NPo-forskning fra Miljøstyrelsen

A - abstracts

Nitrogen and Phosphorus in Soil and Air

Miljøministeriet **Miljøstyrelsen**

Danish Research Programme on Nitrogen, Phosphorus and Organic Matter (NPO)

The aim of the NPO Research Programme is to gather knowledge on the decomposition of Nitrogen (N), Phosporus (P) and organic matter (O) in the soil, and on their impact on lakes, watercourses, inlets, groundwater and the sea.

This report is one of a total of about 50 reports to be issued in connection with the implementation of the NPO Research Programme. The National Agency of Environmental Protection (NAEP) is responsible for the programme, under which about 70 NPO projects have been launched, carried out at 25-30 institutions.

In the 1970's and the beginning of the 1980's there was a growing awareness of the threats to life in watercourses etc. presented by discharges of nutrients – and of the risk of nitrate contamination of groundwater. In 1984 a report was prepared, synthesising existing knowledge in this field. The report, known by the name of NPO Report, was published by the NAEP.

To follow up this report the Dansih Parliament took the first steps in 1985 to reduce pollution with nutrients – laying down requirements for storage and application of farm yard manure in the agricultural sector.

For the purpose of improving our knowledge on the impact of nutrients in nature, the Danish Parliament also reserved 50 million DKK for the research programme, running from 1985 to the end of 1990.

The significance of the NPO Research Programme was further underlined with the Danish Parliament's adoption of the Action Plan on the Aquatic Environment in 1987. The results of the NPO Research Programme will play a vital role in the evaluation of the effects of the Action Plan.

To safeguard the technical and economic interests relating to the research activities a steering group was set up, having the overall responsibility for the implementation of the NPO Research Programme. Furthermore, three coordination groups were formed, each of them responsible for one of the three fields: soil and air, groundwater, and surface water.

The reports are published in the series »NPo-forskning fra Miljøstyrelsen« (NPO Research in the NAEP), divided into three sections:

A: reports on soil and air
B: reports on groundwater
C: reports on watercourses, lakes and marine waters.

The NAEP has been secretariat for the research programme. The reports published in this series are edited by the Agency with the assistance of the coordination groups.

NPo-forskning fra Miljøstyrelsen
Nr. A abstracts

1991

Nitrogen and Phosporus in Soil and Air

Project Abstracts of the Danish
NPo Research Programme

Miljøministeriet
Miljøstyrelsen

List of Contents:

Emissions of the nutrients nitrogen and phosphorus from cities, industries and agriculture are associated with environmental impacts in atmosphere, soils, groundwater and aquatic ecosystems.

In Denmark, the dominating source of nitrogen is related to agricultural production. In 1985, the Danish Parliament established the NPo-action plan with its primary objective to reduce nitrogen losses from agriculture, in particular in connection with application of manure and slurry. At the same time it was realized that the scientific basis was insufficient to provide a reliable evaluation of the effects of the proposed measures.

Accordingly, the NPo research program was initiated to provide a multidisciplinary and comprehensive study of the entire transport- and transformation cycle of nitrogen (N) and phosphorus (P), as schematically shown in figure 1.1.

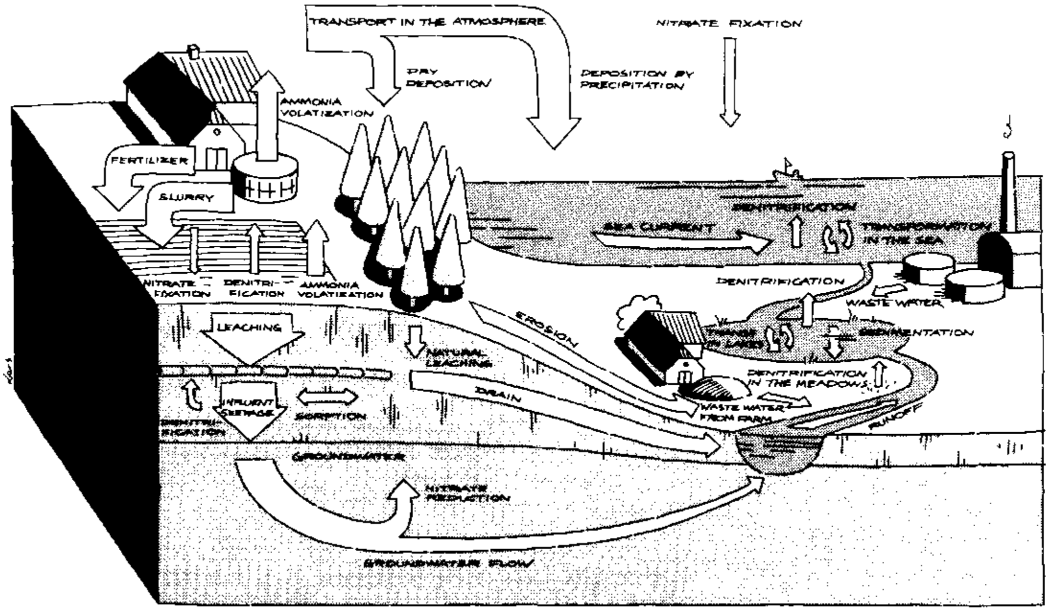

Figure 1.1 Transport and transformation of nitrogen and phosphorus in the environment

The Parliament allocated 50 million Danish kroner for the program and put the National Agency of Environmental Protection in charge of the execution. After a planning phase in the winter of 1986 the program was initiated by spring 1986 with about 50 interrelated projects and participation of about 25 Danish research institutes.

The projects were divided in three groups:

- Group A: Soil and atmosphere:
  * Farming practices in application of mineral fertilizers and manure
  * Ammonia volatilization
  * Nitrogen transport and transformation in the atmosphere
  * Nitrogen transformation in soil
  * Nitrogen leaching from the rootzone

- Group B: Groundwater:
  * Surveys of extent of nitrate contamination
  * Nitrate transport and transformation in unconfined alluvial aquifers
  * Nitrate transport and transformation in confined limestone aquifers
  * Nitrate reduction processes in groundwater
  * Modelling of nitrate transport and transformation in regional aquifers.

- Group C: Meadows, streams, lakes and marine waters:
  * Nutrient transport and accumulation in sediments
  * Internal phosphorous load from sediments in lakes
  * Denitrification in sediments
  * Effects of nutrient load on biological structures.

The results have been published as a summary report (Dyhr-Nielsen et al. 1991: Nitrogen and Phosphorus in Soil and Water, NPo-forskning fra Miljøstyrelsen, National Agency of Environmental protection, Denmark), as three abstract volumes in English and as 56 project reports, mainly in Danish.

The project reports may be grouped as presented in table 1.1-3.

Table 1.1 Reports in Group A: Soil and atmosphere

	Measurements and interview	Modelling
Farming practices in application of mineral fertilizers and manure	A2, A21	A1
Ammonia volatilization	A7, A11, A12, A15	
Nitrogen transport and transformation in the atmosphere	A4, A5, A6	A18, A22
Nitrogen transformation in soil	A3, A9, A13, A16, A19	A10, A20
Nitrogen leaching from the rootzone	A8, A9, A13, A17	A10, A14, A20

Table 1.2 Reports in Group B: Groundwater

	Unconfined aquifers	Confined aquifers
Surveys of nitrate contamination	B4, B16, B18	B4, B16, B18
Climate and discharge data	B9, B17	B9, B17
Nitrate reduction processes	B3	B1, B2, B6
Nitrate transport and transformation	B5, B7, B8, B10, B11, B12,B17	B7, B17, B19
Modelstudies	B8, B13, B15	B14, B15

Table 1.3 Reports in Group C: Meadows, streams, lakes and marine water

	Meadows	Streams	Lakes	Marine Waters
Erosion and leaching	C12,C13 C14	C12		
Transport and accumulation	C10, C11		C11	C6
Internal load			C4, C5	C8
Denitrification	C13,C14 C15	C2	C9	C1
Effects on biological structure		C7, C10	C9	C3, C5, C8.

In the planning of the research programme, a close integration of field- and laboratory studies with mathematical modelstudies has been emphasized. Accordingly, the program was established around three main activities:

- Detailed investigations of particular subsystems, performed as field and laboratory studies,
- Integrated studies of total systems in selected catchments,
- Synthesis of field- and laboratory findings in mathematical models

The field studies of particular subsystems have been located in representative regions all over Denmark, as shown in figure 1.2.

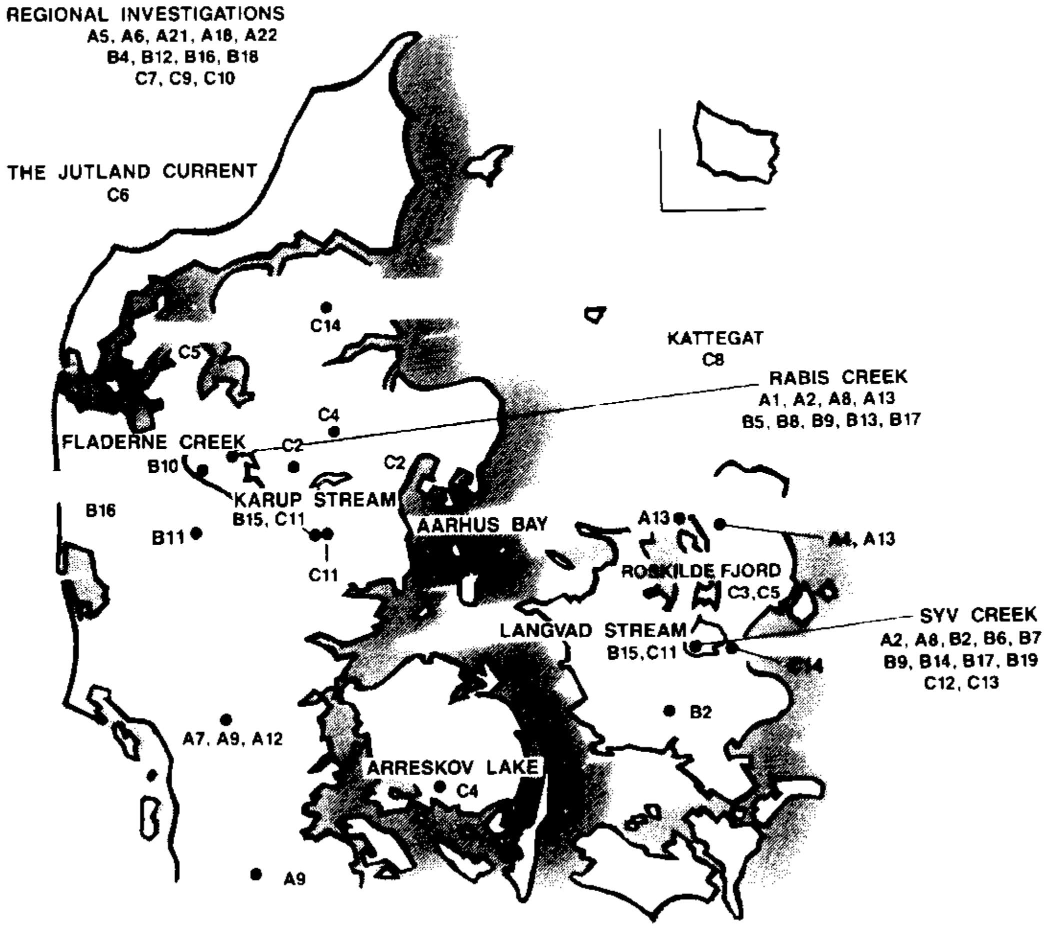

Figure 1.2 Location of the NPo-projects.

The integrated studies of transport and transformation processes have been situated in two small catchments, Syv creek and Rabis creek.

Rabis creek is located in western Jutland, as shown in figure 1.3. The geology and agricultural practices are characteristic for large regions in western and central Jutland. Ground water aquifers are found in unconfined aquifers in glacial outwash plains, highly vulnerable to nitrate leaching. The runoff is dominated by ground water baseflow. Manure and slurry are important nitrogen sources, as some of the highest concentrations of animal production are found in these regions.

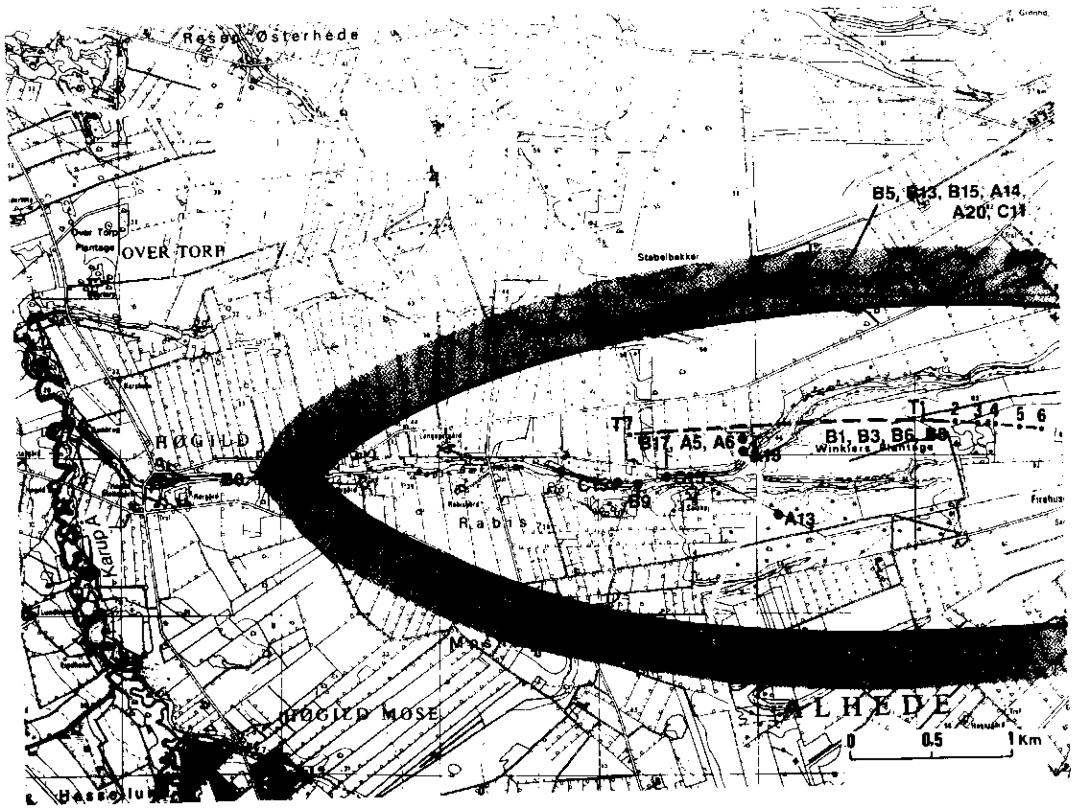

Figure 1.3 The study basin Rabis creek in Jutland.

Syv creek is located in Sealand, as shown in figure 1.4. The geology and the agricultural practices are characteristic for the eastern islands Sealand and Funen. Ground water aquifers are confined and protected by thick layers of moraine till. Runoff is dominated by contributions from tile drains of the loamy soils. Mineral fertilizer is the dominating nitrogen source, as the region has a relatively small animal production.

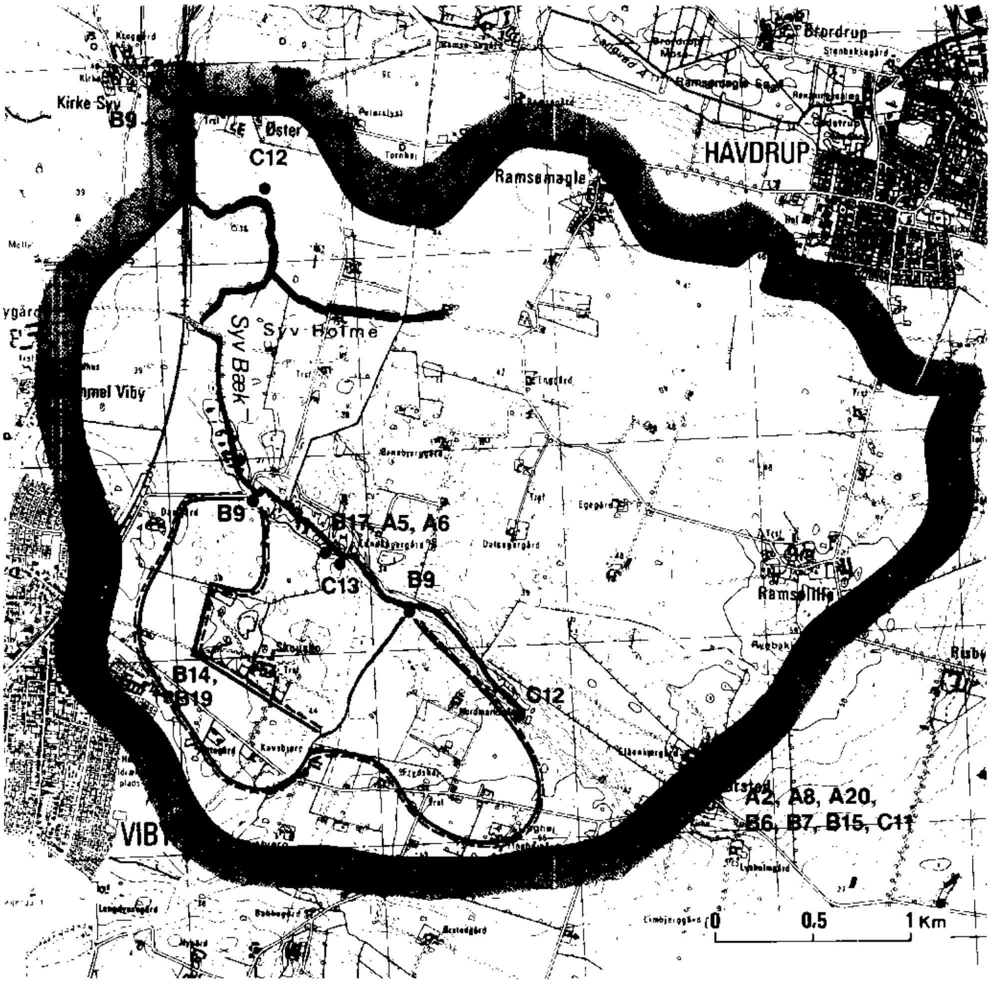

Figure 1.4 The study basin Syv creek on Sealand.

The present volume is one of three abstract volumes containing abstracts from Group A on Soil and Atmosphere, Group B on Groundwater and Group C on Meadows, Streams, Lakes and marine waters.

Ministry of the Environment
National Agency of Environmental Protection
Denmark

The N, P and Organic Matter Research Program 1985-1990

Number A1

Nitrogen and Phosphorus-Balances for Cattle and Pig Farming

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Summary

Procedures for calculating the utilization and excretion of nitrogen (N) and phosphorus (P) have been set up for cattle and pigs. Annual net purchase of N and P, calculated as amounts in purchased products minus amounts in sold products have been determined for individual farms.

Subsequently calculations of N and P-amounts in animal excreta were carried out using, a) standard values from tables of feed-consumption and -composition, b) values from individual farms. Calculations were made for dairy cows, heifers, fattening bulls, porkers and sows.

Excreted amounts are generally determined with good certainty when the corresponding amounts in the feed are known. Partition of excreted amounts between faeces and urine is mostly determined with good certainty, too.

Calculated N- and P-amounts in feed and excreta using standard values matched well with farm mean values. For the separate animal categories the percentages of feed-N and feed-P excreted in faeces and urine do not seem to vary much for practical farming. This means that variation in excreted amounts is primarily caused by variation in the corresponding amounts in the feed.

Net purchase of N, P and K varied much between farms. The calculated annual net inputs of N suggests high losses or accumulations by farms.

Introduction

Loss of nutrients, especially N, from agricultural systems may cause some serious environmental problems. In this context animal production and the use of animal manures has a central position. In order to elaborate good models for nutrient cycles in agricultural systems, knowledge of nutrient balances concerning the animal production is essential.

The project aimed at setting up models for calculation of N- and P-amounts in animal excreta from cattle and pigs, and to determine nutrient balances for a number of farms. Development and evaluation of the models was carried out by Statens Planteavlsforsøg (Danish Institute of Plant and Soil Science). Collection of data and calculation of nutrient balances for practical farming was carried out by Hedeselskabet (Danish Land Development Service).

Animal balance models

Equations exemplified by the N-balance equation for cattle below (eq. 1) were set up for N- and P-balances for cattle and pigs. Procedures for calculating the individual terms from relevant data on livestock, feeding principles and animal production were elaborated on the basis of international and national litterature plus background material when available.

$$N_{feed} = N_{milk} + N_{growth} + N_{faeces} + N_{urine} \qquad \text{(eq 1)}$$

To ensure a sufficient general applicability the models were largely based on physiological principles as far as this did not cause unrealistic demands for input variables.

From the studies it was concluded that within the limits of practical farming N- and P-concentrations in animal products are generally little influenced by the corresponding levels in the feed, making the N and P in animal products proportional to production figures. Faecal excretion was estimated by considering nutrient digestibilities as related to feed composition and feeding intensity.

Model calculations with standard values

Calculations for dairy cattle showed almost no effect of animal performance on utilization and pattern of excretion of N and P (Table 1).

Table 1. Calculated N- and P-balances for dairy cows of large breed, kg/cow/year. Numbers in brackets indicate percentage of amounts in the feed.

Net performance, kg fat corr. milk		feed	milk	growth	faeces	urine
6150	N	163.0	31.7 (19)	2.2 (1)	50.5 (31)	78.6 (48)
	P	24.6*	5.5 (22)	0.6 (2)	18.1 (74)	0.4 (2)
6750	N	171.2	34.8 (20)	2.2 (1)	53.1 (31)	81.1 (47)
	P	26.3*	6.1 (23)	0.6 (2)	19.2 (73)	0.4 (2)
7180	N	178.0	37.1 (21)	2.2 (1)	55.2 (31)	83.5 (47)
	P	27.3*	6.5 (24)	0.6 (2)	19.8 (73)	0.4 (1)

* incl P in feed phosphates

Calculations for fattening bulls, sows and porkers are shown in Tables 2-4.

Table 2. Calculated N- and P-balances for fattening bulls slaughtered at 423 kg liveweight, kg/bull/year. Numbers in brackets indicate percentage of amounts in the feed.

	N	P
Amount in feed	46.0	7.3*
Amount in growth	9.6 (21)	2.3 (31)
Amount in faeces	17.0 (37)	4.8 (66)
Amount in urine	19.4 (42)	0.2 (3)

* incl P in feed phosphates

Table 3. Calculated N- and P-balances for sows, kg/sow/year including the production of 21 piglets of 25 kg liveweight. Numbers in brackets indicate percentage of amounts in the feed.

	N	P
Amount in feed	53.6	14.0
Amount in growth	14.7 (27)	2.9 (21)
Amount in faeces	9.7 (18)	8.5 (61)
Amount in urine	29.2 (55)	2.6 (18)

Table 4. Calculated N- and P-balances for porkers growing from 25 to 95 kg liveweight, kg/produced animal. Numbers in brackets indicate percentage of amounts in the feed.

