Albanian j. agric. sci. 2013;12 (4): 675-681 *Agricultural University of Tirana*

RESEARCH ARTICLE **(Open Access)**

Effect of potassium on fixation of ammonium by clay minerals in different soil layers

AGELDA AJAZI[1*], LIRI MIHO[2], AIDA BANI[1], ARDIAN MAÇI[1]

[1]Agro-Environmental Department, Faculty of Agriculture and Environment, Agricultural University of Tirana, Albania

[2]Center of Agricultural Technology Transfer, Lushnjë

Abstract

In intensive agriculture systems, efficient nutrient use is necessary for high crop yields as well as for sustainable environment management. Fixation of NH_4^+ and K^+ by soil clays affect N and K availability to plants. Latest studies indicates that non-exchangeable NH_4^+, may affect crop productivity and soil N dynamics more than previously thought. An incubation study with K_2SO_4 and NH_4NO_3 was conducted to evaluate NH_4^+ and K^+ fixation in two southern Albanian soils. Soils contained significant amount of native-fixed NH_4^+ and showed relatively high NH_4^+ fixing capacity. Native fixed ammonium content varied for horizons Ap and BCg, from 97 to 133 mg/kg and accounted for between 5 to 19, 8 % of the total nitrogen, respectively . Ammonium fixation was increased with N rates and was reduced with increased K rates. When K was added to the soil prior to the NH4, the amount of ammonium fixed was reduced. By contrast, when K^+ and NH_4^+ were added to the soils simultaneously (equivalent amount; 2mEq/100g), the ammonium fixation was increased somewhat in the BCg horizon , whereas no such preference for ammonium fixation was found in the Ap horizon. In case when NH_4^+ and K^+ were added to the soil samples in form of solutions, containing equal amounts of NH_4^+ (corresponding to 2 mEq NH_4^+/100 g soil) but varying amounts of K^+, the capacity of the soil to fix ammonium was reduced in proportion to the amount of K^+ added. The soil samples incubated anaerobically, were with high differences in clay minerals content. The dominate clay minerals for profile (I-Ap horizon) are smectite > vermiculite > Ilite, while vermiculite plus ilite (as the most important clay fixed minerals), comprised 21% of clay fraction and 13 % of the soil. In the profile (II-BCg horizon), the dominant clay minerals ranged; vermiculite > Ilite > smectite, while (vermiculite + ilite), comprised 52% of the clay fraction and 23, 4 % of the soil. Studies on Ap and BCg horizons comparing the amount of NH_4^+ fixed for equivalent of amount of added cation showed that the NH_4^+ in BCg horizon was fixed in greater quantities than in Ap horizon.

Key words: non-exchangeable NH_4^+, ammonium fixation, clay minerals

1. Introduction

Nitrogen and potassium are major nutrients in crop fertilization. Nitrogen is a unique nutrient that can be absorbed either as the cation NH_4^+ or the anion NO_3^- [12]. For K, the monovalent cation K^+ is the ionic form in soil and is taken up as such by plants. NH_4^+ and K^+ share similar valence and size properties, and consequently compete for the same exchangeable and non-exchangeable sites of soil particles. Many soils have the ability to bind potassium (K^+) and ammonium (NH_4^+) in such a manner that they cannot readily be replaced by other cations [15]. The grater the layer charge, the stronger the interlayer bond. The minerals are non expanding and the interlayer cations are not exchangeable. For vermiculites, forming intermediates in layer charge, the Ca^{2+} , Mg^{2+} and Na^+ ions interlayer position are exchangeable, but K^+ and NH_4^+ are not exchangeable by ordinary procedures (Figure 1).

As reported earlier [13], inorganic cations, e. g. , NH_4^+(radius of 0. 143) or K^+(radius of 0. 133), can be fixed in hexagonal cavity (radius of 0. 140 nm) of silicate tetrahedral sheets of the tetrahedral-substituted or octahedral-substituted layer charges. The K^+ and NH_4^+ are, thereby, “trapped” between the silica sheets, and are largely withdrawn from exchangeable reaction. The equilibrium for fixed soil NH_4^+ ions is based on a scheme for K^+.

$$(NH_4^+ + K)_s \leftrightarrow (NH_4^+ + K)_e \leftrightarrow (NH_4^+ + K)_f$$

In this scheme the intermediate NH_4^+ or (K^+) ions probably occupy interlayer sites close to the edge of the clay crystals either as exchangeable with H^+ or K^+ or recently fixed from fertilizer sources. Therefore, the concentrations of K^+ ions in the soil solution and in the exchange sites are important factors regulating rates of NH_4^+ fixation and release. Reports found that K^+ application enhanced NH_4^+ fixation but reduced the amount of exchangeable NH_4^+ on the clay surface, [9].

