

## **Nitrogen in Soil Water**

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This review comprises a general description of nitrogen in soil water and the use of nitrogen fertilizer. The following investigations on nitrogen leaching and transformations are described: Investigations on drainage water. Losses of nutrients by leaching in agricultural production. Influence of nitrogen fertilizer on nitrate nitrogen content in drainage water.

Nitrate reduction in the subsoil.

Water balance and nitrogen balance by optimum plant production.

The main conclusions are that the leaching of nitrogen as nitrate mainly occurs in the autumn and winter periods as a result of biological degradation of plant residues. Increased plant covering of the soil will decrease the nitrate leaching.

### **Introduction**

The subject of this review is nitrogen in soil water, the source of such nitrogen, its leaching and its possibility of transformations before reaching ground or surface water.

Or in other words: Do the increasing amounts of nitrogen fertilizer used during the year influence the environment of the cropped areas? One of the environments of special interest here is the subsoil very often used as a source of drinking water. Too much nitrogen as nitrate may give rise to health problems.

Another is surface water, lakes and streams. Too much nitrogen here may contribute to eutrophication.

## Nitrogen in the Soil

As mentioned above, the amount of nitrogen fertilizer has increased, especially during the last 10-15 years. The increasing rate will appear from Table 1, where the consumption of plant nutrients in the form of artificial fertilizer is given for the period 1960-1977. During the decade 1960-1970 the amount used increased two or three times, and from 1973 it has been more constant 300,000 to 350,000 tons.

Expressed as nitrogen fertilizer used per area unit, the values for 60/61 would be 40 kg/ha and for 75/76 110 kg/ha.

The use of N in the form of manure has been concentrated in certain areas, but for the years 1970-1975, the Danish Statistical Department has stated 139,000 t N as an average, i.e. about one third of the total artificial nitrogen fertilizer consumption.

Fig. 1 shows a rough calculation of the annual nitrogen »rotation«, i.e. addition, removal and transformation of nitrogen in cropped fields. For comparison, the average content of organic and inorganic nitrogen in the top layer of a field is stated in the same figure.

Until now nitrogen has only been mentioned in general, but of course it exists in different forms in soil as well as in water.

One form of nitrogen, nitrate, is of special interest. One reason is that it is the only form of a plant nutrient, which is totally mobile in the soil; it follows practically the movement of the soil water and is not bound to the soil colloids.

Another reason is that too much nitrate in groundwater used for drinking water is undesirable because of the health problems, which may arise under special conditions (methemoglobinemia).

Fig. 2 shows the possibilities of a nitrate ion to be transformed or transported in the soil system, especially the root zone of a cropped soil, normally reaching a depth of 1-1.5 meter.

Table 1 - Consumption of plant nutrients in the form of artificial fertilizer.

Fertilizer year	Harvest year	1000 tons								
		N	P	K	Na	Mg	Ca	Ca	Cl	S
1960/61	1961	124.8	50.4	144.4	6.1	2.0	258.1	220	138.1	83.4
1970/71	1971	298.8	55.8	151.4	3.5	10.9	121.7	480	122.8	69.9
1971/72	1972	308.7	58.6	158.8	3.1	11.1	117.3	515	130.8	72.4
1972/73	1973	329.9	62.9	169.3	2.8	12.1	117.7	635	138.2	73.7
1973/74	1974	365.2	67.8	179.0	2.4	13.4	122.4	505	154.1	71.3
1974/75	1975	300.4	49.8	132.4	1.0	10.7	81.6	700	112.3	49.8
1975/76	1976	339.1	56.2	142.2	1.2	13.2	95.0	615	122.3	63.7
1976/77	1977	349.6	58.7	139.1	1.5	14.1	85.7	-	118.0	57.0

