Recovery and vertical distribution of ^{15}N labelled fertilizer nitrogen in forest soil

Återvinning och vertikal fördelning av ^{15}N-märkt handelsgödselkväve i skogsmark

by

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ABSTRACT

Laterally isolated micro-plots were used for studying the recovery and vertical distribution of various sources of ^{15}N-labelled fertilizer nitrogen in the soil beneath a 90 years' old stand of Scots pine (*Pinus silvestris* L.). The fate of the added nitrogen was followed by sampling and analysing the field layer vegetation, litter and soil after different time intervals during the growing season 1968 (4 times) and also in spring 1969 (once). Of the calcium nitrate, ammonium sulphate and urea-N added, the amounts recovered at the end of the experiment (i.e. after 12 months' exposure) were 23, 63 and 76 per cent, respectively. Less than ten per cent of the recovered N was in inorganic form. Urea-N showed the lowest mobility of the fertilizers applied, and tended to accumulate in the litter and humus layers.

1. Introduction

According to investigations hitherto carried out in Sweden, the degree of uptake of fertilizer nitrogen in middle-aged stands of both pine and spruce is usually less than 20 per cent (Tamm 1963). What happens to that part of the fertilizer nitrogen which is not taken up by the forest stand, is a question not fully understood. In an investigation carried out on a poor pine forest, employing ^{15}N-labelled nitrogen sources and rootisolated plots, Björkman *et al.* (1967) showed that no less than 50—60 per cent of the calcium nitrate and ammonium sulphate N supplied was immobilised during one growing season and could therefore be recovered in the soil profile in organically bound form. A relatively high recovery, and hence a small loss by leaching, of commercial fertilizer nitrogen has also been reported from lysimeter experiments performed by Cole & Gessel (1965) and Overrein (1968). Of the form of nitrogen tested, urea has proved to be especially affected by microbial immobilisation, and its mobility in the soil has been found to be markedly lower than for the nitrogen in ammonium sulphate (Roberge & Knowles 1966, Overrein 1967, 1970). As regards the extent of nitrogen loss by volatilisation of ammonia, this may be significant for urea, even when it is applied on forest soil covered with a layer of acid raw humus (Hüser 1969, Volk 1970, Overrein 1970).

The aim of the present study was to assess the quantitative recovery, transformation and vertical distribution of different sources of fertilizer nitrogen in forest soil under field conditions.

2. Materials and methods

The experimental site is situated ca 15 km SW of Stockholm, in the State forest of Lindhof. The topography of the experimental area is almost flat, but with a very slight slope towards the west. The area is otherwise fairly hilly. Geologically, the entire area is part of the Uppsala eskar (de Geer 1932), and the solid geology consists of massive blocks of granitic gneiss or gneissose granite (Sundius 1948).
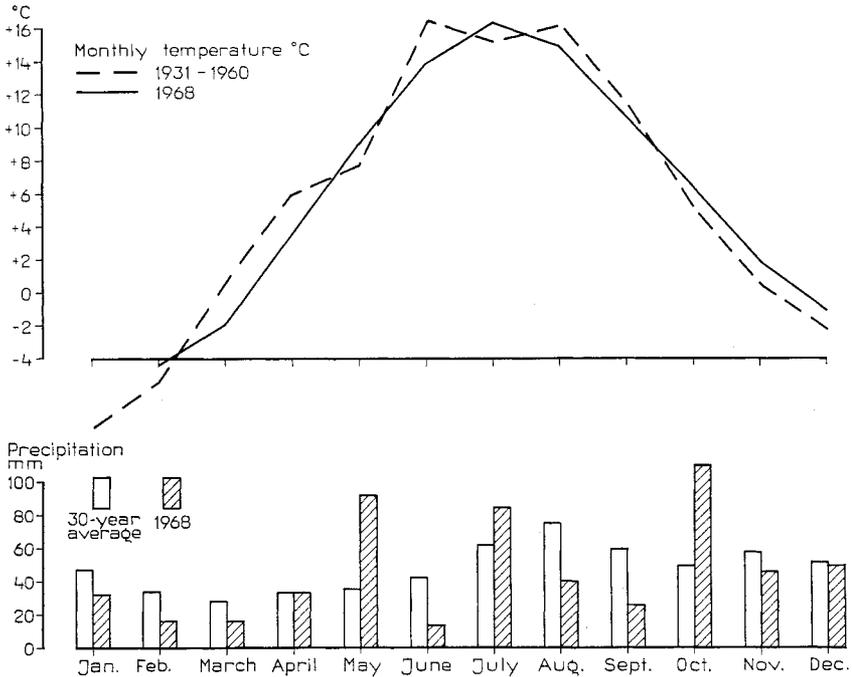
Figure 1. Monthly mean temperature and precipitation for 1968 and mean values for period 1931—1960. Meteorological station Tullinge (Riksten).

The soil may be classified as an iron-humus podzol with a marked mor layer, 5—7 cm in thickness, and an A_2-horizon varying in thickness between 3 and 8 cm. Analytical data for soil properties (Table 1) indicate a poor (oligotrophic) soil, with a low nitrogen content and a C/N ratio of more than 40 in the mor layer.

From data on textural composition (Table 2) it is apparent that the soil is an almost pure sand, low in silt and clay. The tree stand consisted mainly of pine with occasional spruces. The stand had a mean height of 21 m, and an age of 90 years. The site class (Jonson) was III, equivalent to T-24 according to the H_{100} system of the Royal College of Foresty. The field layer consisted mainly of *Vaccinium myrtillus, V. vitis-idaea* and *Deschampsia flexuosa*. The ground layer consisted of mosses such as *Pleurozium schreberi, Dicranum* sp. etc.

