

Potassium→ammonium exchange of two benchmark soils from Botswana and its implication for nitrogen economy of the soils

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Ion exchange preferences for NH_4^+ and K^+ by soil exchanger surface can greatly affect the NO_3^- leaching into groundwater and nitrogen-use efficiency in agricultural production. Since NH_4^+ and K^+ salts are usually applied together as fertilizers, the binary $\text{K} \rightarrow \text{NH}_4$ exchange of two benchmark Botswana soils, Pellustert and a Haplustalf, was studied to determine the selectivity coefficients and the thermodynamic exchange constant with special reference to N economy. The Vanselow and the Gaines and Thomas coefficients indicated preference for NH_4^+ by the Pellustert and K by the Haplustalf across the exchanger phase composition. The equilibrium constant (K_{ex}) was 1.807 for the Pellustert and 0.174 for the Haplustalf. The exchange free energy (ΔG_{ex}^0) was $-1.467 \text{ kJ mol}^{-1}$ for the Pellustert and $4.334 \text{ kJ mol}^{-1}$ for the Haplustalf. Negative ΔG_{ex}^0 for the Pellustert is consistent with preference for NH_4^+ to K^+ in contrast to positive ΔG_{ex}^0 for the Haplustalf. The greater stability of NH_4X than KX complex in the Pellustert, and KX than NH_4X in the Haplustalf, would mean increased residence time of NH_4^+ in the Pellustert than the Haplustalf. The implication of short residence time of NH_4^+ in soil is rapid nitrification, thereby leading to NO_3^- -N leaching losses and possible groundwater contamination.

Keywords: ion exchange; cation selectivity; exchange equilibrium constant; free energy

Introduction

Ammonium (NH_4^+) and potassium (K^+) salts are widely applied as fertilizers in Sub-Saharan Africa (SSA) including Botswana. Accurate estimates of amounts of inorganic fertilizers applied to arable fields annually may be difficult to come by in SSA, but not less than 1.5 million metric tons, consisting of 600,000 metric tons of N and 300,000 metric tons of K that are consumed annually in SSA (Naseem & Kelly 1999). The efficiency of fertilizer use is abysmally low in SSA because the theoretical bases for fertilizer recommendations are rarely founded on the understanding of basic soil chemical processes but on empirical field response trials. Consequently, high unintended nutrient losses from inorganic fertilizer applications occur frequently in the soils.

The effectiveness of N and K utilization by field crops not only depends on the cation exchange behaviour of NH_4^+ and K^+ dissociated or ionized from inorganic fertilizer salts but may also be strongly affected by calcium (Ca) and aluminium (Al) depending on soil pH (Evangelou & Lumbanraja 2002). The general preference of soils for monovalent cations, based on the lyotropic series, is $\text{Cs} > \text{Rb} > \text{K} = \text{NH}_4 > \text{Na} > \text{Li}$ (Talibudeen 1981).

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There can be exceptions to this general trend depending on the mineralogical composition of soils. In soils with micas, NH_4^+ might be strongly preferred to K^+ (Talibudeen 1981) because of the strong $-\text{NH}-\text{O}$ bond in the hexagonal cavity of the $\text{Si}-\text{O}$ tetrahedral sheet (van Bladel 1967). Lumbanraja and Evangelou (1990) who studied the exchange behaviour of K^+ and NH_4^+ in Kentucky soils, dominated by vermiculite, found that added K^+ stimulated the adsorption of NH_4^+ and consequently decreased the potential K buffering capacity of the soils. They, thus, hypothesized that adsorption of K^+ probably expanded the interlayer space of the clay, rather than inducing its collapse, thus making more sorption sites available for cation exchange reactions. The K^+ stimulation of NH_4^+ retention can only be explained by the interlayer expansion of silicate clays or simply due to a synergistic effect of K^+ (Lumbanraja & Evangelou 1990).

The cation exchange chemistry of NH_4^+ in tropical soils is not as well studied as in some temperate soils dominated by expanding layer silicate clay minerals considering the fact that N deficiency remains the main constraint to soil productivity in SSA and the transitory nature of NH_4^+ added to the soil (Brady & Weil 2004). Opuwaribo and Odu (1978) showed that K application to illitic soils from Nigeria increased NH_4^+ fixation. Ammonium fixation was reportedly greater in fine-textured soils formed from igneous and metamorphic rocks than coarser or sandy soils derived from sandy parent material (Opuwaribo & Odu 1974). In a separate study, Opuwaribo and Odu (1975) found that NH_4^+ fixation or specifically adsorbed NH_4^+ correlated with clay and cation exchange capacity, except for soils where OM was high.

The N economy of soils is greatly regulated by cation exchange characteristics. The adsorption of NH_4^+ regulates its leaching, oxidation and volatilization (Brady & Weil 2004), hence the ability of soils to preferentially adsorb NH_4^+ to other cations should make a significant contribution to N-use efficiency (NUE) and availability. Our objectives in this study were to determine the selectivity coefficients and thermodynamic exchange constant of $\text{K}^+ \rightarrow \text{NH}_4^+$ exchange reactions in two benchmark soils from Botswana, and examine the implication for N and K fertilization practices.