## Nitrogen in Soil Water

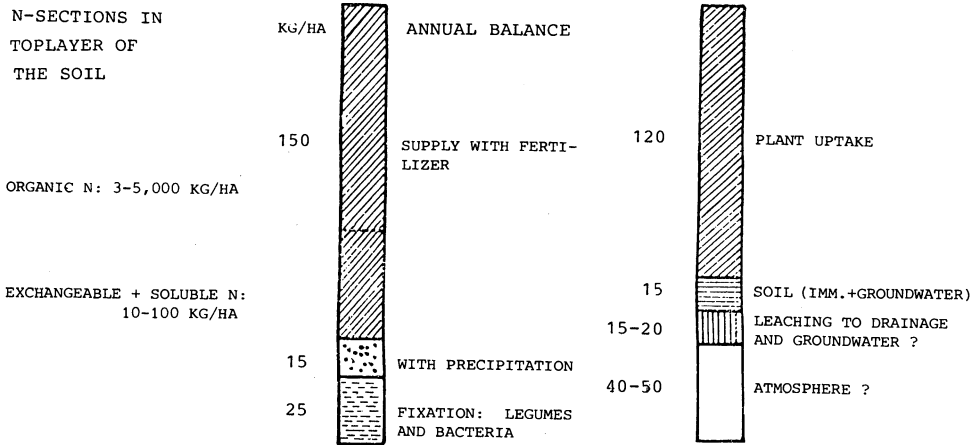
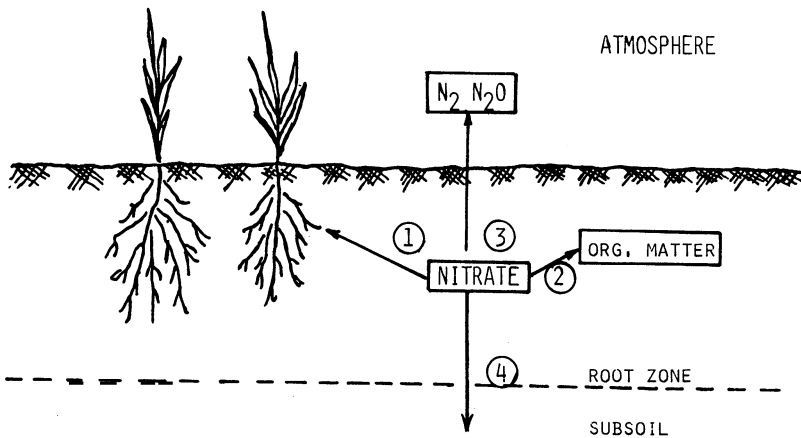


Fig. 1. Nitrogen sections in the soil and an approximate annual balance. Partly from Aslyng (1973) and Scheffer, Schachtschabel (1976).



- 1) It can be removed by plants.
- 2) It can be incorporated in organic matter i.e. immobilized.
- 3) It can be denitrified i.e. reduced anaerobically by bacteria into gaseous nitrogen compounds,  $N_2$  and  $N_2O$ .
- 4) Nitrate not used or removed in the above mentioned ways is leached, partly by drainage, and partly to the underlying soil layers and to the groundwater.

Fig. 2. Nitrate in the root zone.

## Investigations on Drainage Water

Since 1971 samples of drainage water from 20 different sites have been examined.

It started as a joint investigation between the Danish Heath Society and the Danish Marsh Experimental Station. Samples were collected weekly and measured for run-off amounts and quality with respect to plant nutrients.

From 1974 the registration of run-off was automatized, and the number of sampling sites were reduced from 20 to 15.

It should be noticed that all the sampling sites are situated in clayey soil areas. The basic and essential requirements of these investigations was that the areas should be uniformly and systematically drained, and these conditions are only available for clay soils, since sandy soil areas very seldom are drained in Denmark.

Table 2 shows the annual average amounts and concentration of phosphorous, ammonium and nitrate nitrogen at the 15 different sites. Furthermore, the

Table 2 – Leaching of some nutrients through drainage, 1971-74 and 71-77.

Site	NH <sub>4</sub> <sup>+</sup> – N		P		NO <sub>3</sub> – N	
	g/ha	mg/l	g/ha	mg/l	kg/ha	mg/l
5	32	0.03	17	0.02	23.0	24.8
7	53	0.04	84	0.06	36.5	25.6
8	71	0.04	32	0.02	30.5	18.8
9	51	0.04	41	0.03	24.1	17.9
12	29	0.04	16	0.02	18.7	23.3
13	71	0.06	35	0.03	14.6	12.1
14	44	0.04	72	0.06	21.7	18.5
15	47	0.05	17	0.02	14.9	17.4
16	53	0.05	22	0.03	16.4	14.5
17	87	0.04	26	0.01	32.2	14.9
19	103	0.10	17	0.02	16.6	15.9
20	52	0.06	55	0.06	18.3	21.4
22	62	0.10	12	0.02	9.1	14.5
24	37	0.05	7	0.01	16.9	23.2
28	66	0.04	149	0.09	22.4	13.3
<b>Average for all sites</b>	57	0.05	40	0.04	21.1	18.4
<b>Average 1971/77</b>	60	0.06			21.2	19

From Hansen and Pedersen 1975 and Hansen 1977.

average for all sites in the period 1971-74 is given together with the average for 1971-77.

