

FIXATION AND RELEASE OF POTASSIUM AND AMMONIUM IONS IN DANISH SOILS

by J. DISSING NIELSEN

State Laboratory for Soil and Crop Research Lyngby, Denmark

SUMMARY

Results of a laboratory investigation showed that among soils in Denmark it are chiefly those rich in clay minerals that will fix and release potassium and ammonium. The two cations were fixed in nearly equivalent proportions, but ammonium was fixed preferentially to potassium when added together to the soil.

The maximum fixation reached 20 to 30 per cent of the addition in top soil layer but 50 to 80 in subsoil.

Soils from a permanent fertilizer experiment showed the strongest fixation and least release of potassium where no potassic fertilizer had been applied for more than 70 years. In soils from another field experiment on residual effect of various nitrogenous fertilizers there was a small but significant increase in content of inorganically fixed ammonium where urea had been applied.

INTRODUCTION

Most soils contain considerable amounts of non-exchangeable potassium and ammonium which to a greater or lesser extent may be released and taken up by plants. Conversely, many soils have the property of immobilizing potassium and ammonium ions in a non-exchangeable form; this process is called fixation, regardless of the plant availability of the cations involved.

Fixation and release of potassium and ammonium is predominantly associated with the fraction of clay minerals which partly structurally and partly electrostatically are able to fix potassium, ammonium and other monovalent as well as also divalent cations. Exchangeable potassium and ammonium ions are mainly attached to the surfaces of clay and humus particles, while fixed potassium and ammonium ions are trapped between the replicate layers of the clay

minerals, particularly illite, montmorillonite and vermiculite, among which the first two are predominant clay minerals in Danish soils. ⁴

For evaluating the effect of potassium and ammonium fertilizers it is essential to know if parts of the applied plant nutrients are converted into forms more or less available to the crops. The present paper records the results of a laboratory investigation on the extent and degree of potassium and ammonium fixation and release, which has not hitherto been studied in Danish soils. The processes of fixation and release can go on as well under wet as under dry conditions and both principles were used in the investigations.

METHODS

Exchangeable potassium is determined by shaking 10 g dry soil for one hour with 50 ml 0.5 N ammonium acetate.

Potassium released by ignition ⁶ is estimated after similar extraction of 10 g soil followed by filtration and washing of the soil residue with 3 × 15 ml 0.5 N ammonium acetate. Soil + filter paper is ignited for 2 hours at 500°C and extracted with 50 ml 0.5 N ammonium acetate.

For determination of *potassium released by hydrochloric acid*, 2.0 g soil and 50 ml 2 N HCl are placed in a 100-ml flask which is kept for 2 hours in a boiling waterbath; after cooling, the flask is filled up to volume with distilled H₂O and the soil removed by filtration. The difference between extracted potassium and the fraction of exchangeable potassium expresses the content of potassium released by 2 N hydrochloric acid.

'*Wet fixation*' of potassium ⁹ is determined by shaking 20 g soil for one hour with 50 ml 0.01 N KCl, addition of 50 ml 1 N ammonium acetate, and shaking for 1 hour more, followed by filtration. Fixed potassium is expressed as the sum of added and exchangeable potassium minus exchangeable potassium after reaction with 0.01 N KCl.

'*Dry fixation*' of potassium is determined by shaking 10 g of soil for one hour with 25 ml 0.01 N KCl, evaporating the soil suspension to dryness, and desiccating for 16 hours at 70°C, followed by shaking for one hour with 50 ml 0.5 N ammonium acetate. Fixed potassium is calculated as in the 'wet fixation' process.

Potassium in all extracts is determined by flame photometry.

Exchangeable ammonium is determined by three successive extractions of 5 g soil with 25 ml 1 N KCl, followed by 3 × 25 ml distilled H₂O and centrifugation after each washing. The determination of exchangeable ammonium is of analytical importance only because part of the soluble ammonium will probably be nitrified during the time interval between sampling and analysis

Naturally fixed ammonium ¹ is released after removal of the exchangeable

fraction by shaking 5 g of extracted soil for 20 hours with 200 ml (1-N HCl and 1-N HF).

'Wet fixation' of ammonium¹¹ is determined in 5 g soil by adding first 2.5 ml 0.05-N HN₄Cl and then 2.5 ml H₂O, to make a soil/liquid ratio of 1:1. The samples are left at 5°C for at least 2 × 24 hours, with addition of two drops of toluene to prevent nitrification. The difference between ammonium fixed after contact with ammonium and naturally fixed ammonium expresses the amount of 'wet-fixed' ammonium. As a check on the directly determined ammonium fixation it was determined indirectly in the KCl extract.

'Dry fixation' of ammonium¹¹ is determined as above, except that after addition of NH₄Cl-solution and water the soil samples are dried for at least 24 hours at 55°C.

Determination of ammonium-N. Ammonia (NH₃) is liberated by addition of an excess (5 g) of magnesium oxide to the acid- or KCl-extract and recovered by distillation. For its quantitative determination the more sensitive colorimetric method with Nessler's reagent was preferred to acid-titration. A volume of distillate corresponding to 2.10⁻³ to 15.10⁻³ me ammonium was transferred to a 100 ml measuring flask half filled with water, 2 ml of a 1% solution of gum arabic was added to stabilize the colour that ensued by addition of 5 ml Nessler-reagent³. The flask was filled to volume with distilled water, and after 15 min the colour intensity was measured in an Engell colorimeter with filter no. 43 (420-465mμ).