Theory

It is almost conventional to describe cation exchange reactions of soils by, first of all, giving a brief theoretical framework on which the experimental data will be analysed by the investigators. The binary exchange reaction of $\text{K} \rightarrow \text{NH}^+$ in a soil can be written as in Equation (1):



where X is the soil exchanger surface. The exchange reactions above can be described by a thermodynamic equilibrium constant (K_{ex}) given by Equation (2):

$$K_{\text{ex}} = \frac{(\text{NH}_4\text{X})(\text{K}^+)}{(\text{KX})(\text{NH}_4^+)} \quad (2)$$

where (NH_4X) and (KX) are the activities of adsorbed NH_4^+ and K^+ in the soil exchanger surface and (NH_4^+) and (K^+) are the activities of NH_4^+ and K^+ in soil solution. Equation (2) cannot be realistically evaluated in soils for ion exchange reactions because the activities of adsorbed cations (NH_4X) and (KX) cannot be determined (Sposito 2008), hence selectivity coefficients are commonly employed to index cation preference of soils.

There are several selectivity coefficients for describing ion exchange reactions but only a few of them have thermodynamic meanings and significance, from which actual thermodynamic equilibrium constant (K_{ex}) can be derived. Two of these selectivity coefficients are the Vanselow selectivity coefficient (K_v) and the Gaines and Thomas selectivity coefficient (K_{gt}) (Goulding 1983). Selectivity coefficients are *quasi* equilibrium constants that often vary with exchanger phase composition (Essington 2004). The K_v for $K \rightarrow NH^+$ exchange reaction described in Equation (1) can be written as Equation (3)

$$K_v = \frac{N_{NH_4}(K^+)}{N_K(NH_4^+)} \quad (3)$$

where N_{NH_4} and N_K refer to the mole fractions of NH_4X and KX , respectively. Vanselow (1932) thus equated the activities of adsorbed ions to their mole fractions in the soil exchanger surface. The mole fractions of NH_4X and KX are computed according to Equations (4) and (5):

$$N_{NH_4} = \frac{q_{NH_4}}{q_K + q_{NH_4}} \quad (4)$$

$$N_K = \frac{q_K}{q_K + q_{NH_4}} \quad (5)$$

where q_{NH_4} is the concentration of NH_4X and q_K is the concentration of KX in the soil exchange complex. The Gaines and Thomas selectivity coefficient (K_{gt}) is similar to the K_v except that the concept of equivalent fraction of an adsorbed ion is introduced (Gaines & Thomas 1953) to account for the activity of adsorbed ions. The Gaines and Thomas selectivity coefficient for the $K \rightarrow NH_4$ exchange reaction is given by Equation (6):

$$K_{gt} = \frac{E_{NH_4}(K^+)}{E_K(NH_4^+)} \quad (6)$$

where E_{NH_4} and E_K refer to the equivalent fractions of NH_4X and KX , respectively. The equivalent fractions of NH_4X and KX are computed according to Equations (7) and (8):

$$E_{NH_4} = \frac{q_{NH_4}}{q_K + q_{NH_4}} \quad (7)$$

$$E_K = \frac{q_K}{q_K + q_{NH_4}} \quad (8)$$

But, for homovalent ion exchange, in contrast to heterovalent ion exchange, K_v is numerically equal to K_{gt} because Equations (7) and (8) are mathematically the same as Equations (4) and (5). A value of K_v or $K_{gt} > 1$ shows a preference or selectivity for NH_4^+ by the soil, otherwise, there is preference for K^+ . But when K_v or $K_{gt} = 1$, the exchanger surface shows no preference to either NH_4^+ or K^+ (Sposito 2008).

Materials and methods

Experimental soils

The Ap horizons (0–20 cm) of two soils from Pandamatenga (northern Botswana) and Sunnyside (southern Botswana) were sampled for this study. The soil from Pandamatenga is dark in colour, highly productive with cracking properties tentatively classified as Pellic Vertisol in the FAO system or Typic Pellustert according to soil taxonomy (Pardo et al. 2003) with clay mineralogy consisting of some 2:1 layer silicates and kaolinite. Actually, the soils might be Alfisols or Ultisols, except that they have some cracking characteristics that intergrade at the subgroup level to Vertisols (Buol et al. 1980). The soil from Sunnyside was loamy sand classified as a Lixisol in the FAO system or a Haplustalf in soil taxonomy, with textural B horizon dominated by low activity clays but with high base saturation (Table 1).

Routine analysis

The mechanical analysis of the two experimental soils was determined by standard hydrometer method after dispersing the soil particles with sodium hexametaphosphate solution as described by Gee and Bauder (1986). The pH of the soils was measured in 1:1 0.01 M KCl with a glass pH electrode after calibrating with pH buffers at 4 and 7. The soil organic carbon (OC) was determined by dichromate oxidation method as described by Nelson and Sommers (1982). The soil exchange acidity was displaced with 1.0 M KCl solution and titrated with 0.1 NaOH (Agbenin 1995). Exchangeable bases were displaced with neutral 1.0 N ammonium acetate (NH₄OAc) solution (Rhoades 1982). K, Ca, Mg and Na in the soil filtrates were determined in inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Perkin Elmer, Rodgau, Germany). The cation exchange capacity was the summation of exchangeable bases and exchange acidity (Rhoades 1982). Selected physico-chemical properties of the soils are given in Table 1.

