The Ammonium Fixation in Great Soil Groups of Tokat Region and Some Factors Affecting The Fixation I. The Affect of Potassium on Ammonium Fixation

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Abstract: The objective of this study was to evaluate the fixation of ammonium in the soils of Tokat region to find out the important factors influencing them. For this purpose 12 representative soil samples were collected from different Great Soil Groups in the region.

The amount of ammonium fixed naturally in the samples was found between 41.62-66.90 ppm ammonium (0.29-0.47 me NH_{a} -N/100 g. soil).

The amounts of ammonium fixed by the soils where increasing amounts of ammonium applied were found between 0.63-1.29%. There was a significant effect from application of potassium to the soils on the fixation of ammonium.

Potassium applied before ammonium decreased the ammonium fixation in all soils, but when it was applied with ammonium it increased the ammonium fixation in other soils except in Ustifluvent 1-2, Ustorthent 2 and Haplustalf 1-2.

Tokat Bölgesi Büyük Toprak Gruplarında Amonyum Fiksasyonu ve Fiksasyonu Etkileyen Bazı Faktörler

I. Amonyum Fiksasyonuna Potasyumun Etkisi

Özet: Bu çalışmanın amacı, Tokat bölgesi topraklarında amonyum fiksasyonunu değerlendirmek ve bunu etkileyen önemli faktörleri bulmaktır. Bu amaçla 12 toprak örneği bölgedeki farklı büyük toprak gruplarından alınmıştır.

Örneklerde doğal olarak fikse edilen amonyum miktarı 41.02-66.90 ppm amonyum (0.29-0.47 me NH₄-N /100 g. toprak) arasında bulunmuştur.

Artan miktarlarda uygulanan amonyumun topraklar tarafından fikse edilen miktarı % 0.63-1.29 arasındadır. Amonyum fiksasyonuna, topraklara uygulanan potasyumun önemli bir etkisi vardır.

Bu topraklarda, amonyumdan önce uygulanan potasyum, amonyum fiksasyonunu azaltmış, fakat amonyum ile uygulandığında ustifluvent 1-2, ustorthent 2 ve haplustalf 1-2 hariç diğer topraklarda artmıştır.

Introduction

Ammonium is generally held in soils as an exchangeable cation, but it can be fixed in soils which contain 2:1 clay minerals (e.g., illites, vermiculites and montmorillonites). Fixation involves the entrapment NH_4^+ and K⁺ions within the interlayer of the 2:1 type clay minerals. Soils vary greatly in their ability to fix NH_4^+ ions depending on their content of these clay minerals.

Potassium is fixed by the same mechanism as ammonium thus potassium effects the fixation of the ammonium and its availability to plants. Nommik (1) have proposed an explanation for the difference in availability of "native" and recently fixed ammonium ions. The equilibrium for fixed soil $\rm NH_4^{\ +}$ ions is based on a scheme for $\rm K^+.$

$$(NH_4+K)_s \longrightarrow (NH_4+K)_e \longrightarrow (NH_4+K)_f$$

In this scheme the intermediate NH_4^+ (or K⁺) ions probably occupy interlayer sites close to the edge of the clay crystal either as exchangeable with H⁺ or K⁺ or recently fixed from fertilizer sources. Therefore, the concentration of K⁺ ions in the soil solution and in the exchange sites are important factors regulating rates of NH_4^+ fixation and release. The Ammonium Fixation in Great Soil Groups of Tokat Region and Some Factors Affecting The Fixation I. The Affect of Potassium on Ammonium Fixation

Naturally fixed ammonium content in some Ontario soils varied from 57 to 367 mg/g, and accounted for between 3 and 44 % of the total nitrogen (2). Crush and Evans (3) found that the quantities of naturally fixed ammonium in four Manawatu Pasture soils of New Zealand varied between 170 to 250 ppm. Soils containing the clay minerals, vermiculite, illite and montmorillonite have shown to fix added ammonium (4). Özgümü_ (5) found a significant correlation between clay contents and naturally fixed ammonium in Cukurova region soils, southern part of Turkey. Opuwaribo and Odu (6) found that the application of potassium before ammonium stimulated ammonium fixation in three clayey soils containing some illite. The soil's mineralogical and mechanical composition influences the process of ammonium fixation (7). Bajwa (8) reported that montmorillonite clay is the greatest fixer of ammonium, but not of potassium. Chen et al. (9) observed that the Beaumont soil fixed ammonium more than the Nada soil because the Beaumont soil was higher in soil potassium and smectite. Mamo et al. (10) found that the vermiculite clay lattice collapses from an initial d-spacing of 13.1 angstrom to 10.4 angstrom after desorption by KCI. Sağlam (11) found that the quantities of naturally fixed ammonium in the soils of Erzurum-Hasankale and Erzincan plains, Eastern part of Turkey, varied between 18,4 to 164 ppm.