	N	P
Amount in feed	5.9	1.36
Amount in growth	1.8 (30)	0.36 (26)
Amount in faeces	1.0 (17)	0.77 (57)
Amount in urine	3.1 (53)	0.23 (17)

Calculations for normal farming practices

Calculations with data from normal farming practices shows, as an average, good agreement between amount of N and P in the feed and standard values, except that the amount of P in feed for dairy cattle was less than the standard values. Howewer, in some cases deviations from standard values were high.

Figure 1 shows the variations in amounts of N and P in feed and manure for dairy cows. Considerable variations in amount of N in manure pr animal was found between the farms. On the countrary the percentages of feed-N and P excreted in manure do not seem to vary much for dairy cattle.

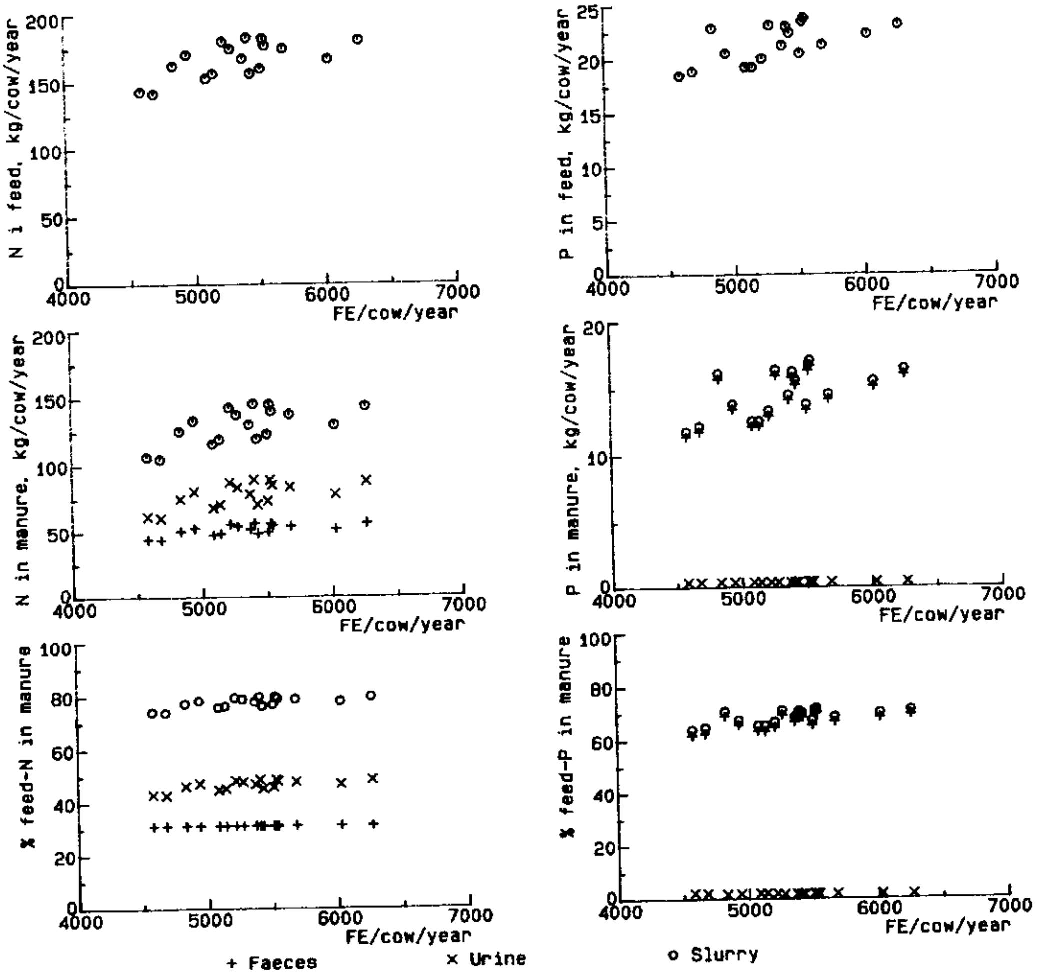

Figure 1. Calculated amounts of N and P in feed and manure pr. dairy cow and percentages of amount in feed excreted in manure related to amount of feed pr cow.

Similar results were found for heifers, porkers and sows. For the separate animal categories the calculated percentages of feed-N and feed-P excreted in faeces and urine did not vary much and were in good agreement with the values found in the calculations with standard values (Tables 1-4).

Nutrient balance for farms

Calculations of amount of plant nutrients in purchased products and sold products is carried out for single farms within the two research areas which have been selected for the experimental investigations in connections with the NPo-projects

The calculated net purchases of plant nutrients are shown in Table 5. Net purchases refers to the difference in the nutrient content between the purchaced and the sold products.

Table 5. Net purchases of Nutrients, kg/ha cultivated Area.

	N	P	K
Purchase			
Chemical Fertilizer	122	18	51
Feed	52	11	12
Total Purchase	174	29	63
Sale			
Animal Products	18	4	3
Vegetable Products	46	8	19
Total Sale	64	12	22
Net Purchase	110	17	41

In most cases the greatest source of nutrients is provided through the purchase of chemical fertilizers, although 1/3 of the P purchased is in the form of feed. Purchases of N, P and K significantly exeeded the content of the products being sold. These differences along with the nutrients contained in precipitation and N-fixation of legumes will either be lost or accumulated by the farms.

Net purchase of N, P and K pr. ha on single farms related to concentration of live-stock is shown in Figure 2.

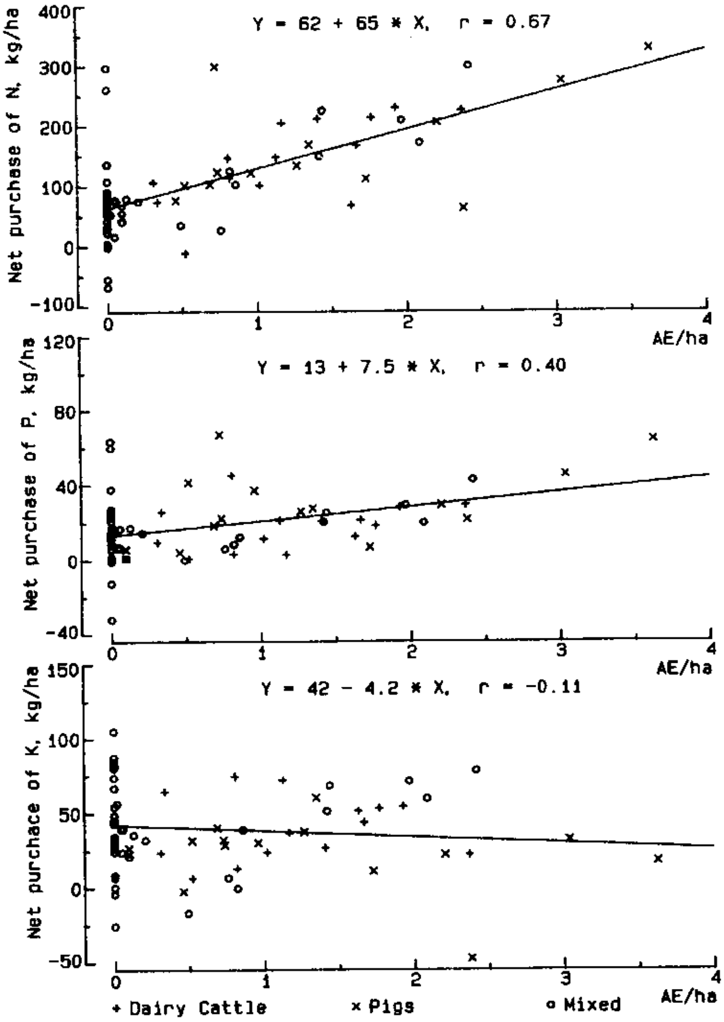

Figure 2. Net purchase of N, P and K related to Animal Equvivalent pr ha.

Net purchase of N is increased by 65 kg N pr Animal Equivalent, AE (approx. one dairy cow) or approx. 2/3 of N in manure. The main reason for this seems to be the high losses from manure, partly by evaporation and partly by leaching from cultivated fields where manure were applied. The calculations shows high variations between farms but the increased losses are significant at a 99% level.

For P the net purchase seems to increase with size of the live-stock but for K no relations were found.

Discussion

Animal N- and P-intakes calculated from standard values are in good accordance with calculated intakes on the farms. Calculated P-intake of cattle, however, is somewhat higher for standard conditions than found on the farms. This inconcistency is mainly due to a lower consumption of P in feed phosphates than assumed as standard.

For all animal categories calculations show N-excretions in urine highly exceeding those in faeces. This is particularly marked for pigs, excreting 2.5 to 3 times as much N in the urine than in the faeces. Urine N is mainly excreted as urea which decomposes to ammonium within few hours, increasing the risk of ammonia volatilization.

The percentages of feed-N and feed-P excreeted in faeces and urine are found to be relatively constant for the single animal categories. For calculations in normal farming practice variation in amount and composition of feed seems to give greather errors than using a fixed part of nutrients in the feed in the calculations.

The amount of N, P and K purchased is significantly greather than which is sold. The difference being either accumulated or lost. For K and especially P the net purchases is a resonable measure for the nutrient balance on a farm.

Ministry of the Environment
National Agency of Environmental Protection
Denmark

The N, P and Organic Matter Research Program 1985-1990

Number A2

Mapping of Farming Practices in the NPo-Research Areas

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Purpose	The purpose of this project was to collect information regarding the actual farming practices within the two NPo-research watershed areas surrounding Rabis Brook and Syv Brook.
Live-stock	Dairy cattle is the principle live-stock of the Rabis area while that of the Syv area is swine. Total live-stock concentrations for both areas were approx. 90% and 47% of the national average.
Cropland Use	The principle crops grown in the Rabis area are spring barley, grass, sugarbeet (feed) and potatoes while the principle crops for the Syv area are cereal grains and rape.
Fertilizer Use	There is considerable variation in fertilizer application from one field to another. The application of substantially more N than is optimum is generally due to inexpedient application of manure.
Manure	In 1987 there was still insufficient storage capacity for manure and especially for urine and slurry. In the sandy soils of the Rabis area, most of the manure is spread in the spring and summer whereas manure is spread in the clay soils of the Syv area during the autumn.
Net Purchase of nutrients	The amount of N, P and K purchased is significantly greater than that which is sold. The difference being either accumulated or lost.

1. Introduction

Purpose

The purpose of this project was to collect information about the farming practices within the two research areas which have been selected for some of the experimental investigations in connection with the NPO-projects. The results of this project will be used to support and improve the possibilities to explain the results of other studies within these areas. Project investigations for farms within these two areas have included: Cropland use, fertilizer applications, etc. for individual field as well as application of plant nutrients, especially Nitrogen, Phosphorus and Potassium in order to explore the potential for leaching, accumulation in the soil etc. Storage capacity and facilities for manure and silage as well as sewage facilities have been studied.

2. Materials and Methods

Data Collection

In order to collect information pertaining to the farming practices within both watersheds, all farms within the two areas were visited. Detailed information was collected for 1987. In order to be able to compare changes in farming practices occuring in recent years information about previous years was also collected although this was less detailed.

Manure

Nutrient application rates for fields on which manure is spread have been calculated using standard content of nutrients as provided by the Agricultural Information Office (LIK, 1988).

Calculation
of Nutrients

Plant nutrients in purchased and sold products have been calculated as described by Kofoed & Hansen (1990).

3. Results

Rabis

The study area of the Rabis Brook watershed comprises 908 ha or approx. 92% of the total area of the 970 ha watershed. At Syv Brook the study area includes 84% of the approx. 1170 ha watershed. Half of the remaining 16% of the watershed area is comprised of town buildings, roads, etc. while the rest belongs to landowners who did not want to participate in the study.

Live-stock

Live-stock ratios for the watersheds are shown in Figure 1. It can be seen that total live-stock ratio for both watersheds has decreased over the last 10 years, especially for Syv. Of Rabis 75% of all live-stock is dairy cattle and 25% swine whereas the ratio for Syv is 70% swine, 15% cattle and 15% other, primarily poultry. The number of Animal Equivalents (AE) has been calculated as indicated by the National Agency for Environmental Protection (Miljøministeriet, 1988).

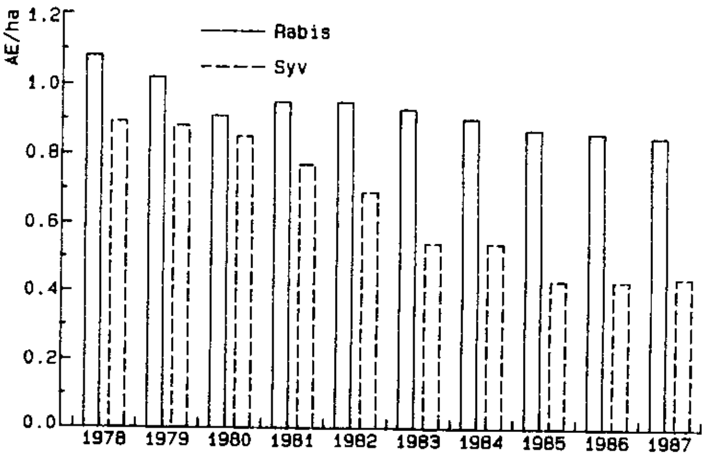

Figure 1. Development in the Live-Stock Ratios for the two Watersheds During the Period 1978-1987. (One AE ~ one Dairy Cattle).

Distribution of Live-stock

24% of the Rabis farms and 56% of the Syv farms were without live-stock. The largest concentration of live-stock of Rabis is just slightly smaller than the 2 AE/ha. Live-stock concentrations are greater than 2 AE/ha for approx. 12% of the Syv farms. Approx. 1/3 of these farms had agreements to supply neighbours or others with excess manure.

Land Use

Of the Rabis area included in the study approx. 79% of the total area is farmed, approx. 9% is forested and approx. 12% is uncultivated, the largest part being heath and the rest farm yards, gardens, etc. Of the Syv study area 91% is farmed, 2% is forested and 7% is uncultivated.

Development of Cropland Use

An outline of the development on cropland use is shown in Tabel 1. Spring cereals has been reduced while the proportion of winter cereals has increased in recent years for both watersheds.

Tabel 1. Development in Cropland Use for the Investigated Watersheds During the Period 1978-1987.

Rabis	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987
Spring Cereals	49.8	56.3	55.6	60.3	54.1	51.9	47.6	48.9	43.3	42.0
Winter Cereals	4.1	3.2	3.1	2.6	2.5	2.3	3.5	3.9	4.4	6.2
Sugarbeets	10.5	10.2	10.0	9.9	10.6	10.3	9.9	9.3	9.4	5.6
Potatoes	6.0	5.5	5.7	4.8	5.4	7.7	9.4	8.1	8.1	7.5
Grazing-land in Rotation	25.1	19.7	20.6	17.8	22.7	23.6	23.2	20.9	20.5	18.6
Grazing-land	3.0	4.0	3.9	3.7	4.0	3.6	3.2	3.6	5.0	7.4
Legumes	0.8	0.6	0.6	0.5	0.4	0.4	1.8	2.9	6.7	9.2
Winter Rape	0.7	0.6	0.5	0.4	0.3	0.3	0.3	1.8	2.0	0.0
Spring Rape										0.8
Other	0.0	0.0	0.0	0.0	0.0	0.0	1.2	0.6	0.8	2.6
Syv	**1978**	**1979**	**1980**	**1981**	**1982**	**1983**	**1984**	**1985**	**1986**	**1987**
Spring Cereals	63.0	59.7	54.3	48.0	44.3	33.3	32.8	41.3	36.4	34.3
Winter Cereals	14.7	16.3	17.4	27.2	32.6	35.8	38.6	26.0	33.1	25.0
Sugarbeets	2.1	2.1	2.1	1.6	1.7	3.3	3.0	2.6	2.6	2.4
Potatoes	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1
Grazing-land in Rotation	2.3	2.3	2.3	1.8	1.7	1.3	1.0	0.8	0.7	0.8
Grazing-land		2.6	2.6	2.3	2.3	1.8	1.8	1.6	1.5	1.4
Legumes	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.0	4.2	5.2
Winter Rape	7.1	8.8	11.2	11.7	11.6	13.2	11.8	12.4	11.3	11.9
Spring Rape										9.5
Other	8.3	8.3	10.2	7.4	5.8	11.3	11.1	12.3	10.1	10.3

The total area planted with rape and legumes (peas) has also increased. Within the Rabis area, total area planted with legumes has increased dramatically over the last years within the period 1978-1987. Within the Syv area, the total area planted with grass and root crops has been minimal during the entire period.

Fertilizer Rates Within the Watersheds

An outline of the average fertilizer rates within the watersheds is shown in Table 2. Because N-requirements are dependent upon the crop blend, there are also an economic optimum rate of N which can be calculated on the basis of crop distribution within the individual watersheds as well as optimum rates of N required for specific crops as indicated by the National Agency of Environmental Protection (Miljøstyrelsen, 1984). Values indicated by the Agricultural Information Office (LIK, 1980) have been used to calculate the effective application rate of N from manure.

Table 2. Average Fertilizer Consumption for the Watershed Study Areas, kg/ha Cultivated Area.

	Rabis	Syv	Denmark
N from manure 1)	87	43	92
N - - 2)	77	35	
N - chemical fertilizer	113	125	135
N total	200	168	227
N effective 2)		142	138
Optimum N	161	137	160
P from manure 1)	14	11	18
P - - 2)	12	9	
P - chemical fertilizer	18	17	17
P total	32	28	35
K from manure 1)	80	30	77
K - - 2)	72	25	
K - chemical fertilizer	53	45	45
K total	133	75	122

1) Total rates calculated for total live-stock
2) Only stall produced manure

Rabis

As seen in Table 2, the effective rate of N application for Rabis was 15-20 kg/ha less than which was calculated as the economic optimum.

Syv

For Syv there is good agreement between the average effective rate of N application and the calculated economic optimum for N.

Variation in N-applications

The variation in N-application rates for the individual watersheds in comparison to the economic optimum rates are shown in Figure 2. All crops except legumes which have an optimum rate of zero have been included in the figure.

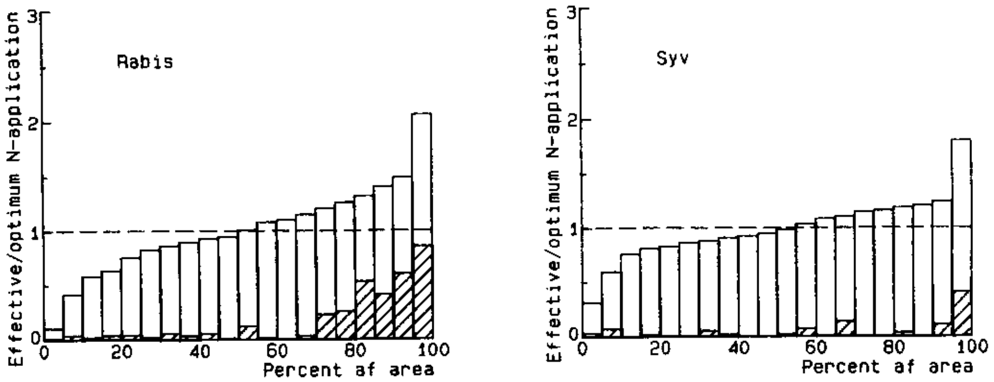

Figure 2. Variations in Relation to Effective/Optimum N-Application Rates. The Cross-Hatched Portion of the Columns Indicate Effective N-Application from Manure whereas the Rest of the Column (no Cross-Hatch) Indicates Application for Chemical Fertilizer.

From the figure it appears that there are for some fields large discrepanies between effective and economic rates of N applied. A smaller part of this discrepancy is, however, due to the fact that in practice the economic optimum rate for N is not the same for all fields having the same crop but depends on the previous crop and fertilization, etc.

The effective N-application rate is less than half of the economic optimum for approx. 10% of the total area and more than 1.5 times the optimum for other 5% of the total area. Nearly all of those fields showing a larger rate of applied N compared to the optimum rate are those to which manure has been applied. This is true especially for the root crops. The economic optimum rate is seldom exceeded with the application of chemical fertilizer alone. Large variations in N-application rates and excesses for root crops in comparison to other crops occurs because a greater portion of manure is commonly applied to root crops.

Changes in Purchase Patterns of Chemical Fertilizers

Purchases of N, P and K for the Rabis area have been relatively consistent throughout the research period whereas the purchase of N, P and K have increased for the Syv area. This has primarily occured as a result of the shift in crop type. Acreage devoted to spring cereals have been reduced in favour of winter cereals and rape which require more fertilizer. Simultaneously, the live-stock ratio has been reduced, thereby reducing the actual amount of manure.

Storage Capacity for Manure

In 1987, storage capacity exceeded 6 months for approx. 95% of the manure (solid) total with 65-70% of the storage capacity exceeding 9 months. Only 55% of the urine storage capacity exceeded 6 months and only 18% exceeded 9 months. In some instances storage capacity is especially limited for urine. In both watersheds, 90-95% of the run-off from the manure was collected.

Time of Manure Application

Leaching from manure varies greatly with respect to the time in which it is applied. Leaching is more prominent when manure is applied in the autumn than in the spring especially on sandy soils. As in previous studies (Hansen & Sommer, 1987), manure has primarily been applied to clay soils during the autumn and sandy soils during the spring, Table 3.

Table 3. Time of Application for Manure, Percent of Total.

	Rabis	Syv
autumn	35	65
winter	5	5
spring+summer	60	30

Silage

Most grass silage is pre-dried hereby reducing the total run-off from grass silage. 15% of all grass made into silage was stored without being pre-dried and without collecting the run-off. Approx. 50% of the sugarbeet top silage is stored without collection of the silage run-off.

Sewage Treatment

Most of the wastewater within the sandy Rabis watershed is infiltrated. Approx. 1/3 of the wastewater from the cleaning of milking equipment, etc. is collected. Within the Syv watershed, most of the wastewater is removed through drainage systems or directly to streams.

Purchase and Sale of Products

The calculated net purchase of plant nutrients is shown in Table 4. Net purchase refers to the difference in the nutrient content between the purchased product and the sold product.

Table 4. Net Purchases of Nutrients, kg/ha cultivated Area.

		Rabis			Syv		
		N	P	K	N	P	K
Purchase	Chemical Fertilizer	114	19	55	129	18	47
	Feed	48	10	12	52	13	12
	Total Purchase	162	29	67	181	31	59
Sale	Animal Products	24	5	5	12	3	1
	Vegetable Products	24	5	18	64	11	19
	Total Sale	48	10	23	76	14	20
Net Purchase		114	19	44	104	17	39

In most cases, the greatest source of nutrients is provided through the purchase of chemical fertilizers, although 1/3 of the P purchased in both watersheds is in the form of feed. Purchases of N, P and K significantly exceeded the content of the products being sold.

Drainage

There are no drained areas within the Rabis area whereas 50% the Syv area has been subsurface drained.

Irrigation

Because rainfall in 1987 was above average during the growing season, only 7% of the fields in the Rabis area were irrigated. Irrigation rates averaged 43 mm. Typically the irrigation rate for approx. 25% of the cultivated fields is 80 mm (Hansen, 1985). None of the fields in the Syv area were irrigated.

4. Discussion and Conclusion

Watersheds Investigated

The farms in the Rabis and Syv watersheds were found to be roughly represent prevalent farming practices within their respective areas. The Western area (Rabis) is dominated by dairy farms and the Eastern area (Syv) has few dairy farms. Both areas had live-stock concentrations below the national average.