Ion exchange procedure

Ten grams of <2-mm sieved soil were weighed into centrifuge tube in three replications and 50 mL of solution containing variable amounts of K⁺–NH₄⁺ were added to the soil, along with 4–5 drops of acetone to inhibit microbial activity, and shaken for 30 min. The solution containing variable amounts of K⁺–NH₄⁺ consisted of a constant chloride concentration (0.1 M). The initial NH₄⁺ equivalent of the K⁺–NH₄⁺ mixture was made to

Table 1. The selected properties of the experimental soils.

Soil properties	Pellustert	Haplustalf
Textural class	Sandy clay loam (SCL)	Loamy sand (LS)
pH (KCl)	7.0	5.7
Sand (%)	59.0	78.5
Silt (%)	9.0	13.0
Clay (%)	32.0	8.5
Organic carbon (g kg ⁻¹)	6.6	8.7
Exchange acidity (mmol _c kg ⁻¹)	3.5	6.0
Effective CEC (mmol _c kg ⁻¹)	140	32
Base saturation (%)	98	81

increase from 0 to 1 while the K^+ equivalent was decreased from 1 to 0 in the mixture. The soil suspension was centrifuged and the supernatant solution discarded. The soil was re-suspended two times with the variable $K-NH_4$ solution and centrifuged, but saving the third supernatant solution to determine the equilibrium concentration of K^+ , NH_4^+ and other cations. Thereafter, the soil was repeatedly washed with ethanol solution until free of Cl^- ions tested by adding a few drops of 0.1 M $AgNO_3$ solution to the supernatant. Absence of white precipitate indicated that the soil was free of Cl^- . Adsorbed NH_4^+ and K^+ were displaced by adding 50 mL of 0.5 N $LiCl$ solution to the centrifuge tubes, shaken for 30 min and centrifuged. The clear supernatant solution was saved into 200-mL volumetric flasks. This step was repeated twice, each time saving the supernatant in the same container for the determination of K^+ and NH_4^+ . The concentrations of K^+ , Ca^{2+} , Mg^{2+} and Na^+ in the supernatant solution were determined in ICP-AES, while the concentration of NH_4 in the solution was determined by the Kjeldahl method (Bremner & Mulvaney 1982).

Data analysis

The adsorbed metal charge (Q_i) of the soil was calculated as the summation of the surface excess of NH_4 (q_{NH_4}) and K (q_K) (Suarez & Zahou 1989; Agbenin & Yakubu 2006). The ion exchange data were fitted to the Vanselow and the Gaines and Thomas selectivity equations described in Equations (3) and (6) to determine K_v and K_{gt} . The activities of NH_4^+ and K^+ in the equilibrium soil solution were determined by multiplying their concentration with their respective activity coefficients. The activity coefficient (γ) of NH_4^+ or K^+ was determined by the Davies equation (Sposito 2008) according to Equation (9):

$$\log Y = -0.512 Z^2 \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.3\mu \quad (9)$$

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 using the Marion–Babcock equation that relates EC_e to μ , given below as Equation (10) (Sposito 2008):

$$\log \mu = 1.159 + 1.009 \log EC_e \quad (10)$$

The ion exchange data reported in the paper were the means and standard deviations of three replicates.

Results and discussion

Soil properties

The two experimental soils had significant differences in physico-chemical characteristics, except for the high base saturation status that exceeded 80% in both soils (Table 1). Whereas the textural class of the Pellustert was sandy clay loam (SCL) with 32% clay, the textural class of the Haplustalf was loamy sand having less than 10% clay. The pH of the soils varied from neutral in the Pellustert to acidic in the Haplustalf. Expectedly, the effective cation exchange capacity (ECEC) was nearly four times greater in the Pellustert than the Haplustalf, apparently reflecting differences in clay quantity in addition to the

differences in pH. The mineralogy of this Pellustert reportedly consisted of some amounts of smectite and illite (Pardo et al. 2003), whereas, the mineralogical composition of the Haplustalf was mostly dominated by kaolinite (Ekosse et al. 2003). Typical of tropical soils, OC was low (less than 1%) because of the rapid rate of decomposition of organic residues. The concentration of OC was, however, slightly greater in the Haplustalf than the Pellustert.

Adsorbed cationic charge

The adsorbed metal charge (Q_i), measured as the summation of surface excess of NH_4^+ (q_{NH_4}) and K^+ (q_{K}) was less than the ECEC of the Pellustert, but was over two times greater than the ECEC of the Haplustalf (Table 2). Although there are similar reports in soils from other parts of the world (Deist & Talibudeen 1967; Evangelou & Lumbanraja 2002), the mechanisms leading to increased or decreased adsorbed metal charge in ion exchange experiments vary from one soil to the other. The relatively lower Q_i than ECEC in this Pellustert might be due to interlayer dehydration of clay colloids, particularly smectite and illite due to NH_4^+ and K^+ adsorption (Deist & Talibudeen 1967). The collapse or dehydration of the interlayer spaces precludes internal sites from participating in the exchange reactions, thereby restricting ion exchange to the external surface sites in the Pellustert.