The weather during the summer of 1968 differed somewhat from the normal as far as rainfall is concerned, in that June and September were drier but May, July and October much more rainy than usual (see Figure 1).

Table 1. Data for some chemical properties of the soil.

Sample	pH (H_2O)	P AL[a]	P HCl[b]	K AL[a]	K HCl[b]	Ignition loss, % dry wt	C, %	N, %	C/N ratio
Humus, A_0 -horizon	4.0	6.8	37	28.2	57	52.6	30.9	0.759	40.7
Mineral soil									
0— 5 cm	4.4	2.8	28	4.2	42	3.5	1.52	0.044	34.5
5—10 cm	4.8	1.7	35	3.5	52	1.6	0.45	0.021	21.4
10—20 cm	5.1	3.0	37	2.7	60	1.4	0.32	0.019	16.8

[a] Ammonium lactate soluble, mg/100 g
[b] HCl-soluble, mg/100 g

Table 2. Mechanical analysis for mineral soil. Percentage of dry wt.

Layer	Sand	Fine sand	Silt	Clay	Organic matter
0— 5 cm	86	6	3	3	2.3
5—10 cm	89	6	2	2	0.7
10—20 cm	93	5	1	1	0.5

Experimental technique

The field technique involved the use of laterally isolated micro-plots (cf. Björkman *et al.* 1967, Nömmik 1967), employing sheet metal rings having an inside diameter of 570 mm, and height of 450 mm. The plot area was 0.255 m². The cylinders were buried into the soil, assisted by digging, without however disturbing the natural stratification and drainage conditions inside the cylinder. A margin of 5 cm of the cylinder remained above the soil surface.

The experiment was laid out in three blocks, with 20 micro-plots in each (four nitrogen sources with five replications of each for varying length of exposure). The treatments within a block were distributed randomly. The plots were placed not less than 50 cm from each other and not less than 4 m from the nearest pine stem. The area of one block did not exceed 100 m² and all three blocks were situated within an area 40 × 40 m.

The experiment was started on 29 May 1968, when the ^{15}N-labelled nitrogen materials were applied. The application was by topdressing, the nitrogen doses corresponding to 100 kg N/ha.

As may be seen from the experimental plan (see below), the plots were sampled on five different dates, 3 × 4 plots on every occasion.

The sampling included the following fractions: field layer vegetation (1), litter, including mosses and lichens (2), humus (3), mineral soil 0—5 cm beneath the humus layer (4), mineral soil 5—10 cm (5), mineral soil 10—20 cm (6), roots in the humus layer (7) and roots in the mineral soil layers (8). The material of fractions Nos. 1, 2, 3, 7 and 8 was in its entirety taken into the laboratory, dried rapidly at 30°C, weighed and ground to pass a 2 mm sieve. The material from mineral soil layers (samples 4—6), on the other hand, was transferred to 50-litre plastic containers, the stones and roots were removed, the material was homogenised carefully by mixing, weighed and a representative sample of approximately 1 kg of the moist soil was taken out for laboratory investigations, including the determination of moisture content. From the weighing values in the field and the moisture content of the material, the total amount of dry matter included in the chemical tests was obtained for each layer of mineral soil.

Experimental plan

The experimental plan comprised the following treatments:
(a) Untreated
(b) Calcium nitrate, 100 kg N/ha, top-dressed
(c) Ammonium sulphate, 100 kg N/ha, top-dressed
(d) Urea, 100 kg N/ha, top-dressed

As described above, every treatment was laid out in 15 replications, of which three were sampled on each of the five sampling dates. Sampling took place on the following dates: 5 July (1), 15 August (2), 30 September (3), 12 November 1968 (4), and 22 May 1969 (5).

Nitrogen materials

(1) Calcium nitrate—14.2 % N, 1.723 atomic-% $^{15}N_{exc}$, crystalline,
(2) Ammonium sulphate—21.2 % N, 1.981 atomic-% $^{15}N_{exc}$, crystalline,
(3) Urea—46.0 % N, 1.607 atomic-% $^{15}N_{exc}$, granulated.

Analytical methods

Total nitrogen was determined by the macro-Kjeldahl procedure, including pretreatment with salicylic acid to include nitrate (see Bremner 1965).

Exchangeable ammonium and nitrate were determined in the 1 M KCl extract of the soil. Ammonium-N in the extract was separated by

distillation in the presence of borate buffer (pH 8.8), and determined in the distillate by acidometric titration. Nitrate-N in the distillation residue was determined using Devarda's alloy.

Isotopic abundance measurements for N were carried out by LKB-9000 Gas Chromatograph-Masspectrometer, provided with equipment for isotope-ratio analysis.

pH in the soil-water suspensions (ratio 1 : 5) was determined with a glass electrode.

3. Results

An assessment of the quantitative losses and vertical distribution of the residual fertilizer nitrogen in a soil profile may be obtained by two, in principle entirely different, methods. The one, which has frequently been used on uncropped arable soils, involves a determination of the quantity of inorganic nitrogen present in the soil profile of both treated and control soil. The excess of inorganic nitrogen in treated soil, expressed per unit area, is considered to be derived from the nitrogen source added. This "difference method" is based on the assumption that none of the added nitrogen is removed from the inorganic nitrogen pool by immobilisation and that the fertilizer treatment does not affect the net mineralization of the native organic nitrogen of the soil. It is known that these conditions are only exceptionally fulfilled entirely (Nömmik 1968 *a, b*). Nevertheless, for practical purposes the method gives acceptable results in many cases.