The average values show no real increase, when the last 4 years are included. The amount of nitrogen applied was 90-120 kg/ha.

Some of the results of these drainage investigations have been published by Hansen and Pedersen (1975), but they are continued so as to include 1978, and all results will then be published in detail in the Danish periodical »Tidsskrift for Planteavl«.

### **Influence of Nitrogen Fertilizer on Nitrate Nitrogen Content in Drainage Water**

The State Experimental Station in Askov in south Jutland has established 2 experimental areas in the field. One area with a clay soil was established in southeast Jutland in 1973 and was also used for the lysimeter experiment. And in 1977 a similar field experimental area was established in an area with sandy soil in western Jutland.

Some preliminary results have been published by Kjellerup (1975), and they will be discussed in the following.

In the area, 4 different levels of nitrogen fertilizer have been used:

- 1) No N-fertilizer
- 2) 55 kg/ha N
- 3) 110 kg/ha N
- 4) 165 kg/ha N as calcium ammonium nitrate

The third level, No. 3, must be characterized as normal, while No. 4 is more than the average. Fig. 3 shows the concentration of nitrate-N for the different fertilizing levels during the winter period 1974-1975. The highest nitrate-N concentrations are found in the beginning of the period. The concentration increases with an increasing use of nitrogen, and shows a marked increase, when

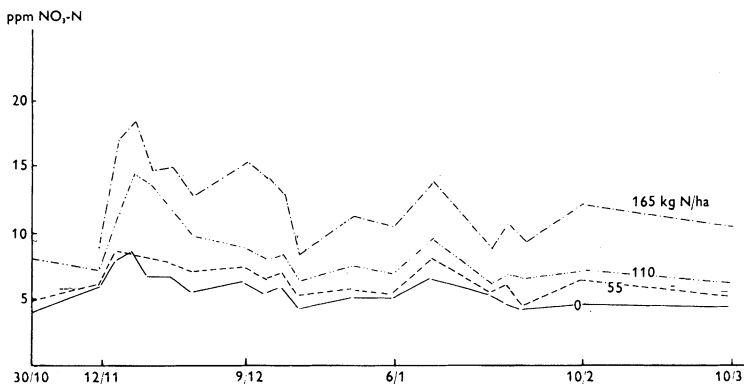


Fig. 3. Concentration of nitrate-N in drainage water 1974-75, Kjellerup (1975).

the amount of N-fertilizer exceeds the normal consumption, 110 kg N.

Table 3 gives the results of 4 years, 1973-76, the cropping in this experimental area together with the precipitation in and the run-off from the area. From the table it appears that in years with normal precipitation the yield was reduced in the plots with the largest nitrogen addition. The plant uptake of nitrogen, however, increases with increasing nitrogen for all levels. The leaching of nitrogen is for each nitrogen level dependent on the annual precipitation and the run-off. The leached amount of nitrogen increases moderately with the increasing amounts of nitrogen fertilizer. The leached nitrogen originates partly in the added fertilizer and partly in mineralization, i.e. biological liberation of a minor part of the 3-5,000 kg N/ha, which the soil contains in the top-layer.

Table 3 – N-uptake in barley and rape, and N-loss with drainage water, Sdr. Stenderup 1973-76.

Added N kg/ha	Yield harvested seed hkg/ha	Removed N kg/ha		Precipitation 1/7-30/6 mm	Run off mm
		crop	water		
1973 barley					
0	36	54	13	736	150
55	48	80	14		156
110	52	98	16		148
165	46	104	18		138
1974 barley					
0	41	58	15	778	252
55	57	89	17		257
110	61	110	21		229
165	59	114	31		256
1975 barley					
0	26	36	2	574	14
55	50	71	1		6
110	64	105	0		3
165	71	129	0		0
1976 rape					
0	16	41	3	625	114
75	25	72	5		111
150	30	107	6		74
225	31	116	15		91
Precipitation mm		73/74	74/75	75/76	
		736	778	574	

From Kjellerup 1975.