That Q_i was nearly twice greater than the ECEC of the Haplustalf can be partly explained by displacement of H^+ from pH-dependent charge component of the CEC (Suarez & Zahou 1989; Agbenin & Yakubu 2006). This may, therefore, imply specific adsorption of NH_4^+ and K^+ by the soil. However, more importantly, colloidal particle dispersion from the weakly aggregated Haplustalf as a result of mechanical agitation or shaking adopted in the batch experiment could also have contributed to the high Q_i values. The dispersion of colloidal particles would have made more surfaces available for ion exchange reaction. Nonetheless, all these factors such as interlayer charge collapse, specific adsorption and displacement of H^+ from pH-dependent charge and dispersion of

Table 2. The equilibrium concentration of K^+ and NH_4^+ (Equil) in soil solution and the concentration of K^+ and NH_4^+ adsorbed by the soil exchanger phase (Exch).

Equil NH_4 conc. (mmol L^{-1})	Equil K conc. (mmol L^{-1})	Exch NH_4 conc. (mmol _c kg^{-1})	Exch K conc. (mmol _c kg^{-1})	Q_i (mmol _c kg^{-1})
Pellustert				
0.04 ± 0.02	101.4 ± 13.9	1.20 ± 0.67	100.9 ± 7.19	102.1 ± 7.63
4.24 ± 0.18	91.9 ± 13.8	48.4 ± 14.6	59.4 ± 7.71	107.8 ± 7.27
17.4 ± 1.46	71.5 ± 4.60	69.0 ± 8.10	51.6 ± 4.83	120.9 ± 7.24
35.0 ± 1.40	40.9 ± 4.11	73.2 ± 7.48	46.6 ± 2.51	119.8 ± 4.97
58.23 ± 2.64	23.6 ± 9.38	83.0 ± 9.08	39.4 ± 5.05	119.4 ± 3.22
78.22 ± 8.11	6.11 ± 0.17	98.1 ± 5.31	25.8 ± 2.90	124.0 ± 7.93
Haplustalf				
0.07 ± 0.01	129.1 ± 2.90	0.10 ± 0.00	88.0 ± 5.20	88.1 ± 5.20
4.62 ± 0.45	123.3 ± 5.68	4.95 ± 0.59	76.8 ± 3.16	81.8 ± 3.16
7.51 ± 0.71	100.1 ± 8.59	7.79 ± 0.28	74.0 ± 5.09	81.8 ± 5.09
30.0 ± 4.07	52.8 ± 16.8	14.2 ± 2.10	71.7 ± 3.42	85.9 ± 3.15
81.4 ± 15.9	4.92 ± 1.53	16.1 ± 1.67	70.0 ± 2.66	86.1 ± 2.49
87.0 ± 4.86	1.36 ± 0.37	29.7 ± 5.49	56.4 ± 5.16	86.0 ± 1.51

soil components are usually responsible for hysteresis in cation exchange (Verbug & Baveye 1994), hence the little or no apparent agreement between Q_i and ECEC of these soils is not entirely surprising.

The $K \rightarrow NH_4$ selectivity coefficients

For the $K \rightarrow NH_4$ exchange, the Vanselow (K_v) and the Gaines and Thomas (K_{gt}) selectivity coefficients were the same (Table 3) because there is no difference between mole fraction and equivalent fraction used to correct exchange phase activities in homovalent exchange (see Equations (3) and (6)). This is, however, in contrast to heterovalent cation exchange where K_v and K_{gt} are not numerically the same (Essington 2004; Sposito 2008). The K_v or K_{gt} for $K \rightarrow NH_4$ in the soils decreased with increasing surface saturation of adsorbed NH_4^+ ($E_{NH_4}E_{NH_4}$) for both the Pellustert and the Haplustalf (Table 3). The decreasing K_v and K_{gt} with exchanger phase composition indicated the heterogeneity of the exchange sites with regard to differences in adsorption energies (Verbug & Baveye 1994; Bricio et al. 1997). The most energetically active sites are first occupied, and with increasing surface saturation, the less energetically active sites are occupied last.

The K_v or K_{gt} values for the Pellustert were far greater than unity with surface saturation up to $N_{NH_4} = 0.39$, above which K_{gt} or K_v decreased to less than 1. In other words, the Pellustert showed preference for NH_4^+ across a wide range of exchanger surface saturation in contrast to the Haplustalf where K_v or K_{gt} was only slightly greater than 1 at $N_{NH_4} \leq 0.10$ (Table 3), suggesting that at more than 90% surface saturation there was selectivity for K^+ . The greater selectivity for NH_4^+ in the Pellustert than the Haplustalf probably reflects differences in mineralogical composition of the Pellustert and the Haplustalf. Whereas the Pellustert contains some amounts of 2:1 layer silicates in its mineralogical suite (Pardo et al. 2003), the Haplustalf's mineralogy is dominated by kaolinite (Ekosse et al. 2003).