The other method is based on the use of isotopically labelled nitrogen sources, which have the advantage that they are easily traced and quantitatively estimated in the soil. A limitation of this technique, besides the high experimental cost, is the uncontrolled effects of the isotope exchange reactions occurring between the ammonium-N and the organic nitrogen pools of the soil (see Jansson 1958, Nömmik 1968 *b*). The consequences of these reactions are difficult to evaluate quantitatively. It seems probable that the microbial nitrogen turnover tends to give too high figures for the net immobilisation of inorganic nitrogen and, conversely, too low figures for nitrogen loss by leaching and volatilisation. In general, this interference is the more significant the higher is the soil content of organic matter, and the longer the fertilizer nitrogen remains in ammonium form.

In the present study, the recovery of added fertilizer nitrogen in the soil profile is estimated by both the difference method and the isotopic tracer technique.

Table 3. Total amount of labelled fertilizer nitrogen recovered in the field layer vegetation and in the soil profile on different sampling dates, percentage of amount applied (= kg N/ha). Refer to Kjeldahl-N, incl. nitrate-N. Nitrogen application rate 100 kg N/ha. Application time 29/5 1968.

| Nitrogen source | Sampling dates | | | | |
	5/7 (1)	15/8 (2)	30/9 (3)	12/11 (4)	22/5-69 (5)
Calcium nitrate					
Vegetation	3.9	10.3	20.3	2.2	2.5
Litter	19.3	8.1	8.8	8.5	4.0
Humus	46.9	8.9	7.5	5.9	4.4
Mineral soil 0— 5 cm	18.6	10.0	6.7	4.6	3.5
5—10 cm	5.3	5.3	6.0	2.9	2.8
10—20 cm	4.0	8.5	5.3	6.1	3.9
Roots, humus layer	7.2	1.8	6.1	4.0	1.1
Roots, mineral soil	0.5	1.5	1.3	0.7	0.6
Total	*105.7*	*54.4*	*62.0*	*34.9*	*22.8*
Ammonium sulphate					
Vegetation	4.7	6.4	15.8	2.7	3.7
Litter	29.6	17.7	16.1	14.1	13.4
Humus	24.0	14.0	19.9	19.9	15.4
Mineral soil 0— 5 cm	18.7	23.7	15.2	20.0	16.8
5—10 cm	4.8	7.0	6.4	8.2	5.2
10—20 cm	3.7	6.1	5.2	8.3	6.2
Roots, humus layer	4.5	3.4	1.6	2.3	1.6
Roots, mineral soil	0.4	1.0	0.8	0.8	0.3
Total	*90.4*	*79.3*	*81.0*	*76.3*	*62.6*
Urea					
Vegetation	6.2	3.6	10.8	2.2	3.3
Litter	46.3	44.0	37.2	35.0	25.3
Humus	26.8	20.7	28.1	24.9	29.9
Mineral soil 0— 5 cm	5.7	11.4	4.5	6.7	10.8
5—10 cm	2.0	3.6	2.4	2.3	2.3
10—20 cm	1.4	4.4	1.7	2.2	2.0
Roots, humus layer	2.0	0.9	2.2	1.2	2.0
Roots, mineral soil	0.2	0.6	0.2	0.4	0.4
Total	*90.7*	*89.2*	*87.1*	*74.9*	*76.0*

Table 3 and Figure 2 give data on the total recovery of added, ^{15}N-labelled nitrogen in the field layer vegetation and in the different soil layers & on different sampling dates after the nitrogen application. The figures are based on the Kjeldahl-N fraction (sum of organic and inorganic nitrogen). It appears that on the first sampling date (approximately five weeks after application of fertilizer nitrogen), the recovery figures for calcium nitrate-, ammonium sulphate- and urea-N were 106, 90 and 91 per cent, respectively. According to the statistical ana-
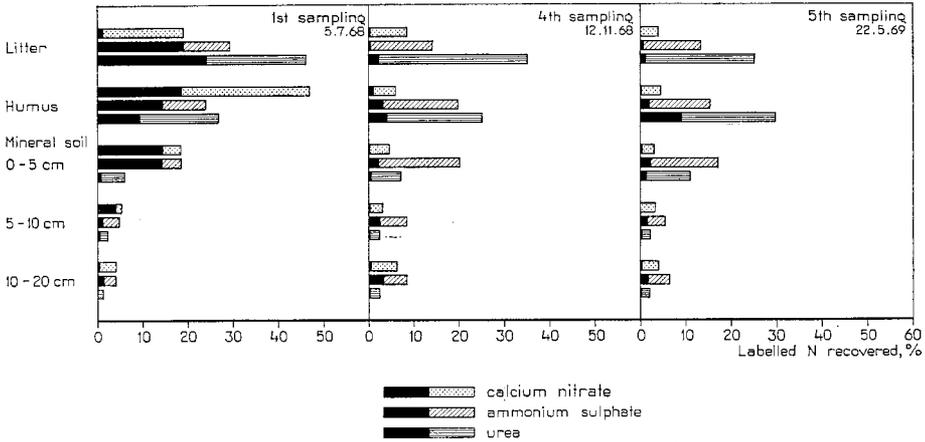
Figure 2. Labelled nitrogen recovered at different depths in the soil profile, per cent. Total length of bars refers to total amount of labelled nitrogen recovered, per cent of added. Black part of bars refers to labelled nitrogen recovered in inorganic form, per cent of added.
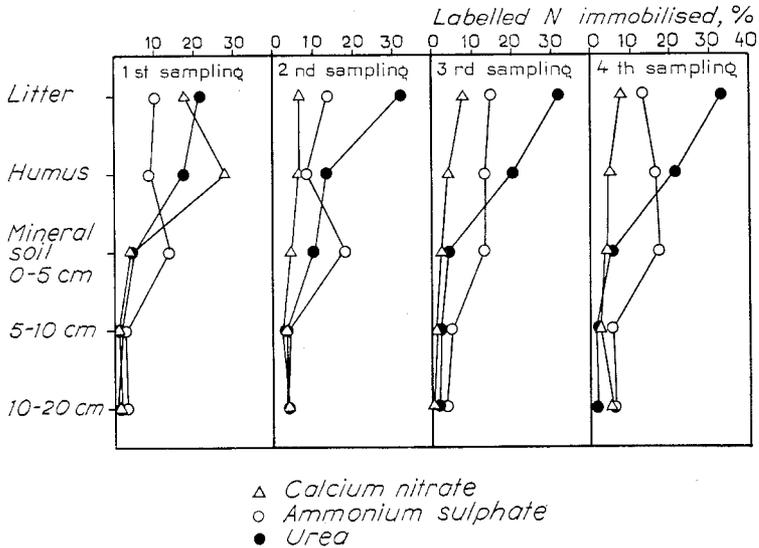

