NH4+ Fixation and Ionic Competition with K+ in a Clayey Soil from Ocumare Del Tuy, Venezuela

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ABSTRACT

Ammonium and potassium are essential for plant production, both share an ionic potential capable of entering the structure of some 2:1 type clay minerals, remaining fixed. Although, in Venezuela there are abundant areas with the presence of this type of clays, ammonium fixation (NH_4f) has been little studied. The soil studied located in Los Valles del Tuy, Miranda State, presented clayey texture, some textural homogenization, and little differentiation in horizons, which is characteristic of Inceptisols. That soil also evidenced by XRD the abundant presence of nontronite / montmorillonite, resulting in a semi-quantification of 20% and 16.4% for the surface and subsoil horizons, respectively. The fixation of ammonium and the competition with potassium to occupy the fixed sites of these clays were studied by means of an incubation experiment, varying the concentration of K^+ and keeping the concentration of NH_4^+ fixed, then extracting and determining the fixed ammonium by a photocolorimetry method. The soil presented a great ammonium fixing capacity, 49% of the total added was fixed in the absence of the competitive ion; however, NH_4f fell drastically when both ions were added simultaneously, decreasing exponentially under increasing amounts of the competitive ion and staying constant around 8%. It seems possible that, the high toxicity induced by excessive fertilisation with ammonium sulfate could be counteracted in soils with capacity to retain K, if, at the expense of Kf, the levels of K in the soil solution are increased causing a decrease in the concentrations of N in the tissue.

Keywords: *2:1 Clays, Ionic competition, Potassium, Nontronite, Montmorillonite, Fertilization.*

Highlights of this paper

- An incubation experiment was used to study the competition between ammonium and potassium for fixed adsorption sites in 2:1 clays.
- Toxicity induced by ammonium fertilization could be counteracted, if, at the expense of ammonium fixed, levels of K in soil are increased, causing a decrease in N concentrations in plant-tissues.

1. INTRODUCTION

Nitrogen (N), potassium (K) and phosphorus (P) represent the main essential elements for plant production. N plays a primary role in growth, development and multiple functions in plants. In soil, N is found in: i) organic forms, as part of the organic matter, either in the process of decomposition, and/or in the highly decomposed organic form (humus), ii) in inorganic forms as ammonium (NH_4^+) and nitrate (NO_3^-) ions, and to a lesser extent as nitrite (NO_2^-) [1, 2].

Natural ecosystems are supplied with N basically through the N biological fixation processes [1, 3], and to a lesser extent by contributions from wet and dry precipitations. However, intensive-managed agrosystems, in order to achieve adequate biomass production, need to use generous amounts of nitrogenous fertilisers, generally based on nitrate or ammonium salts. It is noteworthy that in agrosystems, a significant proportion of this N, is also lost through leaching, volatilisation and denitrification, thus strongly contributing to environmental deterioration and global warming [4].

Losses of N by leaching are more accentuated in soils with coarse textures and in soils with a high rate of nitrification (e.g. microbiological oxidation of ammonium to nitrates) as the nitrate ion, is not mostly adsorbed in the fine fraction of the soil [1, 5]. However, if 2:1 type clays such as illite, montmorillonite and vermiculite are presented in the soil, N-NH_4 losses can be minimised due to the high capacity of these clays to irreversibly retain the ammonium that reaches the system. This form of ammonium immobilised in the soil has been called "fixed ammonium" (NH_4f). NH_4f corresponds, therefore, to the adsorption or absorption of partially irreversible ammonium ions by the mineral or organic fraction of the soil, in such form, that these ions are not exchangeable by traditional cation exchange methods [6-9].

When considering the levels of adsorbed ammonium, and the greater or lesser facility of its exchange, it is convenient to differentiate, the fixed ammonium in a "native" form from the ammonium fixed "artificially", the former referring to the ammonium originally retained during the processes of soil formation, and the second, to an additional fixation (adsorption) product of the application of ammoniacal fertilisers or generated by the soil internal processes of mineralisation-ammonification [8, 10, 11].

NH_4^+ and K^+ ions have a very similar physical appearance since they have similar ionic radii (0.143Å, 0.133Å, respectively) and low hydration energy, moreover, both ions fit exactly into the ditrigonal holes in the basal oxygen plane of the 2:1 type clay minerals. Therefore, in those clays, NH_4^+ and K^+ ions present the same fixation mechanism, which results in a competition of both ions for the same exchangeable and non-exchangeable sites (adsorbed and fixed) [8, 12-14].