### **Nitrate Reduction in the Subsoil**

In 1976 investigations on nitrate reduction in the subsoil were finished (Lind and Pedersen 1976; Pedersen and Lind 1976).

The purpose of the investigations was to find out what possibilities the different subsoils have to react with nitrate leached from the root zone before reaching the groundwater. On the basis of a number of analyses of drinking water samples from the whole country, combined with geological knowledge of the area around the sample sites, it has been postulated that chemically reduced substances in the subsoil, especially ferrous iron compounds, are responsible for a reduction of the leaching nitrate (Christensen 1970).

3 boring sites were selected in 3 areas, which were widely different regarding soil chemical and physical properties.

Borings were made to a depth of about 20 m and a special technique ensured that the soil cores were intact when taken up.

Figs. 4, 5, and 6 give the variation of nitrate-N, ferrous iron and ammonia-N with the depth together with a visual geological evaluation of the profiles.

In the figures and in the description, the expression "weathering limit" is used for the transition zone between oxidized and reduced soil layers, especially referring to the soil content of iron. The oxidation condition in the profiles appears from the colours of the soil: Reddish or brown colours indicate oxidized or weathered soil layers, and bluish or greyish colours indicate reduced or unweathered soil layers.

Herlufmagle (Fig. 4) is situated in an area of homogeneous clay with a high content of lime. In this profile the nitrate content of the soil disappears 1-2 m below the weathering limit, while the ferrous iron content simultaneously increases strongly. This relationship between nitrate and ferrous iron is in fact what theoretically should be expected in a homogeneous soil.

Bramminge (Fig. 5) is situated in an area consisting of an inhomogeneous, mainly sandy soil. In this profile the ferrous iron content is fluctuating at a low level, and there is a low content of nitrate throughout the profile to the weathering limit. Below this limit, it disappears, while the content of ferrous iron slowly increases. This differing picture of nitrate-ferrous iron relationship is caused by the stratification and coarse texture of this soil profile.

Skælskør (Fig. 6) is situated in an area of inhomogeneous mainly clayey sediments. In this profile the ferrous iron content follows the same picture as in that of Herlufmagle: A very small amount above the weathering limit, and below this a sharply increased amount. The content of nitrate decreases at the weathering limit, but a small amount still remains throughout the profile. This is surprising in view of the very high level of ferrous iron, but is explained by the inhomogeneity of the profile.

As a further supplement to characterize the nitrate reducing ability of the soil profiles, samples from different depths have been used for nitrate reduction

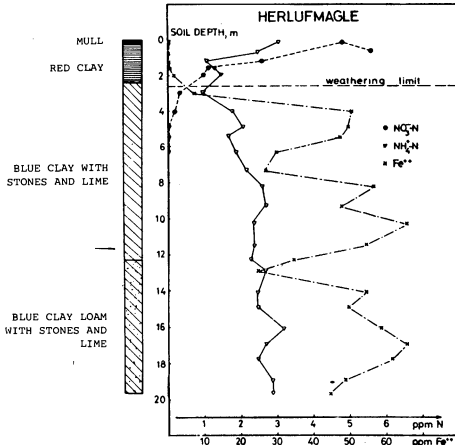


Fig. 4.

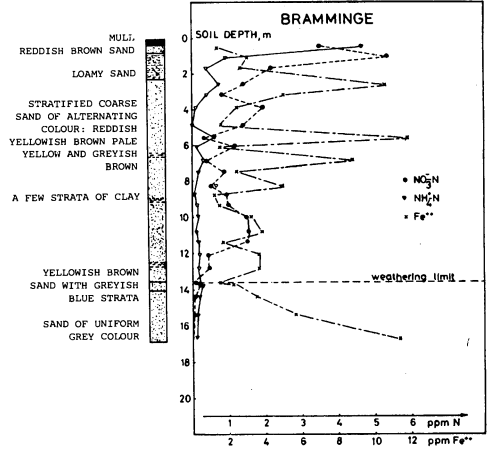


Fig. 5.