Figure 3. Labelled fertilizer nitrogen immobilised in different soil layers. Per cent of nitrogen added.

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Table 4. Fertilizer nitrogen immobilised per unit of organic matter present in different soil horizons, ppm. Refer to the 3rd sampling date.

	Calcium nitrate	Ammonium sulphate	Urea
Litter	420	930	2670
Humus	110	460	940
Mineral soil, 0— 5 cm	110	550	170
5—10 cm	20	50	30
10—20 cm	<10	20	<10

Table 5. Recovery of inorganic nitrogen in the soil profile on different sampling dates, mg N/plot. Nitrogen application rate 2550 mg N/plot (= 100 kg N/ha).

Nitrogen source	Sampling dates									
	5/7 (1)		15/8 (2)		30/9 (3)		12/11 (4)		22/5—69 (5)	
	Total[a]	Labelled	Total[a]	Labelled	Total[a]	Labelled	Total[a]	Labelled	Total[a]	Labelled
Control										
Litter	22		49		21		24		57	
Humus	116		171		106		225		104	
Mineral soil 0— 5 cm	38		93		112		193		101	
5—10 cm	76		76		131		195		63	
10—20 cm	64		81		183		259		82	
Total	*316*		*470*		*553*		*906*		*407*	
Calcium nitrate										
Litter	+89	31	+88	42	+47	11	+9	7	− 26	3
Humus	+744	478	+107	69	+161	69	− 34	18	− 7	7
Mineral soil 0— 5 cm	+427	372	+240	137	+103	108	− 1	7	+10	8
5—10 cm	+85	104	+79	63	+115	124	− 14	6	+23	6
10—20 cm	+54	49	+168	114	+92	136	+15	9	+33	8
Total	*+1399*	*1034*	*+668*	*425*	*+518*	*448*	*− 35*	*47*	*+33*	*32*
Ammonium sulphate										
Litter	+553	489	+193	91	+48	24	+12	9	+9	14
Humus	+694	373	+199	128	+420	158	+159	80	+146	51
Mineral soil 0— 5 cm	+210	119	+386	139	+108	53	+161	59	+143	55
5—10 cm	+36	43	+145	85	+64	39	+125	61	+102	39
10—20 cm	+40	36	+113	73	+54	37	+156	82	+75	41
Total	*+1533*	*1060*	*+1036*	*516*	*+694*	*311*	*+603*	*291*	*+475*	*200*
Urea										
Litter	+769	612	+423	296	+211	126	+99	57	+21	34
Humus	+361	240	+269	181	+352	191	+211	97	+339	113
Mineral soil 0— 5 cm	+38	17	+158	30	+100	22	− 3	15	+139	30
5—10 cm	− 18	6	+5	20	+24	8	− 31	6	+46	11
10—20 cm	+1	6	+36	14	+36	6	− 15	5	+26	9
Total	*+1151*	*881*	*+908*	*541*	*+723*	*353*	*+251*	*180*	*+571*	*197*

[a] The figures for treated plots refer to amounts of inorganic nitrogen excess over the control treatment.

lysis, none of the above recovery figures differs significantly from 100. It is assumed that the main source of error originates from the sampling operation in the field.

The figures for the vertical distribution of labelled N in the soil profile on the first sampling occasion indicate some definite differences for the three nitrogen sources tested. As regards e.g. the *litter layer,* no less than 47 per cent of the added urea-N could be recovered in this horizon. The corresponding figures for ammonium sulphate and calcium nitrate were 30 and 19 per cent, respectively. Except for the calcium nitrate treatment, not more than approximately half of the labelled nitrogen recovered in the litter layer was in inorganic form (see Figure 2 and Table 5). In the *humus layer* the recovery of tracer nitrogen was for calcium nitrate 47, for ammonium sulphate 24 and for urea 27 per cent. The amounts of recovered fertilizer nitrogen in the three *mineral soil layers* were 28, 27 and 9 per cent for calcium nitrate, ammonium sulphate and urea, respectively.

On the second and third sampling dates (15 August and 30 September, respectively) the total recovery figures for labelled nitrogen had decreased markedly, being for calcium nitrate 54 and 62, ammonium sulphate 79 and 81, and urea 89 and 87 per cent, respectively. The tendency towards an accumulation of urea-N in the litter layer was still very clear. The higher mobility of nitrogen in calcium nitrate and ammonium sulphate was evident from the relatively high levels of labelled inorganic nitrogen in the mineral soil.