The plot of E_{NH_4} or E_K with charged fraction in soil solution (\dot{E}_{NH_4} or \dot{E}_K) in relation to the thermodynamic non-preference isotherm line clearly indicated the preferential adsorption of NH_4^+ to K^+ by the Pellustert, and the preferential adsorption of K^+ to

Table 3. The mole fractions (N_K , N_{NH_4}) and the Vanselow (K_v) and Gaines and Thomas (K_{gt}) selectivity coefficients for $K \rightarrow NH_4$ binary exchange in two benchmark soils from Botswana.

N_K	N_{NH_4}	K_v	K_{gt}
Pellustert			
0.988 ± 0.006	0.012 ± 0.006	29.69 ± 3.50	29.69 ± 3.50
0.555 ± 0.103	0.445 ± 0.103	17.96 ± 6.69	17.96 ± 6.69
0.429 ± 0.043	0.5826 ± 0.094	5.64 ± 1.60	5.64 ± 1.60
0.390 ± 0.036	0.610 ± 0.036	1.82 ± 0.12	1.82 ± 0.12
0.3230 ± 0.051	0.677 ± 0.051	0.82 ± 0.094	0.82 ± 0.094
0.208 ± 0.011	0.792 ± 0.011	0.29 ± 0.02	0.29 ± 0.02
Haplustalf			
0.999 ± 0.000	0.001 ± 0.000	2.01 ± 0.22	2.01 ± 0.22
0.939 ± 0.009	0.061 ± 0.009	1.72 ± 0.07	1.72 ± 0.07
0.904 ± 0.009	0.096 ± 0.009	1.41 ± 0.12	1.41 ± 0.12
0.835 ± 0.027	0.165 ± 0.027	0.71 ± 0.06	0.71 ± 0.06
0.813 ± 0.019	0.187 ± 0.019	0.03 ± 0.01	0.03 ± 0.01
0.655 ± 0.061	0.345 ± 0.061	0.02 ± 0.00	0.02 ± 0.00

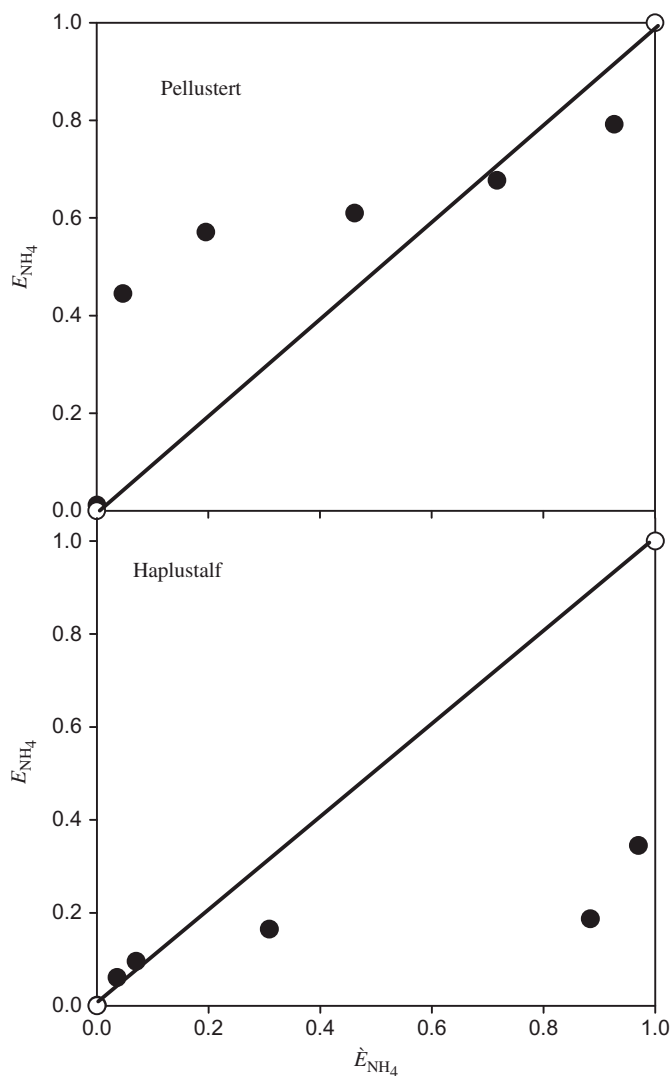


Figure 1. The 1:1 non-preference isotherm lines in relation to NH_4^+ adsorption isotherms plotted as equivalent fraction of NH_4 (E_{NH_4}) in the exchange complex versus the charge fraction (\dot{E}_{NH_4}) in soil solution.

NH_4^+ by the Haplustalf across a wide range of exchanger surface composition (Figures 1 and 2). For homovalent ion exchange the thermodynamic non-preference isotherm is $E_i = \dot{E}_i$. In other words, the equivalent fraction of the adsorbed ion i is equal to charged fraction of the ion i in soil solution (Sposito 2008). Thus, E_{NH_4} or E_K falling above the thermodynamic non-preference isotherm line indicated preference for NH_4^+ or K^+ by the soil. Across a wide range of soil exchanger surface composition, the E_{NH_4} data were above the non-preference isotherm line in the Pellustert, whereas its E_K was below the non-preference line. In contrast, whereas E_{NH_4} data points were clearly below the non-preference isotherm in the Haplustalf, the E_K values were above the isotherm line across a wide range of the soil exchanger phase composition.