The penetration of NH_4^+ and K^+ ions into the intermediate layers of clay minerals causes the silicate layers to collapse at 1 nm, the ions are then trapped between the clay layers and, consequently, they do not participate to a greater extent in the exchange reactions [15].

Despite the fact that in Venezuela there are important geographical areas with abundance of 2:1 clays [11, 16], many under intensive agriculture, in which nitrogenous fertilisers are used [11], there are no major publications on the fixation of ammonium in clays of Venezuelan soils. 2:1 clays are capable of immobilise significant amounts of

nitrogenous fertilisers that can interfere with the potassium fertilisation and induce K deficiencies in plants [17]. Likewise, high percentages of NH₄f in soils can function as a potential reservoir of exchangeable ammonium [8, 11].

This contribution presents information on the mineralogical characterisation and the ammonium fixation in a Venezuelan expansive clay, emphasis will also be placed on an incubation experiment, where the process of competition between the ammonium (NH_4^+) and potassium (K^+) ions for adsorption sites on that clay will be studied.

2. MATERIALS AND METHODS

2.1. Study Site

The studied soil comes from the sub-region Valle del Tuy, Miranda state, with a monsoon climate zone, transitional between tropical savannah and forest, typical of foothill regions or intramontane valleys and with temperatures that vary between 22 and 29ºC, the area has poorly consolidated sediments belonging to the Tuy and Tucutunemo geological formations with a predominance of savannah-type vegetation [18].

2.2. Soil Sampling

The sampling corresponds to a profile previously described [14]. Sampling was carried out from several subsamples, both from the surface horizon and from the subsoil, to form two composite samples.

2.3. Physical, Mineralogical and Chemical Characterisations

2.3.1.Physical Characterisation

The Bouyoucos method was used for the determination of the textural classification of the sediments, in triplicate samples for both soil horizons.

2.3.2. Mineralogical Characterisation

It was performed by X-ray diffraction (XRD) using the powder method, according to the procedure described by Moore and Reynolds [19]. The minerals present in both profile depths were semi-quantified according to the treatment described by Pozas, et al. [20].

2.3.3. Chemical Characterisation

2.3.3.1. Determination of Ammonium Fixation

The fixed ammonium from the deep horizon (subsoil) was determined by a modification of the method proposed by Zhan, et al. [21].

5g of soil were weighed in two flasks, and sterilisation was carried out using the Autoclave at 120ºC and 1 atm pressure, then $2\ mEq.100g^{-1}$ soil was added to one of the flasks as 5 mL of NH₄Cl, and in the other, 5 mL of deionized water, to obtain a 1:1 soil:solution ratio. To further inhibit microbial activity, a couple of drops of toluene were added to each vial. Treated samples were left to incubate in the laboratory for 48 h. Once the equilibrium was completed, the unfixed ammonium (sample treatment with NH₄Cl), and the original exchangeable NH_4^+ (sample without addition of NH₄Cl) were extracted by adding 50 mL of a KCl solution (1 M) to each vial, following this, samples were stirred at a speed of approximately 100 rpm for 2 h. Once the period of agitation was over, they were allowed to decant, filtered and the extracts were transferred to flasks. After this, it was necessary to add another 45 mL of the KCl solution in each vial to ensure that all the ammonium was extracted, solutions were shaken and left to decant for 10 min to filter again and calibrate to 100 mL, Finally, the extracts were transferred to bottles for later analysis.

Ammonium determination was carried out by means of a colorimetric method through the formation of a coloured complex of indophenol blue according to the procedure described by Wang and Oien [22]. The determinations were performed in triplicate.

Fixed ammonia was calculated using the following equations:

NH_4^+ (not fixed) = NH_4^+ (in filtrate) - NH_4^+ (exchangeable).

NH_4^+ (fixed) = NH_4^+ (added) - NH_4^+ (not fixed).

2.3.3.2. Competition Experiments

It was carried out through an experiment similar to the one previously described, but with the addition of ammonium and potassium salts simultaneously, the ammonium concentration being constant in all cases of $2mEq.100g^{-1}$ soil and the potassium level variable (0, 2, 5, 10 and 20 $mEq.100g^{-1}$ soil, respectively). The amount of ammonia fixed in each experimental point was calculated using the same equations than above.

2.4. Statistical

All measurements were performed in triplicate in order to evaluate the precision of the techniques and methods. The values were reported as the arithmetic mean of the triplicates followed by the standard error calculated for each one.

