca^{2+} by Pellustert and Haplustalf from Botswana. The K_{RS} was the most stable selectivity coefficient across all exchanger phase compositions of the soils. Because K_{RS} was as consistent as K_{ex} across all exchanger phase composition, prediction of Ca^{2+}/NH_4^+ exchange and aqueous phase composition would be better made by the regular solution model than by any of the semi-empirical selectivity models. Further studies of ion exchanges in weathered tropical soils of Africa are becoming imperative in view of the severe fertilizer wastages reported in tropical Africa because of poor understanding of chemistry of the soils. This has resulted in inaccurate estimates of aqueous solution composition of soils from which plants derive the bulk of their nutrients. Soil solution composition can only be best predicted from a fairly robust ion exchange selectivity coefficient for that soil as shown by K_{RS} for the two soils evaluated in this study.

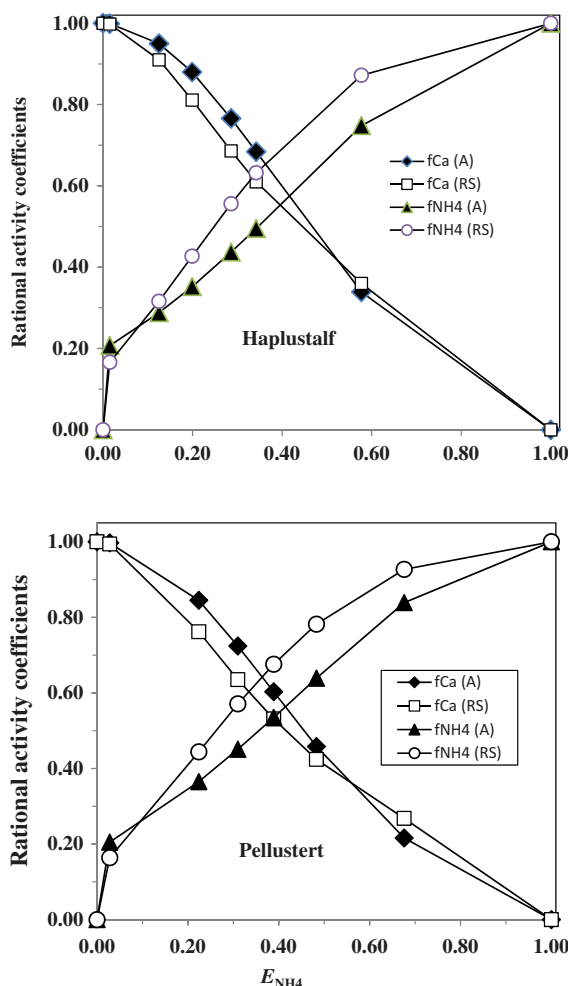


Figure 6. Rational activity coefficients of adsorbed NH_4 (f_{NH_4}) and Ca (f_{Ca}) determined by the regular solution model (RS) and Argesinger approach (A) based on Eqs. [17] and [18].

Table 5

Overall K_{ex} and K_{RS} of $\text{Ca} \rightarrow \text{NH}_4$ exchange reaction and the free energy of exchange in the two soils from Botswana

Experimental	ΔG_{ex}			
soil	${}^a \ln K_{\text{RS}}$	K_{ex}	${}^b \ln K_{\text{ex}}$	(kJ mol^{-1})
Pellustert	3.11 ± 0.23 (3.10)	5.75 ± 1.24 (5.21)	1.72 ± 0.24 (1.65)	-4.26 ± 0.59 (-4.09)
Haplustalf	1.54 ± 0.32 (1.50)	0.92 ± 0.27 (0.75)	-0.136 ± 0.35 (-0.293)	0.34 ± 0.87 (0.73)

^aMean $\ln K_{\text{RS}}$ and standard deviations were determined from Eq. [8] as a function of exchanger phase composition while the values in parentheses were based on graphical estimation using Eq. [15].

^bMean K_{ex} or $\ln K_{\text{ex}}$ values and standard deviations were computed from Eq. [18] as a function of exchanger phase composition while K_{ex} or $\ln K_{\text{ex}}$ values in parentheses were determined from Eq. [20]

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