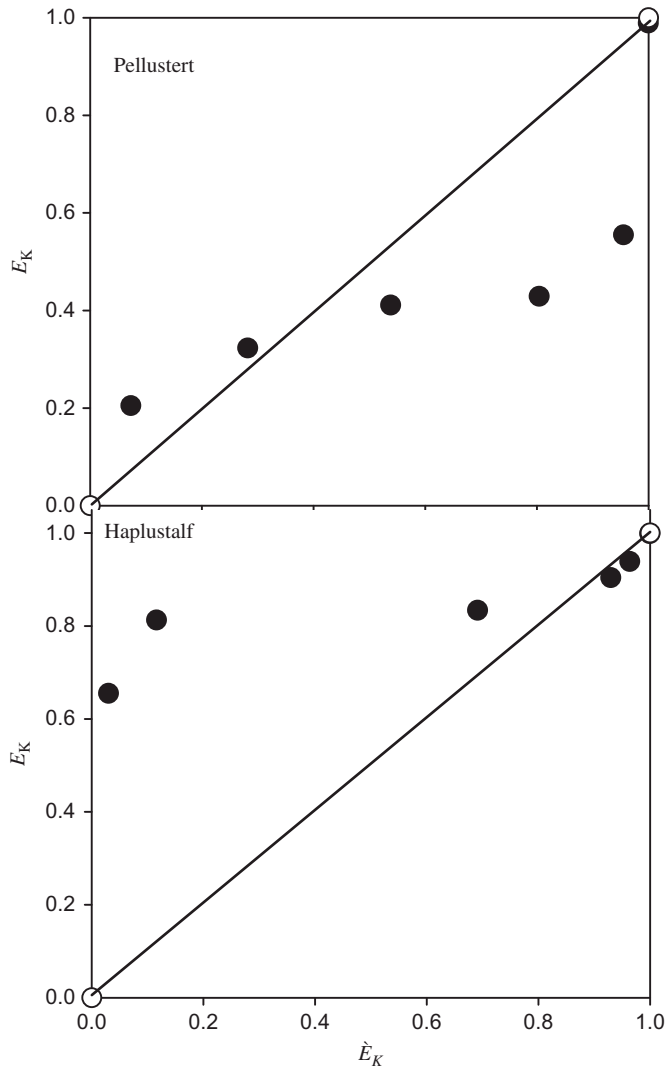


Figure 2. The 1:1 non-preference isotherm lines in relation to K^+ adsorption isotherms plotted as equivalent fraction of K (E_K) in the exchange complex versus the charge fraction (\dot{E}_K) in soil solution.

Although the crystal chemistry of K^+ and NH_4^+ is quite similar, NH_4^+ might be more strongly preferred to K^+ by smectite and micas because of the strong $-NH-O$ bond that can be formed in the hexagonal cavity of Si-O tetrahedral structure (Talibudeen 1981), and the $-OH-N-OH$ bond with the oxygen planes in the interlayer space (van Bladel 1967). Thus, the preference of NH_4^+ to K^+ by the Pellustert is somewhat consistent with the presence of smectite and illite as reported by Pardo et al. (2003) in contrast to Haplustalf. The apparent selectivity of NH_4^+ by this Pellustert whose mineralogy had some 2:1 layer aluminosilicates is in agreement with the selectivity of NH_4^+ over K^+ in vermiculite reported by Evangelou and Lumbanraja (2002) and Chappell and Evangelou (2002). On the other hand, the preference of K^+ by this Haplustalf has also been reported

for Alfisols from other tropical savanna (Udo 1978; Agbenin & Yakubu 2006; Yakubu & Agbenin 2010).

Thermodynamic exchange constant

The ultimate goal of ion exchange studies is to determine the thermodynamic exchange constant (K_{ex}) and possibly the free energy of the exchange because selectivity coefficients are mere pseudo-equilibrium constants that often vary with the soil exchanger phase composition. Thermodynamic equilibrium constant K_{ex} is usually invariant with exchanger phase composition (Goulding 1983). The K_{ex} for the $\text{K} \rightarrow \text{NH}_4$ exchange can be determined by inserting the rational or exchange phase activity coefficients (f_{NH_4}) and (f_{K}) into the Vanselow equation (Equation (3)) corrected for exchange phase activity according to Equation (11):

$$K_{\text{ex}} = \frac{(N_{\text{NH}_4} f_{\text{NH}_4})(\text{K}^+)}{(N_{\text{K}} f_{\text{K}})(\text{NH}_4^+)} \quad (11)$$

where f_{NH_4} and f_{K} are rational activity coefficients of adsorbed NH_4^+ and K^+ , respectively. If Equation (11) is compared with Equation (3), it becomes clear that K_{ex} can be determined from K_{v} by substituting Equation (3) into Equation (9) to yield the following Equation (12) (Essington 2004).