3. RESULTS AND DISCUSSION

3.1. Soil Textural Characterisation

The studied soil can be classified according to the taxonomy (USDA Taxonomy Soil) as an Inceptisol due to its, field observed incipient development of horizons. The textural classification of the soil indicates a very similar grain size distribution, which can be attributed to the low soil evolution, which generates low differentiation and textural homogenization throughout the profile. Both horizons presented a predominance of the clay fraction (<2 μ) with more than 40%, followed by silt (approximately 39%) and finally, a low percentage of sand, less than 20% (Table 1), both horizons were textural classified as clay.

Table 1. Textural characterisation of the samples.

Soil Horizon	% Sand	% Silt	% Clay	Texture
Surface	20.0 ± 0.1	38.7 ± 0.1	41.3 ± 0.1	Clay
Subsoil	19.0 ± 0.7	39.1 ± 0.7	41.9 ± 0.1	Clay

3.2. Mineralogical Classification of Soil By X-Ray Diffraction

In the surface horizon, the presence of quartz, albite, nontronite and kaolinite was evidenced (Table 2), coinciding with a previous report which pointed out the existence, in the zone, of 2:1 clays, specifically of the smectite group [18, 23].

The presence of this clay may be due to the little soil evolution, in which the incipient weathering has not completely altered the structure of the nontronite, avoiding its dealkalinisation to cause a subsequent formation of kaolinite. On the other hand, the subsoil presented, the predominance of practically the same minerals found in the surficial soil. The mineralogical similarity in both horizons highlights, the incipient alteration, and the consequent little differentiation of the soil profile, which is characteristic of the Inceptisols.

The semi-quantification of the minerals showed predominance of quartz in both analysed horizons (37.5%), which can be attributed to the high stability of this mineral to be altered, with a relative accumulation in relation to the other minerals (Table 2); it is followed in abundance by albite (25.0-31.5%).

Soil Horizon	%Quartz	%Albite	%Nontronite/ Montmorillonite	%Kaolinite
Surface	37.2	25.0	20.0	17.8
Subsoil	37.5	31.5	16.4	14.6

In the superficial horizon the content of nontronite (smectite) is important (20%), while in the deeper horizon, the 2:1 clay is of the montmorillonite type and reaches 16.4%. Likewise, the presence of 1:1 clays of the kaolinite type with values of 17.8 and 14.6% in the superficial and deep horizon, respectively, was also reported (Table 2).

3.3. Exchangeable Ammonium and Ammonium Fixing Capacity

The (original) exchangeable ammonium value of the soil is relatively high (0.53 ± 0.1 $mEq.100g^{-1}$), taking into consideration, that it is a deep horizon with very little root activity and no major presence of organic matter, which could have influenced those values (Table 3). The value is higher than the one reported ($0.07\,mEq.100g^{-1}$) in savannahs with weathered soils of Central Venezuela, characterised by abundance of kaolinitic clays [24], or with those of an Entisol cultivated with rice in Japan (0.19 $mEq.100g^{-1}$) [25].

Table 3. Exchangeable ammonium content and ammonium fixation capacity of the sediment.

Exchangeable NH₄ $mEq.100g^{-1}$	Fixed Ammonium $mEq.100g^{-1}$	% NH₄ fixed
0.53 ± 0.1	$0.98\ \pm\ 0.04$	49

In the studied subsoil, in the absence of competitive ions, half of the NH_4 added in the form of NH_4Cl was fixed (0.98 ± 0.04, Table 3), which highlights the importance of NH_4f in nitrogenous nutrition for crops growing in that soil. Under this strong ammonium fixation, N–NH_4 is not immediately usable for crops, however, it remains protected from losses due to leaching, nitrification and potential gaseous losses, therefore, it constitutes a soil potential reserve of N in periods of high demand or/and low availability for crops.

It has been pointed out that NH_4f in soils has a wide range, which is related to differences in parent materials [9]. There may also be large differences at the regional scale [8, 26]. Nieder, et al. [8] in soils with high 2:1 clay content, recorded NH_4f values as high as 7.7 $mEq.100g^{-1}$.

3.4. Competition Between NH_4^+ and K^+ for Fixed Adsorption Sites

The deep horizon sediment used in this experiment showed a high capacity to fix ammonium, which is probably a consequence of its abundance in bentonite clays (Table 2). This high fixation, however, was strongly affected by the presence of the potassium ion, which competes in this montmorillonite clay with NH_4^+ to occupy the fixed adsorption sites. Consequently, the amount of NH_4^+ retained in an environment without competitive ion (without addition of K ion) drops drastically when similar doses of potassium and ammonium are supplied (Table 4). Figure 1 illustrates how the fixation process decreases exponentially with increasing doses of potassium in solution, reaching low levels of fixation after a potassium dose of 5 $mEq.100g^{-1}$ Figure 1, Table 4. At higher K concentration, a minimum of ammonium fixation was reached, maintaining a constant fixation behaviour around 0.17 mEq $NH_4^+.100g^{-1}$ fixed Table 4, this value may be taken as the minimum capacity of ammonium fixation in that clay.