Cropland Use

In the Rabis area spring cereals are primarily grown, yet during the period 1978-1987, the total area was reduced from 60% to 40%. There are larger areas, approx. 30% comprised of feed crops (sugarbeet, grass, silage crops). Areas supporting legumes have increased in recent years from <1% to approx. 10%.

Over the last 10 years, cereal grains and rape have made up 80-85% of the cultivated area within the Syv watershed. There has been an increase in the area with winter cereal grains and rape and a decrease in area with spring cereal grains during this period. Areas with legumes have increased in recent years from zero to approx. 5% while fruit and nursery production made up approx. 3% of the area.

Live-stock

Dairy cattle predominates in the Rabis area while swine predominates in the Syv area. Livestock concentrations have been significantly reduced over the last 10 years, and in 1987 totalled approx. 90% and approx. 47% of the national average, respectively.

Fertilizer Use

The effective rate of N-application for Rabis has on the average been approx. 15% less than the economic optimum rate, whereas Syv has had an effective rate similar to the economic optimum for a given combination of crops. N-application rates vary considerably within single fields. Manure spread inexpediently can be blamed for most of the higher N-application rates than the optimum. Differences in actual and optimum N-rates have been less than in previous studies (Hansen & Sommer, 1987).

Collection of Manure Heap Run-Off

In 1987, 90-95% of all manure heap run-off was collected. Although gains had been in fulfilling the requirements for collection and storage, there was still a lack of sufficient storage capacity, especially for urine and slurry in 1987.

Application of Manure

Most of the manure being applied to the sandy Rabis area is spread in the spring or summer, whereas, most of the manure being applied to the clayey Syv area is spread in the autumn. Spreding manure in the spring, especially in sandy areas, is particularly desirable in order to increase nutrient utilization and reduce leaching.

Silage Storage

In 1987 storage facilities for silage were inadequate. The run-off from 15% of the grass silage and from 50% of the sugarbeet top silage was not being collected. Storage facilities had improved since earlier studies (Hansen & Sommer, 1987).

Net Purchase of Nutrients

The application rates of N, P and K are significantly higher than the amount of N, P and K in the sold product. These differences along with the nutrients contained in rainfall and nitrogen fixation of legumes will either be lost or accumulated by the farm. Earlier studies (Hansen & Sommer, 1987) indicate that surplus P accumulates primarily in the plow layer and K will leach to under the plow layer only to accumulate and/or leach under the rootzone.

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Ministry of the Environment
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Number A3

Temperature and Denitrification

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Résumé.

The denitrification activity in two different agricultural soils, a coarse sandy soil and a sandy loam soil, was investigated in the laboratory. Soil samples were incubated under different temperature and moisture conditions, and were added pig slurry at varying amounts.

By using the acetylene inhibition technique it was possible to calculate both the denitrification activity and the ratio between N_2 and N_2O.

In the coarse sandy soil the denitrification activity was very low. Only after addition of large amounts of slurry and incubating at high temperature (25°C) a significant activity could be measured.

In the sandy loam soil both the denitrification activity and the ratio between N_2 and N_2O was affected by temperature as well as by soil moisture. At soil moisture contents above water holding capacity, the N_2/N_2O-ratio was positively correlated with the temperature.

1. Introduction.

The reduction of nitrate to gaseous products can be more or less complete (e.g. to N_2O or to N_2) depending on different environmental factors such as soil pH, soil temperature, oxygen status in the soil and plant growth (Nömmik, 1956; Bailey and Beauchamp, 1973; Bailey, 1976; Keeney et al., 1979; Chalamet, 1985; Klemedtsson et al., 1988; Ottow et al., 1985; Vinther, 1984).

Bailey and Beauchamp (1973) found that the soil temperature did not have any significant effect on the ratio between N_2 and N_2O, whereas other investigations showed an effect of temperature (Nömmik, 1956; Bailey, 1976; Keeney et al., 1979).

The purpose of the present investigation was to study the effect of soil temperature and moisture content on the denitrification activity and on the ratio between N_2 and N_2O.

2. Materials and methods.

This study was performed purely as laboratory investigation including two different soil types: A coarse sandy soil from Jyndevad Experimental Station located in Southern Jutland and a sandy loam soil from Askov Experimental Station in Eastern Jutland.

Some of the main chemical and physical characteristics of the two soils are presented in Table 1.

The experiments were carried out with airdried soil, of which 40 g was placed in 300 ml infusion flasks and the desired applications (e.g. water and glucose) were added. In experiments with pig slurry, the slurry was mixed with soil before distributed into

Table 1. Chemical and physical characteristics of soils (Partly after Hansen, 1978).

	Coarse sandy soil	Sandy loam soil
ppm NO_3-N*	3.4	8.7
ppm NH_4-N*	1.3	1.6
% total N	1.2	1.7
% total C	1.7	1.4
pH(H_2O)	6.0	6.6
Weight pct.:		
Clay	3.9	10.6
Silt	4.1	11.8
Fine sand	12.2	37.0
Coarse sand	76.8	37.6
Humus	3.0	3.0
Weightpct. water at field capacity	18	25

* determined prior to start of experiments.

the flasks. Three levels of slurry application were used: 10, 20 and 40 g slurry kg soil^{-1}, which correspond to approximately 25, 50 and 100 tons ha^{-1}. The slurry used contained 7.1 % dry matter, 0.5 % total N and 0.3 % NH_4-N.

Incubations were carried out as indicated in Fig. 1.

The samples were incubated for about 24 hrs (A to B) without acetylene (C_2H_2), whereafter a 1 ml gas sample was analyzed for N_2O on gaschromatograph. Acetylene was added (app. 10 vol %), and the soil sample was incubated for another 24 hrs before a second gas sample was analyzed for N_2O.

Assuming that C_2H_2 completely inhibits the reduction of N_2O to N_2, the ratio between N_2 and N_2O can be calculated in the following

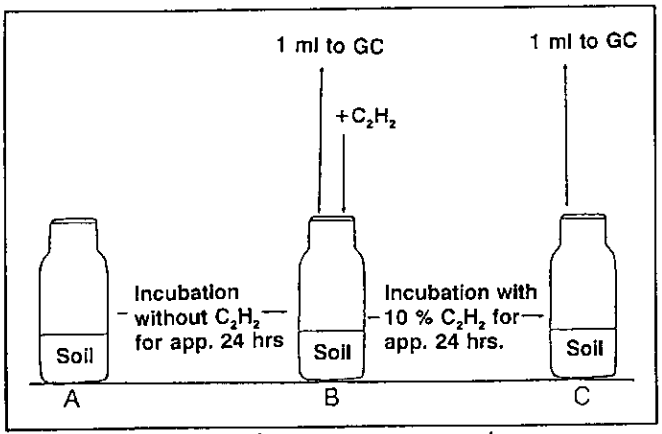

Fig. 1. Incubation and meausuring procedure.

way:

$$N_2/N_2O\text{-ratio} = \frac{(N_2O(C)-N_2O(B)) - (N_2O(B)-N_2O(A))}{(N_2O(B) - N_2O(A))}$$

The atmosphere contains 0.3 ppm N_2O, and this concentration is used in $N_2O(A)$.
The denitrification activity is expressed as $(N_2O(C)-N_2O(B))$ hour^{-1}.
The gas analyses were carried out on a Varian-3000 gaschromatograph equipped with an ^{63}Ni electron capture detector and a Poropak T column. Detector and column temperatures were 350 and 45 °C, respectively. As carrier gas a mixture of Ar (95 %) and CH_4 (5 %) was used at a flow rate of 25 ml min^{-1}.

3. Results and discussion.

3.1 Denitrification activity.

There was a significantly higher denitrification activity in the sandy loam soil than in the coarse sandy soil (Table 2). The activity in the coarse sandy soil did not increase appreciably by increasing the soil moisture from 80 to 140 % FC, which indicates that the potential for denitrification in the coarse sandy soil was very low. Field measurements of the denitrification activity in the same soil gave similar low rates (Andersen et al., 1983), which resently was confirmed by Lind et al. (1990). On the other hand there was a significant activity in the sandy loam soil, especially after increasing the soil moisture content from 75 to 125 % FC and after slurry application (Table 2).

Table 2. Denitrification activity (μg N_2O-N kg soil^{-1} h^{-1}) in a coarse sandy soil and a sandy loam soil at different temperatures and soil moisture contents and after slurry application.

Temp. °C	Coarse sandy soil		Sandy loam soil	
	% FC			
	80	140	75	125
10	0.01	0.01	0.05	0.44
20	0.05	0.08	0.34	2.49
	40 g slurry kg soil^{-1}			
10	0.22		2.75	
20	3.36		68.79	

Studies of the relationships between temperature and denitrification activity has shown, that at low temperatures (< 10°C), the tem-

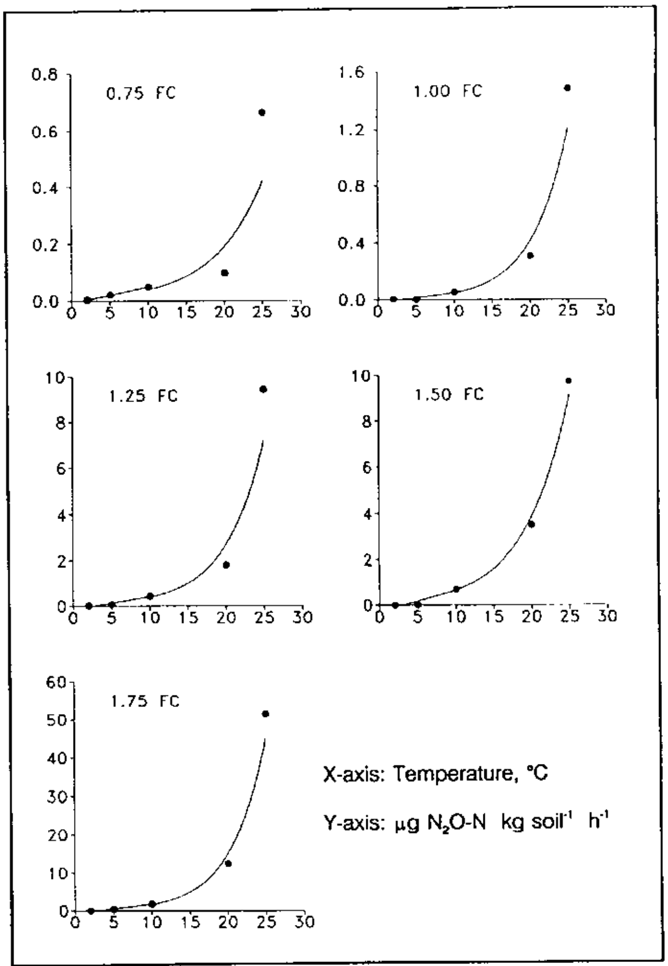

Fig. 2. Relationships between temperature, soil moisture content and denitrification activity.

perature effect is minimal and that there is a linear relationship between temperature and denitrification activity (Bremner & Shaw, 1958; Stanford et al., 1975; Smid & Beauchamp, 1976;). At higher temperatures there is an exponential relationship between temperature and activity (Focht & Verstrate, 1977; Doner & MacLaren, 1978; Stanford et al., 1975). This means that the relationship between temperature and denitrification activity can be expressed as follows:

$$Y_{(0\text{-}10\,^\circ C)} = a \cdot t + b$$

$$Y_{(10\text{-}25\,^\circ C)} = c \cdot e^{t \cdot d}$$

where Y = denitrification activity ($\mu g\ N_2O\text{-}N\ kg^{-1}\ h^{-1}$), t = temperature (°C) and a, b, c and d are constants.

Based on this assumption and on the results of the present experiments, the relationship between denitrification activity and temperature can be expressed as shown in Fig. 2, where also the best fit functions are presented. Calculated constants for the two functions are shown in table 3.

At low temperatures (< 10°C), the effect of temperature on the denitrification activity also in the present investigation was found to be small, which is indicated by the relatively low Q_{10} values (Table 3). In the coarse sandy soil no activity at all could be measured at 2 and 5°C.

At temperatures above 10°C the denitrification activity increased significantly with increasing temperatures, as indicated by Q_{10}-values from 5 to 11 in the sandy loam soil. Also in the coarse sandy soil the similar effect of temperature could be seen, but only after addition of slurry. If only water was added to the coarse sandy soil, the temperature did not have any effect on the denitrification activity.

Addition of water is causing an increase in the denitrification activity in at least two ways: 1. Increasing amounts of water means less oxygen in the soil and thereby more anaearobic sites. 2. By adding water to the soil more organic material will be solubilized and brought into contact with denitrifying bacteria.

From the results in Table 3 it can be seen

Table 3. Calculated constanst (a, b, c and d) for the best fit relationships between temperature and denitrification activity after addition of different amounts of water and slurry.

Sandy loam soil						
Water-content/ slurry-application	Temperature regime					
	0 - 10 °C $Y=a*t+b$			10 - 25 °C $Y=c*e^{t*d}$		
	a	b	Q_{10}	c	d	Q_{10}
75% FC	.006	-.007	.1	.008	.159	4.9
100% FC	.006	-.017	.1	.005	.217	8.7
125% FC	.056	-.143	.6	.055	.195	7.1
150% FC	.094	-.267	.9	.123	.173	5.6
175% FC	.230	-.564	2.3	.189	.219	8.9
10*	.004	-.007	.1	.003	.240	11.0
20	.129	-.378	1.3	.121	.212	8.3
40	.351	-.922	3.5	.313	.238	10.8
Coarse sandy soil						
80% FC	At the temperatures 2 and 5°C no activity.			.003	.113	3.1
110% FC				.008	.066	1.9
140% FC				.122	.003	1.0
10*	At the temperatures 2 and 5°C no activity.			.004	.209	8.1
20				.004	.242	11.2
40				.009	.276	15.8

* g slurry kg soil^{-1}.

that both addition of water as well as organic material in the form of slurry caused an significant increase in the denitrification activity in the sandy loam soil. The constant c increased from 0.008 to 0.189 after increasing the water content from 75 to 175 % FC, and was 0.003, 0.121 and 0.313 after addition of 10, 20 and 40 g slurry kg soil^{-1} respectively. In all the treaments the constant d remained around 0.2 in the sandy loam soil. This means that the relative increase in denitrification activity caused by an increase in temperature was similar independent of treatments.

In other words, an increase in the temperature causes an increased respiration of the denitrifying bacteria, and addition of water or organic material increases the number of sites where denitrification can take place.

3.2 The ratio between N_2 and N_2O.

Table 4. The ratio between N_2 and N_2O in the coarse sandy soil at different temperatures.

Temp °C	Without additions			Addition of 0,2 % glucose		Addition of slurry.		
	Moisture % FC			Moisture % FC		g/kg soil		
	80	110	140	110	140	10	20	40
2	0	0.3	0	0	2.7	0	0.5	0
5	0	0.4	0	1.0	2.1	-	1.7	0
10	0	0.2	0.3	0.1	2.5	3.9	2.3	2.8
15	0	0.0	0.6	-	-	-	-	-
20	0	0.8	1.2	4.8	11.1	7.8	4.2	9.3
25	-	-	-	-	-	9.8	6.8	9.0

- = not measured. Moisture content after addition of slurry was app. 110 % FC.

In the coarse sandy soil the N_2/N_2O-ratio was generally low in treatments without additions (Table 4). A N_2/N_2O-ratio equal to zero means that only N_2O was produced. From these series of expriments it is not possible to say whether the N_2O originated from the denitrification process or from the nitrification process, but considering the low moisture content (80 % FC) it is most evident that the nitrification process in this case was responsible for the N_2O. One of the reasons for the low denitrification activities and the low N_2/N_2O-ratios in the coarse sandy soil could be lack of easily available organic material.

To get an answer of this assumption, glucose and slurry was added (Table 4). This resulted in higher N_2/N_2O-ratios and the ratios seemed to be positivily correlated with temperature.

Table 5. The ratio between N_2 and N_2O in the sandy loam soil at different temperatures.

	Without additions					Addition of slurry *		
Temp	Moisture content: % FC					g kg soil^{-1}		
°C	75	100	125	150	175	10	20	40
2	2.5	0.6	1.9	0.6	0.5	0.1	0	0
5	3.2	0.3	1.5	0.1	0.0	0	0	6.9
10	0.4	1.6	2.9	2.1	1.6	0.7	0.7	30.1
20	0.3	2.8	6.2	9.7	4.8	2.4	4.6	63.1
25	1.7	6.2	10.7	13.2	15.9	5.0	3.1	23.2

* moisture content after addition of slurry was 80-90 % FC.

In the sandy loam soil there was a clear effect of both temperature and moisture content on the N_2/N_2O-ratio (Table 5). At moisture contents above 100 % FC there was a positive correlation between temperature and the N_2/N_2O-ratio.
The results of these experiments indicate that there is a close relationship between the denitrification activity and the N_2/N_2O-ratio. By increasing the temperature the N_2/N_2O-ratio increases exponentially, which is exemplified in Fig. 3.

The relationship between the N_2/N_2O-ratio and the temperature found in the present investigation is in good agreement with earlier reports. Nömmik (1956) measured the N_2- and the N_2O-production at the temperatures 3, 12-13, 20-22, 28 and 37 °C, and found N_2/N_2O-ratios of 0, 0.2, 0.7, 1.6 and 30.7 respectively.

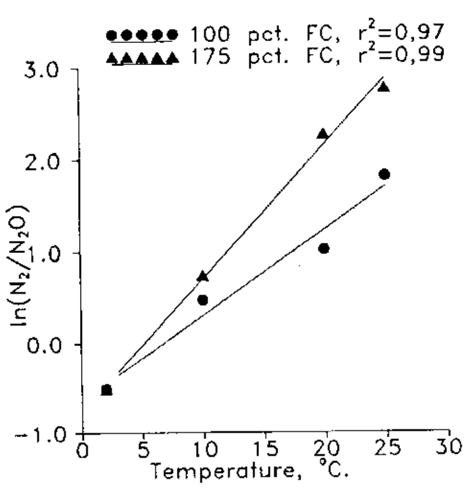

Fig. 3. Relationship between temperature and the N_2/N_2O-ratio.

Furthermore Keeney et al. (1979) found that by increasing the temperature from 7 to 25 °C, the N_2/N_2O-ratio increased from 1.3 to 4.4.

Also with respect to soil moisture content or oxygen status, the present results seems to be in agreement earlier investigations. Nömmik (1956) mention that "... it should be pointed out that at lower moisture content the denitrification gas consisted chiefly of nitrous oxide. This indicate that the degree of anaerobity is one of the factors which determines the composition of the denitrification." This has later been confirmed by Letey et al. (1981).

Whether the nitrous oxide originates from the nitrification process or from the denitrification process was investigated in an experiment with addition of ammonium and incubation with acetylene. Besides inhibiting the reduction of N_2O to N_2, acetylene also block the nitrification process (Berg et al., 1982), so by optimizing the conditions for nitrification (addition of 100 ppm NH_4-N and a moisture content of 80 % FC) and incubating samples both with and without acetylene, the contribution of nitrification-N_2O can be evaluated.

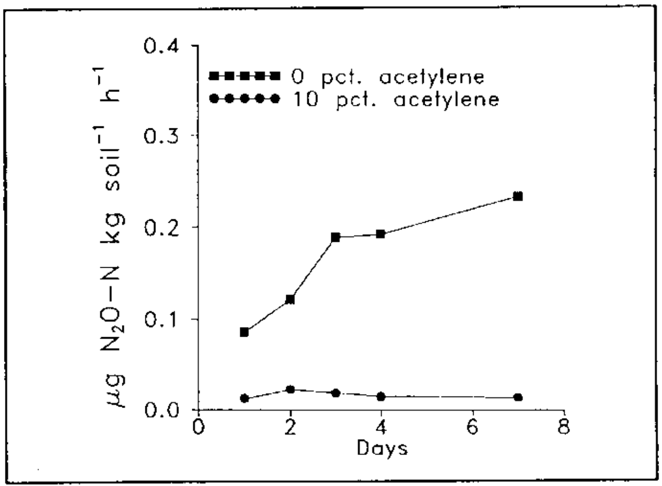

Fig. 4. N2O-production in a sandy loam soil incubated with 10 % acetylene and without acetylene.

The production of nitrous oxide was 7 - 15 times higher in samples where the nitrification was not affected by acetylene. These results, which also have been found by Bremner and Blackmer (1978) and Klemedtsson et al. (1989), show that the nitrification process under certain circumstances can contribute with considerable amounts of nitrous oxide. These results can also explain why low N_2/N_2O-ratios was found at low moisture contents.

4. Conclusions.

- the denitrification activity was in most cases negligible in the coarse sandy soil.
- the denitrification activity was negligible at temperatures below 10°C in the sandy loam soil.
- at temperatures above 10°C the denitrification activity increased exponentially by increasing temperature as a result of increased respiratory activity.
- increasing the soil moisture contents caused increased denitrification activity, which was a result of an increased number of sites where denitrification could take place.
- factors which caused an increased denitrification activity (temperature, soil moisture and organic material) also affected the N_2/N_2O-ratio: higher activity gave higher ratios.
- at soil moisture contents below 100 % FC the N_2/N_2O-ratio in most cases was less than 1, which might be due to N_2O produced from the nitrification process.

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Deposition of Ammonia near a Dairy Farm

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Summary

Deposition of ammonia from a dairy farm

Decreasing concentrations of atmospheric ammonia at increasing distances from a dairy farm will result in a decline in the deposition of nitrogen. Changes in the deposition of total N to vegetation near a dairy farm are thus a result of changes in ammonia deposition.

Total N deposition measured with biomonitors

The deposition of total N was measured by means of biomonitors, in 1987 as the difference between the quantity of nitrogen applied and the quantity of nitrogen harvested, and in 1988 as the dilution of ^{15}N in the plants exposed. During the periods of exposure, nitrate and ammonium concentrations in rain collected in permanently open funnels (i.e. bulk deposition) and concentrations of atmospheric ammonia were measured at increasing distances from the buildings of the dairy farm situated 20 km north of Copenhagen.

Bulk deposition of ammonium and nitrate

The bulk deposition of ammonium was related to the atmospheric ammonia concentration, the bulk deposition being 1.7 to 2 times higher near the farm than 150 to 300 m from the farm. The deposition velocities of ammonia to grass, calculated on the basis of measurements of total N deposition and atmospheric ammonia concentrations, were 1.6 cm s^{-1} (s.d. 1.2 cm s^{-1}) in 1988 and 3.8 cm s^{-1} (s.d. 5 cm cm s^{-1}) in 1987.

Calculation of ammonia deposition

The decline in ammonia deposition at increasing distances from a dairy farm was calculated by means of a surface depletion model (Asman et al., 1989). The model predicted the decline in ammonia deposition very well, but the deposition calculated was too low and the decline in calculated ammonia deposition (resulting from decreasing atmospheric ammonia concentrations) was not as steep as the decline measured in the deposition of total N. This may be due to an inadequate knowledge of both the rate of ammonia evaporation from manure and the rate of ammonia deposition to plants.

Introduction

Livestock production the source of atmospheric ammonia

Ammonia evaporation from livestock is high but unevenly distributed over the country (Buijsman et al., 1987; Kruse et al., 1989). Dung yards and stables are the source of almost half of the ammonia emitted from livestock. It is therefore of great importance to know the degree to which ammonia evaporation affects the local deposition of ammonia, as nitrogen deposited in natural ecosystems may be detrimental to such ecosystems (Roelofs, 1986; Schulze et al. 1989; Dijk et al., 1989).