$$K_{\text{ex}} = \frac{f_{\text{NH}_4}}{f_{\text{K}}} K_{\text{v}} \quad (12)$$

where f_{NH_4} and f_{K} were determined by the Argesinger approach according to Equations (13) and (14) (Sposito 2008):

$$\ln f_{\text{NH}_4} = -(1 - N_{\text{NH}_4}) \ln K_{\text{v}} - \int_{N_{\text{NH}_4}}^1 \ln K_{\text{v}} dN_{\text{NH}_4} \quad (13)$$

$$\ln f_{\text{K}} = N_{\text{NH}_4} \ln K_{\text{v}} + \int_1^{N_{\text{NH}_4}} \ln K_{\text{v}} dN_{\text{NH}_4} \quad (14)$$

The exchange phase activity coefficients represented by Equations (13) and (14) were determined from the linear relations between $\ln K_{\text{v}}$ and N_{NH_4} . Since the resulting relation was not linear throughout the soil exchanger phase composition (Figure 3), the linear portion of the curve was employed to evaluate Equations (13) and (14) as described elsewhere (Essington 2004; Agbenin & Yakubu 2006; Sposito 2008). Table 4 gives the exchange phase activity coefficients and K_{ex} as a function of the soil exchanger phase composition. As a true thermodynamic exchange constant, K_{ex} was fairly consistent throughout the exchanger phase composition in contrast to the decreasing K_{v} or K_{gt} with increasing surface saturation of NH_4^+ . The K_{ex} of the Pellustert was greater than unity (mean $K_{\text{ex}} = 1.988$; $\ln K_{\text{ex}} = 0.687$) at every exchanger phase composition, whereas for the Haplustalf, its mean K_{ex} was less than unity (mean $K_{\text{ex}} = 0.173$, $\ln K_{\text{ex}} = -1.754$).

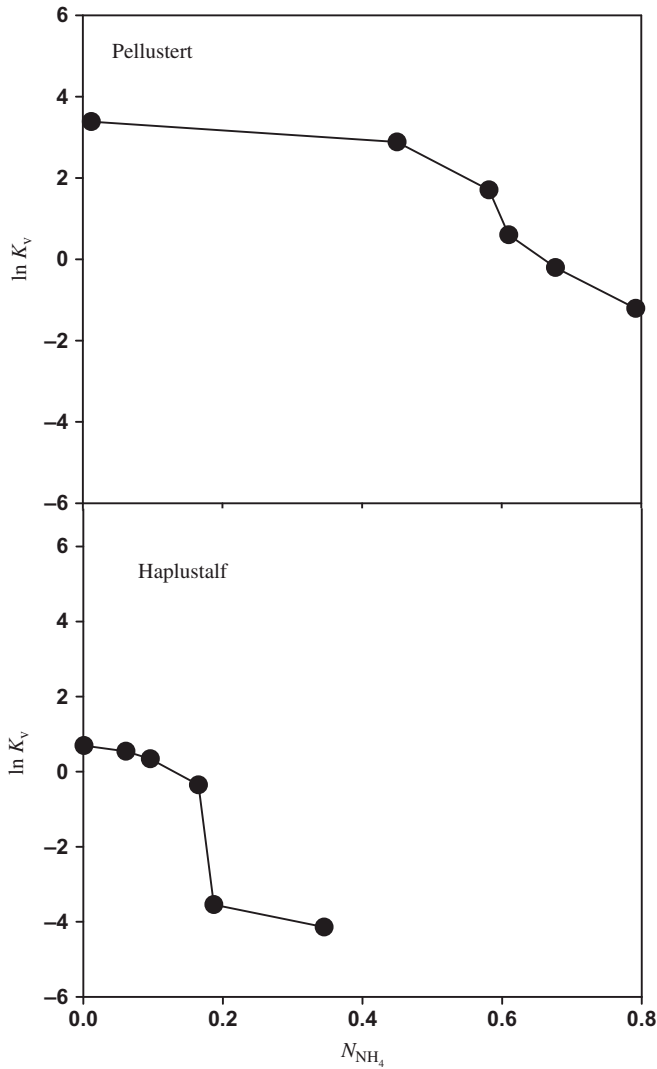


Figure 3. The relationship between $\ln K_v$ and the mole fraction of adsorbed NH_4 by the two soils.

The overall K_{ex} determined by integrating $\ln K_v$ over the whole range of the exchanger surface composition according to Equation (15):

$$\ln K_{ex} = \int_0^1 \ln K_v \, dN_{NH_4} \quad (15)$$

gave K_{ex} value of 1.807 or $\ln K_{ex} = 0.592$ for the Pellustert and 0.174 $\ln K_{ex} = -1.747$ for the Haplustalf (Table 5) which were fairly consistent with mean values of K_{ex} from Equation (12). The free energy of exchange reaction (ΔG_{ex}^0) was derived from Equation (16):

Table 4. The rational activity coefficients (f_{NH_4} , f_{K}) and thermodynamic equilibrium constants (K_{ex}) in relation to the exchanger phase composition of K \rightarrow NH $_4$ exchange (N_{NH_4} , N_{K}) in the soils.