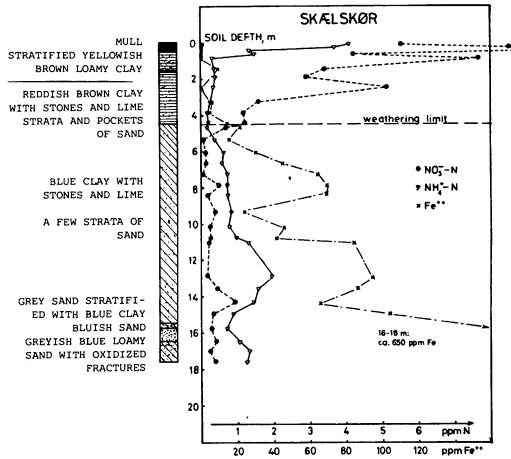


Fig. 6.

Profile description, and variation of contents of nitrate-N, ammonia-N and ferrous iron with soil depth.



experiments in the laboratory. These experiments have proved that the soil ferrous iron under anaerobic condition is able to reduce nitrate added to the soil, to gaseous nitrogen compounds.

The conclusion of the investigation was as follows:

The evaluation of the nitrate reducing ability of the three profiles is based on both the chemical, the physical and the nitrate reduction investigations.

The Herlufmagle profile has in all respects the most favourable possibilities of reducing nitrate, and owing to the pronounced homogeneity all parts of the profile are able to take an active part in the reduction. There is no risk at all of nitrate leaching through profiles of this type.

The Bramminge profile does not offer favourable conditions for nitrate reduction. The reduction experiments indicate that certain parts of the profile are able to reduce nitrate in spite of the low content of ferrous iron. However, the physical and chemical investigations indicate that nitrate leaching may occur without contact with the limited zones which possess reducing properties. A further complication is that the water movement is not only vertical, but must be horizontal, too, in certain soil layers. In an area of this type, nitrate is often found in the upper groundwater.

Great parts of the Skælskør profile have chemically good possibilities of reducing nitrate because of their large content of ferrous iron. The reduction experiments indicate a slowly proceeding nitrate reduction compared with the Herlufmagle profile. The physical investigations show insufficient contact between leaching nitrate and the reducing parts of the profile. The occurrence of considerable amounts of nitrate in the groundwater is unlikely, but a weak leaching of nitrate will always occur.

A real evaluation of the risk of nitrate leaching into the groundwater within an area would require comprehensive geological mapping combined with the above described chemical, physical and nitrate reduction investigations.

## **Water and Nitrogen Balance by Optimum Plant Production**

The State Experiment on Marsh Land in Højer has carried out investigations of the movement of water and nitrate in unsaturated soil layers.

Two experimental areas were used, one in a clay soil area in South Jutland (Aarslev), and the other at the State Experimental Station at Jyndevad in a sandy soil area.

The investigations comprised registration of water potentials at different soil depths amount and intensity of drainage run-off and precipitation. Furthermore, an extraction system for the soil water of varying depths down to 30 m was used.

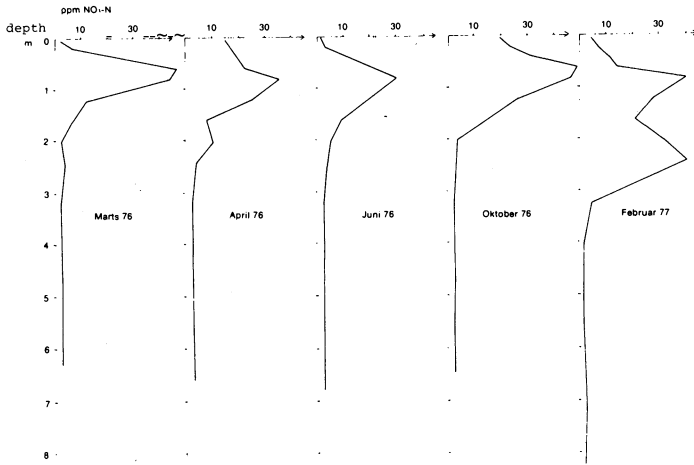


Fig. 7. Nitrate concentration in soil water at varying depth clay soil, cereal. Bennetzen (1978).