On the last sampling date, i.e. in the following spring, only 23 per cent of the added calcium nitrate-N could be recovered in the field layer vegetation and in the soil layers investigated. For ammonium sulphate and urea, the recovery was considerably higher, amounting to 63 and 76 per cent, respectively. Of the labelled nitrogen recovered, less than one-fifth was present in inorganic form (cf. Table 5).

When using the "difference method" for estimating fertilizer nitrogen recovery in soils, i.e. the excess amounts of inorganic nitrogen recovered on treated plots as compared with control plots, it is evident that the figures obtained are substantially lower than those obtained from ^{15}N data (cf. Table 5, Fig. 4). Thus, for calcium nitrate the nitrogen recovery at the end of the experiment is approximately ± 0, and for ammonium sulphate and urea, about 20 per cent. The recovery figures for labelled inorganic nitrogen are still lower.

As regards the soil content of *inorganic nitrogen,* it was in general significantly increased by fertilizer application. Since the acid forest soil in question was characterised by an extremely low nitrification
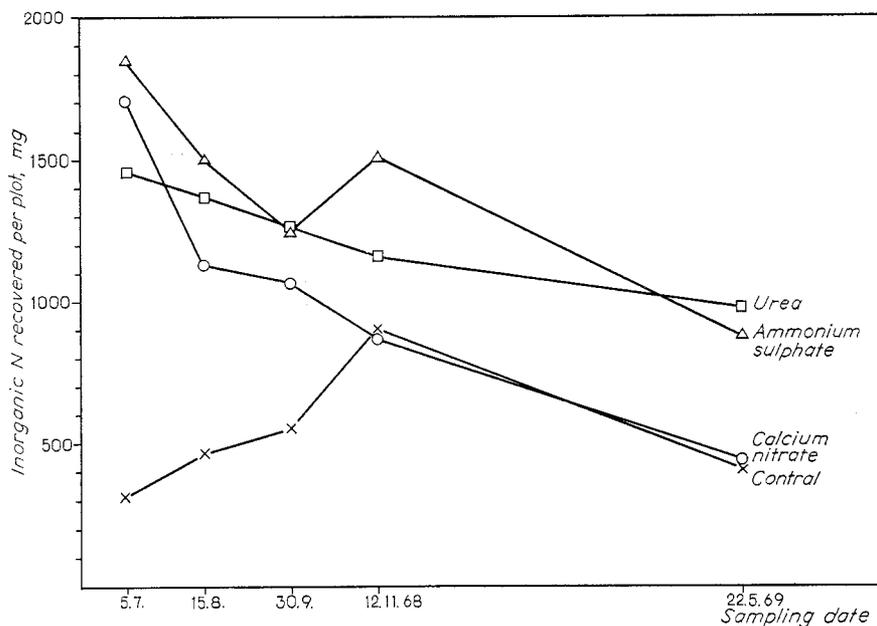
Figure 4. Total amounts of inorganic nitrogen, labelled and non-labelled, recovered in soil profile.

capacity, the nitrate content of the soil was not measureably changed by the addition of ammonium sulphate or urea. On the other hand, the soil content of exchangeable ammonium was markedly increased by the addition of the nitrate form of nitrogen. Thus it is evident from Table 5 and Figure 5 that on the first sampling date, the soil on calcium nitrate treated plots showed an ammonium-N content which was approximately 400 mg (corresponding to 15.7 kg N/ha) higher than that from control plots. It may be noted that not more than a quarter of this ammonium-N was derived from the labelled calcium nitrate added.

The figures for the vertical distribution of labelled N in the soil profile show some characteristic features of the mobility of various nitrogen sources used. As regards nitrogen in *calcium nitrate*, it was exceedingly mobile in the soil media in question. The figures show that in spite of the low precipitation during the spring and summer, about half of the added nitrate N had passed the soil layers investigated by the middle of August. Furthermore, it may be concluded that on the last sampling date in the autumn (12 November), only traces of the
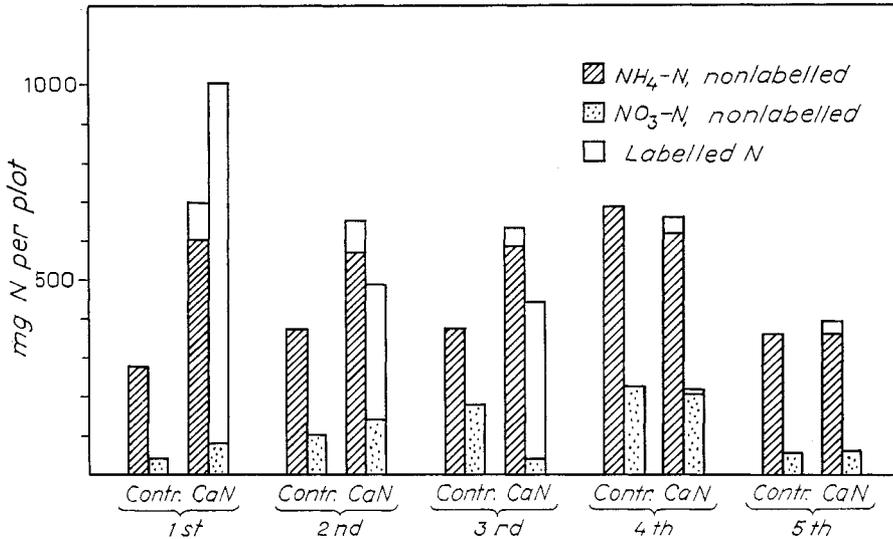
Figure 5. Amounts of ammonium and nitrate nitrogen, both labelled and non-labelled, in soil from control plots and plots treated with calcium nitrate.

labelled N added as calcium nitrate could be recovered in inorganic forms. Evidently, under the climatic conditions prevailing in Central Sweden, the nitrate in forest soils is not carried over from one season to another.