The trend obtained in the NH_4-K competition experiment was, in general, the same as that found in other incubation experiments already done in soils with 2:1 clays [8, 12, 13, 21].
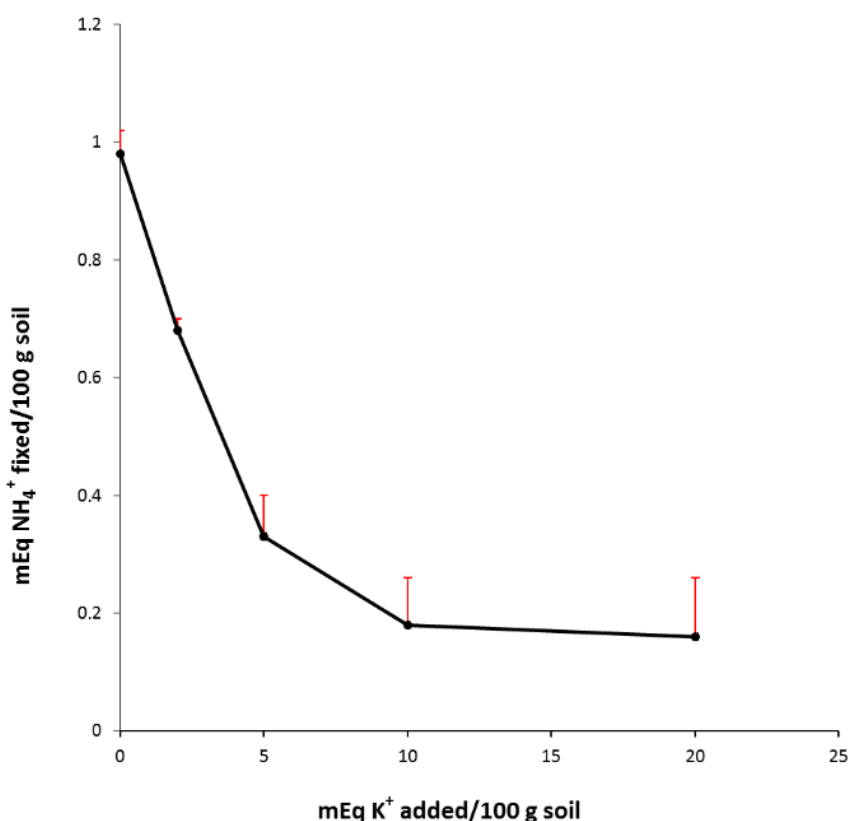
Figure 1. Variation of fixed ammonium with different doses of potassium (KCl). Ammonia (NH₄Cl) was applied in constant doses of $2\ mEq.100g^{-1}$.

Fertilisation with high levels of ammonium sulfate can induce a toxicity problem in plants [27] mainly due to a reduction in K incorporation [17]. Therefore, if, at the expense of K immobilised in 2:1 clays, the levels of K in soil solution are increased, the toxicity of ammonium may decrease as a result of K-NH₄ competition which, in turn, might cause a reduction in N concentrations in plant tissue [28]. On the other hand, a moderately low ammonia fertilisation would favour the fixation of potassium, thus serving as a potential reserve of this nutrient for future use by plants.

Table 4. NH₃⁺ fixation, when K⁺ and NH₄⁺ ($2\ mEq.100g^{-1}$) were added simultaneously.

K⁺ added $mEq.100g^{-1}$ soil	NH₄⁺ Fixed $mEq.100g^{-1}$ soil	% NH₄ fixed
0	0.98 ± 0.04	49
2	0.68 ± 0.02	34
5	0.33 ± 0.07	16.5
10	0.18 ± 0.08	9
20	0.16 ± 0.10	8

4. CONCLUSIONS

The studied montmorillonite clay has a high ammonium fixation capacity. This high ammonium fixation decreases drastically when similar doses of ammonium and potassium salts ($2.0\ mEq.100\ g^{-1}$ of NH₄Cl and KCl) are added simultaneously to the soil. Under higher doses of KCl, NH₄ fixation reaches very low levels (8%).

The high toxicity that can be induced by excessive fertilisation with ammonium sulfate could be counteracted in soils with capacity to retain K, if at the expense of Kf, the levels of K in the external concentration are increased, which could reduce the toxicity of the ammonium by causing a decrease in N concentrations in the tissue.

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44

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