Correspondence: Agelda Ajazi; *Agricultural University of Tirana, Albania*; Email: **agelda. ajazi@gmail. com**

(Accepted for publication 24 November 2013)

***ISSN**: 2218-2020, © Agricultural University of Tirana*

Application of the fertilizer ammonium sulfate to different soil types from China in incubation experiments significantly altered the distribution between pools of native K and added K in the soils, [18]. The depressive effect of K^+ on fixation of NH_4^+ has been the subject of a number of investigations. The fixation of NH_4^+ was reduced by K addition before NH_4^+, and the reduction was proportional to the amount of K previously fixed, [7]. In the presence of K, NH_4^+-N concentrations increased 4. 1 fold when N fertilizer was applied and 3. 5 times in absence of N application [17]. Non-exchangeable ammonium is not a static fraction, but may be involved in the N dynamics of soils [11].This mean that, the pool of non-exchangeable ammonium can thus fraction as a kind of buffer which contributes to reduction of N emission from soils on the one hand and provides mineral N to crops on the other hand [14]. Increasing NH_4^+ fixation can be a way in building up an available N pool in soils to optimize crop recovery and minimize N losses into the environment [10], as the NH_4^+ ions after penetration into the clay minerals interlayers are excluded from nitrification [6], and are thus protected against leaching. It was the purpose therefore of this study to determine the capacity of the soil to fix ammonium and to relate this fixation to their clay mineralogy. In addition studies were conducted on e comparison of fixed ammonium to the interrelationship between K^+ and NH_4^+. We want to add in the present paper, that this is the first scientific study about the ability of Albanian soils to fix NH_4^+.

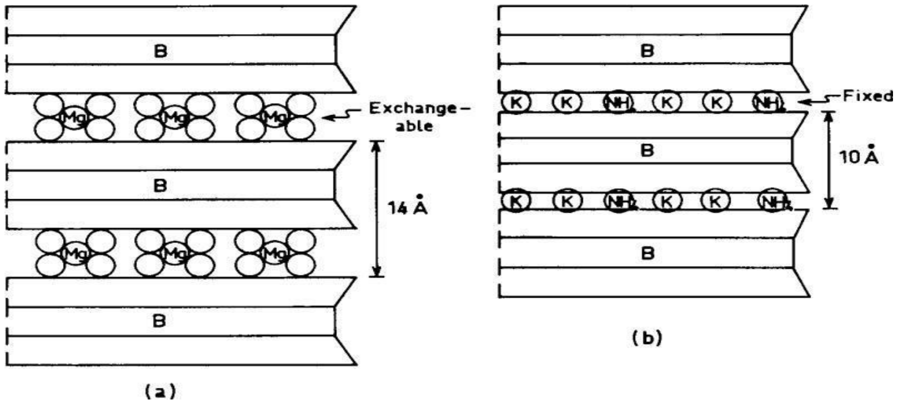

Figure1-Schematic picture of the structure of vermiculite (Nommik & Vahtras 1982); (a) Expanded vermiculite lattice with Mg^{2+} ions (hydrated) in the interlayer position; (b) Collapsed lattice of vermiculite after K^+ or NH_4^+ saturation; B-brucite layer

2. Materials and methods

2. 1. Experiment design

An extraction method was developed that enables measurements of fixed NH_4^+ in two different layers with different content of clay minerals, after extraction of exchangeable NH_4^+ (Fig. 2). In the soil samples, increasing of K^+ were added in form of K_2SO_4 solutions of varying concentration. The volume of added solutions was kept constant. After 48 hours, NH_4^+ in quantities corresponding to 2 mEq per 100 g soil were added to the sample. NH_4^+ and K^+ were added to a series of soil samples in the form of mix solutions containing equal amounts of NH_4^+ (corresponding to 2 mEq NH_4^+ per 100 g soil) but varying amounts of K^+ .