N_{NH_4}	N_{K}	f_{NH_4}	f_{K}	K_{ex}
Pellustert				
0.012 \pm 0.006	0.988 \pm 0.006	0.999 \pm 0.000	0.001 \pm 0.000	2.42 \pm 0.28
0.445 \pm 0.103	0.555 \pm 0.103	0.894 \pm 0.016	0.1068 \pm 0.016	1.84 \pm 0.71
0.5826 \pm 0.094	0.429 \pm 0.043	0.615 \pm 0.024	0.385 \pm 0.024	1.21 \pm 0.25
0.610 \pm 0.036	0.390 \pm 0.036	0.314 \pm 0.017	0.686 \pm 0.017	1.52 \pm 0.28
0.677 \pm 0.051	0.3230 \pm 0.051	0.167 \pm 0.030	0.833 \pm 0.030	2.48 \pm 0.58
0.792 \pm 0.011	0.208 \pm 0.011	0.098 \pm 0.001	0.902 \pm 0.001	2.46 \pm 0.10
Haplustalf				
0.001 \pm 0.000	0.999 \pm 0.000	0.999 \pm 0.000	0.082 \pm 0.000	0.16 \pm 0.02
0.061 \pm 0.009	0.939 \pm 0.009	0.913 \pm 0.011	0.089 \pm 0.001	0.17 \pm 0.01
0.096 \pm 0.009	0.904 \pm 0.009	0.838 \pm 0.024	0.097 \pm 0.003	0.16 \pm 0.01
0.165 \pm 0.027	0.835 \pm 0.027	0.577 \pm 0.069	0.143 \pm 0.017	0.18 \pm 0.03
0.187 \pm 0.019	0.813 \pm 0.019	0.109 \pm 0.010	0.750 \pm 0.073	0.20 \pm 0.02
0.345 \pm 0.061	0.655 \pm 0.061	0.088 \pm 0.002	0.927 \pm 0.018	0.17 \pm 0.02

Table 5. The overall equilibrium constant (K_{ex}) and free energy of exchange (ΔG_{ex}^0) for K \rightarrow NH $_4$ exchange calculated from Equations (15) and (16), respectively, for the two benchmark soils from Botswana.

Experimental soils	K_{ex}	$\ln K_{\text{ex}}$	ΔG_{ex}^0 (kJ mol $^{-1}$)
Pellustert	1.807	0.592	-1.467
Haplustalf	0.174	-1.747	4.328

$$\Delta G_{\text{ex}}^0 = -RT \ln K_{\text{ex}} \quad (16)$$

where R is the universal gas constant and T is the absolute temperature. The negative ΔG_{ex}^0 for the K \rightarrow NH $_4$ in the Pellustert (Table 5) clearly indicated that NH $_4X$ was more stable than KX . Similarly, the positive ΔG_{ex}^0 value in the Haplustalf showed that NH $_4X$ was less stable than KX . Clearly, the binary K \rightarrow NH $_4$ exchange characteristics between the Pellustert and Haplustalf from Botswana are quite different from each other. While the Pellustert had preference for NH $_4^+$ to K $^+$ the Haplustalf had preference for K $^+$ to NH $_4^+$.

Soil N economy and environmental implications

The K-NH $_4$ interactions in the soils were not straightforward and did not behave as true chemical exchange partners with equal preference by the soils. The results of the K \rightarrow NH $_4$ exchange in the two soils have some implications for N and K fertilization and the use of ammonium acetate for assessing cation exchange characteristics of the soils. The greater stability of NH $_4X$ complex in the Pellustert than the Haplustalf is quite advantageous for NUE in this soil. In most soils, added NH $_4^+$ has a short residence time of a few hours to 96 hours before it is completely oxidized or nitrified to NO $_3^-$ -N (Brady & Weil 2004). Soil NO $_3^-$ -N is highly mobile and susceptible to leaching losses, hence the preferential retention of NH $_4^+$ by any soil curtails the amount of NH $_4^+$ available for microbial nitrification or oxidation to NO $_3^-$ -N at any given time (Chappell & Evangelou 2000).

Consequently, NO_3^- -N leaching losses in this Pellustert will be significantly less than the Haplustalf.

In the Haplustalf, however, K^+ was preferred to NH_4^+ , suggesting that K^+ can effectively displace NH_4^+ in the exchange complex of the soil. Displacement of NH_4^+ by K^+ from the soil exchange sites makes added NH_4^+ susceptible to microbial oxidation or rapid nitrification. Consequently, leaching losses of NO_3^- -N will be predictably higher in this Haplustalf than the Pellustert when NH_4^+ and K^+ salts are applied together as fertilizers. The low NUE in SSA can be partly explained by the preferential retention of K^+ when compound NPK fertilizers are applied to the soils. A less important observation, however, is the appropriateness of the use of ammonium acetate for displacing exchangeable K and determination of CEC in weathered soils of tropical semi-arid regions like the Alfisols with high selectivity for K^+ . These measurements may be prone to errors, but the errors are, however, unlikely to be significant though because of the relatively high concentration of ammonium acetate (1.0 N) employed in displacing cations from the exchange sites.

Conclusion

In conclusion, NUE and leaching in soils of SSA are more likely to be controlled by cation exchange behaviour between NH_4^+ and other cations, particularly K^+ , Ca^{2+} and Mg^{2+} , than by any other soil properties.

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