For *ammonium sulphate-* and *urea-N* the distribution pattern in the soil profile is completely different from that for calcium nitrate, depending to a large extent on the incapacity of the soil to nitrify. The high retention by the litter layer is especially striking in the case of urea. The low mobility of added urea-N is illustrated conclusively also by data for amounts of labelled nitrogen recovered in the mineral soil layers in inorganic forms. A comparison with ammonium sulphate gives the following recovery figures (expressed in per cent of the labelled nitrogen added):

	Sampling date				
	1	2	3	4	5
Ammonium sulphate	7.8	11.6	5.1	7.9	5.3
Urea	1.1	2.5	1.4	1.0	2.0

As to the inorganic nitrogen content of soil on the control plots, it appears that this showed a substantial increase from the start in the

Table 6. pH of litter, humus and mineral soil as influenced by nitrogen fertilizer treatment[a].

	Litter		Humus		Mineral soil, 0—5 cm	
	(1)	(5)	(1)	(5)	(1)	(5)
Control	4.3	4.3	3.9	3.8	4.1	4.1
Calcium nitrate	4.4	4.4	3.8	3.9	3.9	4.1
Ammonium sulphate	3.8	4.1	3.7	3.8	—	4.1
Urea	5.4	4.6	4.1	4.2	4.0	4.2

[a] Refer to the first (1) and fifth (5) sampling date, respectively. Means of three replicate treatments.

Table 7. F-test values for different forms of nitrogen in mg/plot. Lindhof 1968—1969.

Source of variation	$^{15}N_{tot}$	$^{15}N_{ammon}$	N_{ammon}	$^{15}N_{inorg}$	N_{inorg}
Block	0.46	1.69	5.34**	2.03	5.67**
Treatment	26.53***	88.56***	50.33***	9.36***	44.91***
Sampling date	18.16***	45.41***	7.79***	33.92***	15.46***
Interaction treatment × time	5.03**	13.54***	2.12*	1.48	3.81**

spring to the last sampling date in the autumn (Table 5, Figures 3—5). This increase was most marked for nitrate nitrogen. On sampling in November, the soil on the control plots contained not less than 27 kg inorganic nitrogen per ha. During the winter nearly all of the nitrate and half of the ammonium nitrogen accumulated during the growing season was lost, possibly by leaching. The nitrate distribution pattern in the soil profile indicates that most of the nitrate formation probably occurred in the mineral soil layers.

In Table 6 are given data on pH changes in soil as a consequence of fertilizer treatment. It may be concluded that on the first sampling (1), the pH of the litter was decreased by ammonium sulphate addition, whereas treatment with urea resulted in a marked increase of pH. Calcium nitrate was indifferent in this respect. The pH of the humus and the uppermost mineral soil layer was only insignificantly influenced by the application of nitrogenous materials. The above trend in pH changes of the litter diminished with time but was still significant at the end of the experiment.

In Table 7 are given data on F-test values for different forms of labelled and nonlabelled nitrogen. The high significance for treatment and sampling date should be observed.

4. Discussion

The mobility of nitrogen in the various nitrogen sources used is rather instructively demonstrated by data on labelled nitrogen distribution in the soil profile. Most striking is the high retention capacity of the litter and mor layers for urea nitrogen. This observation is in good agreement with the results obtained by other workers (Cole & Gessel 1965, Overrein 1968). The relatively rapid downward displacement of ammonium sulphate nitrogen in this non nitrifying forest soil was however rather remarkable, indicating a considerable risk of leaching loss even for the ammonium form of nitrogen. From Table 3 it may be concluded that not more than 63 per cent of the added ammonium sulphate nitrogen could be recovered in the soil and field layer vegetation after 12 months' exposure (cf. Overrein 1970). It may also be seen from Fig. 5 that approximately half of the ammonium-N accumulated on control plots during the growing season was lost from the soil during the winter. As the loss of ammonia by volatilization is rather unlikely on the acid soil in question, the part of the ammonium sulphate-N not recovered may most probably have been removed from the uppermost soil layers by leaching. For urea, a loss of nitrogen by volatilization of ammonia should not, however, be excluded.

The high retention of urea-N in the litter, and even in the humus layers, is to a large extent explicable in terms of intensive microbial immobilization, induced primarily by the pH increase produced by urea hydrolysis. But this is unlikely to be the whole truth. According to the figures in Table 5, the litter and humus layers of plots treated with urea also contained larger amounts of exchangeable ammonium than those on the ammonium sulphate plots. The ammonium formed on hydrolysis of urea thus appears to be less subject to leaching than ammonium from added sulphate. This is not at variance with previous observations showing that the mobility of the ammonium ion is greatly influenced by the presence of easily diffusible anions, e.g. chloride, nitrate, sulphate. It may be considered, furthermore, that the increase of pH resulting from urea application will increase the cation exchange capacity of the organic material in the litter and mor layers, and thus increase their capacity for retaining ammonium ions in exchangeable form.