EXPERIMENTAL

A. - Fixation and release of potassium and ammonium in 'specimen' soils.

The soils to be studied were taken from a collection of samples representing most Danish soil types and selected from 17 localities, each at 0-20, 20-50 and 50-100 cm depth. Since the capacity for potassium and ammonium fixation depends strongly on the clay minerals and typical sand soils show no fixation, only soils with a comparatively high clay and silt content were chosen for the investigation.

1. The fixation processes. Fig. 1 shows the relations between wet and dry fixation of the two cations. The determinations of fixations under wet and dry conditions show correlation coefficients (r) of 0.87 and 0.76 for potassium and ammonium, respectively, and dry fixation of both cations is higher than wet fixation.

The potassium and the ammonium ion have many physical and chemical properties in common:— they both carry a single positive

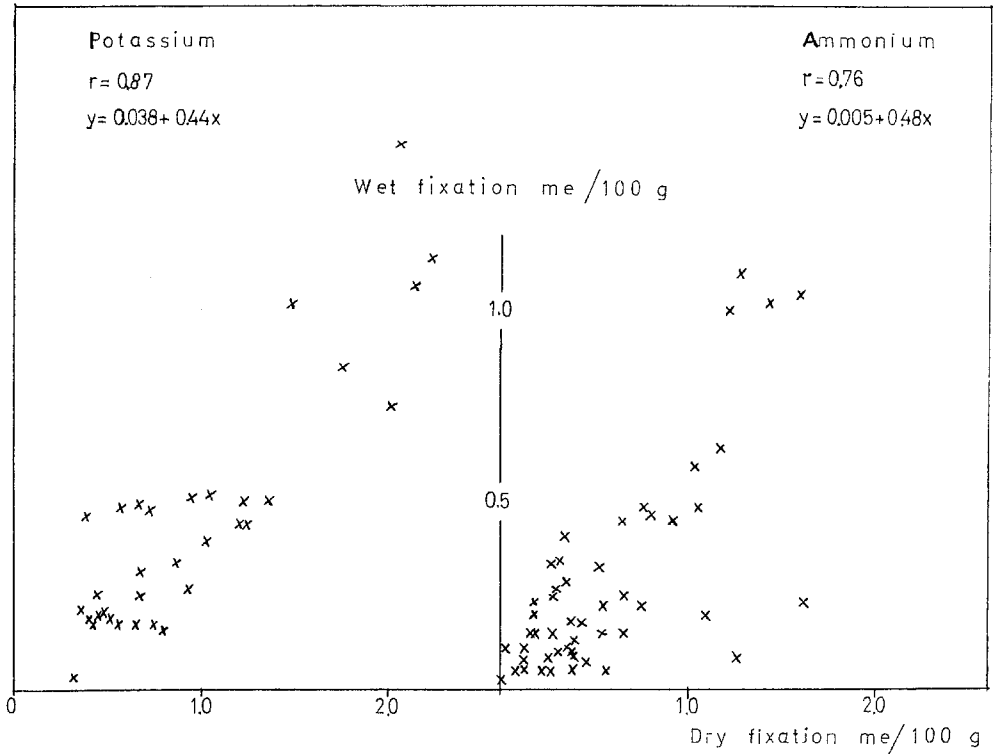


Fig. 1. Relationship between wet and dry fixation of K and NH_4 . Fixation estimated in soil samples from varying depths, added 2.5 me of K or NH_4 .

electric charge, and with most anions they form readily soluble salts that are completely dissociated in aqueous solution; their ionic radius is approximately the same, and they take part in cationic exchange processes in the soil where they are mutually interchangeable. Owing to these analogies, both ions are liable to fixation in the clay minerals of the soil, and significant correlations have been found (10) between the amounts of potassium and ammonium ions liable to wet fixation when added in equivalent concentration.

Fig. 2 shows the relationships between potassium and ammonium fixation in a series of samples from different localities and at varying depths. There is a significant correlation between the fixation of the two cations under wet as well as dry conditions; in the first case the fixed amounts are nearly equivalent, but dry fixation shows an