Higher plants and microorganisms can not take up ammonium ions fixed by clay minerals in soils. Considerably longer time is needed for the utilization of such fixed ammonium ions. Therefore, it is very important to know about the changes in the NH, status in soils for determination of its amount that will be added as fertilizer to soils.

The objective of this research work was to study the naturally fixed ammonium and the factors affecting the fixation of ammonium such as wetting and drying, freezing and thawing, and the interactions between ammonium and potassium with respect to fixation processes.

Material and Method

Material

Soil samples used in the experiment were collected from Tokat region of Turkey. Soil samples were taken from six different great soil groups from 0-20 cm and 20-40 cm depths according to the procedure outlined by Jackson (12). These soils have been described as Ustifluvent, Ustorthent, Haplustoll, Argiustoll, Ustochrept, Haplustalf according to Soil Taxonomy (13).

Method

The naturally fixed ammonium was determined according to Silva and Bremner (14). The soil samples were treated with alkaline potassium hypobromite (KOBr-KOH) solution to remove exchangeable ammonium and organic-N compounds which may yield ammonium under the conditions employed to release and estimate non-exchangeable ammonium, and the residue from this treatment was washed with 0,5 N KCl and shaken with 5 N HF-1 N HCl solution for 24 hours to decompose minerals containing non-exchangeable ammonium. The ammonium released by HF-HCl treatment was then

 Table 1.
 Some physical and chemical properties of the experimental soils.

Great Soil	Depth Mechanical Composition		n (%) pH		0.M.	CaCO ₃	C.E.C.	Total N	E.C. (me/100 g)		Naturally fixed	
Groups	(cm)	Sand	Silt	Clay	(water)	(%)		(me/100 g.)	(ppm)	К	$^{\rm NH}_{4}$	NH_ (ppm)
							(%)				·	
Ustifluvent	0-20	32.02	29.01	38.97	7.50	1.16	8.60	21.79	731	0.695	0.013	41.72
	20-40	30.91	23.33	45.76	7.54	2.80	9.50	20.13	937	0.642	0.012	41.62
Uslorthent	0-20	41.28	25.98	32.74	7.48	2.40	2.50	23.08	974	0.715	0.016	47.09
	20-40	20.74	29.75	49.51	7.51	1.90	2.55	24.10	981	0.570	0.014	49.61
Ustochrept	0-20	33.00	32.00	35.00	7.25	1.75	13.40	26.92	641	0.733	0.019	50.23
	20-40	36.19	29.04	34.77	7.32	1.43	16.60	26.54	579	0.602	0.020	50.54
Haplustoll	0-20	63.61	16.36	20.03	7.09	2.55	2.80	29.23	1113	0.890	0.027	62.21
	20-40	58.23	21.27	20.50	7.16	2.18	1.40	32.82	1130	0.710	0.028	61.03
Argiustoll	0-20	41.64	17.24	41.12	7.33	2.55	1.90	37.59	1142	0.930	0.025	66.90
	20-40	30.05	25.86	44.09	7.45	2.10	2.35	39.10	1105	0.953	0.025	66.11
Haplustalf	0-20	31.84	15.66	52.50	7.55	2.50	15.20	28.46	1120	1.600	0.026	48.53
	20-40	26.94	17.67	55.39	7.61	1.95	15.55	27.31	1075	1.340	0.026	51.91