It is a well-known fact that atmospheric ammonia may be absorbed as well as released by plants. The vertical flux of ammonia is to some extent determined by the atmospheric ammonia concentration, as plants may absorb ammonia at high concentrations of atmospheric ammonia and emit ammonia at low concentrations (Farquhar et al., 1980; Roger & Aneja, 1980).

NH_3 deposition measured by means of biomonitor

Continous measurements are therefore necessary in order to estimate the net flux of ammonia to a plant community during a given growth period. Unfortunately, however, continuous measuring of the net deposition of ammonia throughout the growth season by means of technical equipment would be laborious and expensive. Consequently, a biomonitor in the form of rye grass (Sommer, 1988; Sommer & Jensen, 1991) grown in pots was used to measure the effect of ammonia emitted from a dairy farm on the deposition of nitrogenous compounds.

The measurements of ammonia concentrations were taken simultaneously with the biomonitor measurements. It was thus possible to determine whether a correlation existed between the deposition of nitrogen and the atmospheric ammonia concentration and to calculate the deposition velocities of ammonia. The results were used to verify a transport and deposition model (Asman et al., 1989).

Wet deposition of ammonium (i.e. bulk deposition) was measured by means of permanently open funnels at various distances from the farm buildings. It is therefore possible to study dry weather deposition on the funnels may have contributed to the differences in the ammonium content measured in the rain collected.

Methods

Measurement of total N deposition

The deposition of total N was measured in the growth seasons of 1987 and 1988. In 1987 the uptake of atmospheric ammonia and inorganic nitrogen was measured as the difference between applied fertiliser nitrogen and harvested plant nitrogen. In 1988 the deposition of total N was measured as the dilution of ^{15}N in the plants exposed.

The N-difference method

In 1987 the deposition of total N was estimated by growing Italian rye grass (Lolium multiflorum Lam.) in pots containing N-free rockwool (Table 1). The seeds were spread on the rockwool and covered with sand. During the first month after germination, the plants were kept in a greenhouse. Nutrients were added to the solution (Sommer, 1988) used for watering the plants, a total of 0.896 g N being supplied to each pot (no nitrogen was applied during the period of exposure in the field). The plants were harvested once during the period of exposure and dried at 80°C, and after the period of exposure the grass was harvested and oven-dried at 80°C. The dried plant material was weighed and total N was measured by means of the Kjeldahl digestion procedure. Total N of the rockwool was measured twice -before commencement of the experiment and after the experiment (including the roots of the plants), and the deposition of nitrogen was calculated by means of the "N-difference method" (the "N-balance method"):

The ^{15}N-dilution method

In 1988 Italian rye grass was grown in N-free sand (Table 1) and 0.224 g N (KNO_3) with 2.786 atom % ^{15}N excess was applied to each pot with the nutrient solution. With these exceptions, the biomonitors were treated in the same way as in 1987 (Table 1). After 47 days of exposure, the grass was harvested and the sand was gently washed off the roots. The plant material was oven-dried and weighed and total N and ^{15}N enrichment were determined by means of an elemental analyser (Carlo Erba NA 1500) interfaced to an isotopic ratio mass spectrometer (Delta, Finnegan MAT). When the pots were placed in the field five pots were harvested and analysed in order to control the ^{15}N concentration of the plant material. The atom % ^{15}N excess thus measured was used as the basis for calculating the dilution of fertilizer during the exposure period and could thus also be used to estimate the deposition of total N (Sommer & Jensen, 1991). The results of these measurements has been presented elsewhere (Sommer & Jensen, 1991).

Table 1
Area of pots, content of rockwool or sand, quantity of seeds, and quantity of fertiliser nitrogen added.

Method	N-Difference Method			^{15}N-Dilution Method
Pot area, cm^2	491			491
Pot volume, litres	8.8			8.8
Rockwool weight, kg	1.3			
Weight of sand, kg	0.3			7.4
Weight of seeds, g	0.705 75		N content of seeds,	0.01[illegible]8
Fertiliser N, g N	0.896	0.448	Period of exposure	2.06-
8.09/87				17.06-2.08/88
Length of exposure, days	99			47

Measurements of atmospheric ammonia and inorganic N in rainwater

Atmospheric ammonia was measured by sucking air through a gas washing trap containing sulphuric acid at 0.5 l min^{-1}, the measuring periods ranging from 3 to 7 days. The ammonium concentrations were determined colorimetrically by means of an indophenol blue reaction. The traps were positioned 1.2 m above the crops.

Inorganic N in rainwater was measured by collecting rain in permanently open funnels (area: 452 cm^2). The funnels were placed in black plastic pipes in order to prevent growth of microorganisms and positioned at the same height as the biomonitors. The ammonium concentrations were determined colorimetrically and the nitrate concentrations determined by means of an HPLC (Perkin Elmer, series 10):

Site description. The deposition of N was measured near a dairy farm with a herd of 80 cows, the calculated annual emission of NH_3-N from the dung yard and the stable amounting to 1100 kg. There were no hedges or trees within 300 m east and 210 m west of the farm. Biomonitors, funnels and gas washing traps were placed east and west of the farm (Fig. 1). The deposition of N for each location was estimated as the mean of the results of three or four biomonitor measurements. Furthermore, wet deposition was measured at St. Lyngby in 1987, in an area with no animal production within five km north of the farm. Bulk deposition was measured during the entire period of exposure and atmospheric ammonia concentrations were measured five times during the exposure period in 1987 and twice in 1988.

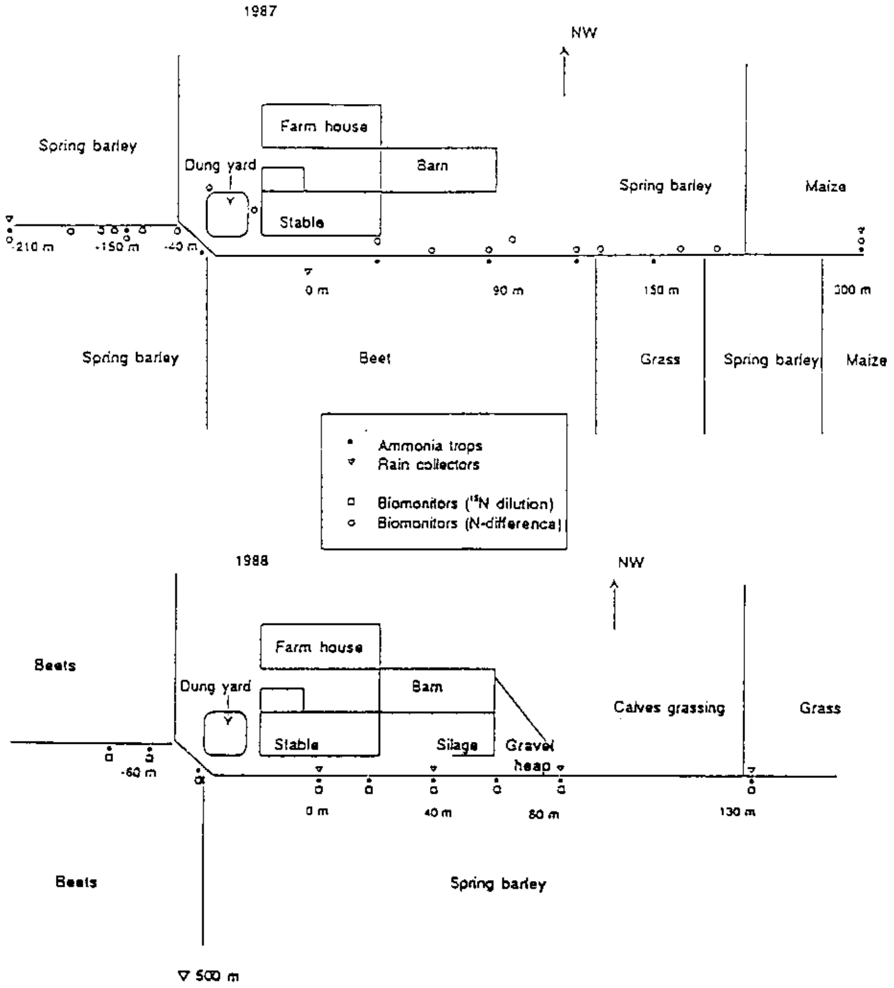

Figure 1.

Map showing locations of biomonitors, ammonia traps and funnels for collecting rain-water.

Results and Discussion

Atmospheric ammonia concentrations

In 1987 concentrations of atmospheric ammonia near the farm were lower than in 1988 (Fig. 2), as the summer of 1987 was quite windy. At distances over 40 m from the farm, however, concentrations were higher in 1987 than in 1988, probably as a result of ammonia volatilization from a small dung yard in the field 300 m south-west of the farm and a composting plant 600 m east of the farm. Thus, both the highest and the lowest concentration of atmospheric ammonia were measured in 1988, being 6 μg m^{-3} and 89 μg m^{-3}, respectively.

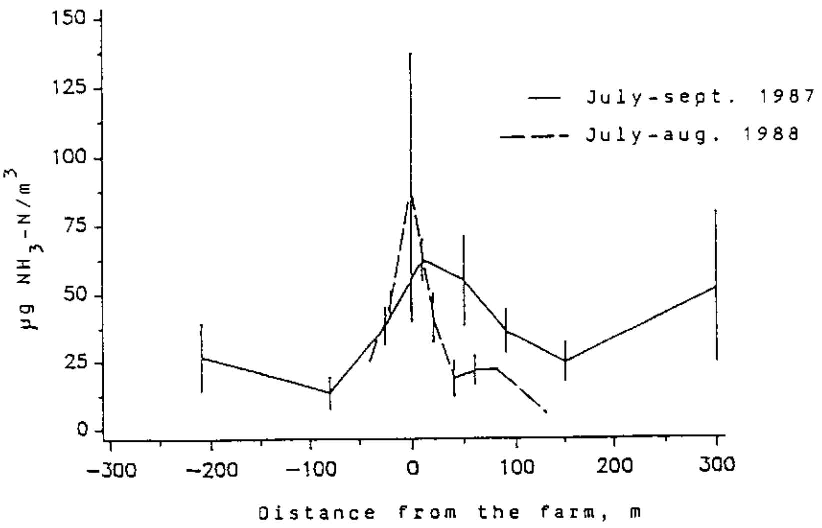

Figure 2.

Atmospheric ammonia concentrations est (+) and west (−) of the dung yard. Bars indication 1 standard deviation.

Ammonium in rain collected in open funnels

Near the buildings, the concentrations of ammonium in collected rain-water were 1.7 - 2 times the concentrations measured 150 - 300 m from the farm (Fig. 3). The high concentrations corresponded to atmospheric ammonia concentrations of approx. 70 µg NH_3-N m^{-3} and the low concentrations to approx. 25 µg NH_3-N m^{-3}. There was no difference between the concentrations of nitrate in rain-water collected near the farm and those in rain-water collected at greater distances from the farm. This indicates that dust deposited on the funnels as a result of traffic near the farm did not cause the inorganic nitrogen content of the collected rain-water to increase.

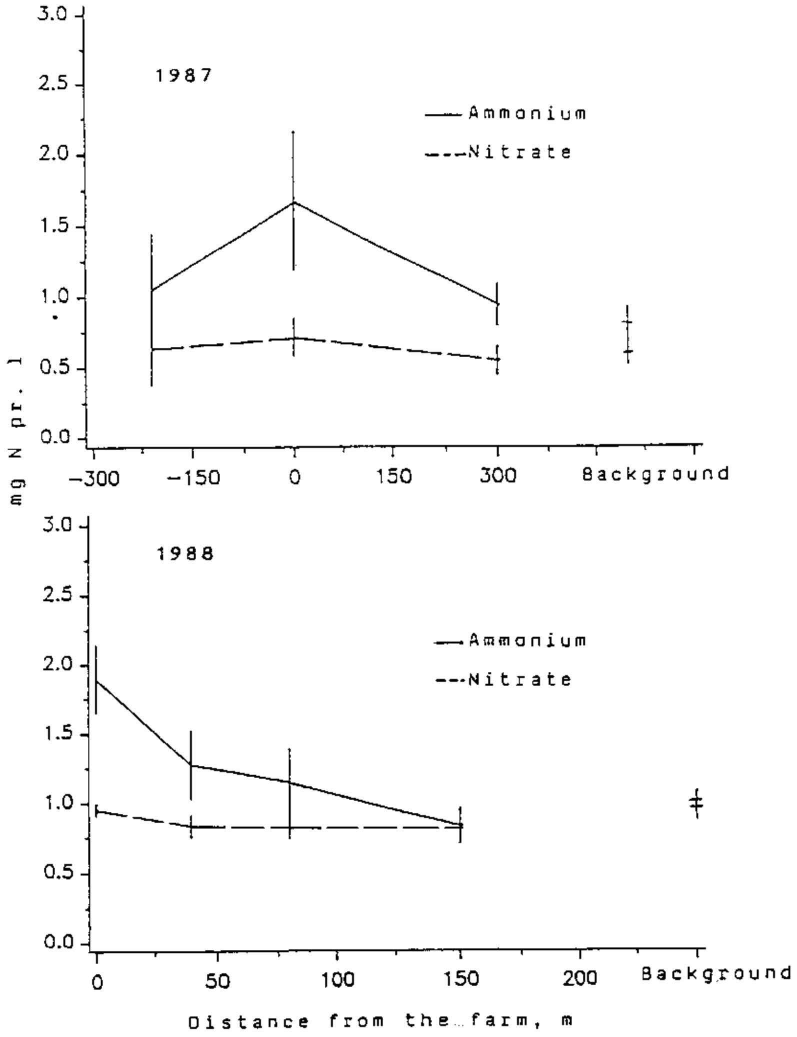

Figure 3.

Concentrations of ammonium and nitrate in rain (bulk deposition) eat (+) and west (−) of th dunk yard in year 1987 and 1988.

High ammonium concentrations in rain-water near farm

The results indicate that with increasing concentrations of atmospheric ammonia an increasing proportion of the inorganic nitrogen in rain-water will be ammonium. In rain-water collected in a forest, 21% of the ammonium content was deposited on the sides of the open funnel in the form of ammonia or particulate ammonium (Grennfelt et al., 1985). This could explain why Draaijers et al. (1989) did not find decreasing ammonium concentrations at increasing distances from an ammonia emission area in rain collected in funnels which were cleaned before it started raining. This, however, contrasts with the decline found by Schuurkes et al. (1988) in the ammonium content of rain collected in open funnels at increasing distances from an ammonia source.

In 1987 precipitation in the period of exposure totalled 343 mm and the bulk deposition of inorganic N was 0.48 g $(NH_4^+ + NO_3^-)$ N m^{-2}. In the exposure period in 1988, precipitation totalled 94 mm and the bulk deposition amounted to 0.14 g $(NH_4^+ + NO_3^-)$ N m^{-2}. The deposition is calculated from NH_4^+ and NO_3^- concentrations determined in funnels situated more than 500 m from the farm.

The differences between the results arrived at when calculating the deposition of N by means of the N-difference method and the ^{15}N-dilution method have been studied by Sommer & Jensen (1991), who demonstrated that the N-difference method did underestimate the deposition of N. The differences between the results were due to ammonia volatilisation from the seedlings. There may also have been some loss of ammonia during treatment of the samples prior to the analyses. The measurements taken in 1987 were corrected for losses of ammonia occurring while the plants were kept in the greenhouse, assuming that the same amount of nitrogen was lost with both methods.

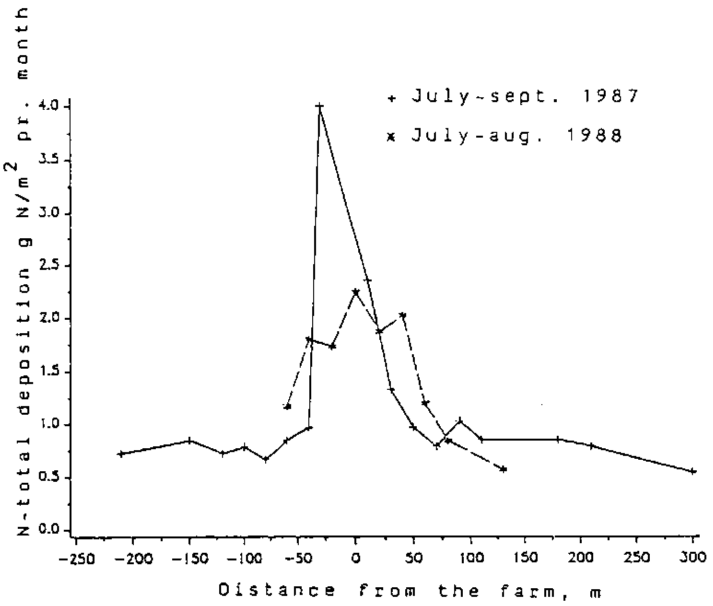

Figure 4.

Depostition of N-total eat (+) and west (-) of the dung yard measured with biomonitors, area 492 cm

Total N deposition low 150 m from farm

In both years, the deposition of total N declined sharply east and west of the farm (Fig. 4). In 1987 the highest total N deposition (4.0 g N m^{-2} $month^{-1}$) was measured one metre from the dung yard. That year the biomonitors were placed along an east-west line running one metre south of the stable and the dung yard. In 1988 the biomonitors were placed along a line 10 m south of the stable and the dung yard, and the deposition measured was 2.1 g N m^{-2} $month^{-1}$. The lowest deposition (0.4 g N m^{-2} $month^{-1}$) was measured in 1988, 130 m from the farm. The higher concentrations of atmospheric ammonia measured in 1987 at distances over 100 m from the farm seem to have resulted in the higher deposition of N-total that year - approx. 0.8 g N m^{-2} $month^{-1}$, which is twice the deposition measured 130 m east of the farm in 1988.

Deposition of other nitrogenous compounds to plants

There will be no differences in atmospheric concentrations of NO_x, NO_3^- or HNO_3 at increasing distances from a dairy farm as there is no NO_x source on such a farm. Furthermore, transformation of ammonia to ammonium will be slow, with a pseudo-first order rate constant of 10^{-3} -10^{-5} s^{-1} (Asman & Janssen, 1987). Differences in total N deposition at increasing distances from a dairy farm must therefore be due to differences in the deposition of ammonia. Taking this into account, it is possible to calculate an average deposition velocity for a given growth period on the basis of measurements of nitrogen deposition and atmospheric ammonia concentrations. In order to eliminate the deposition of other nitrogenous compounds, the difference in total N deposition in different locations should be divided by the difference in atmospheric ammonia concentrations and the period of exposure.

Deposition velocities

The estimated deposition velocities in 1987 and 1988 were 3.8 cm s^{-1} (S.D. 5 cm s^{-1}) and 1.6 cm s^{-1} (S.D. 1.2 cm s^{-1}), respectively. The great standard deviation in 1987 is probably a result of the N-difference method being less accurate than the ^{15}N-dilution method. Duyzer et al. (1987) estimated a Vd of 1.92 cm s^{-1} (S.D. 1.09 cm s^{-1}) on a moor by means of the micrometeorological mass balance method, and Draijers et al. (1989) calculated a Vd of 2.7 cm s^{-1} on the basis of throughfall measurements and model calculations of atmospheric ammonia concentrations. The deposition velocities estimated during the present study are thus within the range estimated elsewhere.

The model for calculating ammonia deposition

A surface depletion model (Asman et al., 1989) was used to calculate the ammonia concentrations east and west of the farm, the calculations being made on the basis of climatic data from a station 4 - 5 km from the experimental field. A Vd of 1.2 cm s^{-1} and a simple daily average of the annual emission of 1100 kg NH_3-N $year^{-1}$ were used for the calculations. Near a dairy farm, however, the model will fail in predicting the deposition of ammonia because the source is diffuse and not a single source as assumed in the calculations and because wind conditions will be affected by the buildings. For this reason, the results of measurements taken between 0 and 30 m east and west of the farm have not been used in the comparison of modelled ammonia deposition and measured N-total depostion.

Inaccurate estimates of ammonia volatilisation

There is a linear relationship between the calculated ammonia deposition and the deposition of total N (which means that the model predicts the deposition of ammonia from the farm very well (Fig. 5)). The difference bet

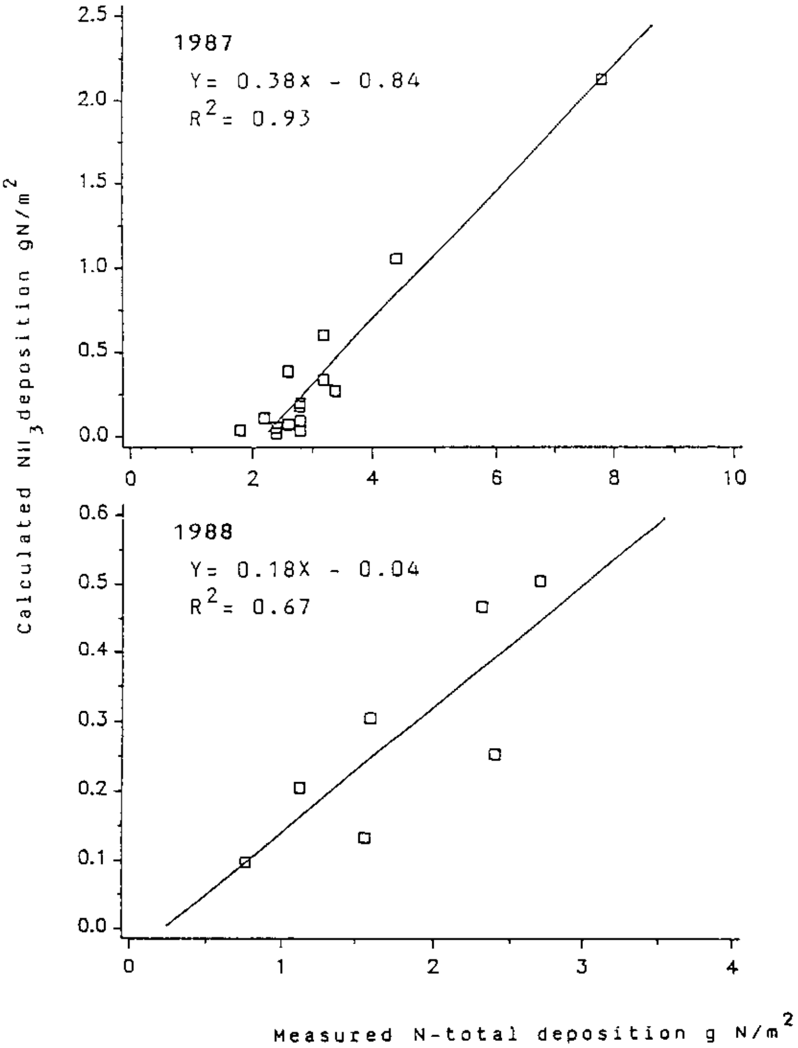

Figure 5.