2. 2 Soil used in this experiment

Soil samples used in the experiment were collected from Synej (Kavajë) 0-27 cm (Ap-horison) and Dajc (Shkodër) 110-140 cm(BCg-horison) depth, respectively identified as Soil (I) and Soil (II) . Synej provinces extends between 19^{o}30'39" East and 41^{0}11'51" North, located in the Western Lowlands regions of Albania. Dajc provinces extends between 19^{o}25'50" East and 41^{0}57'94" North, located in northwestern of Albania. Soil samples were air-dried and ground to pass a 2-mm sieve prior to incubation. A full description of the results is given in (table 1).

These soils, respectively, have been described as Vertisols and Eutric Gleysol according to Classification of FAO-UNESCO. To obtain information on the mineralogical composition of the soil, it was fractionated with respect to the particle size, and the various fractions were then subjected to X-ray diffraction analysis (table 2).

Table 1. Characteristics of soil used in this study

Soil (1) profile	**Horizons**	**Depth, cm**	**pH (2)**	**EC (3) μgS/cm**	**$CaCO_3$ (4)**	**Clay (5) %**	**C. E. C (6) (meq/100g)**	**Naturally(7) fixed N-NH_4^+ (mg/kg))**	**C_{org} (8) %**	**N_t(9) %**	**C:N**
I	Ap	0-27	7. 45	418	6. 8	62	25	97	3. 0	0. 19	15. 8
II	BCg	110-140	7. 39	n. m*	0, 95	45	21	133	0, 53	0, 067	7, 9

(1) (I)- Vertisols; (II)- Eutric Gleysol, according to FAO-UNESCO classification.

(2) Soil pH was determined on 1: 2, 5 (soil:water) suspensions with a glass electrode.

(3) Soil EC was determined on 1:5 (soil:water) suspensions with a conductivity cell

(5) clay content was determined by the pipette method.

(6) Cation exchange capacity was determinded using hexamminecobalt trichloride solution, (ISO method).

(7) Fixed N-NH_4^+ was determined according to an adaption of the Silva and Bremner, [16].

(8) organic C was measured using Chromic acid oxidation for determination of easily oxidized material.

(9) Total N was measured by sample digestion with H_2SO_4/Se/Salicylic acid and H_2O_2, (total N finally measured as NH_4^+), [8].
*non measured

Table 2. Clay mineralogy of the soil layers

Soil Depth (cm)	*4, 18 Å*	*7 Å*	*10 Å*	*10Å-14Å*	*14 Å*	*14Å*	*18 Å*	*6, 26 Å*
I 0-27	--	5	**7**	5	**14**	5	**64**	--
II 110-140	--	20	**18**	6	**34**	7	**15**	--
Mineral % *	Goethit	Kaolinit	**Illit**	WL I/V/S	**Vermiculit**	Chlorit	**Smectit**	Lepido.

* clay mineralogy was analyzed using X-ray diffraction *(University of Hohenheim, Germany*).

2. 3. Soil Incubation

The soil samples were incubated anaerobically at 21^{0}C for 48 and 96 hours with and without application of soil sterilization as a pre-treatment.

- A series of 10 g of the air-dried soil were weighed out in 200 ml extraction flask , and sterilized using an autoclave in temperature 120^{o}C for three times. After that, was added 10 ml potassium sulfate solution that contained 0, 2, 5, 10 and 20 mEq K^+/100g of soil. After 48 hours in room temperature (21^{o}C), using a sterile fume hood we added in all samples 10 ml ammonium sulfate that contained 2 mEq NH_4^+ /100g soil . After addition of some drops of toluene, the flasks were closed and allowed to stand at room temperature (21^{o}C) for another 48 hours.
- In the same series of soil samples, using the same procedure, were added in the form of a mix solutions containing equal amount of NH_4^+ (corresponding to 2 mEq NH_4^+ per 100 g soil) but varying amounts of K^+. The volume of the added solutions was kept constant.

After incubation time, the amount of fixed ammonium were determined by shaking the soil samples with 100 ml 1N KCl solution during 2 hours and then filtrated and washed in small portions with further 100-150 ml of KCl solution. In the filtrate the ammonium was determined calorimetrically on a spectrophotometer at 660 nm wavelength. The amount of ammonium not fixed by the soil was calculated as the difference between the amount of NH_4^+ found and the amount of NH_4^+ in another 10 g of the soil, which was treated with 10 ml of H_2O instead of the ammonium sulfate solution.The amount of NH_4^+ fixed was expressed as mEq NH_4^+ per 100 g of soil. Each treatment was performed in triplicate

.