Two different procedures were used for estimating the quantitative recovery of added fertilizer nitrogen in the soil profile. The first was based on the use of labelled nitrogen data and the second on the difference in inorganic nitrogen content on treated and control plots. It was shown that even after correction for labelled nitrogen in the ground vegetations the methods gave rather divergent results, the recovery figures being significantly higher for the tracer nitrogen technique than for the indirect difference procedure. This discrepancy is largely explicable by the capacity of the litter and humus layer to immobilise added fertilizer nitrogen. As may be seen from Table 1, the C/N ratio in organic matter of the above soil layers exceeded 40 indicating a low degree of decomposition. It is recognised that the microbial decomposition of this type of acid and only slightly transformed organic matter is accompanied by a net immobilisation of inorganic nitrogen. Owing to this, fertilizer nitrogen, when applied to such a soil, is more or less quantitatively taken up by the microbial flora and removed from the available nitrogen pool of the soil. A non-enzymatic fixation of ammonia by the soil organic matter is less probable on this acid soil. The effect of isotopic exchange on the amounts of labelled nitrogen incorporated into the soil organic nitrogen fraction, should be considered, however.

Figure 2 and 3 show that not only ammonium, but also added nitrate nitrogen, is subject to microbial immobilisation in the soil, the most extensive immobilisation occurring in the litter layer. As a result of fertilizer treatment, the organic nitrogen content of the litter increased from 0.91 (in control plots) to 0.97, 0.96 and 1.18 per cent for calcium nitrate, ammonium sulphate and urea treatments respectively. The immobilisation per unit of organic matter was lower for the other soil layers, than for the litter (Table 4).

As mentioned above, urea showed the highest tendency to be immobilised in the soil, compared with calcium nitrate and ammonium sulphate. Of urea-N added, approximately 30 per cent was immobilized in the litter layer, 20 per cent in the humus layer and 10 per cent in the mineral soil layers studied. The high relative immobilisation in the litter layer was closely related to the pH increase following the addition of urea. From recent studies by Tamm & Pettersson (1969) and Nömmik (1968 a, b), it was evident that the increase of pH in the acid raw humus brought about by the addition of lime resulted in a marked decrease in the amounts of inorganic nitrogen accumulated on incubation. It was shown, furthermore, that liming induced a substantial immobilisation of added inorganic nitrogen. By use of the ^{15}N tech-

nique, it could be demonstrated that the added ammonium-N was successively incorporated into the stable humic fraction of the soil organic matter. It was concluded that the immobilisation reaction was principally enzymatic in nature. This is in accordance with the results of Overrein (1967), showing that the amount of urea-N immobilised in raw humus was markedly influenced by the temperature of incubation.

It was demonstrated that a treatment with calcium nitrate increased the amounts of exchangeable ammonium accumulated in all the soil layers studied. It was interesting that only a fractional part of this ammonium was derived from the added, labelled nitrate. Most of it was released from the native soil organic matter by mineralisation. This nitrate-induced organic nitrogen mineralisation has previously been described by Zöttl (1960) and Nömmik (1968 b). Zöttl is inclined to believe that the accumulation of ammonium on nitrate application is a result of partial sterilisation, as the carbon mineralisation was depressed by nitrate treatment. The last observation is in agreement with the results of recent investigations by one of the present authors (Nömmik, unpublished).

Figures on the isotopic composition of the exchangeable ammonium fraction showed that the addition of labelled fertilizer nitrogen consistently increased the release of unlabelled nitrogen from the native humus nitrogen pool. An increased accumulation of unlabelled ammonium-N, in comparison with the control, was evident for all of the sampling periods employed. This "priming effect" has been characterized by Jansson (1958) and Nömmik (1968 b) as a chimaera, being a result of isotopic exchange. Overrein (1970), on the other hand, has reported data on real positive priming effects, showing that the increase of exchangeable ammonium-N was in some cases higher than the total amount of labelled inorganic nitrogen added. It should be realised, however, that the priming effect described by some workers, obviously is to be related to uncritical interpretation of tracer data.

5. Summary

Using micro-plots, of 0.255 m², isolated laterally to a depth of 40 cm by sheet metal rings, the recovery and vertical distribution of various sources of 15N-labelled nitrogen were studied on an acid, poorly nitrifying forest soil (podzol). Fertilizer nitrogen recovery in the various soil layers and in the field layer vegetation was examined after different time intervals, the last occasion being in the spring one year after fertilizer application.

It was found that of the nitrogen added as calcium nitrate, ammonium sulphate and urea, the amounts recovered at the end of the experiment (i.e. after 12 months' exposure) were 23, 63 and 76 per cent, respectively. Less than ten per cent of the recovered N was in inorganic form.

From data on the distribution of labelled nitrogen in the soil profile, it was concluded that of the nitrogen sources tested, the urea-N showed the lowest mobility, and tended to accumulate in the litter and humus layers. The relatively highest accumulation in mineral soil layers was found for ammonium sulphate-N. The capacity of the litter and raw humus to immobilise added fertilizer nitrogen, and conditions for this, are discussed.

It was evident from the nitrogen distribution data that only traces of nitrate were carried over from one season to another. Nor was the ammonium form of nitrogen resistant to & leaching under the climatic and soil conditions studied. The relatively high retention of added fertilizer 15N by the soil was mainly due to microbial immobilisation.

REFERENCES

Björkman, E., Lundeberg, G. & Nömmik, H. 1967. Distribution and balance of ^{15}N labelled fertilizer nitrogen applied to young pine trees (*Pinus silvestris* L.) *Stud. For. Suec.*, *48*, 1—23.