Measured N-total deposition related to calculated deposition of ammonia. Data collected nearer than 30 m from farm yard is not included.

ween predicted ammonia deposition and total-N deposition is due not only to the deposition of NH_4^+, NO_x, NO_3^- and HNO_3 but also to the deposition of atmospheric ammonia from the surroundings. One more reason for the difference is presumably that the emission of ammonia from stables is much higher in the summer than in the winter (Ryden et al., 1987). The ammonia emisssion per day should therefore be weighted using a factor to account for seasonal differences.

The deposition velocity (Vd) estimated by means of the biomonitors was higher than that used for calculating the deposition of ammonia. If a Vd which is too low is used in the model, the deposition of ammonia near the farm thus calculated would be too low and the calculated atmospheric ammonia concentrations at greater distances from the farm would thus be too high. This explains why the measured deposition of total N declines more sharply at increasing distances from the farm than calculated ammonia deposition, giving a coefficient of inclination lower than 1 for correlation lines (Fig. 5).

Conclusion

Ammonium in collected rain-water

As a result of dry deposition of ammonia on the sides of the funnels, the bulk deposition of ammonia is related to the concentration of atmospheric ammonia. The ammonium concentrations in collected rain-water were 1.7 - 2 times higher near the dairy farm used in this study than 100 to 300 m from the farm. The influence of local sources of atmospheric ammonia must therefore be taken into account when ammonium deposition in rain-water is calculated on the basis of measurements with open funnels.

Total N deposition and calculations of ammonia deposition

There was a correlation between the measured deposition of total N and the predicted deposition of ammonia (results from measurements between 0 and 30 m from the farm were not included in the comparison). The model did predict the changes in deposition resulting from declining concentrations of atmospheric ammonia very well. The coefficients of correlation for the linear relationship between measured total N deposition and calculated ammonia deposition were 0.93 in 1987 and 0.67 in 1988. This linear relationship was expected, as differences in atmospheric ammonia concentrations is the parameter varying in the ammonia plume at increasing distances from the farm.

By predicting the deposition of ammonia, one does get an idea of the parameters of importance for the deposition process. The results of such a validation show that it is possible to calculate deposition trends, but the ammonia deposition thus calculated is too low. The reason for this is presumably that the rate of ammonia emission from manure and the rate of ammonia deposition are too low.

Acknowledgements

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Ammonia Monitoring
Passive Diffusion Tube Sampling

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Abstract.

This paper presents the results from an ammonia monitoring programme in Denmark using passive diffusion tube samplers. The programme was carried out from April 1988 to May 1989. The passive diffusion tube provides a two week average value of the ammonia concentration. Measurements at three different localities in Zealand and four different localities in Jutland were carried out. These included both background and emission areas. Results from a local investigation in an emission area and inside and outside three forests are also presented.

The data show differences in ammonia levels in the background and the emission areas and are agreeable to emission inventories. Furthermore they show concentration gradients in emission areas and inside and outside forests.

The passive diffusion tube is useful for the determination of ammonia levels and for the determination of the representativity of samplings sites.

Contents

1. Introduction.

There is a growing concern at the levels of ammonia in the atmosphere and their role in nutrient cycles and environmental acidification. In response to this, a monitoring programme to determine gaseous atmospheric ammonia in Denmark was carried out from April

Monitoring network

1988 to May 1989. Monitoring was carried out at seven localities, with one or more measuring sites in each. The localities comprise areas with low as well as high ammonia emission densities and forest locations.

Ammonia

Ammonia is mainly emitted from livestock (both stables and manure spreading), fertilizers and biological activities in the soil. Since the emission is mainly caused by biological activities the atmospheric concentrations are dependent on the season. Further, because the solubility of ammonia in water is temperature dependent, the concentration varies with temperature and humidity. Ammonia reacts readily with nitric acid and other acidic species in the atmosphere and dissolves in droplets or in aqueous layer on wet surfaces. These processes may be reversible (Ferm, M., 1986). The gas has a high deposition velocity (v_g) to the ground and this fact, together with its emission exclusively from ground level sources, accounts for its rapid fall in concentration with distance from source. Conversion to particulate forms (e.g. $[NH4]_2SO4$ with a typically sub-micron mass median diameter, Stern, A.C., 1976 and Milford, J.B. & Davidson, C.I., 1987) leads to a reduction of several orders of magnitude in the deposition velocity and the dry deposition ceases to be an important removal process.

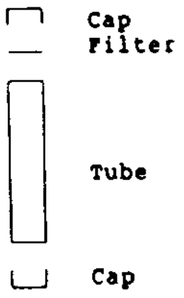
Passive diffusion tubes

In the monitoring programme passive diffusion tube samplers were used to determine the gaseous ammonia concentration. These samplers collect the gas by molecular diffusion along the tube to an absorbing medium. Aerosols, because they have a much lower diffusion rate, are not sampled. The passive diffusion tube gives an integrated concentration measured over the sampling period. In this monitoring programme the tubes were exposed for periods of approximately 14 days.

Comparison to reference method

At two of the measuring sites the passive devices were compared to a denuder reference method. The comparison showed, that the measurements done by the passive device not correspond to the teoretical expectation, but they do correlate to the reference method. The results from the passive device are therefore corrected by a calibration factor.

2. Measurement technique.



The passive sampler for ammonia consists of a 7 cm long P.T.F.E. tube of 1 cm internal diameter. A glass fiber filter (Whatman GF/A), impregnated with 30 μl 1 % (w/v) sulphuric acid, which serves as an ammonia absorbent, is held in position at one end of the tube with a coloured polythene cap. The other end of the tube is sealed with a plain cap.

The tubes were mounted vertically, with the coloured cap upwards and at a height of 2 m. Sampling was started by removing the plain cap, allowing ammonia in the air to diffuse along the tube to the absorbing filter. After exposure the tubes were sealed and sent to the laboratory together with information about their exact time of exposure. In the laboratory the filters were removed from the tubes and extracted with water and the ammonia determined by the indophenol method (Searle, 1984).

The tubes were exposed for periods of about 14 days, starting the first and fifteenth of every month. At each measuring site four tubes were exposed in parallel. The mean value of the four tubes defines the result from a measuring site.

2.1 Theory of the diffusion tube sampler

For a tube of a known length and internal diameter, with an efficient absorbent at one end, the sampling rate can be calculated using Fick's law for the flow of gas (ammonia, NH3) through a gas mixture (NH3 in air) under conditions of constant temperature :

Fick's law

$$F_{NH3} = - D_{NH3} \frac{d\, c_{NH3}}{d\, z} \qquad (1)$$

F_{NH3} = flux of ammonia in air; [mol/cm²s]
D_{NH3} = molecular diffusion coefficient of ammonia in air; [cm²/s]
c_{NH3} = concentration of ammonia in air; [mol/cm³]
z = length of diffusion path; [cm]

The minus sign indicates flux in the direction of a decreasing concentration gradient. It has no numerical significance.

The flux of ammonia F_{NH3} through a certain area, in this case the crosssectional area of the tube ($\Pi/4\ d^2$), in a certain time (t) is given by :

$$Q_{NH3} = F_{NH3}\ \Pi/4\ d^2\ t \qquad (2)$$

With an ammonia concentration $c_{NH3(e)}$ at the entrance of the tube and $c_{NH3(z)}$ after the length z, (1) and (2) gives :

$$- D_{NH3} \frac{(c_{NH3(e)} - c_{NH3(z)})}{z}\ \Pi/4\ d^2\ t$$

if $c_{NH3(z)}$ is taken as zero, due to efficient absorption at the filter surface then

$$Q_{NH3} = \frac{-D_{NH3}\ c_{NH3(e)}}{z}\ \Pi/4\ d^2\ t \qquad \text{and}$$

Calculation of outdoor concentration

$$c_{NH3(e)} = \frac{Q_{NH3}\ z}{D_{NH3}\ \Pi/4\ d^2\ t} = \frac{Q_{NH3}}{t}\ \text{const.} \qquad (3)$$

where Q_{NH3} is the amount of ammonia absorbed on the filter, corrected for blank values.

Equation (3) relates the average outdoor concentration of ammonia (the concentration at the entrance of the tube) to the amount of material absorbed on the filter in a certain time period.

Temperature dependence of diffusion coefficient

The molecular diffusion coefficient D is temperature dependent :

$$D = D' \left(\frac{T}{T'}\right)^{3/2} \qquad (4)$$

T = temperature; [K]

The diffusion coefficient of ammonia is 0.236 cm²/s at 25°C (Coulson & Ricardson, 1954). At 10°C the diffusion coefficient is 0.218 cm²/s, at 5°C 0.213 cm²/s etc. according to (4). In the calculation of concentrations from the measured values, monthly average temperatures in the intervals -5°C - 0°C - 5°C - 10°C - 15°C - 20°C are used to get suitable diffusion coefficients.

2.2 Detection limit.

Accept level

For one sampling period one batch of tubes including blanks are prepared. The blanks are kept in refrigerator, while the tubes are exposed. The value of a given quantity Q of ammonia on a filter is then accepted if the value is greater than twice the standard deviation of the blank values on the day of analysis in question. There are 8 blanks on each day of analysis. If the value was lower, it was recorded as zero. The blank values showed a day to day variation and a seasonal variation with higher values in winter and spring. This is probably due to contamination from the indoor environment and in winter time higher concentrations resulting from reduced ventilation and perhaps in springtime to manure spreading.

Contamination

Variating accept level

Since the blank values were variable, the accept levels were also variable. When the filter values got below the accepted level, this was about 0.3 µg NH3-N/m^3 in terms of an outdoor concentration using the calibration factor introduced below for two week sampling periods.

2.3 Parallel measurements.

At Risø four tubes were exposed at each of two sites 10 meters apart for 15 two weeks periods. The results are shown in Figure 1.

Risø 1 against Risø 2

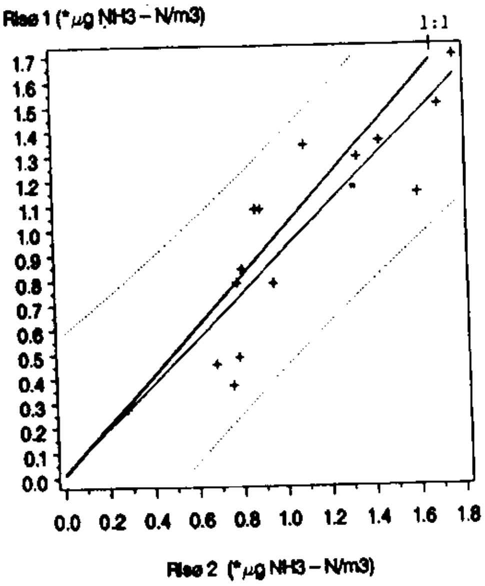


Figure 1
Plot of passive diffusion tube measurements at Risø 1 against Risø 2. The line 1:1, the best linear fit and 95 % confidence limits for observations are shown. (* : concentration calculated from equation (3)).

The two stations at Risø showed good agreement and were identical at the 95 % confidence level.

2.4 Comparison with denuder measurements.

The passive diffusion tube was compared with a denuder reference method, (Ferm, 1979). The comparison took place at two measuring sites, Risø (Oct.'88 - June'89) and Tange (Dec.'88 - May'89), (the locations of the sites are shown in Figure 3).

Scientifically the denuder method is believed to be the most reliable method for the determination of gaseous ammonia. It is very labour intensive, however, and is therefore only used when circumstances may require it.

Denuder technique

The denuder sampler resembles the passive sampler in utilizing the difference in diffusion rates of gases and aerosols. However it differs from the passive device, by sucking air through the tube, the airflow and tube dimensions being optimized to give laminar flow conditions. The aerosols move with the laminar flow through the tube and are not collected, while the gas with a higher diffusion coefficient diffuses to the acid coated inner wall of the tube and is absorbed. A detailed description of the denuder used in this survey is given by Ferm, 1979.

In the comparison between passive diffusion tubes and the denuder method, the denuder determined 24 hour mean values of the ammonia concentration. The denuder measurements were then calculated to an average value for the period in which the diffusion tubes were exposed. Each point for comparison is then an average of 14 or more denuder measurements and as a consequence it might be associated with some measure of uncertainty.

Logaritmic transformation

In the comparison between the two methods and in further statistical calculations on the measurements with passive diffusion tubes, the values were transformed logaritmically (ln(conc. + 1)) to obtain a normal distribution.

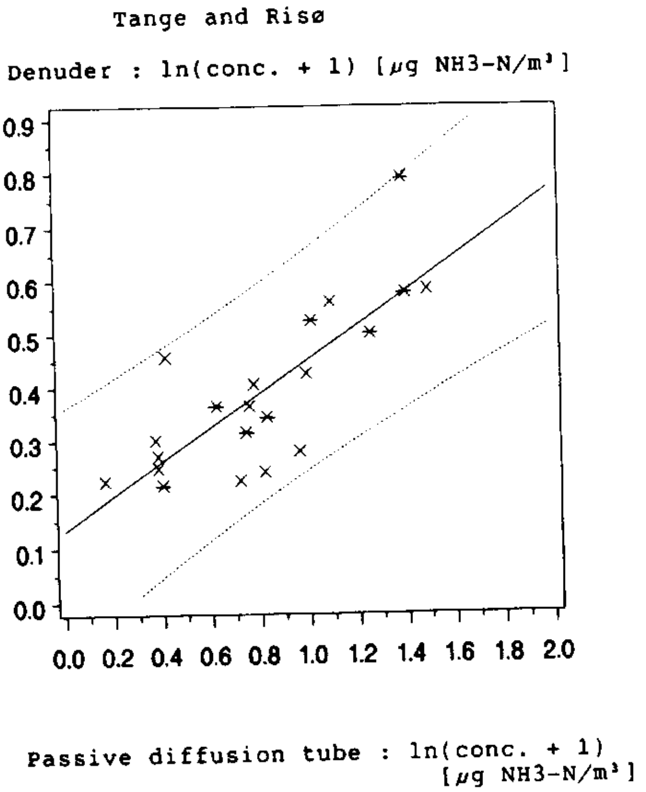


Figure 2
Plot of denuder measurements against passive diffusion tube measurements on data from Tange and Risø. Best linear fit, 95 % confidence limits for observations and correlation coefficient (corr.) are shown.

The data from Tange and Risø are correlated with the denuder measurements (corr.(r) 0.80). The data from the two measuring sites are in the same concentration range, though the data from Risø are more scattered.

A principal component analysis on the data from both Risø and Tange gives :

$$\ln(\text{denuder}+1) = 0.33*\ln(\text{passive}+1) + 0.130 \qquad (5)$$

with a correlation coefficient (r) on 0.80.

A principal component analysis on Tange data alone gives :

$$\ln(\text{denuder}+1) = 0.46*\ln(\text{passive}+1) + 0.012 \qquad (6)$$

with a correlation coefficient (r) on 0.90.

A principal component analysis on Risø data alone gives :

$$\ln(\text{denuder}+1) = 0.24*\ln(\text{passive}+1) + 0.187 \qquad (7)$$

with a correlation coefficient (r) on 0.69.

At the 95 % confidence level equation (5) is equal to equation (6) and (7). Equation (5) is used to relate the measurements with passive diffusion tubes to an atmospheric concentration of ammonia. No explanation has yet been found for the relation, which disagrees with the theory of passive diffusion tube samplers. The theoretical expression (3) assumes, that the diffusion path is equal to the length of the tube. This may not be true due to some turbulent effect at the entrance of the tube. Probably equation (3) for the concentration calculation should be corrected for an "effective length of diffusion", but even halving the diffusion path would not explain the empirical relation found with denuder measurements.

Linear extrapolation

The linear relation between denuder and passive diffusion tube measurements are found in a concentration interval from 0.2 - 0.9 μg NH_3-N/m^3 (measured by denuder). Some of the results from the different measuring sites are above this level. The conversion from passive diffusion tube result to "denuder concentration" therefore assumes a continued linear relation above 0.9 μg NH_3-N/m^3.

2.5 Contamination of tube walls

For most of the sampling periods, when returned to the laboratory after exposure, the tubes, after removel of the filter, were extracted with water and analysed for ammonium. The tubes were found to have ammonium species deposited on the inside of the walls. The distribution by season and measuring site of the tube content of ammonium indicates a particle deposition related to windspeed. Static electricity is also known to have an influence. The tube content of ammonium species might have an influence on the collection of gas, either by absorbing or releasing ammonia. This tube contamination may explain at least in part the relation found between the tubes and the denuder measurements.

3. Measuring sites.

The measuring localities are marked on the map in Figure 3. Each locality has one or more measuring sites within the local area.

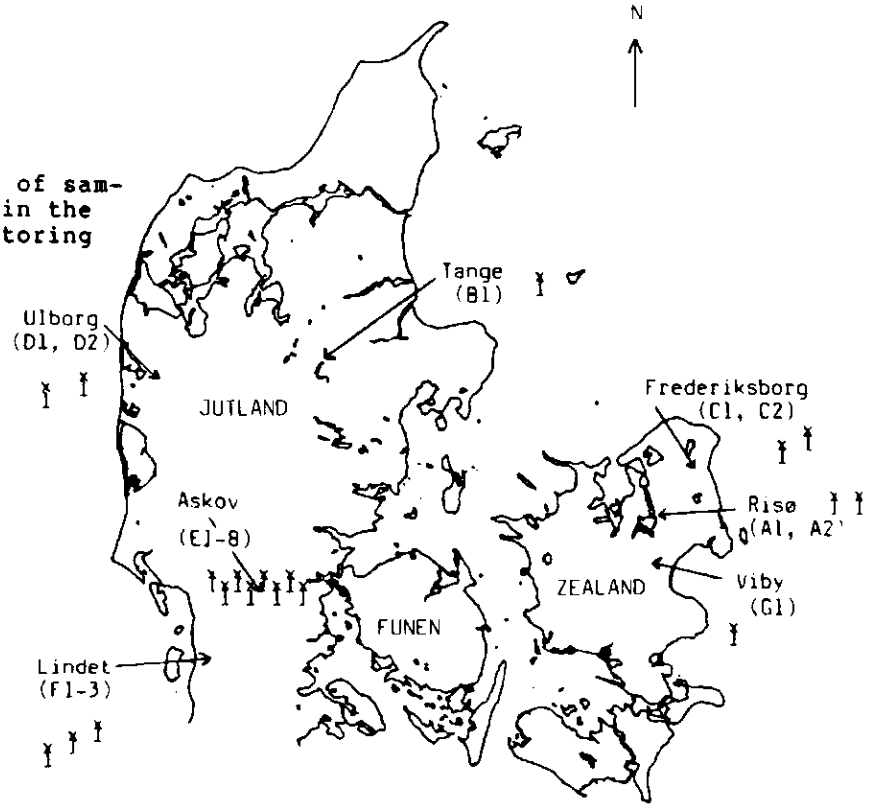


Figure 3
Distribution of sampling sites in the ammonia monitoring network.

As shown previous a denuder reference method, was used to determine ammonia at the Risø and Tange (EMEP-station) measuring sites for a part of the monitoring programme.

Risø 1 and 2 (A1 & A2) are located on a grassland area ten meters apart near a shallow bay and used as "parallel" measurement sites.

The station Viby (G1) is situated in a small meadow between two cultivated fields.

Frederiksborg 1 (C1) and Ulborg 1 (D1) are in forest clearings, surrounded by evergreen trees.

Frederiksborg 2 (C2) is located in a grass field about 2 km south-east of Frederiksborg 1 (C1) and about 1.7 km from the forest edge.

Ulborg 2 (D2) is on heathland 200-300 m west of Ulborg 1 (D1) and about 100 m from the forest edge.

The measuring sites at Askov are in an area of about 500 m x 500 m. A pigfarm is located approximately 500 m west of the area. The measuring sites at Askov are shown below.

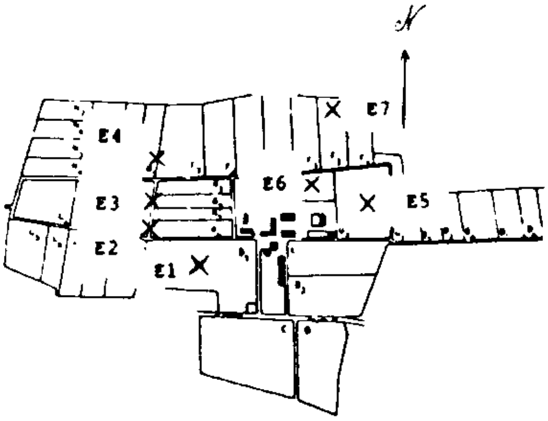


Figure 4
Measuring sites at Askov. The stations E2, E3 & E4 are located in a windbreak. The other stations are in grassland or meadow surrounded by agricultural fields.

Lindet 2 (F2) is at the edge of a forest, about 200 m northwest of a pigfarm producing 3000 pigs yearly. Lindet 1 (F1) is in a clearing in the forest about 200 m northwest of Lindet 2 (F2). Lindet 3 (F3) is located beneath the canopy of a young beech wood, about 1 km west of Lindet 1 (F1) and about 300 m south-east of the forest edge to the west.

4. Results and discussion.

The yearly average contrations of ammonia at the different measuring sites are shown in Table 1. The coefficients of variation are also given.

Table 1
The annual average concentration of ammonia at each measuring site, converted using the relation to denuder measurements (equation (5)), and assuming linear extrapolation of the relation to higher concentration ranges than measured. The 95 % confidence limits on the yearly average are in the range 0.16-0.18 µg NH3-N/m³. The coefficient of variation at each measuring site is also included. No allowance is made for missing data at some sites.

Measuring site		Average concentration (15.04.88-15.04.89) µg NH3-N/m³	Coefficient of variation %
Risø 1	A1	0.55	18.4
Tange	B1	0.72	14.1
Frederiksborg 1	C1	0.32	52.7
Frederiksborg 2	C2	0.39	30.5
Ulborg 1	D1	0.35	40.5
Ulborg 2	D2	0.49	27.4
Lindet 1	F1	0.62	14.2
Lindet 2	F2	1.14	7.4
Lindet 3	F3	0.42	33.5
Viby	G1	0.54	15.4
Askov 1	E1	0.91	8.5
Askov 2	E2	1.11	7.7
Askov 3	E3	1.11	6.7
Askov 4	E4	1.11	7.4
Askov 5	E5	0.84	10.8
Askov 6	E6	0.88	10.2
Askov 7	E7	0.92 *	9.8

* Half of the exposure periods are missing.

The annual average concentrations of ammonia (Table 1) show a close inverse relation to the coefficient of variation at the measurement sites. This is probable due to an increasing contribution from analytical errors at the lower concentrations and less natural variation at the sites with high concentrations, which are more constantly influenced by high emission density areas.

4.1 Comparison to emission inventories.

All measuring sites except those at Askov and Lindet were placed in areas with no emission sources within a distance of at least 1-2 km. Askov and Lindet were placed in areas close to emission sources and in areas with high emission densities. The annual average concentrations of ammonia (Table 1) show very good agreement with the distribution of emissions (Asman, 1990). Low concentrations are found in areas with low emission densities and increasing emission densities are followed by increasing concentrations. The emission inventory cover domestic animals and fertilizers in a 5 km x 5 km grid (Asman, 1990).

4.2 Seasonal variations.

The seasonal variations of ammonia concentrations show a pattern with maximum in spring and early summer, decreasing concentrations, with some evidence for an increase in late autumn, before falling to a minimum in wintertime (Figure 7-12 below). The pattern is less well characterized at Askov and Lindet, which were located near emission sources (Figure 5 and 6 below). Lindet shows a different pattern, probably due to the influence of a local source to the east, the non-dominating wind direction (Figure 6 below). The late autumn increase in concentration was better characterized at the Jutland measuring sites (Figure 12). This may indicate more agricultural activity and perhaps different agricultural practices compared to Zealand.