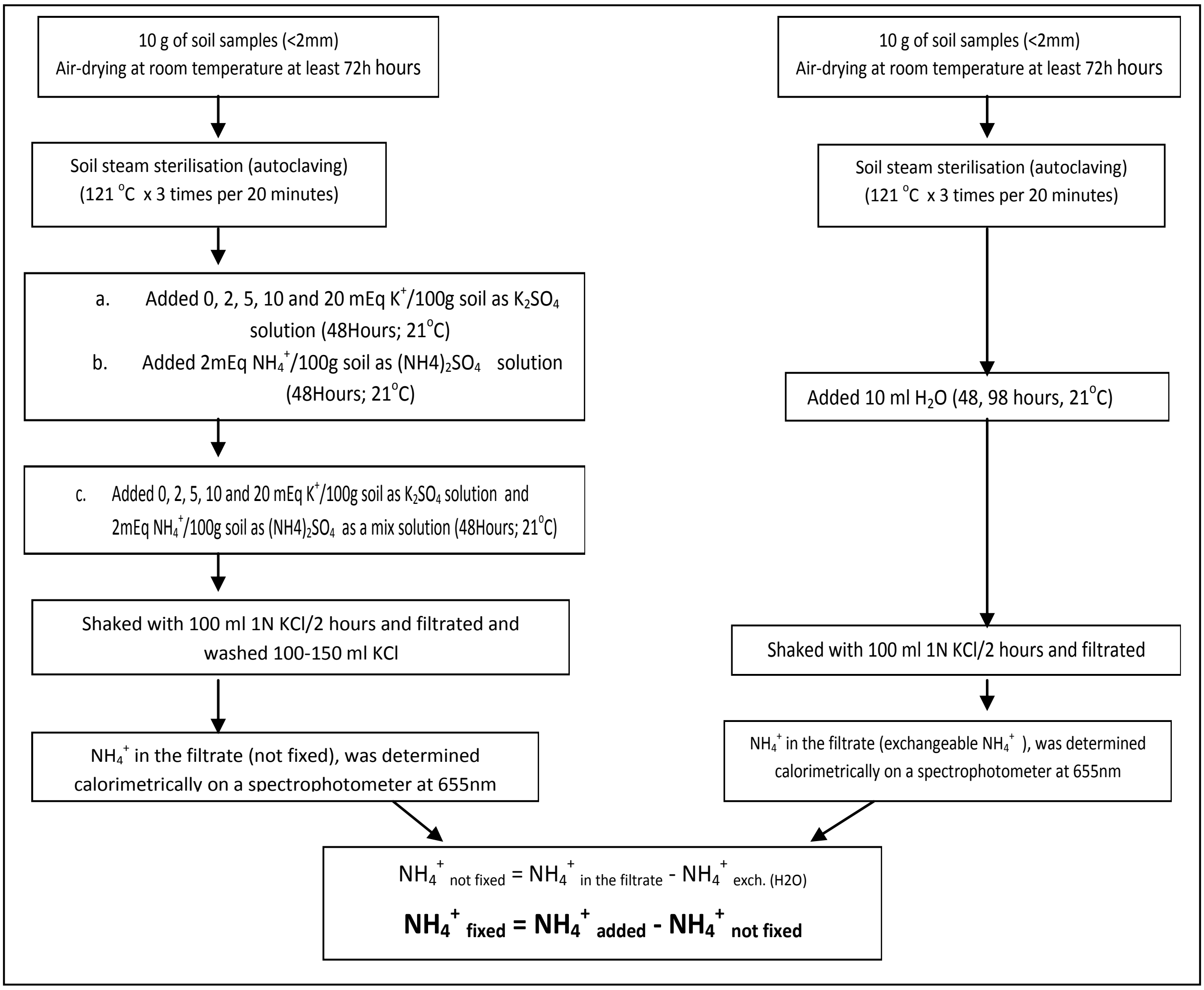

Figure 2. Experiment design for identification of the effect of potassium on fixation of ammonium by clay minerals. Exchangeable NH_4^+ and NH_4^+ in the filtrate was determined calorimetrically on a spectrophotometer at 655 nm wavelength, [8]. In this method, the ammonium reacts with salicylate in the presence of hypochlorite (oxidizer) and nitroprusside (catalyst) to form an emerald green complex.