Great Soil	Smee	tite	Kaolii	nite	Illite		
Groups	Dominancy	Crystallinity	Dominancy	Crystallinity	Dominancy	Crystallinity	
Ustifluvent	++++	*	+++	***	++	**	
	+++++	***	++++	***	++	**	
Ustorthent	+++++	***	++++	***	++	**	
	+++++	***	++++	***	+	*	
Ustochrept	++++	**	+++	**	-	-	
	++++	*	++++	***	+	*	
Haplustoll	+++++	***	+++	***	-	-	
	+++++	***	++	***	-	-	
Argiustol	+++++	***	++	***	-	-	
	+++++	**	++	***	+	*	
Haplustalf	++++	*	+	*	+	*	
	+++	*	+	*	-	-	

Table 2.Mineralogical properties of the
experimental soils

determined by collection and titration of the ammonia liberated by steam distillation of the soil-acid mixture with KOH. Exchangeable ammonium, extracted with 1 M KCI was steam distilled with MgO and, After collection in boric acid-mixed indicator solution, was estimated by titration with standard sulphuric acid (15).

The percentage of the ammonium fixed from ammonium nitrate applied to soil was determined in the following way :

 NH_4NO_3 solutions containing amount of NH_4 (2000 ppm) was applied to one gram of soil and was dried under the laboratory conditions (at $20\pm2^{\circ}C$) for a period of 48 hours. After that the total quantity of ammonium fixed by the soil was determined according to Silva and Bremner (14), and from this value the quantity of the naturally fixed ammonium was substracted and the percentage of fixed ammonium was determined.

The effect of potassium on the rate of ammonium fixation was determined in the following way : One gram soil samples, after applying 2 ml of KCI solution of increasing concentrations (2000, 4000 and 6000 ppm KCI) were kept under laboratory conditions (at $20\pm2^{\circ}C$) for a period of 24 hours. Than 2 ml of NH4NO3 solutions of increasing concentrations (2000, 4000 and 6000 ppm NH4NO3) were added to the corresponding samples and they were kept under laboratory conditions (at $20\pm2^{\circ}C$) for 48 hours. The ammonium fixed in these samples were determined according to Silva and Bremner (14) and from these values the quantities of naturally fixed ammonium were subracted and the quantities of fixed ammonium from the added ammonium were calculated.

The effect of ammonium and potassium added together on the rate of ammonium fixation was determined in the following way : The soil samples

simultaneous after application of 2 ml of KCI and $\rm NH_4NO_3$ solutions at increasing concentrations (2000, 4000 and 6000 ppm) they were kept under laboratory conditions (at 20±2°C) for a period of 24 hours. The ammonium fixed in the soil was determined according to Silva and Bremner (14). From these values the quantities of naturally fixed ammonium were subtracted and the quantities of ammonium fixed from the added ammonium in presence of potassium were calculated.

The statistical analysis of the results were done according to Steel and Torrie (16).

Results and Discussion

Naturally fixed ammonium

The quantities of the naturally fixed ammonium in the soils of Tokat region are given in table 1. The naturally fixed ammonium varied between 0.29-0.47 me/100 g. soil with a mean value of 0.29 me/100 g. (41.02 -66.90 ppm NH₄-N). It was found maximum in Argiustoll and was followed by Haplustoll. The naturally fixed ammonium was found minimum in Ustifluvent. Naturally fixed ammonium as the percentage of total nitrogen varies between 4.3-8.7.

Naturally fixed ammonium in soil Ustifluvent is the lowest (Table 1). Illite is predominant in this soil. Ammonium fixation is the lowest because of dominance of illite. At the same time, Cation exchange capacity of this soil is the lowest among other soils.

The Effect of potassium on ammonium fixation

Potassium had a depressive effect on the fixation of added ammonium in soils. Usually, there was as much as 10 percent decreasing or increasing in ammonium

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fixation of all soils. The results agree with those obtained by Opuwaribo and Odu (17), and Drury and Beauchamp (18). Increase and decrease in ammonium fixation may have resulted from the blocking of some exchange sites by potassium. The fixation of ammonium was reduced by potassium added before ammonium. This reduction was proportional to the amount of potassium previously fixed.

Simultaneous addition of equivalent amounts of ammonium and potassium, addition of potassium prior to or after ammonium addition caused important differences in the amounts of ammonium fixed by all soils (Figure 1,2,3). Usually, potassium added after ammonium resulted in high ammonium fixation in soils, but there was an appreciable decrease in the amounts of ammonium fixed by soils Ustifluvent and Ustorthent.