The seasonal pattern of ammonia levels with increases in spring and autumn are consistent with the agricultural activities of manure spreading at these times. The low level of agricultural activity and low temperatures in wintertime also relate to the concentration minima found in this period.

4.3 Local variation.

Askov

Seven measuring sites were placed in an area of about 500 x 500 m at Askov (shown in Figure 4). The measuring sites towards the west were placed in a windbreak (E2, E3 & E4) and gave the same results. E1 showed lower concentrations than the three sites towards west, but a little higher than E5, E6 and E7, which were very similar. Not all the sites are shown in Figure 5. The concentration gradient going from west to east (Figure 5, below) is most apparent and indicates a considerable deposition in the windbreak. The sites E2, E3 and E4 were about 20 % higher than the rest of the stations (Table 1).

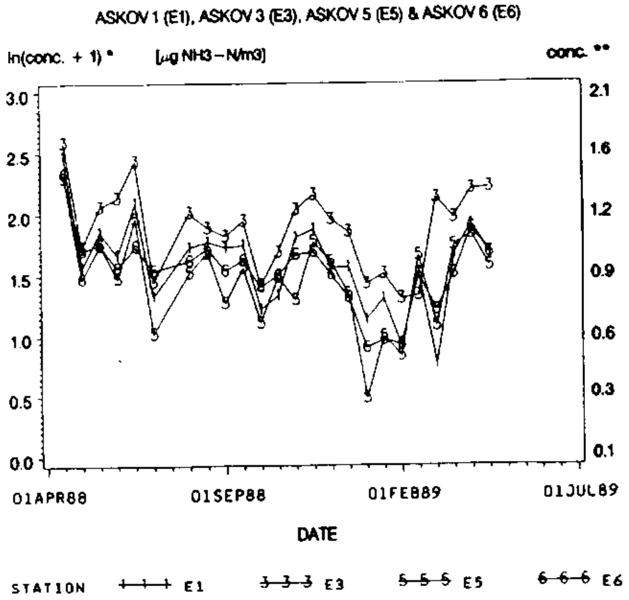


Figure 5
Plot of 14 days average concentration of ammonia against time at Askov.
* : "ln(conc. + 1)" is the logaritm of the concentration calculated from equation (3) - the theoretical concentration.
** : "conc." is the concentration converted using the calibration between denuder and passive diffusion tube [µg NH3-N/m³].

Lindet

The measuring site Lindet 2 (F2) was strongly influenced by a local emission source (pigfarm) located 200 m southeast of the site. Peaks in concentrations are therefore often seen with easterly winds. If the exposure periods starting 01.07.88, 01.09.88 and 01.10.88 in Figure 6 (below) are compared with the same periods at Askov (Figure 5, above), Lindet 2 (F2) shows peaks when Askov sites show low values and a smaller tendency to differences between the sites (notice logaritmic scale). This could very well indicate wind directions from the east, influencing Lindet 2 (F2), while Askov sites at the same time are less influenced by the sources located to the west.

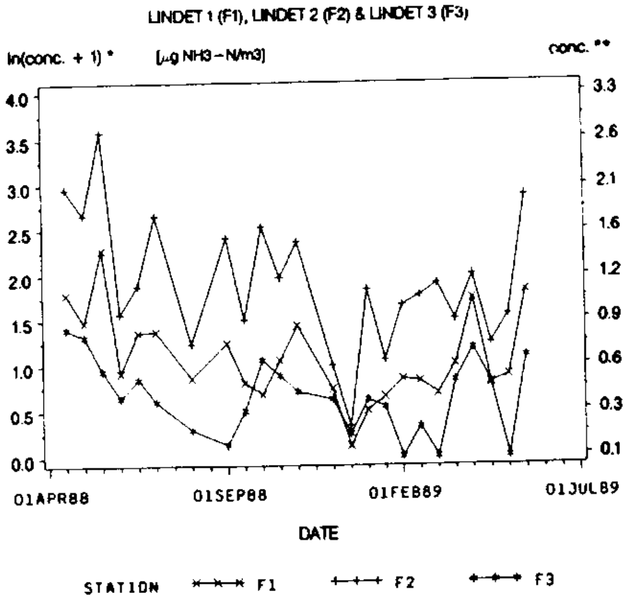


Figure 6
Plot of 14 days average concentration of ammonia against time at Lindet.
* : "ln(conc. + 1)" is the logaritm of the concentration calculated using equation (3) - the theoretical concentration.
** : "conc." is the concentration converted from the calibration between denuder and passive diffusion tube [µg NH3-N/m³].

We have seen that the measuring site Lindet 1 (F1) was situated in a forest clearing, about 200 m north-west of Lindet 2 (F2). Lindet 1 (F1) is at a higher ammonia concentration level than the other forest clearing sites Frederiksborg 1 (C1) and Ulborg 1 (D1), (Figure 7, below). The Lindet 1 site was influenced by a pigfarm and showed the same pattern, as Lindet 2 (F2) except that concentration levels were lower (Table 1 and Figure 6, above). This indicates a deposition of ammonia in the forest. The site Lindet 1 was located in an area with higher emission densities than the other forest measuring sites.

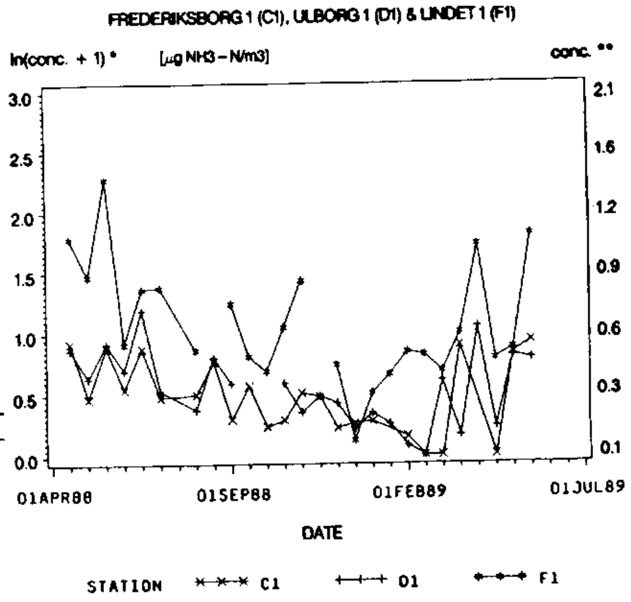


Figure 7
Plot of 14 days average concentration of ammonia against time at Frederiksborg 1, Ulborg 1 and Lindet 1.
* : "ln(conc. + 1)" is the logaritm of the concentration calculated using equation (3) - the theoretical concentration.
** : "conc." is the concentration converted from the calibration between denuder and passive diffusion tube [µg NH3-N/m³].

Lindet 3 (F3) was placed beneath the canopy of a young beech wood about 1 km west of Lindet 1 (F1) and about 300 m south-east of the forest edge to the west. The concentrations at this site was lower than Lindet 1 (F1) (Table 1 and Figure 6, above). The pattern is a little different from Lindet 1 (F1) and Lindet 2 (F2) (Figure 6, above), which might suggest, that this site was also dominated by other sources than the pigfarm. From about 15.09.88 Lindet 3 (F3) showed an increase in concentration, which might be caused by manure spreading and later on leaf fall which might reduce deposition of ammonia at this measuring site.

Frederiksborg Ulborg

The measurements showed a clear decrease in concentration levels inside the forests compared with outside, both on Frederiksborg 1 and 2 (C1 & C2)(Figure 8, below) and Ulborg 1 and 2 (D1 & D2)(Figure 9, below). The decrease is caused by deposition in the forest edge and uptake of ammonia in the leaves (Gundersen, P., 1989). The concentration patterns inside and outside the forest were similar at both locations (Figure 8 & 9, below).

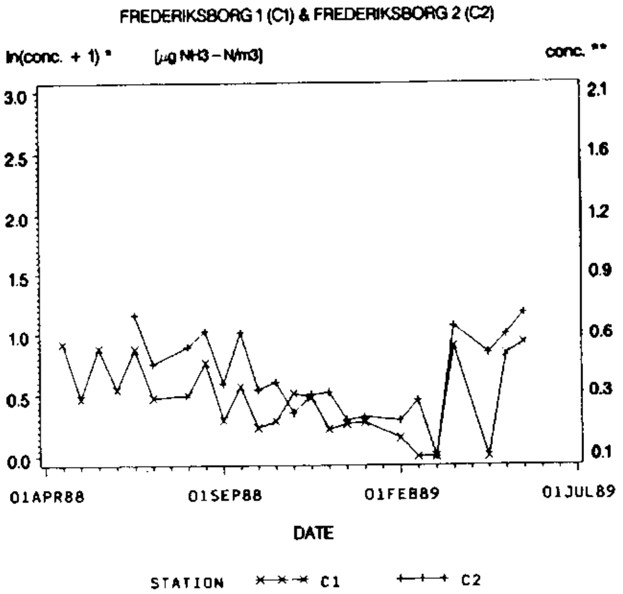


Figure 8
Plot of 14 days average concentration of ammonia against time at Frederiksborg 1 and 2.
* : "ln(conc. + 1)" is the logaritm of the concentration calculated using equation (3) - the theoretical concentration.
** : "conc." is the concentration converted from the calibration between denuder and passive diffusion tube [µg NH3-N/m³].

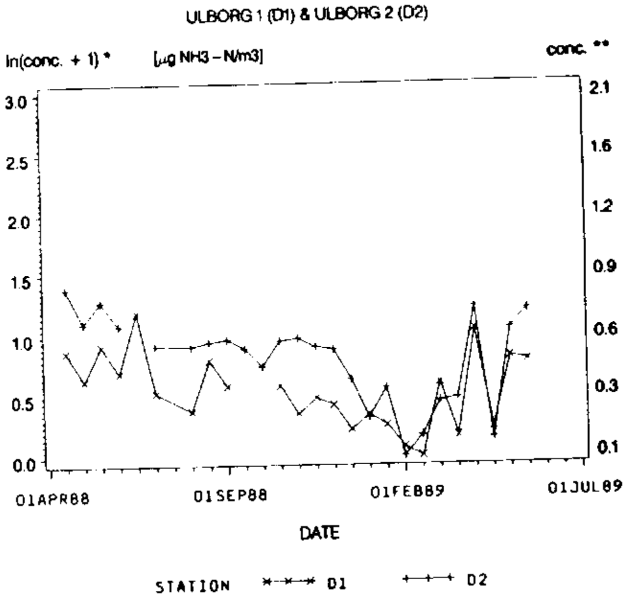


Figure 9
Plot of 14 days average concentration of ammonia against time at Ulborg 1 and 2.
* : "ln(conc. + 1)" is the logaritm of the concentration calculated using equation (3) - the theoretical concentration.
** : "conc." is the concentration converted from the calibration between denuder and passive diffusion tube [µg NH3-N/m³].

4.4 Regional variation.

Zealand

On Zealand Risø 1 (A1) and Viby (G1) were at approximately the same concentration levels (Table 1 and Figure 10, below). The sites Frederiksborg 1 and 2 (C1 & C2) had lower concentration levels (Table 1 and Figure 8 & 10). Comparing the concentration patterns at the Zealand measuring sites (Figure 8 & 10), the same trends are apparent although the concentrations differ.

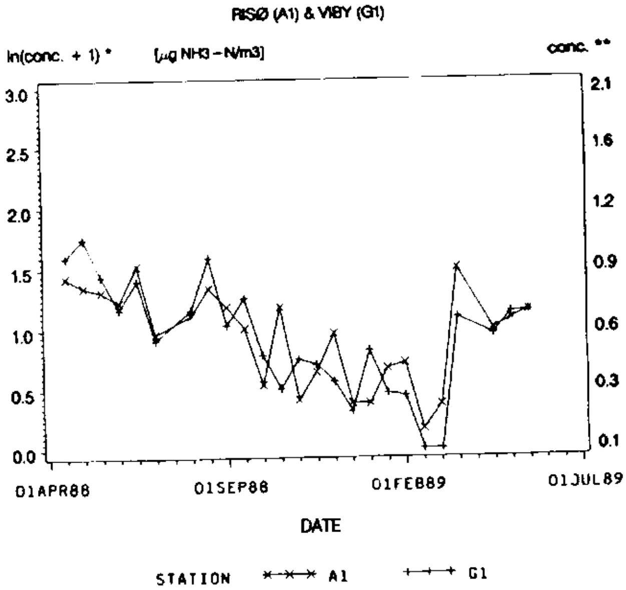


Figure 10
Plot of 14 days average concentration of ammonia against time at Risø and Viby.
* : "ln(conc. + 1)" is the logaritm of the concentration calculated using equation (3) - the theoretical concentration.
** : "conc." is the concentration converted from the calibration between denuder and passive diffusion tube [µg NH3-N/m³].

Jutland

In Jutland the sites at the southern part, Askov (E1-7) and Lindet 2 (F2), had highest concentrations (Table 1). These are followed, in decreasing order by Tange (B1), Lindet 1 (F1), Ulborg 2 (D2), Lindet 3 (F3) and Ulborg 1 (D1) (Table 1). When compared with the concentration patterns at the Jutland sites (Figure 5, 6, 9 & 11), Lindet is an outlier, while all the other sites show the same tendencies. The Lindet sites are probably different because of the strong influence from an emission source east of the sites.

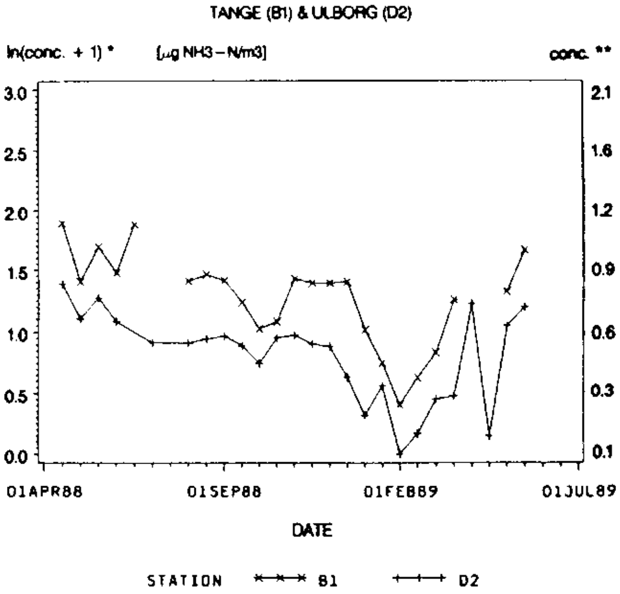


Figure 11
Plot of 14 days average concentration of ammonia against time at Tange and Ulborg 2.
* : "ln(conc. + 1)" is the logaritm of the concentration calculated using equation (3) - the theoretical concentration.
** : "conc." is the concentration converted from the calibration between denuder and passive diffusion tube [µg NH3-N/m³].

The uniformity in the concentration patterns may be due to some meteorological factors. Comparing the concentration patterns at Zealand to the ones at Jutland (Figure 5 - 12), the Jutland sites show a higher increase in late autumn, as mentioned in the passage on seasonal variation.

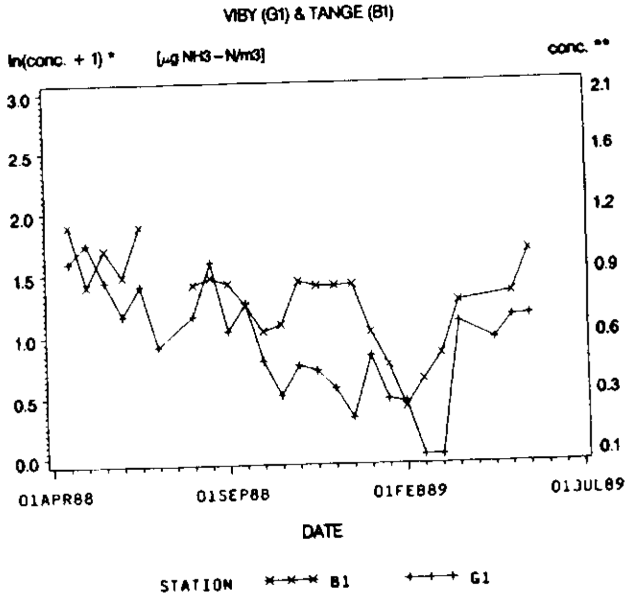


Figure 12
Plot of 14 days average concentration of ammonia against time at Viby and Tange.
* : "ln(conc. + 1)" is the logaritm of the concentration calculated using equation (3) - the theoretical concentration.
** : "conc." is the concentration converted from the calibration between denuder and passive diffusion tube [μg NH3-N/m³].

4.5 Dry deposition

There are different approaches by which air concentration data can be used to derive dry deposition information. In the simplest approach, assumptions are made concerning an appropriate dry deposition velocity constant which, when multiplied by the concentrations of the relevant species, yields the deposition rate. A more sophisticated approach considers the dry deposition velocity as a function of time and changes in surface properties, and may also involve local measurements of variables (among others meteorological factors), which have an influence on the deposition velocity. This sophisticated approach is typically wholly or partly used in modelling work to estimate the deposition.

$v_g * c$

The dry deposition rates are here estimated by the simplest method with the annual average concentration multiplied by a constant dry deposition velocity. The chosen deposition velocity (0.8 cm/sec. W.A.H. Asman & A.J. Janssen, 1986) lies in the middle of the range of dry deposition velocities for ammonia cited in literature. This value is also used to estimate dry deposition rates in Scania by M. Ferm & P. Grennfelt, 1986.

Since the ammonia measurement itself may not be very representative of an area, the dry deposition rates are also very restricted in area representativity. It is assumed that the simple approach gives an estimate with an uncertainty of a factor 2-3. Table 2 below gives the annual estimates of the dry deposition rate at the stations.

Table 2
The annual dry deposition rates at the stations. The estimates are derived from the annual average concentration (Table 1) multiplied with an assumed dry deposition velocity constant on 0.8 cm/sec.

Measuring site		Dry deposition rate g NH_3-N/m² year
Risø 1	A1	0.14
Tange	B1	0.18
Frederiksborg 1	C1	0.08
Frederiksborg 2	C2	0.10
Ulborg 1	D1	0.09
Ulborg 2	D2	0.12
Lindet 1	F1	0.16
Lindet 2	F2	0.29
Lindet 3	F3	0.11
Viby	G1	0.14
Askov 1	E1	0.23
Askov 2	E2	0.28
Askov 3	E3	0.28
Askov 4	E4	0.28
Askov 5	E5	0.21
Askov 6	E6	0.22

The dry deposition rates are in agreement with estimates made for Danish background localities reported by M.F. Hovmand, 1990.

4.6 Conclusion

The conclusions about the passive diffusion tube method and the results from the monitoring network are the following :

1. The passive diffusion tube :

- the results from the measuring sites agree with the emission inventories.
- the tubes need further investigation con-

cerning the relation to denuder measurements and influence from tube contamination.

2. The monitoring programme showed :

- seasonal variation with high values in spring and early summer followed by declining concentrations, with some evidence for an increase in autumn before falling to minimum values in winter. The late autumn increase was more charateristic at the Jutland measuring sites. The variations were less characteristic at measuring sites in high emission density areas.
- decreasing gradient (about 20 %) going west - east in a local area with high emission density.
- decreasing gradient (about 30%) going from the outside to the inside of a forest (low emission density areas).
- background concentrations from 0.3 - 0.8 μg NH_3-N/m^3 as an yearly average.
- estimated dry deposition rates at the background stations in the range 0.1 - 0.2 g NH_3-N/m^2 year.

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Denmark

The N, P and Organic Matter Research Program 1985-1990

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Chemical composition of Bulk Precipitation

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Summary

Increased nitrogen deposition

Earlier studies on precipitation chemistry in agricultural areas in Denmark have shown an increase in average bulk deposition of nitrogen from 7 kg N/ha/year in the fifties to 12 kg N/ha/year in the seventies. Bulk deposition is the sum of wet and dry deposition. Results from the present investigation including the years 1987-89 and 11 sampling sites show a further increase up to 14 kg N/ha/year. The highest depositions of nitrogen, 16-17 kg N/ha/year are found in the middle-, west and the south of Jutland. The same areas have had the highest increase in nitrogen deposition since the seventies. The increase in nitrogen deposition is probably caused by an increase in precipitation of 200-300 mm per year since the seventies and a relative high emission of ammonia from intensive livestock farming in the same areas. At Tystofte on Zealand where livestock farming is low, no changes in nitrogen deposition or precipitation are found since the seventies.

Regional variation

Seasonal variation

The seasonal variation in the concentrations of NH_4-N and SO_4-S shows a peak in April, and the ratio, NH_4/SO_4, is relative high in spring and autumn. Such peaks are not seen in data for the period 1970-77.

Decreased Sulphur deposition

The average bulk deposition of total sulphate in Denmark has decreased from 16 kg S/ha/year in the seventies to 11 kg S/ha/year in the late eighties. The deposition of sulphate is 11-15 kg S/ha/year at sampling sites in the middle-, west and the south of Jutland. In the eastern part of Jutland and on the islands, Zealand and Funen, the deposition is 8-10 kg S/ha/year. The lowest deposition, 8 kg S/ha/year, is found at Tystofte on Zealand.

Bulk and wet deposition

For ammonium and nitrate, bulk deposition is estimated to be 0-30 % higher than wet deposition. The same estimate for sulphate is 0-15 %.

1. Introduction

The aim of the study

This monitoring programme was a continuation on previous measurements of precipitation chemistry in Denmark (Hansen, 1931; Jensen, 1962; Jørgensen, 1979). The aim was to identify levels of concentrations and depositions of the major ions in precipitation in the late eighties, and to identify possible trends in depositions, by comparing present results with earlier data from the same sampling sites. The aim was further, to examine the seasonal and regional variation in concentration and deposition.

2. Materials and methods

Sampling sites

The sampling sites are shown in Figure 1. All stations are located in agricultural areas. Bulk precipitation were sampled each fortnight in the period 1.4.1987 to 31.9.1989 with funnels of the NILU type (Norwegian Institute for Air Research). One NILU collector was placed at each location, except at Rabis Bæk where 5 collectors were located in the period 1.5 1988 to 30.9 1989.

Chemical analysis

The collector design includes arrangements to minimize contamination from bird droppings and the effect of solar heating of the collected precipitation. The sampled precipitation were analyzed for pH, NH_4, NO_3, SO_4, Cl, Na, K, Mg Ca and PO_4. PO_4 was primarily used as an indicator of contamination by organic material. Before data processing the results were scrutinized by several methods described by details in Grundahl and Hansen (1990).

Different collectors

In the earlier studies of precipitation chemistry in Denmark funnels of the Hellmann type were used (Jørgensen, 1979). In addition to the NILU collector, a Hellmann collector was placed at two sampling sites to improve the comparison with earlier results. At one site a wet-only collector was placed in order to estimate the level of dry deposition in the bulk collector (bulk minus wet-only deposition). All collectors were placed according to WMO standards (Lövblad and Westling, 1988).