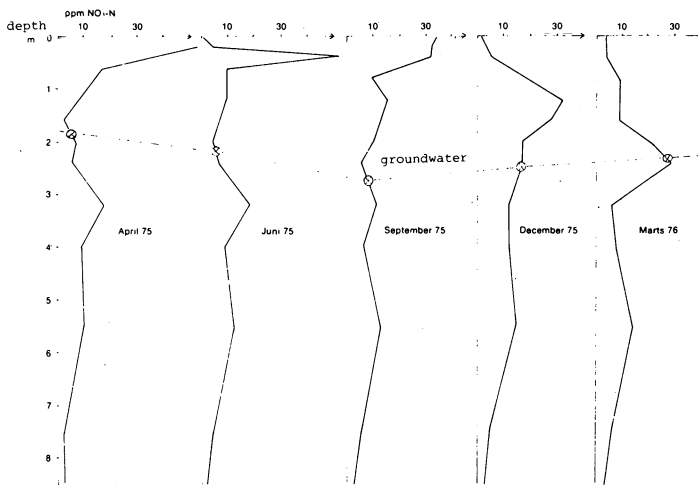


Fig. 8. Nitrate concentration in soil water at varying depths, sandy soil, irrigated cereal. Bennetzen (1978).

In the extracted samples the content of nutrients was estimated.

A few of the results were published by Hansen in 1977. The total publication will appear in 1978 in *Tidsskrift for Planteavl*, Bennetzen (1978).

Figs. 7, 8, and 9 show the nitrate profile during a year for the clay soil with cereal and for the sandy soil with two different crops.

From Fig. 7 it can be seen how the nitrate originating in fertilizer and mineralized plant residues moves in the root zone and in soil layers down to a

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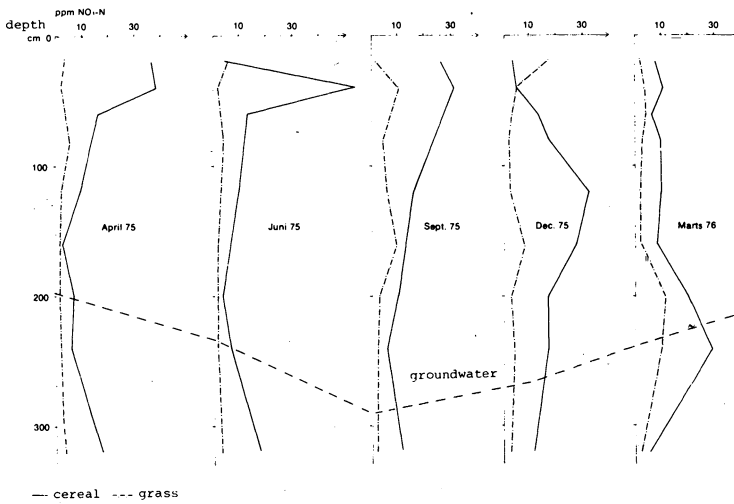


Fig. 9. Nitrate concentration in soil water at varying depths sandy soil, irrigated cereal and grass. Bennetzen (1978).

depth of 3 m. Nitrate has never been found to exceed 1-2 ppm N in soil layers below 3 m, either in clay layers down to a depth of 9 m or in real ground water from 26 to 30 m, the deepest sampling depth.

Fig. 8 and Fig. 9 give the nitrate profiles for the sandy soil with irrigated cereal and one with irrigated cereal related to a grass crop. Fig. 9 shows the difference between the ability of the two crops to use nitrate. Grass is much more efficient.

The residual nitrate concentration peaks can be detected in a part of the groundwater. The concentration of nitrate in water samples from a depth of 10 metres is normally a few ppm N and varies very little during the year.

Table 4 shows a nitrogen balance for all the areas investigated, given as an average of 3 years with added and removed amounts of nitrogen.

The values for nitrogen leached from the root zone show the influence of the sort of crop, and that more nitrate is leached from the grass not irrigated owing to poorer growth and consequently smaller uptake of N.

The conclusion of these investigations is as follows:

- 1) The water balance and with that the nutrient balance is determined by soil type, precipitation, evaporation and choice of crop. The growth seasons of 1975 and 1976 were very dry, and therefore it is not possible to generalize on the basis of the exact values, but only on the basis of the tendency.
- 2) On a sandy soil the entire netto-precipitation quickly reaches the groundwater. On a clayey soil the run-off to the groundwater is approximately constant during the year. The remaining excess precipitation runs off as drainage water.