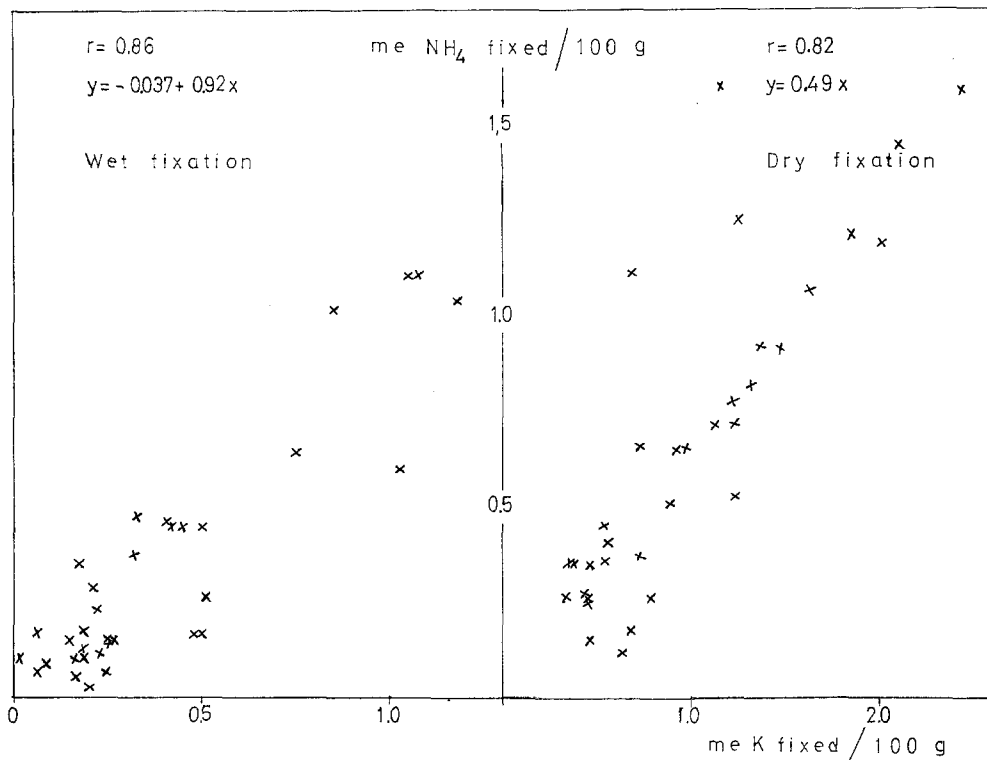


Fig. 2. Relationship between fixation of K and NH₄. Fixation estimated in soil samples from varying depths, added 2.5 me of K or NH₄.

excess of potassium compared to ammonium. In the next experiments the two cations were added together, such as is the case in practical use of mixed fertilizers containing potassium and ammonium in ionic form; under such conditions the two ions will compete for the sites of fixation on the clay minerals, and since they are unable mutually to displace each other from the sites, the rates of fixation will decide which ion will predominantly be fixed.

The fixation of ammonium added in rising doses, was studied in four soils with comparatively high fixing capacities. Table 1 shows some of their physical and chemical properties. The experiment was divided into three sections: (a) ammonium alone, (b) ammonium + 2 me potassium/100 g soil, and (c) the same but potassium added 24 hours before ammonium. Fig. 3 shows the results for ammonium fixation.

TABLE 1

Texture and pH

Locality	Depth cm	Percent				Humus	pH	
		Clay	Silt	Fine sand	Coarse sand			
5b Abed.	Lolland	20-50	14.2	30.0	36.4	18.5	0.8	8.2
7a Blangstedgaard	Funen	0-20	13.3	15.4	42.2	26.9	2.2	6.7
7b	-	20-50	14.1	16.8	39.1	28.8	1.2	7.7
7c	-	50-100	14.5	20.5	37.9	26.5	0.6	8.3

By addition alone of 1 me/100 g to the subsoil samples the wet fixation amounts to 50 per cent and the dry fixation to 75 per cent, approximately. The fixation in the 0-20 cm layer is much less than in the deeper layers although the clay content is much the same. In all the tested soils the ammonium fixation is constantly stronger under dry than under wet conditions, and the dry fixation is almost proportional to the amount of added ammonium even up to 2 me/100 g. The relationship between the soils is the same with regard to the wet and the dry fixation. Addition of 2 me potassium/100 g soil together with ammonium has only a slight influence on the latter, but the ammonium fixation is considerably reduced if the soil has already fixed some potassium before ammonium; this applies particularly to the wet fixation but is also noticeable in the dry process.

Nömmik⁷ has studied the effect of increasing amounts of potassium on the fixation of simultaneously added ammonium in a vermiculite soil. When equivalent amounts (1 me/100 g) were added, ammonium and potassium were fixed in the ratio of 3.4/1. Addition of potassium resulted at lower concentrations in a small increase in ammonium fixation, but apart from this the relatively large additions of potassium did not influence the wet fixation of ammonium.

In Fig. 4 the fixation of added potassium is shown in the presence and absence of simultaneously added ammonium (2 me/100 g). Within the range of concentrations tested, the fixation, wet as well as dry, increases with increasing amount of potassium, and the relationship between the various soils is the same as in ammonium fixation.