3. Results and discutions

3. 1 Clay minerals

Soils classified as Vertisols and Eutric Gleysol, contained considerable amount of 2:1 type clay minerals detectable by X-ray diffraction analysis. Smectite (64%) was found to be the dominant clay mineral in Ap-horison, with vermiculite(14%) and illite (7%) occurring in minor amounts. The opposite was found to be in BCg horizon, profile(II). In this horizon(BCg), the vermiculite (34%) was found to be the dominant clay mineral, with illite (18%) and smectite (15%) into a moderate amount (table2). The soils in question, contained 3. 0 to 0. 53 % organic carbon and the pH in water was 7. 45 to 7. 39, respectively(table 1).

3. 2 Effect of K^+ on fixation of NH_4^+

The main chemical difference between K^+ and NH_4^+ is that the latter can also be oxidized to nitrite and NO_3^- mainly through microbial activity. Only the fixed phase NH_4^+ is relatively protected from the oxidation process and can be retained in the clay interlayers from long periods. The similar properties of K^+ and NH_4^+ ions leads to strong interactions between them in the soil. Both ions are held by the same non-exchangeable sites in the interalyers and edges of interlayers of 2:1 clay minerals. Consequently, a simple competition where application of one ion should displace the other and increase its fraction in soil solution is to be expected. however, the reality is more complex and application of NH_4^+ or K^+ to soil may lead to increases as well as decreases in the non-exchangeable pool of the counter ion [3]. As pointed out previously, the depressive effect of K^+ on fixation of NH_4^+ has been the subject of a number of investigations. In field experiments, the soil fixation capacities for both NH_4^+ and K^+ were significantly reduced by sustained high rates of K fertilization, but not by N fertilization, [9]. Also was found that the fixation of NH_4^+ was reduced by K^+ addition before NH_4^+ was added, and that the reduction was proportional to the amount of K^+ previously fixed [7]. The sequence of NH_4^+ and K^+ application may influence K^+ fixation. It has been found that the effect may vary, depending on whether K^+ is added simultaneously, prior to, or after the addition of NH_4^+. Application of NH_4^+ at high rates before K fertilization to rice plants resulted in poor growth and reduced K^+ uptake compared to NH_4^+ application after K fertilization, [4]. It is highly probable that NH_4^+ is fixed by a mechanism similar to that of K^+, since the prior addition of either ion seems to block the fixation of the other. Some date illustrating this question are presented in (Table 3). When K^+ was added to the soil prior to the NH_4^+, the amount of ammonium fixed was reduced in proportion to the amount of K^+ previously added to the soil. As is seen from the Figure 3, the fixation of NH_4^+, decreased strongly with increasing amount of K^+ previously added. In case when NH_4^+ and K^+ are added to the soil simultaneously, when equivalent amounts of ammonium and potassium were added, the first soil fixed more NH_4^+ than K^+, whereas no such preference for ammonium fixation was found in the other soil.

Table 3. Fixation of NH_4^+, when K^+ was added to the soils before the addition of NH_4^+. The data refer to 100 g of soil, (96 hours).

K^+ added mEq I + II	***NH_4^+ added mEq I + II***	***NH_4^+ fixed mEq Profile (I)***	***NH_4^+ fixed mEq Profile (II)***
0	2	1, 42	1, 96
2	2	0, 62	1, 04
5	2	0, 32	0, 65
10	2	0, 22	0, 47
20	2	0, 12	0, 37