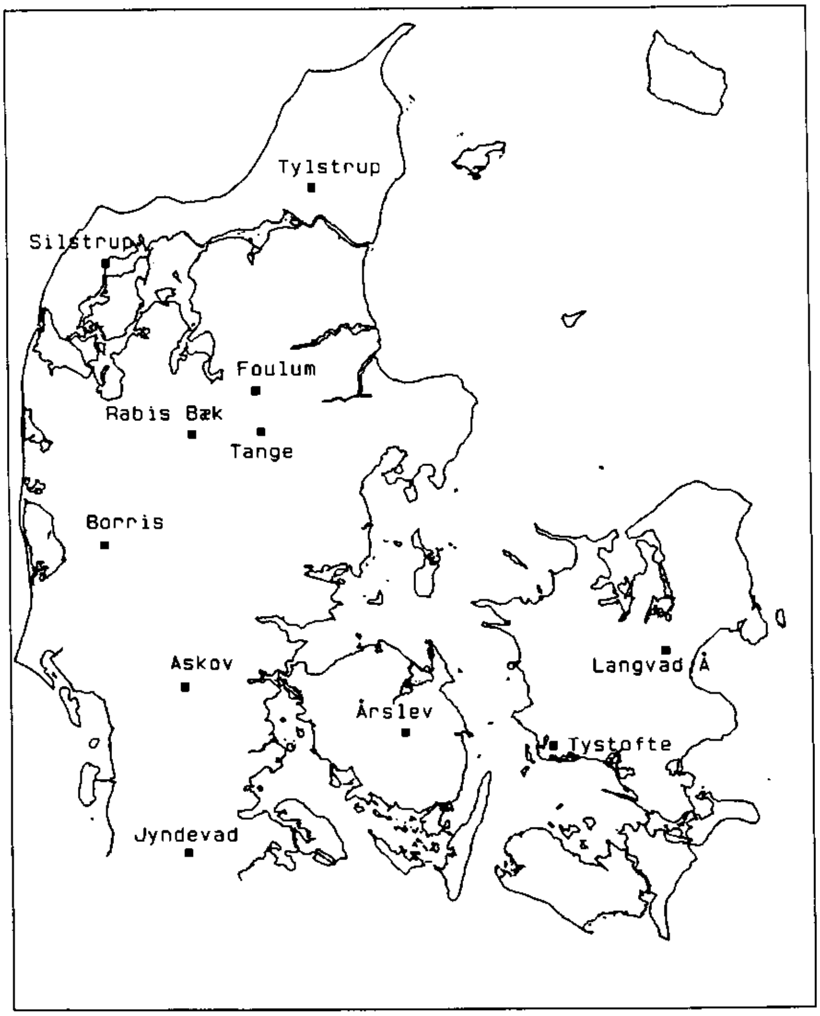

Figure 1. Geographical position of precipitation sampling sites.

3. Results

Orthophosphate

Bulk deposition of major ions are shown in Table 1. Results from 5 samplers situated within four square kilometres at Rabis Bæk (Figure 1), indicate a level of orthophosphate bulk deposition of approximately 0.08 kg P/ha/year at this site.

Table 1. Precipitation and bulk deposition af major ions at the 11 sampling sites shown in Figure 1. The year 1987 includes the period 1.6.1987 to 31.5 1988. The year 1988 includes the period 1.6.1988 to 31.5 1989. The means of 1988 are exclusive Langvad Å and Rabis Bæk.

				Deposition kg/ha/year												
	Precipitation			H^+			NH_4-N			NO_3-N			SO_4-S			
Stations	1987	1988	Aver.	1987	1988	Aver.	1987	1988	Aver.	1987	1988	Aver.	1987	1988	Aver.
Tystofte	607	441	524	0.25	0.15	0.20	6.5	4.6	5.5	5.4	4.0	4.7	9.8	6.5	8.2
Jyndevad	1121	872	996	0.26	0.21	0.24	10.5	10.9	10.7	6.6	6.8	6.7	15.9	13.6	14.7
Askov	1092	974	1033	0.30	0.23	0.27	10.0	9.4	9.7	6.8	5.9	6.4	12.7	12.8	12.7
Foulum	842	589	715	0.19	0.14	0.17	7.4	7.3	7.3	4.7	4.9	4.8	9.8	9.5	9.7
Tange	842	657	750	0.16	0.19	0.18	4.6	7.9	6.2	4.4	4.9	4.6	9.3	10.1	9.7
Silstrup	922	867	894	0.17	0.24	0.21	7.6	8.8	8.2	6.8	7.4	7.1	12.0	15.0	13.5
Borris	1071	921	996	0.27	0.25	0.26	12.1	9.2	10.7	6.3	6.5	6.4	13.3	13.1	13.2
Tylstrup	898	755	827	0.21	0.21	0.21	9.4	6.4	7.9	5.6	4.5	5.1	11.1	10.4	10.8
Årslev	689	573	631	0.21	0.14	0.18	7.4	7.8	7.6	4.8	4.9	4.8	9.4	9.7	9.5
Langvad Å		553			0.19			7.0			5.3			9.7	
Rabis Bæk		743			0.23			7.0			5.6			10.8	
Average	898	739	818	0.22	0.20	0.21	8.4	8.0	8.2	5.7	5.5	5.6	11.5	11.2	11.3

	Bulkdeposition (kg/ha/year)														
	Cl			Na			Mg			K			Ca		
Stations	1987	1988	Aver.	1987	1988	Aver.	1987	1988	Aver.	1987	1988	Aver.	1987	1988	Aver.
Tystofte	14.5	17.9	16.2	8.3	10.2	9.2	1.2	1.4	1.3	0.9	0.9	0.9	3.3	2.6	2.9
Jyndevad	50.9	68.7	59.8	29.4	36.3	32.9	3.8	4.7	4.2	1.7	1.9	1.8	6.1	4.1	5.1
Askov	37.7	57.6	47.6	20.0	31.1	25.6	2.6	3.9	3.3	1.3	1.8	1.5	3.2	3.3	3.3
Foulum	20.8	37.8	29.3	12.6	21.3	17.0	1.6	2.6	2.1	1.0	1.6	1.3	3.2	3.2	3.2
Tange	18.5	44.3	31.4	10.2	23.8	17.0	1.6	3.0	2.3	2.6	1.8	2.2	2.7	2.9	2.8
Silstrup	59.2	103.2	81.2	27.2	59.1	43.2	3.7	7.2	5.5	2.4	2.9	2.6	5.2	8.6	6.9
Borris	48.3	73.7	61.0	26.2	41.3	33.8	3.5	5.0	4.2	1.8	2.2	2.0	3.5	3.7	3.6
Tylstrup	21.9	34.9	28.4	11.4	18.2	14.8	1.8	2.5	2.2	2.0	1.8	1.9	4.6	4.0	4.3
Årslev	16.0	27.0	21.5	9.0	14.7	11.8	1.2	2.0	1.6	0.7	1.0	0.9	2.6	2.7	2.7
Langvad Å		19.9			10.5			1.6			1.3			4.3	
Rabis Bæk		50.2			28.7			3.5			1.6			3.1	
Average	32.0	51.7	41.8	17.2	28.5	22.8	2.3	3.6	2.9	1.6	1.8	1.7	3.8	3.9	3.9

Difference, Hellmann and NILU

The comparison between NILU and Hellmann sampling shows a 10 % higher SO_4-S deposition with the NILU collector. A similar difference were found for Cl and Ca, but only at one of the two sites where parallel measurements were made. For all other ions the measured differences were not significant at 5 % level.

Table 2 shows mean annual depositions and concentrations of SO_4-S, NO_3-N and NH_4-N for three time periods, at sampling sites which are included in the earlier and in the present investigation.

Comparison with earlier studies

The mean annual deposition and concentration of SO_4-S has decreased since the seventies at all five stations. The mean annual deposition of NO_3-N and NH_4-N has increased since the seventies at the four stations in Jutland, but is unchanged at Tystofte on Zealand. Trends in NO_3-N and NH_4-N concentrations are not clear, but there is a tendency of a slight decrease in NO_3-N concentrations in Jutland whereas NH_4-N concentrations are unchanged except at Askov.

Precipitation increase

The amount of precipitation has increased considerably especially in the mid, west and the south of Jutland (Table 2). An analysis of 15 year moving average of precipitation from 1881 to 1988 at the 5 stations listed i Table 2 shows an increase in amount of precipitation from late fifties to mid seventies of 100-200 mm per year for stations in Jutland (Grundahl and Hansen, 1990). At Tystofte on Zealand the amount of precipitation shows a small increase in spring and a slight decrease in fall. These findings are in agreement with another precipitation study comprising several stations in Denmark (Mikkelsen, 1990).

Table 2. Deposition of SO_4-S, NO_3-N and NH_4-N at 5 stations included in present and previous studies. Numbers in brackets are mean concentrations in mg/l. SO_4-S is not corrected for sulphate of marine origin. Older data are from Hansen (1931), Jensen (1961) and Jørgensen (1979).

Station and period	Precipitation mm/year	SO_4-S	NO_3-N	NH_4-N	N-total
		kg/ha/year			
Tystofte					
1955-61	505	10.7 (2.11)	2.2 (0.44)	5.1 (1.01)	7.3
1970-77	516	13.2 (2.56)	4.3 (0.83)	5.7 (1.10)	10.0
1987-89	524	8.2 (1.56)	4.7 (0.89)	5.5 (1.06)	10.2
Jyndevad					
1959-61	672	14.3 (2.13)	2.7 (0.40)	4.6 (0.68)	7.3
1970-77	770	17.2 (2.23)	5.8 (0.75)	7.8 (1.01)	13.6
1987-89	996	14.8 (1.49)	6.7 (0.67)	10.7 (1.07)	17.4
Askov					
1921-27	756	- -	2.6 (0.34)	5.2 (0.69)	7.9
1955-61	673	12.5 (1.86)	2.5 (0.37)	5.0 (0.74)	7.5
1970-77	744	19.5 (2.62)	5.9 (0.79)	9.3 (1.25)	15.2
1987-89	1033	12.7 (1.23)	6.4 (0.62)	9.7 (0.94)	16.1
Borris					
1957-61	668	13.0 (1.95)	2.2 (0.33)	4.2 (0.63)	6.4
1970-77	760	15.9 (2.09)	4.3 (0.57)	7.6 (1.00)	11.9
1987-89	996	13.2 (1.33)	6.4 (0.64)	10.7 (1.07)	17.1
Tylstrup					
1957-61	589	11.3 (1.92)	1.9 (0.32)	3.5 (0.59)	5.4
1970-77	614	14.5 (2.36)	4.6 (0.75)	6.4 (1.04)	11.0
1987-89	827	10.8 (1.31)	5.1 (0.62)	7.9 (0.96)	13.0

Concentration and precipitation amount

The depositions of SO_4-S, NO_3-N and NH_4-N in fortnight samples are significantly correlated with the amount of precipitation. Depositions of the three components are also intercorrelated. The concentrations of SO_4-S, NO_3-N and NH_4-N are highly dependent on the amount of precipitation, but the results indicate a nearly constant concentration for fortnight sampled precipitation amounts between 30 and 80 mm (Grundahl and Hansen, 1990).

Sea salt aerosols

The deposition of Na, Cl and Mg, which mainly are of marine origin, are highly intercorrelated, but weaker correlated to the amount of precipitation (Grundahl and Hansen, 1990). This support the theory that the deposition over land of components of marine origin (sea salt aerosols) primarily are due to dry fallout and impaction (Hansen, 1983; Grennfelt et al.,1985).

Regional variation

The regional variation in bulk deposition of NH_4-N and NO_3-N together with the molar ratios NH_4/SO_4 and NH_4/NO_3 are shown in Figure 2. The two sampling sites indicated by an asterisk are placed in forest clearings. The remaining sites are located in agricultural areas.

Seasonal variation in deposition

It is difficult to identify trends in the seasonal variation in concentration and deposition of chemical components in precipitation because of the dependency on amount of precipitation. Therefore the volume-weighted monthly average concentrations for the period studied were calculated. Data for precipitation, number of precipitation days, NH_4-N, SO_4-S in ppm and the molar ratio NH_4/SO_4 as a mean of six sampling sites included in the present and the previous investigation in the seventies, are compared in Figure 3. A peak in concentrations of NH_4-N, SO_4-S and in the molar ratio of the two are seen in April for data from the late eighties, but not for the data from the seventies.

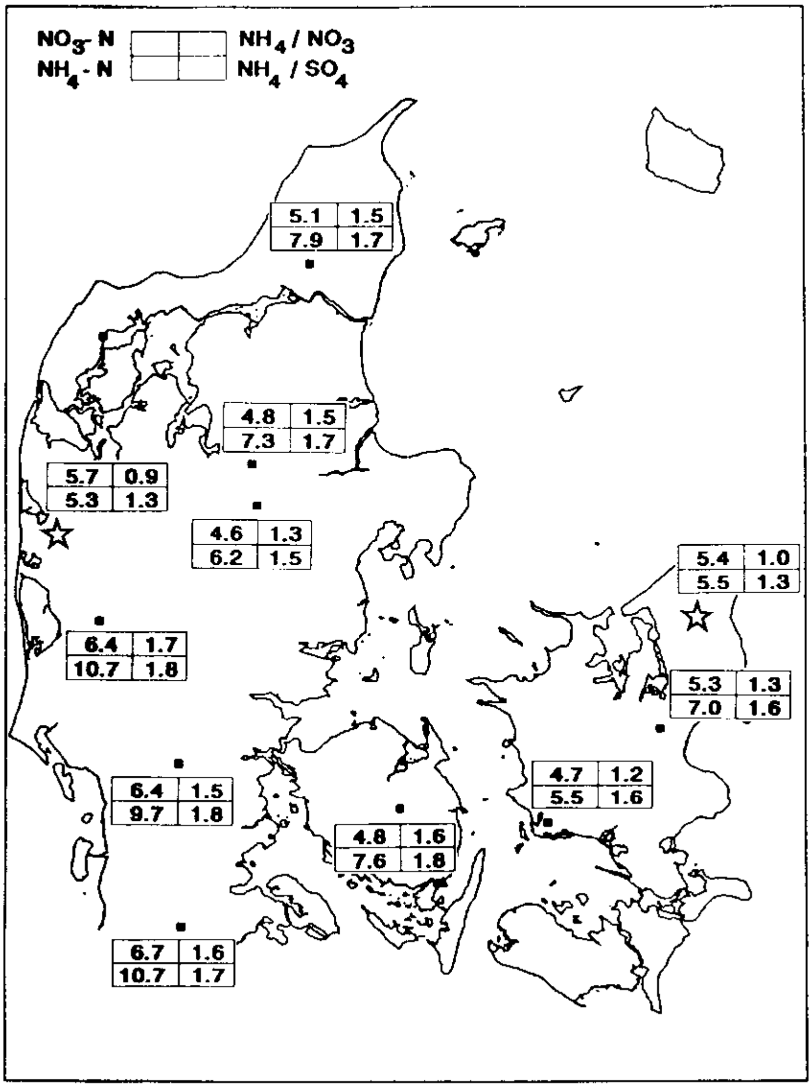

Figure 2. Regional variation of bulk deposition of NH_4-N, NO_3-N in kg/ha/year and the molar ratios of NH_4/SO_4 and NH_4/NO_3. Data represents the period 1.6 1987 to 31.5 1989. The two sites marked with a asterisk are Ulborg in Jutland and Frederiksborg in northern Zealand (Hovmand and Hansen, 1988). Data represents the period 1.6 1987 to 31.5 1988.

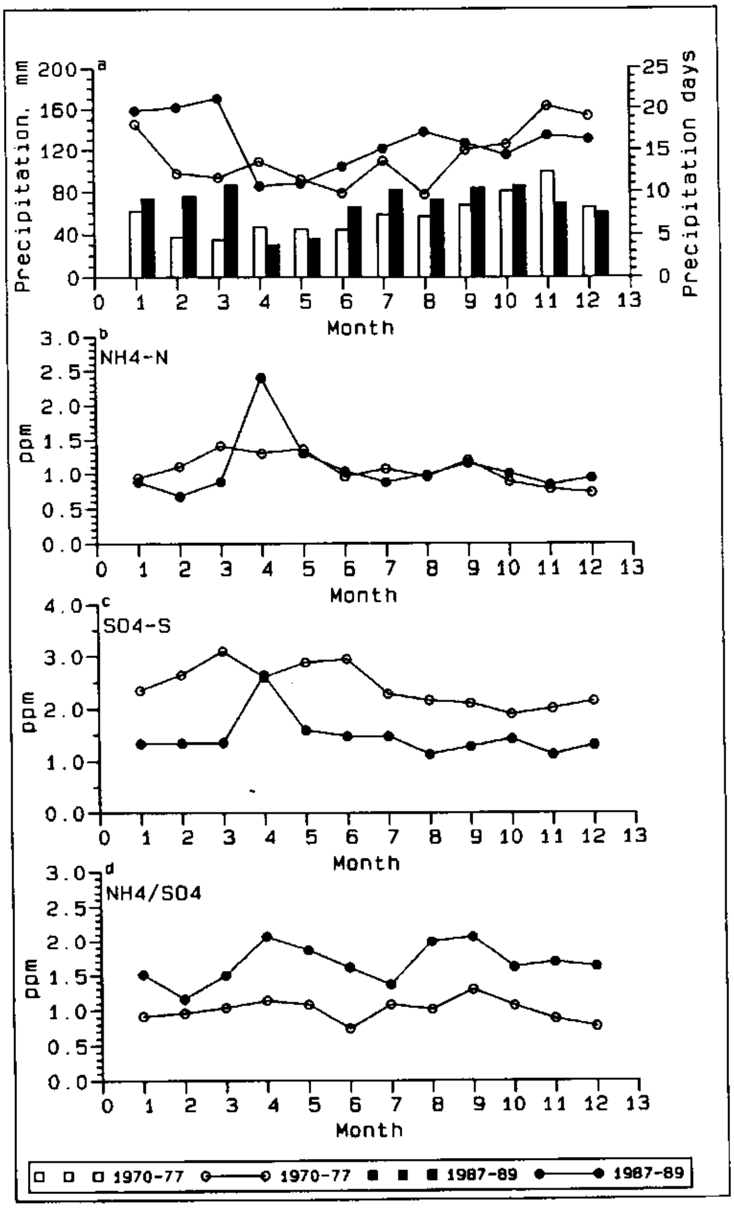

Figure 3. a) Monthly mean precipitation and precipitation days. b) Volume-weighted monthly mean concentrations of NH_4-N (ppm). c) Volume-weighted monthly mean concentrations NO_3-N (ppm). d) Molar ratio of NH_4 and SO_4. All data are an average of 6 sampling sites: Tylstrup, Silstrup, Borris, Askov, Jyndevad, Årslev and Tystofte.

4. Discussion and conclusion

Increased nitrogen deposition

Jørgensen (1979) showed an increase in average bulk deposition of nitrogen from 7 kg N/ha/year in the fifties to 12 kg N/ha/year in the seventies. The same tendency was found by Rohde and Rood (1986), who analysed data from the European Air Chemistry Network, comprising more than 50 stations in the northern and central Europe since 1955. The present results from the late eighties shows a further increase in nitrogen deposition especially on sites in Jutland (Table 2 and Figure 2). At Jyndevad, Askov, Borris and Tylstrup the most recent increases are 30 %, 6 %, 44 % and 18 %, respectively. At Tystofte on Zealand, the bulk deposition of nitrogen was the same as measured in the seventies (Table 2).

Precipitation increase and ammonia emission

At Jyndevad, Askov, Borris and Tylstrup there has been a precipitation increase of 200 to 300 mm per year since the study in the seventies (Table 2). These areas also have the highest production of organic manure from livestock farming (Statens Planteavlsforsøg, 1989) and the highest emission of ammonia (Asman, 1990). Results from this investigation indicate a nearly constant concentration of nitrogen compounds for precipitation amounts between 30 and 80 mm fortnightly. It therefore seems probably, that the increase in nitrogen deposition is caused by a combination of an increase in precipitation (amount and frequency) and a relative high emission of ammonia from intensive livestock farming. At Tystofte where livestock farming is relative low, no changes in nitrogen deposition or precipitation amounts are found since the seventies.

Seasonal variation

The seasonal variation in the concentrations of NH_4-N and SO_4-S show a peak in April, and the ratio, NH_4/SO_4, is relative high in spring and autumn. Such peaks is not seen in data for the period 1970-77 (Figure 3).

Decreased sulphur deposition

The average bulk deposition of SO_4-S (including sulphate of marine origin) has decreased from 16 kg S/ha/year in the seventies to 11 kg S/ha/year in the late eighties. The deposition of sulphate is 11-15 kg S/ha/year at sampling sites in the middle, west and the south of Jutland. At sampling sites in the eastern part of Jutland and on the islands, the deposition is 8-10 kg S/ha/year. The lowest deposition of 8 kg S/ha/year was found at Tystofte.

Bulk and wet deposition

On the basis of a 5 month test period with comparison of bulk- and wet-only sampling of precipitation, bulk deposition of nitrate and ammonium is estimated to be 0-30 % higher than wet deposition of the same components. For sulphate the bulk deposition is estimated to be 0-15 % higher than wet depostion.

Acknowledgement.

We thank Ole Manscher and Jørgen E. Olesen for statistical assistance.

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NH_3 - Volatilization from Fertilizers and Animal Manure

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SUMMARY

Gaseous loss of ammonia during spreading of slurry and from surface applied animal manure and mineral fertilizers was investigated in the period 1986 to 1989. Ammonia loss during spreading represented less than four percent of the applied ammonium. The volatilization loss of ammonia from urea was 20-30% during the summer period and 3-10% during winter. The loss from urea-ammonium-nitrate was lower than that from urea. Irrigation treatments with 5-10 mm reduced the volatilization loss from urea. In a serie of experiments, factors of importance for ammonia volatilization was identified, i.e.: Air temperature, wind speed, air humidity, irrigation, pH of slurry, slurry dry matter content, soil pH, soil water content, soil structure and time of exposure before incorporation of slurry in the soil. It was shown that ammonia loss was exponential related to air temperatur the first 6 hours and linear in the following periods. Ammonia loss rate increased when wind speed were increased up to 2.5 m/s. The relation of ammonia loss tended to be sigmoidally related to slurry dry matter content. Therefore, changes in ammonia loss rates was low from slurry with dry matter content (DM) at DM < 4 % and DM > 12 %.

Great ammonia losses from animal manure

The gaseous loss of ammonia has direct implications for the efficient use of nitrogen in animal manure and mineral fertilizers. The emission of ammonia from manure represents the most important source of atmospheric ammonia in Europe (Buijsman et al., 1987), while emission of ammonia from mineral fertilizers is of minor importance. Deposition of ammonia may detrimentally affect nitrogen-limited natural ecosystems (Schulze et al., 1989).

Ammonia loss from manure is affected by a variety of factors

Ammonia losses related to livestock farming occur from animal housings, manure storages, spreading of manure and from applied manure. When incorporated into the soil, either by direct injection or by cultivation, ammonia losses are believed to be low if the manure are properly covered by soil.

In numerous publications it has been shown that ammonia loss from surface applied slurry were affected by climate, slurry characteristics and soil condition (Pain et al., 1990; Holzer et al., 1988). Therefore volatilization loss of ammonia from surface applied slurry can vary considerably. A throughout understanding of the most important factors affecting ammonia volatilization would be an important tool to improve the efficience of inorganic nitrogen in animal manure.