The surface soil 7a fixed less potassium than the subsoils although the clay content is much the same at all tree depths. Dry fixation,

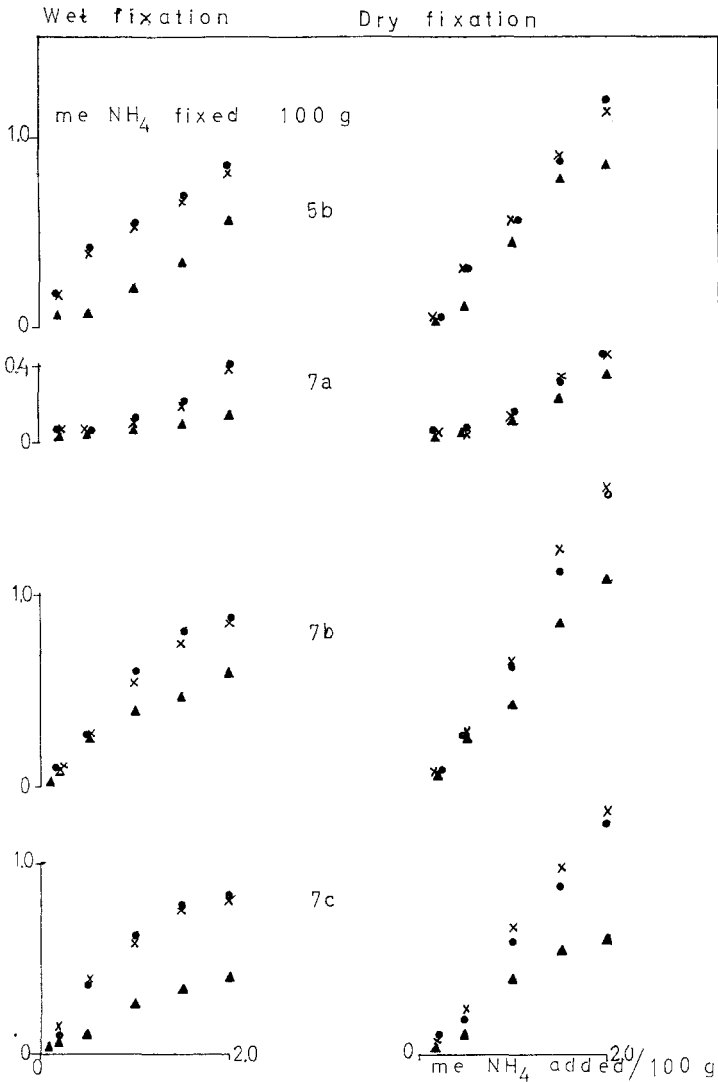


Fig. 3. Effect of K on the fixation of NH₄.

- NH₄Cl
- × NH₄Cl and simultaneously addition of 2 me KCl per 100 g soil.
- ▲ NH₄Cl and previously addition of 2 me KCl per 100 g soil

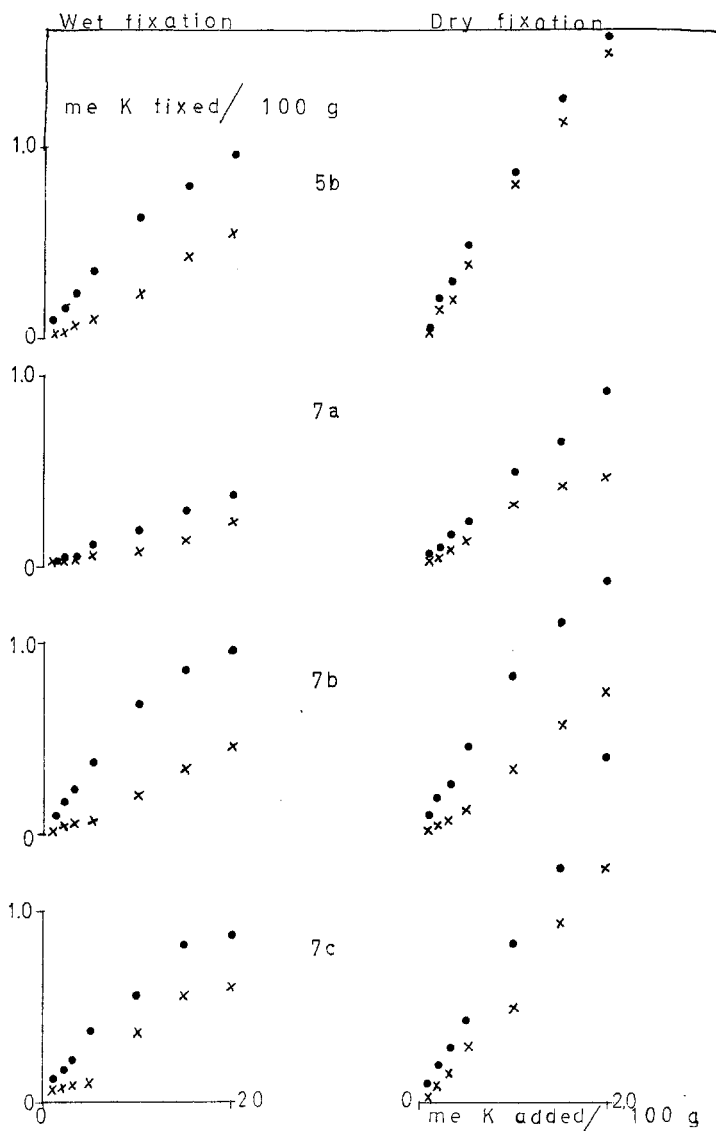


Fig. 4. Effect of NH_4 on the fixation of K.