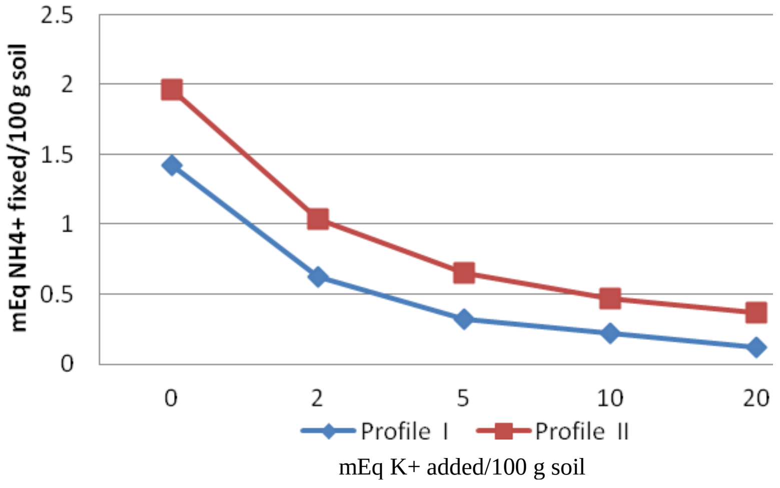

Figura 3. Effect of previously added K^+ on the fixation of NH_4^+. 2mEq NH_4^+ added per 100 g soil two days after the addition of K^+

Table 4. Fixation of NH4+, when NH4+ and K+ are simultaneously added to the soil. The data refer to 100 g of soil, (48 hours).

mix solution			
K^+ added mEq **I + II**	***NH_4^+ added mEq*** **I + II**	***NH_4^+ fixed mEq*** **Profile I**	***NH_4^+ fixed mEq*** **Profile II**
0	2	1, 39	1, 92
2	2	1, 32	2, 15
5	2	1, 11	1, 94
10	2	0, 83	1, 64
20	2	0, 43	1, 02

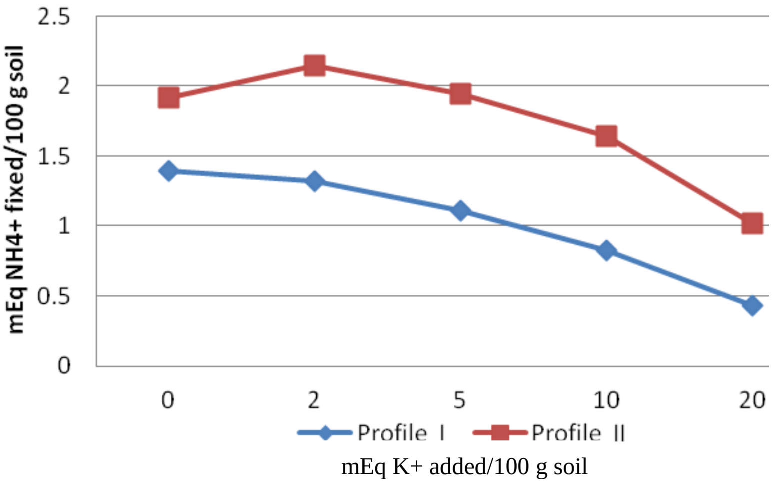

Figura 4. Effect of K^+ on fixation of NH_4^+ added simultaneously in form of a mixed solution.

Availability of applied NH_4^+ in vermiculitic soils would depend on the presence or absence of applied K+[2]. In this case NH_4^+ and K^+ were added to soil samples in form of solutions containing equal amounts of NH_4^+ (corresponding to 2 mEq NH_4^+/100 g soil) but varying amounts of K^+, [5]. From the results, which are recorded in (Table 4), it is seen that the amount of NH_4^+ fixed by the soil of (profile II), was increased by addition of small amounts of K^+.

This difference between plant N and K raises the question of possible interactions or competition between these two nutrients. As pointed out previously, $NH_4^+$and K^+ are both univalent cations and have a similar ionic radius (2. 8 Å). Consequently, they compete for the same exchangeable and non-exchangeable sites of soil particles. Experiments involving additions of NH_4^+-N to air-dry soils have demonstrated that the ability of some soils from Western Lowlands regions of Albania, to fix added ammonium, is related to their content of vermiculite and illite, to a lesser extent, their content of smecite. Also, it has been shown that their contents of naturally fixed NH_4^+-N can best be related to their contents of illite and vermiculite[1]. The results indicates that this soil, which contains considerable amounts of vermiculite, fixes NH_4^+ in preference to K^+. This increase was small but definitely significant. For the higher K^+ concentrations, however, these values were somewhat lower.