A comparative look at the ammonium and potassium fixation in relation to clay mineral composition reveals that kaolinite is the least fixer of ammonium, but smectite is the greatest fixer of ammonium. Kaolinite and illite were mixed with smectite in soils Ustifluvent and Ustorthent, but in these soils rather than other soils, illite was found to be the predominant clay mineral. Results of the variance analysis show that potassium added after ammonium was found to have statistically highly significant effects on the ammonium fixation between great soil groups (P<0,001).

When ammonium and potassium are added simultaneously, various results can be obtained, depending on the type of fixing material, the concentration level. The effect of increasing amounts of simultaneously added potassium and ammonium on the ammonium fixation in soils Ustifluvent, Ustorthent, Ustochrept and Haplustalf have been reduced with increasing concentrations, but the amount of ammonium fixed increased proportionately with the quantities of ammonium and potassium added in the soils Haplustoll and Argiustoll ammonium fixation was highest in this soils.

Potassium applied to soil, prior to the addition of ammonium after a certain concentration decreased the ammonium fixation with increasing concentrations. Ammonium and potassium ions have similar ionic radius and can function as proxy for each other in the interlattice positions of clay minerals. Potassium was fixed by planar sites on the external surfaces of the lattice, edge sites and interlattice sites situated between the layers of the mineral because it was applied to soil, prior to the addition of ammonium. Figure 1 shows that the fixation of ammonium was reduced by potassium added prior to the addition of ammonium and that this reduction was proportional to the amounts of potassium and ammonium added. Similar relationships have been found by some researchers (1, 8, 17).

Finally, The effect of potassium on the ammonium fixation is not only dependent on the amount of potassium added, but also on the time when potassium is added, in relation to the addition of ammonium. The depressive effect of potassium on the ammonium fixation has been shown to be different, depending on whether potassium is added simultaneously, prior to or after the addition of ammonium. In accordance with the discussion above, the addition of potassium prior to the addition of ammonium will depress the ammonium fixation, but the addition of potassium after the addition of ammonium will not appreciably influence the amount of ammonium fixed.



Figure 1. Effects of potassium added after ammonium on ammonium fixation

EFU1: Ustifluvent 1: 0-20 am, EOU1: Ustorthent1: 0-20 cm, IOU1: Ustochrept: 0-20 cm EFU2: Ustifluvent 2: 20-40 cm, EOU2: Ustorthent 2: 20-40 cm, IOU2: Ustochrept: 0-20 cm MUH1: Haplustoll: 0-20 cm, MUA1: Argiustoll: 0-20 cm MUH2: Haplustoll: 20-40 cm, MUA2: Argiustoll: 20-40 cm, AUH1: Haplustalf: 0-20 cm, AUH2: Haplustalf: 20-40 cm

Effects of potassium added

before ammonium on ammo-

nium fixation



Figure 2. Effects of ammonium and potassium added together on ammonium fixation

EFU1: Ustifluvent 1: 0-20 am, EOU1: Ustorthent1: 0-20 cm, IOU1: Ustochrept: 0-20 cm EFU2: Ustifluvent 2: 20-40 cm, EOU2: Ustorthent 2: 20-40 cm, IOU2: Ustochrept: 0-20 cm MUH1: Haplustoll: 0-20 cm, MUA1: Argiustoll: 0-20 cm MUH2: Haplustoll: 20-40 cm, MUA2: Argiustoll: 20-40 cm, AUH1: Haplustalf: 0-20 cm, AUH2: Haplustalf: 20-40 cm



EFU1: Ustifluvent 1: 0-20 am, EOU1: Ustorthent1: 0-20 cm, IOU1: Ustochrept: 0-20 cm EFU2: Ustifluvent 2: 20-40 cm, EOU2: Ustorthent 2: 20-40 cm, IOU2: Ustochrept: 0-20 cm MUH1: Haplustoll: 0-20 cm, MUA1: Argiustoll: 0-20 cm MUH2: Haplustoll: 20-40 cm, MUA2: Argiustoll: 20-40 cm,

AUH1: Haplustalf: 0-20 cm, AUH2: Haplustalf: 20-40 cm

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Figure 3.

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