● KC1

× KC1 and simultaneously addition of 2 me NH_4C_1 per 100 g soil

especially of higher potassium additions, is again somewhat stronger than wet fixation. Percentage fixation is highest with minimum additions and is almost proportional to the actual addition up to 2.0 me/100 g. Addition of potassium does not reduce the fixation of simultaneously added ammonium, but Fig. 4 shows that fixation of potassium is reduced by simultaneous addition of ammonium (2 me/100 g). In most soils wet fixation is reduced by 50 per cent, but the shape of the curves varies strongly in the individual soils. In the top soil 7a the ammonium ion particularly inhibits the dry fixation of potassium, with only a slight effect on the wet process, but in the subsoil 7c it has comparatively little effect on potassium fixation, wet or dry. The inhibitory effect of the ammonium ion is most striking towards small doses of potassium comparable to those used in field practice. Fixation of ammonium thus takes place more rapidly than that of potassium when the two ions are added together and in equimolar concentrations, but potassium appears to be fixed slightly stronger when potassium and ammonium do not compete for the sites of fixation. We may therefore expect that the combination NH₄⁺ versus K⁺ in the fertilizer application will be of importance for the degree of fixation of these two plant nutrients.

Table 2 shows the correlations between potassium and ammonium fixation calculated per 100 g soil and per 100 g clay. Because the same soils and the same clay minerals fix the two cations, the corre-

TABLE 2
Correlation between potassium and ammonium fixation

	Dry fixation of K	Wet fixation of NH ₄	Dry fixation of NH ₄	Content of clay
<i>Calculated per 100 g soil</i>				
Wet fixation of K	0.87***	0.86***	0.77***	0.37**
Dry fixation of K		0.80***	0.82***	0.33*
Wet fixation of NH ₄			0.76***	0.21
Dry fixation of NH ₄				0.22
<i>Calculated per quantity of soil containing 100 g clay</i>				
Wet fixation of K	0.88***	0.87***	0.82***	-0.20
Dry fixation of K		0.88***	0.85***	-0.34*
Wet fixation of NH ₄			0.85***	-0.08
Dry fixation of NH ₄				-0.30

* Significant at $P < 0.05$, ** at $P < 0.01$, *** at $P < 0.01$

lation coefficients remain practically unaltered regardless of the basis for calculation, and potassium and ammonium fixation are positively correlated. There is also a positive correlation between clay content of soils and fixation, but the correlation disappears or becomes slightly negative if calculated per quantity of soil containing 100 g clay.

2. – The processes of release. – Potassium in soil is found partly in a water-soluble and partly in a water-insoluble state, some of the latter in a state readily exchangeable against other cations. The water-soluble and the exchangeable potassium components are usually pooled and represent the fraction of soil potassium most readily taken up by the plants roots. In routine soil analysis in Denmark exchangeable potassium is defined as the amount removed by extraction with 0.5 *N* ammonium acetate. This includes water-soluble potassium but accounts for only a small fraction of total soil potassium. Extraction with dilute mineral acids (8) removes some of the non-exchangeable potassium from the clay minerals without their crystalline structure being destroyed. Another method⁶ for determination of non-exchangeable potassium is based upon saturation of the soil with ammonium and subsequent ignition at 500°C for 2 hours; this removes the ammonium, the clay minerals expand vertically to the orientation of their lamellae, and the non-exchangeable potassium becomes partly exchangeable against ammonium ions.

Fig. 5 and Table 3 show the release of non-exchangeable potassium (*a*) following ignition and (*b*) by extraction with 2 *N* hydrochloric acid. The results of the two methods show a good correlation although ignition releases only 34 per cent of the amount extracted by hydrochloric acid. The correlation becomes less marked when calculated on the basis of clay instead of the soil itself. The same is the case between exchangeable potassium and release and the significant correlation, disappears altogether when calculated per 100 g of clay (Table 3). – The soil also contains certain amounts of naturally fixed ammonium (1) soluble in 1 *N* (HCl + HF). As shown in Table 3, this fraction shows some correlation with the release of potassium after ignition or acid extraction, but the correlation is less than between fixation of potassium and ammonium, and again it disappears when calculated per 100 g clay instead of soil.