Table 4 – Nitrogen balance kg/ha, average of 3 years.

	Clay soil		Sandy soil	
	cereal	cereal irr.	grass irr.	grass not irr.
<b>Added</b>				
Fertilizer	88	99	227	182
Precipitation + water	10	24	37	12
Total	98	123	264	194
<b>Removed</b>				
Crop	119	91	272	125
Change in soil	-54	-27	-31	-17
Leached from root zone	33	59	23	86

**Bennetzen 1978**

- 3) More nitrate is leached from the root zone of a sandy soil than of a clayey soil.
- 4) The amounts of leached nitrate are substantially greater from cereal crops than from grass. The most important reason for this is that nitrogen is liberated by mineralization of plant residues from the harvest, when no growing plants are present to use the liberated nitrogen.
- 5) In a clay soil area with the ground water situated in deeper layers, the leaching of nitrogen can be followed to a depth of 4 m. In the reduced layers below it must be assumed that nitrate reduction takes place, and nitrogen has no possibility of reaching the groundwater.
- 6) In a sandy soil area, the nitrogen is leached to the ground water at a depth of 2-3 m. It has not been possible to prove an increasing nitrate concentration in the deeper lying groundwater. Nitrate reduction may take place in the ground water.

These investigations are continued, but the clay soil area is changed for the sandy soil area used for the drainage investigations performed by State Exp. Station in Askov.

**Nitrate in Surface Water**

Several attempts have been made to evaluate the supply of nitrogen and phosphorus from agricultural areas to surface waters.

Some examples of different investigations are shown in Table 5. The values are stated as average values, kg N/ha/year Roughly it could be said that the nitrogen

## Nitrogen in Soil Water

Table 5 – Load of N and P in streams.

	N kg/ha/year			P kg/ha/year			N:P	
	City			City			Total	Diff.
	Total	Contrib.	Diff.	Total	Contrib.	Diff.		
Gjelbæk <sup>1</sup>	25.2	0.6	24.6	0.43	0.2 <sup>6</sup>	0.2	58	123
Odense A <sup>3</sup>	23.–	10.–	13.–	3.3	3.3	0.0	7	–
Tryggevælde A <sup>2</sup>	21.8	1.3	20.5	0.4	0.4	0.0	55	–
Nældevad A <sup>3</sup>	18.–	2.–	16.–	1.1	0.8	0.3	16	53
Skallebæk <sup>5</sup>	17.4	3.4	14.0	2.4	0.8	1.6	7	9
Voelbæk <sup>1</sup>	13.5	0.6	12.9	0.17	0.2 <sup>6</sup>	–	79	–
Brøns <sup>4</sup>	12.9	0.6	12.3	0.35	0.17	0.18	37	68
Gudenå, A 10 <sup>1</sup>	11.8	2.7	9.1	0.78	0.65	0.13	15	70
Granslev Å <sup>1</sup>	7.8	0.8	6.9	0.39	0.26	0.13	20	53
Karup <sup>2</sup>	6.5	3.1 <sup>7</sup>	3.4	0.14	0.80 <sup>7</sup>	–	46	
Havelse Å <sup>3</sup>	6.–	9.–	–	1.–	3.–	–	17	

1. Gudenårapport No. 12 1976

2. Lønholdt 1973

3. Lønholdt 1975

4. Edens and Solbjerg 1975

5. VKI, Haderslev Dam 1972

6. Larsen 1975

7. Calculation, Lindhard 1978

level is lower than the level for nitrogen leached through the drainage system cf. Tables 2, 3, and 4. Therefore it could be concluded that in most cases the surface water must consist of run-off from the root zone soil mixed with run-off from groundwater, the latter with a lower content of nitrate due to the passage of soil through reducing soil layers. These observations are confirmed by some unpublished investigations on other water streams made by the Danish Geological Survey (Kristiansen 1978).

### Conclusion

An attempt to control or decrease nitrogen leaching from agricultural areas would be very difficult. As it appeared from several of the described investigations, the leached nitrate does not normally originate directly in added nitrogen fertilizer, but mainly as a result of mineralization, i.e. biological degradation of plant residues after the growing season.

Therefore, one possibility of reducing the leaching of nitrogen might be a switch to other cropping methods including a wider use of catch crops to remove a part of the nitrogen liberated during mineralization of plant residues.

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