4. Conclusions

- The K application modes have effects on ammonium availability in soil through exchange and fixation reactions, respectively.
- A quantitative estimate of the clay minerals present was only carried out on vermiculite and illite, since there were the most important clay minerals that are known to fix added NH_4^+. In the Ap-horizon, the vermiculite plus illite, comprised 21% of the clay fraction and 13% of the soil. In the BCg-horizon, the vermiculite plus illite comprised 52% of the clay fraction and 23, 4 % of the soil.
- As heavier-textured soils in Western Albania would be expected to contain more vermiculite and illite than fine-or medium-textured soils, this may be explain in part the differing behavior of the soils in their response to N fixation.
- The capacity of the soil to fix ammonium was much less from topsoil than subsoil as attributed of the dominance of vermiculite and illite minerals.
- The additional of potassium fertilizer before application of ammonium fertilizers can reduce ammonium fixation. Data from this study indicate that recently fixed ammonium can be an important source of N (slow release) and maybe can affect water quality.

5. References

1. Allison F. E, Doetch JH, Roller EM: **Availability of fixed ammonium in soils containing different clay minerals**. Soil Sci. 1953, 75: 373–381.
2. Allison F. E, Roller EM and Doetch JH: **Ammonium fixation and availability in vermiculite** . Soil. Sci. 1953, 75: 173-180.
3. Bar Tal, **Agriculture Research Organization (ARO),** Volcani Center, Israel, Decembre 2010.

4. Chen XQ, Zhou JM, Wang HY, Du CW: **Effect of N varieties application and interaction of N and K fertilizers on rice growth and nutrient uptake**. Chinese Agr Sci Bulletin 2007, 23:376-382.

5. Evangelou V P. , and Lumbanraja J.: **Amonium-Potassium -Calcium Exchange on Vermiculite and Hydroxyl-Aluminum Vermiculite**. Soil Science Society American Journal 2002, 66:445-455.

6. Guo P-C, Bogring J, Scherer HW:**Verhalten von Dünger –NH_4^+ in Böden unterschiedlicher tonmineralischer Zusammensetzung, ZPlflanzenernahr Bodenkd** 1983, 146:752-757.

7. Kenan K, Derici RM, Saltal K:**The ammonium fixation in great soil groups of Tokat region and some factors affecting the fixation**. Turk J Agric For. 1999, 23(6):673-678.

8. Keeney D R. and Nelson D W. **Nitrogen-Inorganic Forms**. Method 1982, 643-698.

9. Liu, Y. D. , D. A. Laird, and P. Barak: **Release and Fixation of Ammonium and Potassium under Long-Term Fertility Management**. Soil **Science Society American Journal 1997, 61:310-314.**

10. Liu YL, Zhang B, Li CL, Hu F, Velde B: **Long-term fertilization influences on clay mineral composition and ammonium adsorption in rice paddy soils**. Soil Sci Sco Am J 2008, 72:1580-1590.

11. Lu CY, Zhang XD, Chen X, Shi Y, Ma J, Zhao M, Chi G, Huang B**: Fixation of labeled $(^{15}NH_4+)_2SO_4$ and its subsequent release in black soil of Northeast China over consecutive crop cultivation**. Soil and Tillage Research 2010, 106:329-334.

12. Marschner H: **Mineral Nutrition of Higher Plants**: 2nd Edition, Academic Press, London;1995.

13. McBride M B: **Environmental chemistry of soils**: Oxford Univ. Press, New York; 1994.

14. Nieder R, Benbi D K. , Scherer H W: **Fixation and defixation of ammonium in soils: A review. Biology and fertility of Soils** 2011, 47: 1-14.

15. Nommik H, Vahtras K: **Retention and fixation of ammonium and ammonia in soils**. In: Stevenson FJ (ed.) **Nitrogen in agricultural soils**. Agronomy 1982, 22:123–171.

16. Silva JA, Bremmer JM: **Determination and isotope-ration analysis of different forms of nitrogen in soils**: 5. Fixed ammonium. Soil Sci. Soc. Am. Proc. 1966, 30: 587-594.

17. Tung PGA, Yusoff MK, Majid NM, Joo GK, Huang GH: **Effect of N and K fertilizers on nutrient leaching and groundwater quality under mature oil palm in Sabah during the monsoon period**. Am J Appl Sci 2009, 6(10):1788-1799.

18. Wang H. Y. , Zhou J. M., Du C.W., and Chen X.Q.: **Potassium Fractions in Soils as Affected by Monocalcium Phosphate, Ammonium sulfate and Potassium Chloride Application**. Pedosphere 2010, 20:368-377.