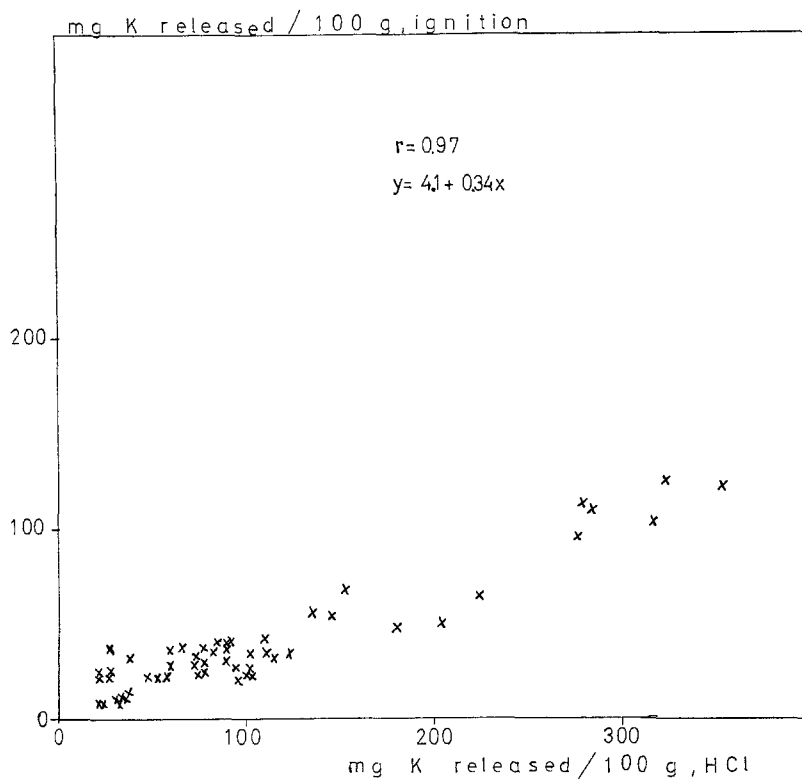


Fig. 5. Relationship between K released by HCl and ignition.

TABLE 3

Correlation between potassium and ammonium release

	K released by ignition	K released by HCl	Naturally fixed NH ₄	Content of clay
<i>Calculated per 100 g soil</i>				
Exchangeable K	0.58***	0.56***	0.52***	0.56***
K released by ignition		0.97***	0.59***	0.89***
K released by HCl			0.69***	0.86***
Naturally fixed NH ₃				0.38**
<i>Calculated per quantity of soil containing 100 g clay</i>				
Exchangeable K	0.20	0.06	0.18	-0.28
K released by ignition		0.69	0.09	-0.01
K released by HCl			0.15	0.16
Naturally fixed NH ₄				-0.19

* Significant at $P < 0.05$, ** at $P < 0.01$, *** $P < 0.001$.

3. — Relationships between fixation and release. As shown in Table 4, certain correlations exist between fixation and release of potassium, which may be explained on the assumption that both processes are connected with the clay fraction. If an equilibrium exists between the three potassium fractions:

exchangeable K \rightleftharpoons fixed K \rightleftharpoons lattice K, a high content of the first two fractions should lower the capacity of the soil for potassium fixation. This does not become apparent when potassium is calculated per 100 g soil. There is no correlation between exchangeable potassium and potassium fixation but contrary to the theory of equilibrium there is a positive correlation between fixation of exchangeable and release of non-exchangeable potassium. When calculated on the basis of 100 g clay, the figures for exchangeable potassium and potassium fixation show no correlation, while the positive correlation between fixation and release of potassium now appears negative. The soil content of naturally fixed ammonium shows little or no correlation with the ammonium fixation, regardless of the basis for calculation.

Table 5 shows fixation and release of potassium and ammonium at different soil depth. As might be expected, the content of exchangeable potassium decreases from top layer to subsoil while fixation of ammonium and potassium increases. The release of potassium (but not of ammonium) also increases with the depth.

TABLE 4

Correlation between fixation and release of potassium and ammonium

	Wet fixation of K	Dry fixation of K	Wet fixation of NH ₄	Dry fixation of NH ₄
<i>Calculated per 100 g of soil</i>				
Exchangeable K	0.05	0.04	0.15	-0.34*
K released by ignition	0.31*	0.23	-0.04	0.02
K released by HCl	0.33*	0.39**	-0.07	0.03
Naturally fixed NH ₄	0.16	0.27	-0.07	0.21
<i>Calculated per quantity of soil containing 100 g clay</i>				
Exchangeable K	-0.05	-0.13	-0.16	-0.41**
K released by ignition	-0.36**	-0.31	-0.32	-0.37**
K released by HCl	0.05	-0.04	-0.12	-0.11
Naturally fixed HN ₄	0.15	-0.10	-0.21	-0.18

* Significant at $P < 0.05$, ** at $P < 0.01$, *** at $P < 0.001$

TABLE 5

Fixation and release of potassium and ammonium in soil profiles (me per 100 g soil). Average and standard deviation in parentheses for samples from 17 localities and 3 depths

Depth	Ex- change- able	Wet fixation		Dry fixation		Release			Con- tent of clay
		K	NH ₄	K	NH ₄	Ignition K	HCl K	Naturally fixed NH ₄	
0-20 cm	0.40(0.20)	0.30(0.14)	0.21(0.16)	0.62(0.41)	0.46(0.35)	0.99(0.72)	2.74(2.09)	0.86(0.63)	13
20-50 cm	0.28(0.21)	0.37(0.33)	0.29(0.32)	0.81(0.67)	0.58(0.53)	1.07(0.87)	2.81(2.32)	0.77(0.61)	15
50-100 cm	0.25(0.28)	0.39(0.32)	0.39(0.32)	0.85(0.54)	0.63(0.43)	1.18(0.85)	3.35(2.37)	0.67(0.51)	17

B. - Fixation and release of potassium and ammonium in soils from fertilizer experiments.

Exhaustion of soil potassium will gradually result from continuous cropping without compensation for the removed potassium. Contents of exchangeable as well as HCl-soluble potassium should then be expected to decrease and the potassium fixation to increase in accordance with the theory of equilibrium. Information on this point was sought through analyses of soils from permanent fertilizer experiments.

Very long-range experiments are found at two experiment stations: Askov, representing medium loam, since 1893, and Studsgaard representing light sandy soil, since 1908. The sampled plots had received no organic manure, but N- and P-fertilizers with or without potassium, or were wholly unmanured.