Bremner, J. M. 1965. Total nitrogen. In: *Methods of soil analysis* (eds C. A. Black *et al.*) Part 2. (Also in *Am. Soc. Agron., No. 9, Ser. Agronomy*, 1149—1178.)

Cole, D. W. & Gessel, S. P. 1965. Movement of elements through a forest soil as influenced by tree removal and fertilizer additions. *Forest Soil Relationships in North America.* Oregon State Univ., Washington.

Geer, G. de. 1932. Stockholmstraktens Kvartärgeologi. *Sver. Geol. Undersökning, Ser. Ba, No. 12.*

Hüser, R. 1969. Harnstoffumsetzung im Rohhumus. *Forstwiss. Cbl.*, *88*, 149—159.

Jansson, S. L. 1958. Tracer studies on nitrogen transformation in soil with special attention to mineralisation-immobilization relationships. *Kungl. Lantbrukshög. Ann.*, *24*, 101—361.

Nömmik, H. 1967. Use of micro-plot technique for studying gaseous loss of ammonia from added nitrogen materials under field conditions. *Acta Agric. Scand.*, *16*, 147—154.

— 1968 *a*. Skogens kväveförsörjning och möjligheterna att påverka den. *Skogs.- o. Lantbruksakad. Tidskr.*, *107*, 43—60.

— 1968 *b*. Nitrogen mineralization and turnover in Norway spruce (*Picea abies* (L.) Karst.) raw humus. *9th Internat. Congr. Soil Sci. Trans., Vol. 2*, 533—545.

Overrein, L. N. 1967. Immobilization and mineralization of tracer nitrogen in forest raw humus. 1. Effect of temperature on the interchange of nitrogen after addition of urea, ammonia and nitrate N[15]. *Plant and Soil*, *27*, 1—19.

— 1968. Lysimeter studies on tracer nitrogen in forest soil. 2. Comparative losses of nitrogen through leaching and volatilization after the addition of urea, ammonia and nitrate N[15]. *Soil Sci.*, *107*, 149—159.

— 1970. Tracer studies on nitrogen immobilization-mineralization relationships in forest raw humus. *Plant and Soil*, *32*, 478—500.

Roberge, M. R. & Knowles, R. 1966. Ureolysis, immobilization and nitrification in black spruce (*Picea mariana* Mill.) humus. *Soil. Sci. Soc. Am. Proc.*, *30*, 201—205.

Sundius, N. 1948. Beskrivning till Berggrundskarta över Stockholmstrakten. *Sver. Geol. Undersökning, Ser. Ba. No. 13.*

Tamm, C. O. 1963. Die Nährstoffaufnahme gedüngter Fichten- und Kiefernbestände. *Archiv f. Forstwesen, 12 (2)*, 211—222.

Tamm, C. O. & Pettersson, A. 1969. Studies on nitrogen mobilization in forest soils. *Stud. For. Suec.*, *75*, 1—39.

Volk, G. M. 1970. Gaseous loss of ammonia from prilled urea applied slash pine. *Soil Sci. Soc. Am. Proc.*, *34*, 513—516.

Zöttl, H. 1960. Dynamik der Stickstoffmineralisation im organischen Waldbodenmaterial. 2. Einfluss des Stickstoffgehaltes auf die Mineralstickstoff Nachlieferung. *Plant and Soil*, *13*, 183—206.

Sammanfattning

Återvinning och vertikal fördelning av ^{15}N-märkt handelsgödselkväve i skogsmark

Lateralt isolerade mikroparceller har använts för att studera kvantitativ återvinning och vertikal transport av ^{15}N-märkt handelsgödselkväve i en skogsmarksprofil på Lindhof, ca 2 mil SV om Stockholm. För isolering användes plåtcylindrar, som grävdes ned till ett djup av 40 cm, utan att den naturliga lagringen av jord inom försöksytan förstördes. Parcellerna, som hade en yta av 0,225 m² placerades under ett 90-årigt tallbestånd. Marken kan karakteriseras som järnhumuspodsol med obetydlig nitrifikationskapacitet.

Undersökningen startades på våren 1968 och avslutades under den därpå följande våren. Provtagningen utfördes vid fem olika tidpunkter och omfattade fältskiktsvegetationen, förnan, måren samt mineraljorden till 20 cm djup. Provmaterialet vägdes och analyserades med avseende på total-, ammonium- och nitratkväve samt på dessa kvävefraktioners isotopsammansättning.

Undersökningsresultaten visar att av tillförda kalciumnitrat-, ammoniumsulfat- resp. ureakvävemängder (100 kg N/ha) återfanns vid försökets avslutning, dvs. efter 12 månader, totalt 23, 63 resp. 76 %. Av det återfunna kvävet var mindre än 10 % i oorganisk form.

Av resultaten av det märkta kvävets vertikala fördelning i markprofilen kan man dra slutsatsen att av de undersökta kväveformerna hade ureakvävet den minsta rörligheten i marken och tenderar att ackumuleras i förna- och humuslagret. Ammoniumsulfatkvävet visade den högsta relativa ansamlingen i den undersökta delen av mineraljorden (0—20 cm). Förnans och humusens förmåga att immobilisera tillfört gödselkväve samt förutsättningarna för detta diskuteras.

Av sammanställningen över kvävets fördelning i markprofilen framgår tydligt att endast ytterst små mängder av nitratkvävet undgick urtvättning under vinterhalvåret. Icke heller ammoniumformen av kvävet var urlakningssäker under gällande klimat- och markförhållanden.

Det relativt höga kvarhållandet av tillsatt ^{15}N-gödselmedel i marken kunde i huvudsak hänföras till mikrobiell immobilisering.