Actually the data in Table 6 show a very low content of exchangeable as well as HCl-soluble potassium in the plots receiving no potassium; this is most pronounced in the plots supplied with N and P fertilizers where larger crops are carried away. The exhaustion has little influence on the fixation, except for a suggestion of lower values in the plots receiving potassium; this applies to both soil types.

The sand soil seems rapidly to reach an equilibrium where the release of HCl-insoluble reserves together with potassium in the precipitation compensates for the removal of potassium in crops and by leaching from the soil. The net removal amounts in the unfertilized plots to some 25 to 30 kg/ha annually, depending on the

TABLE 6

Investigations of fixation and release of potassium in soils (mg K per 100 g soil) from permanent fertilizer experiments.

Treatment	Exchangeable	Dry fixation	Released by HCl
<i>Askov (medium loam) 5 replications</i>			
Unmanured	2.6	15.4	48.2
P + N	2.0	18.4	45.8
N + K	7.2	14.5	56.3
N + P + K	12.6	13.3	59.6
<i>Studsgaard (light sandy soil) 5 replications</i>			
Unmanured	2.6	4.6	24.1
P + N	2.8	5.5	24.8
N + K	7.4	3.9	25.5
N + P + K	8.2	4.2	27.3

crop yield. The progressing exhaustion does not lower the content of HCl-soluble non-exchangeable potassium, which is presumably maintained by release from normally insoluble reserves. In the loam soil plots that receive no potassium the supply seems also to be mainly derived from similar reserves, although there is here a noticeable decrease in the acid-soluble reserves.

As already mentioned there was no correlation between fixation and content of exchangeable potassium in the samples from the soils collection. As shown in Table 7 there is, however, some indication of negative correlation between content and fixation of potassium, as was to be expected according to the theory of equilibrium. No such correlation is visible in the sand soil, perhaps due to its low clay content and low capacity for fixation, while some potassium is released from other soil constituents.

Table 8 records the results of another set of analyses of soils from experiments on the residual effect of nitrogenous fertilizers. The N-fertilized plots were annually added 90 kg N per ha. The samples were taken from the upper 20 cm layer in the autumn 1969, 4 years after the first application of nitrogen. The average contents of naturally fixed ammonium are seen to be highest in the loam soils but differed strongly from one experimental site to another. The figures are upon the whole lower than in the 'collection' soils, most of which came from experimental stations where the applications of nitrogenous fertilizer are probably on the whole more plentiful than in average farm practice.

TABLE 7

Correlation between dry fixation of K, exchangeable K and K released by HCl in samples from permanent fertilizer experiments at Askov (medium clay) and Studsgaard (light sandy soil).

	Dry fixation of K		K released by HCl	
	Askov	Studsgaard	Askov	Studsgaard
Exchangeable K	-0.46	-0.03	0.51	0.26
Dry fixation of K			-0.38	-0.10

TABLE 8

Effect of N-fertilizers on the content of naturally fixed NH₄ (me per 100 g of soil). The N-fertilized soil supplied with 90 kg N/ha annually for 4 years.

	No. of soils	No N-fertilizer	Calcium ammonium				
			NPK	nitrate	Urea	Ammonia	
Averages	Clay	11	0.765	0.762	0.781	0.848	0.796
	Sand	9	0.476	0.439	0.446	0.477	0.451
		20	0.635	0.618	0.630	0.681*	0.641

For 20 samples 0.033 me NH₄ is significant difference (*).

It has often been pointed out that incorporation of anhydrous ammonia in the soil exposes the soil particles to such strong local influences that its value as fertilizer might be lowered. The strongly alkaline reaction which arises locally after application of anhydrous ammonia might well create favourable conditions for ammonia fixation. However, the figures in Table 8 do not show a particularly high content of fixed ammonium after 4 years of treatment with anhydrous ammonia, and if ammonium has been fixed it must apparently be readily released. Urea, which is rapidly ammonified in the soil, differs from other fertilizers in causing a minor but significant increase in fixed ammonium. It might appear as if the scattering of urea on the soil surface causes a stronger fixation of ammonium than other N fertilizers. The surplus fixation, however, amounts merely to 0.08 me/100 g at the highest, or 10 per cent of the applied nitrogen. Possibly a small fraction of ammonium could be fixed below the top soil layer, but experiments at the Askov Station⁵ have shown that practically all spring-applied ammoniacal nitrogen is oxidized to nitrate before being transported to the subsoil by the precipitation.

DISCUSSION

The potassium and ammonium transformations represent an important chapter in soil research and are of equal value in the practical management of fertilizers supplies.

The present investigation dealt with Danish soils mainly rich in clay and silt fractions because previous investigation ⁹ has shown that the processes of potassium and ammonium fixation are of prime importance in soil of this character.

The same soils were responsible for the fixation of potassium and ammonium under wet and dry conditions and the two cations were fixed in nearly equivalent amounts.

The ammonium ion was fixed prior to the potassium ion after simultaneous addition, and their combination in fertilizer application might therefore be of practical significance. Presumably their presence in mixed fertilizers would result in a greater ammonium fixation than would happen after application of potassium a few weeks prior to ammonium, which is usually the case when anhydrous ammonia is used.

The question arises how the degree of fixation under field conditions compares with the results of laboratory experiments where cations are added in concentrations far exceeding the practical use. The actual fixation increases with the concentration of cations but the percentual fixation is strongest at low concentration. Furthermore, under field conditions the fertilizer is allowed to react with the soil for a much longer time than in the laboratory, and intermittent periods of drying and re-wetting may permit the fixation to proceed much longer than in the laboratory. The homogeneous mixing of soil particles and electrolytes favour the fixation in the laboratory, opposite to time and concentration in the field. Upon the whole it is difficult to estimate the amount of field fixation, but the present results indicate that some fixation does take place in clay soils, particularly in the subsoil.

Considerable amounts of non-exchangeable potassium and ammonium were released by acid extraction or ignition, and some relations could be seen between release of the two ions if calculated on the basis of 100 g soil. This might probably be an effect of the clay fraction, and the correlation disappeared when calculated on the basis of 100 g of clay. Our knowledge of the availability of fixed

potassium and ammonium under practical conditions is quite deficient although we may assume that parts of the fixed cations may be released and taken up by the plants. Non-exchangeable potassium is only slowly released under normal soil management, but during the exhaustion of soil for potassium a certain amount becomes available, and under such conditions the plants have recourse to an ultimate reserve of potassium. Fixation and release are supposed to be opposite processes and some negative correlation could be seen for potassium when calculated on the basis of 100 g of clay.

The potassium status of the soil seems decisive for the fixation and the release of fixed ammonium⁷. Potassium has two opposite effects: its addition may reduce the fixation of exchangeable ammonium but counteract its release after fixation. Generally, plant utilization of naturally fixed ammonium seems to be a minor process. Most investigations^{2 12} indicate that considerable release of this fraction only happens when the content of exchangeable potassium is very low. Presumably the ammonium fixed after addition to the soil may be somewhat more available than the naturally fixed fraction.

It might be expected that the use of potassic and ammoniacal fertilizers should increase the soil content of non-exchangeable, acid-soluble potassium and ammonium. This was actually the case with potassium in the long-range experiment on loam soil at Askov (Table 6), and in the 4-year residual experiments (Table 8) where the use of urea led to a small increase in fixed ammonium in comparison with other nitrogenous fertilizers, or no nitrogen.

From these experiments it can be concluded that the same soils may show fixation as well as release, but this relation is mainly due to the clay fraction. Potassium and ammonium ions are fixed in equivalent amounts and the way of application decides which of the two ions will be fixed. Ammonium is fixed in preference to potassium when added simultaneously to the soil. In broad generality the importance of potassium and ammonium fixation in local Danish soils should not be overrated, since the process only reaches significant proportions in soils rich in clay minerals, and here it is chiefly the subsoil that displays a major propensity for fixation of the two cations.

ACKNOWLEDGEMENT

The writer wishes to express his thanks to Dr. H. L. Jensen for valuable assistance in preparation of the manuscript.

Received January 28, 1971

REFERENCES

- 1 Bremner, J., Determination of fixed ammonium in soil. *J. Agr. Sci.* **52**, 147-160 (1959).
- 2 Jansson, S. L., Tracer studies on nitrogen transformations in soil with special attention to mineralisation-immobilisation relationship. *Kungl. Lantbrukshögskolens Ann.*, **24**, 101-361 (1958).
- 3 Egnér, H., Brodin, G., and Johanson, G., Sampling technique and chemical examination of air and precipitation. *Kungl. Lantbrukshögskolens Ann.* **22**, 397 (1955).
- 4 Jensen, E., The mineralogical composition of the finegrained fraction of some typical Danish agricultural soils. *Kgl. Vetr. Landbohøjskole Årskr.*, 13-32 (1955).
- 5 Kofoed, A. D., Lindhard, J., and Søndergaard Klausen, P., Forsøg med flydende ammoniak. *Tidsskr. Planteavl* **71**, 145-225 (1967).
- 6 Kolterman, D. W. and Truog, E., Determination of fixed soil potassium. *Soil Sci. Am. Proc.* **17**, 347-351 (1953).
- 7 Nömmik, H., Fixation and defixation of ammonium in soils. *Acta Agr. Scand.* **7**, 395-436 (1957).
- 8 Reitemeier, R. F., Soil potassium. *Advances Agron.* **3**, 113-164 (1951).
- 9 Schachtschabel, P. and Köster, W., Chemische Untersuchungen an Märgen, 3. Kaliumfixierung und Kaliumnachlieferung. *Pflanzenernchr. Düng.* **89**, 148-159 (1959).
- 10 Stanford, G. and Pierre, W. H., The relation of potassium fixation to ammonium fixation. *Soil Sci. Soc. Am. Proc.* **11**, 155-160 (1946).
- 11 Walsh, L. M. and Murdock, J. T., Native fixed ammonium and fixation of applied ammonium in several Wisconsin soils. *Soil Sci.* **89**, 183-193 (1959).
- 12 Welch, L. F. and Scott, A. D., Nitrification of fixed ammonium in clay minerals as affected by added potassium. *Soil Sci.* **90**, 79-85 (1960).