It has been assumed that substantial amounts of ammonia is lossed during spreading of slurry. Recent studies have shown inconsistent ammonia loss figures ranging from less than 1 % to 10-14 %. (Pain et al, 1989; Besson et al., 1986).

In the present study ammonia loss from fertilizers containing urea has been examined. Ammonia loss during spreading and from surface applied slurry has been determined. The study of ammonia volatilization from sur-

Ammonia loss from fertilizers, spreading of slurry and surface applied slurry was studied

face applied slurry was carried out in two parts. First the factors of importance were identified in a serie of experiments using a wide variety of pig slurries spread on different soil types and run during the whole year. Thereafter selected factors of importance were quantified in experiments in which the other factors were constant.

In this article the author has condensed four years study, which has been presented elsewhere.

2. MATERIAL AND METHODS

2.1 Measurement of ammonia loss during spreading

Loss during spreading, the methodology

The ammonia loss was determined as the difference in the ammonium content in samples taken from the tank of the spreader and in samples collected during spreading in containers placed on the soil surface. The slurry in the tank of the spreader was stirred until the start of the experiments. Samples were taken from the tank before and after an experiment. During an experiment the slurry was collected in three rows of 6 containers. Immediately after spreading the slurry was transfered to small airtight containers (200 ml), and stored at 4°C until analysis. The ammonium content of the slurry samples was determined within 3 days.

2.2 Measurement of ammonia loss from surface applied slurry and fertilizer

Ammonia loss was measured using a wind tunnel system designed like the system described by Lockyer (1984). The four wind tunnel each consists of an transparent polycarbonate inverted U-shaped shell (45 cm high) covering the experimental plot (2 x 0.5 m^2) and a circular steel duct housing a fan driven by an electric powered engine. Each steel duct was equippped with a termocouple sensor and a vane anemometer head, that measured wind speed. Signals from the sensors were scanned at 1 minute intervals and stored as hourly means on a data logger.

Ammonia loss from surface applied manure and fertilizer was studied with a wind tunnel system

After passing the experimental plot and the fan, the air stream was sampled near the outlet of the steel duct with a diaphragm suction pump. The pumps were drawing the air through 100 ml absorption flasks fitted with a sintered glass distribution tube. The flasks contained 50 ml of 0.005 $\underline{M}$ H_3PO_4. Ammonia in the air was trapped in the phosphoric acid and subsequently determined colorimetrically with an indophenol reaction.

Ammonia loss was measured for periods of 6 and 24 h

For each tunnel there was a gas trapping unit consisting of four absorption flasks. A programmable magnetic valve control automatically switched each absorption flask on and of at pre-selected intervals. During the first two days after manure or fertilizer application ammonia was collected for periods of 6 h, during the following four days ammonia collection periods were 24 h long.

Each trial included one untreated reference plot (control) for measurements of background air ammonia concentrations and three treated plots. For a given period, background ammonia concentrations were subtracted from those obtained for treated plots. Ammonia loss was calculated multiplying the net-ammonia concentration with the air flow. The results were corrected by the factor 100/74 in order to correct for recovery percentages (Christensen & Sommer, 1989).

2.3 Meteorological data

Data recorded at the climate station situated at the research station (55°25'N,9°07'E) was used to provide climate parameters not recorded and temperature measurements for periods of datalogger malfunctions. The climate station is lying within a few hundred meters from where the experiments were conducted. Air temperature was measured at a height of 2 meter in a standard screen (Olesen, 1988). An intercallibration showed that tunnel temperature was gererally 1°C lower than air temperatures (2 m) (Sommer et al., 1991). Temperatures was adjusted for the discrepancy.

2.4 Slurry analysis

Determination of slurry characteristics

Total ammoniacal nitrogen (TAN-ammonia + ammonium) content of the slurry was determined by direct distillation of the ammonia with light MgO, collection of ammonia in boric acid-indicator solution and titration with standard HCl solution. Total-N was analysed using the Kjeldahl method and a Tecator kjeltec Auto 1030 analyzer. Dry matter content (DM) was determined gravimetrically upon oven drying at 80°C and slurry bulk pH with a standard electrode (Radiometer).

TAN - ammonium+ammonia

3 DISCUSSION

3.1 Volatilization of ammonia during slurry spreading

With two different slurry spreaders the loss was similar

Two different slurry spreaders equipped with a central sprinkler-plate situated one and two meter above the ground ,respectively, were examined (Sommer, 1989). Irrespective differences in geometry of spreading fan, loss during spreading with the two spreaders were similar. In all experiments losses during spreading represented less than 4% of the amonunt of TAN applied (Tabel 1). In the experiment run the 13. june 1989 only 2% of applied TAN was lost, although air temperature was substantial higher than in the other experiments. In this trial the slurry sampling period was reduced to diminish ammonia loss during the period from the slurry hid the collectors untill it was transferred to the airtight containers. The loss this day with a high ammonia evaporation potential was low indicating that losses during spreading normally is less than 2% of the applied amount of TAN, which is supporting the results reported by Pain et al. (1990).

Probably the loss is < 2% of applied TAN

Tabel 1. Slurry spreader, temperature and loss of ammonia during application of slurry (34 m^3/ha) (Sommer, 1989). Cattle slurry characteristics; TAN 2.45 g N/L, pH 7.7.

Date	*Spreader	Temperature °C	Ammonia loss in % of TAN
12 Oct. 1988	1	9.6	3
	2	9.6	4
14. Dec. 1988	1	3.9	1
17. Feb. 1989	2	2.5	2
10. May 1989	2	11.2	4
13. June 1989	2	23.2	2

* Central sprinkler plate : 1) Height, 1 m; Width of fan, 11 m; Length of fan 9.5 m. 2) Height, 2 m; Width of fan, 6 m; Length of fan 4.2 m.

3.2 Volatilization of ammonia from urea and urea-ammonium-nitrate

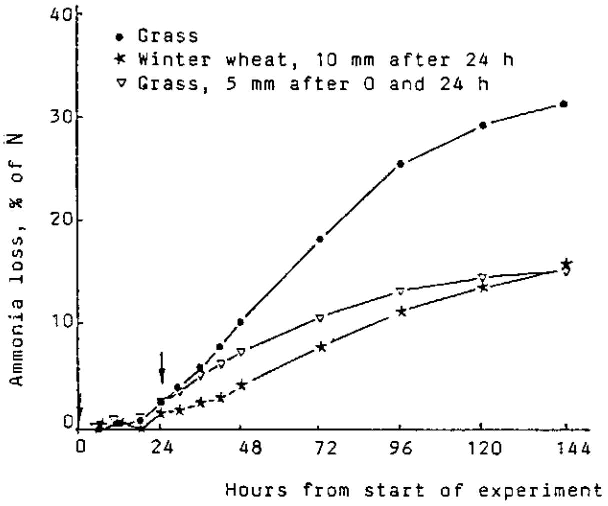
Low losses from urea applied to a dry soil

From urea applied to a dry soil ammonia loss rate during the first day was less than 50% of that found from urea applied during more humid condition (Christensen & Sommer, 1989). Reduction in initial loss from urea applied to a dry soil is probably an effect of restriction in the rate of hydrolyses of urea (McInnes et al., 1986).

In the period May 1987 to February 1988 the lowest ammonia loss-rates were found in February, as low temperatures limited hydrolyses and ammonia transfer from the soil to the air.

Irrigation decreased ammonia loss from urea

The loss of ammonia from urea-ammonium-nitrate was 50% lower than from urea. The reduction in ammonia loss is partly due to a decline in solution pH as nitric acid is formed during ammonia volatilization. Furthermore the urea-ammonium-nitrate was applied in a solution enabling the ammonium to infiltrate the soil. Ammonia loss from urea could be restricted by irrigation treattments with 5-10 mm (Figur 1).



Figur 1. Accumulated loss of ammonia from urea applied 12. May 1987 to winter wheat at a rate of 10 g N/m^2 and on 17. June 1987 to cut grass at a rate of 15 g N/m^2 (Christensen & Sommer, 1989). Air temperature was 6.5-8.6°C and mean wind velocity in the steel duct was 4.3-4.5 m/s. Arrows indicates irrigation.

3.3 Volatilization of ammonia from surface applied slurry

Ammonia loss from animal slurry is presented in p.c. of applied TAN

Results on ammonia volatilization loss are presented as a proportion of TAN in applied slurry to eliminate small differences in the TAN content in slurry (Sommer et al., 1991). The variation in ammonia loss between

In most experiments loss rates were highest the first day

wind tunnels with similar treatments was less than 25% (C.V.) (Figur 2). In most of the experiments more than half of the total loss during the 6 d period took place within the first day, a pattern demonstrated in several other studies (Thompson et al., 1987; Pain et al., 1989). Proton activity has a substantial influence on the flux of ammonia from surface applied slurry. After an initial period with high loss rate (Fig. 2), the ammonia volatilization potential will be reduced by acidification, decreasing concentrations of TAN and infiltration of TAN into the soil (Beauchamp et al., 1978; Lauer et al., 1976).

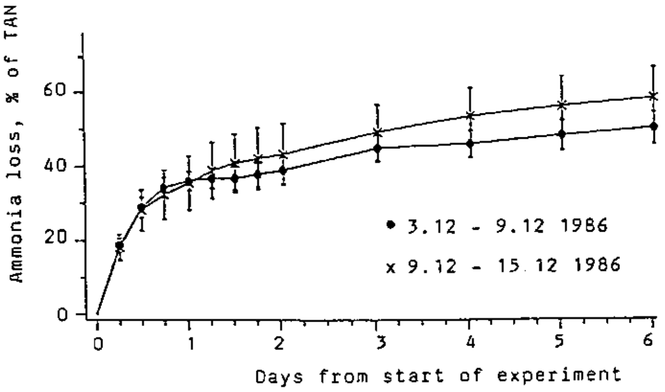


Figure 2. Accumulated ammonia loss in percent of applied TAN in cattle slurry (3 L/m^2) for 4 experiments (Sommer et al., 1991) . Bars indicate ± S.D. of observations. Mean air temperature was 3-6°C, wind speed in the steel-duct 5.0-6.2 m/s and water vapor pressure deficit 0.1-1.5 mbar. Slurry pH was 7.1 and dry matter content 7.2%.

3.3.1 Factors affecting ammonia volatilization

High losses were found during winter and summer periods

Ammonia loss from different pig slurries after surface application to the soil during October 1986 to June 1988 showed that volatilization loss were dependend on pH, temperature and slurry DM content (Sommer & Christensen, 1989). The greatest cumulated loss was found during winter periods when the liquid fraction could not infiltrate the soil due to high soil water content and frost (Fig. 3a). The loss was also high during periods with temperature from 7°C to 16°C. The lowest volatilization loss of ammonia was found when temperatures were between 0°C and 7°C. Increasing initial pH of the slurry resultet in increasing accumulated ammonia loss. Although interaction between initial pH of the slurry and slurry DM content was strong, the loss of ammonia was small when the DM content was less than 1.5% (Sommer & Christensen, 1989). Ammonia loss was increasing with increasing slurry DM content (Fig. 3b).

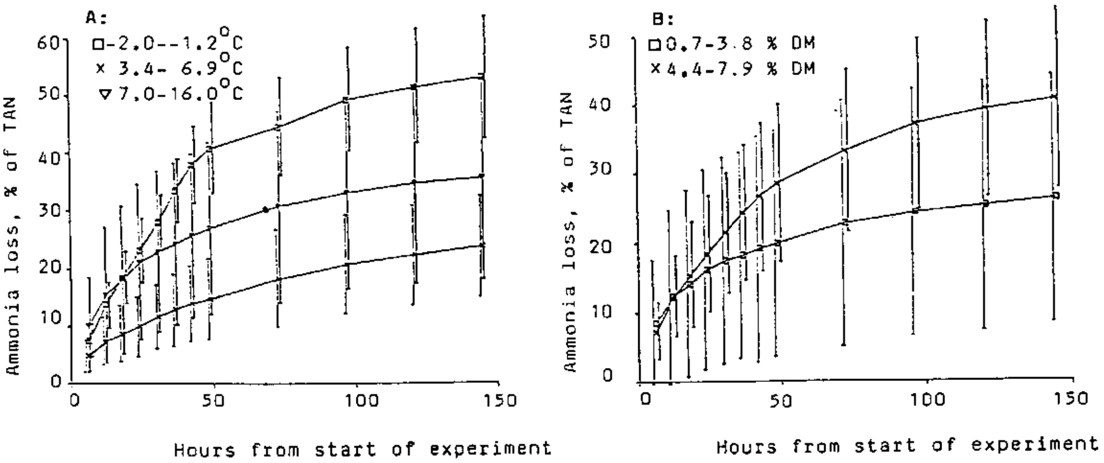


Figure 3. Average accumulate ammonia loss from pig slurry (3 L/m^2) in relation to temperature (A) and dry matter content (B) (Sommer & Christensen, 1989). Slurry pH was 6.4-7.7, DM was 0.7-7.9% and TAN 0.18-0.56%. A: Average temperatures within the interval of -2.0°C-1.2°C, 3.4°C-6.9° and 7°C-16°C. B: Average slurry dry matter contents within the intervals 0.7-3.8% and 4.4-7.9 %

Fermentation had no effect on ammonia loss rate

Fermentation of slurry had no effect on the ammonia loss following landspreading (Fig. 4a). Probably reflecting that fermentation did not change slurry pH and DM content. It was considered (Sommer & Christensen, 1990) that within the same category of manure (e.g. slurries, farmyard manure or urine), the loss of ammonia may be predicted from slurry DM content, pH of slurry and climatic conditions. If viscocity of the slurry is not correlated to DM content differences in viscocity may be of importence. The experiments with the liquid fraction and fibrous fraction confirmed that ammonia volatilization from slurry was strongly affected by slurry dry matter content (Fig. 4b). Interactions of temperature and dry matter content resulted in high losses from the fibrous fraction but not from the liquid fraction in winter experiments (Sommer & Christensen, 1990).

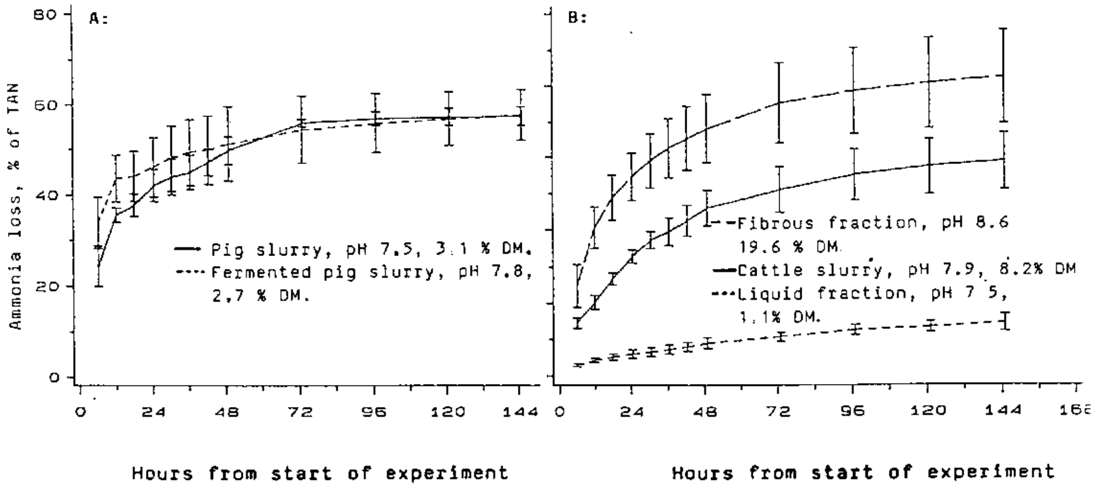


Figure 4. Accumulated ammonia loss from pig and cattle slurry, fermented pig slurry and the liquid and fibrous fraction of pig slurry (3 L/m^2) (Sommer & Christensen, 1989). A: Air temperature was 8.1-17.4°C, wind speed in steel duct 4.3-5.1 m/s and water vapor pressure deficit 1.1-2.7 mbar. B: Air temperature was 1.3-5.5°C, wind speed in steel duct 3.3-3.8 m/s and water vapor pressure deficit 0.7 mbar.

Injection reduced ammonia losses

Injection of slurry into a dry soil reduced the accumulated ammonia loss during 6 d to less than 17 %, whereas 50% of injected ammonium was lost when the soil had a high water content (Sommer and Christensen, 1990). Probably reflecting that the furrow did stay open after the slurry was injected into the soil with a high content of water. Irrigation with 5 and 10 mm at application of pig solid manure and after 1, 2 and 3 days halved the ammonia loss (Sommer & Christensen, 1990). Irrigation with 10 mm had highest effects during the first two days, thereafter the ammonia loss rate increased. After six days the accumulated ammonia loss from the two treatments was similar.

3.3.2 Effect of temperature

It was demonstrated that temperature affected ammoia loss from surface applied slurry. Therefore this factor was examined in a serie of experiments during the period October 1986 to November 1989 (Sommer et al., 1991).

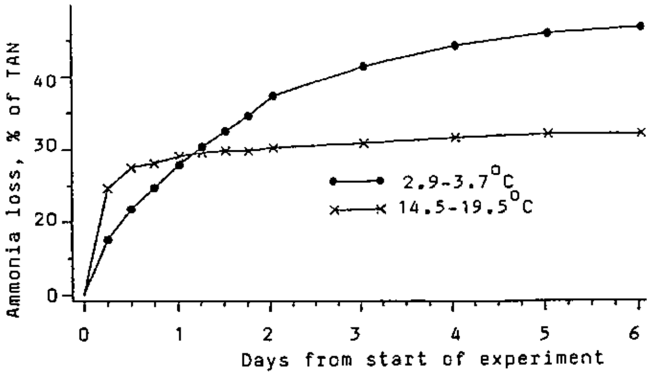


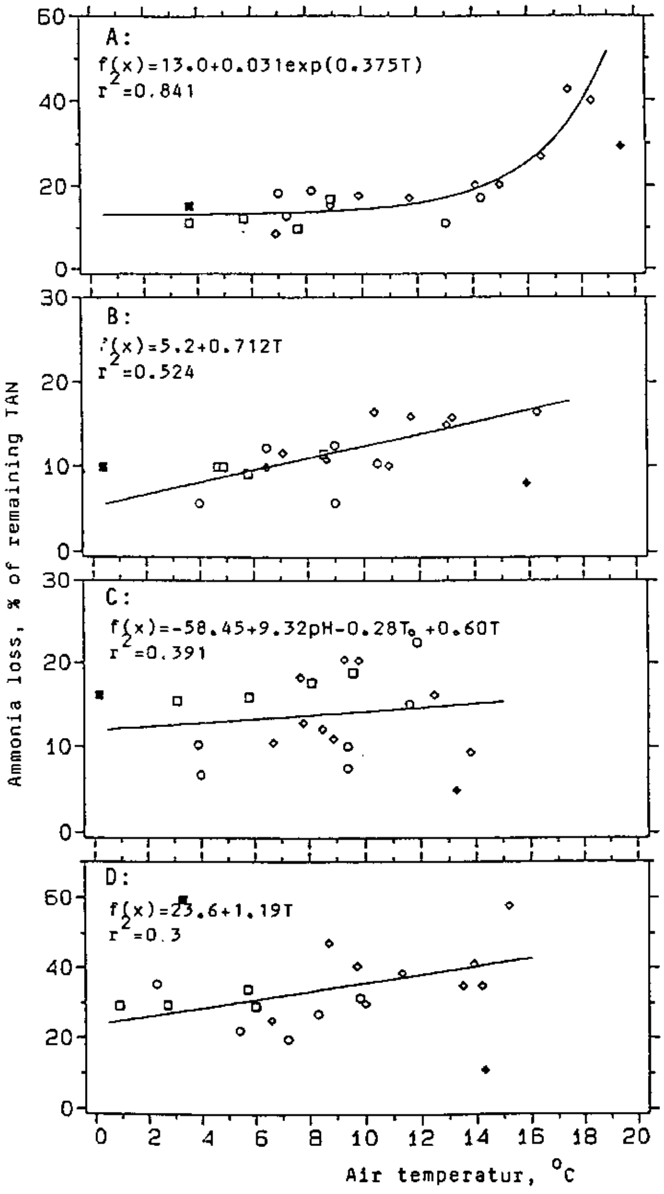
Figure 5. Accumulated ammonia loss in percent of applied TAN in cattle slurry (3 L/m^2) (Sommer et al., 1991). Slurry dry matter content was 7.6%, pH 7.7 and TAN 2.6 g N/L.

Ammonia loss might be high at temperatures near zero

When temperatures were near zero, the rate of ammonia loss was generally low. The accumulated loss over six days was high, however, due to a constant loss rate throughout the period (Fig. 5). In the experiments soil was saturated with water and partially frozen, factors which probably increases ammonia losses. At 19°C initial loss rates were high but after 12 h almost no further loss occured, probably due to surface crusting and rapid infiltration into the dry soil.

The first 6 h loss was exponential related to temperature

During the initial 6 h accumulated ammonia volatilization was exponential related to temperature (Figur 6). During the three succeding periods of 6-12 h, 12-24 h and 24 h - 6 d the ammonia volatilization rate is low and only slightly related to temperatur. In these periods ammonia loss pattern does shift to be linear related to temperature. Four equations describing the relationship between ammonia loss and temperature were determined for the four periods 0-6 h, 6-12 h, 12-24 h and 24 h-6 d (Sommer et al., 1991). Initial pH of the slurry had an effect on ammonia loss in the period 12-24 h and was included in the equation. For all experiments 46% of the measured loss over 6 d was accounted for with the models.



Figur 6. Accumulated ammonia loss from cattle slurry (3 L/m^2) during the periods (A) 0-6 h, (B) 6-12 h, (C) 12-24 h and (D) 24 h-6 d (Sommer et al., 1991). Slurry dry matter content was 7.0-8.2%, pH 7.1-7.5 and TAN 0.26-0.30. Wind speed in metal duct was 2.0-6.2 m/s and water vapor pressure deficit 0.6-11 mbar. T, air mean temperature during the period; T_0 air mean temperature since start of experiment.

3.3.3 Effect of slurry dry matter

The first 6 h loss was linear related to slurry dry matter content

In a study (Sommer & Olesen, 1991) ammonia loss was related to slurry dry matter in cattle slurry adjusted to different dry matter contents. Ammonia losses in the periods 0-6 h, 0-12 h, 0-24 h and 0-6 d were studied. The ammonia loss from 0 to 6 h was linearly related to content of dry matter, while the relationship in the following periods was nonlinear (Fig. 7). The slurry with a high content of dry matter had a low pH, but interaction of acidity on ammonia loss was only partly the reason for the nonlinear relationship.

Excluding temperature from the data showed that losses was sigmoidally related to slurry dry matter content

The effect of temperature and pH was eliminated using the equations calculated in the previous study (Sommer et al., 1991), and adapted to the experimental conditions during the study of the effect of slurry dry matter content. This transformation of data showed, that ammonia loss tended to be sigmoidally related to dry matter content in the four periods 0-6 h, 6-12 h, 12-24 h and 1-6 d. This indicated that at low and high contents of dry matter, small changes in dry matter content had a limited influence on ammonia loss. At dry matter content from 4 to 12% ammonia loss increased as dry matter content increased.

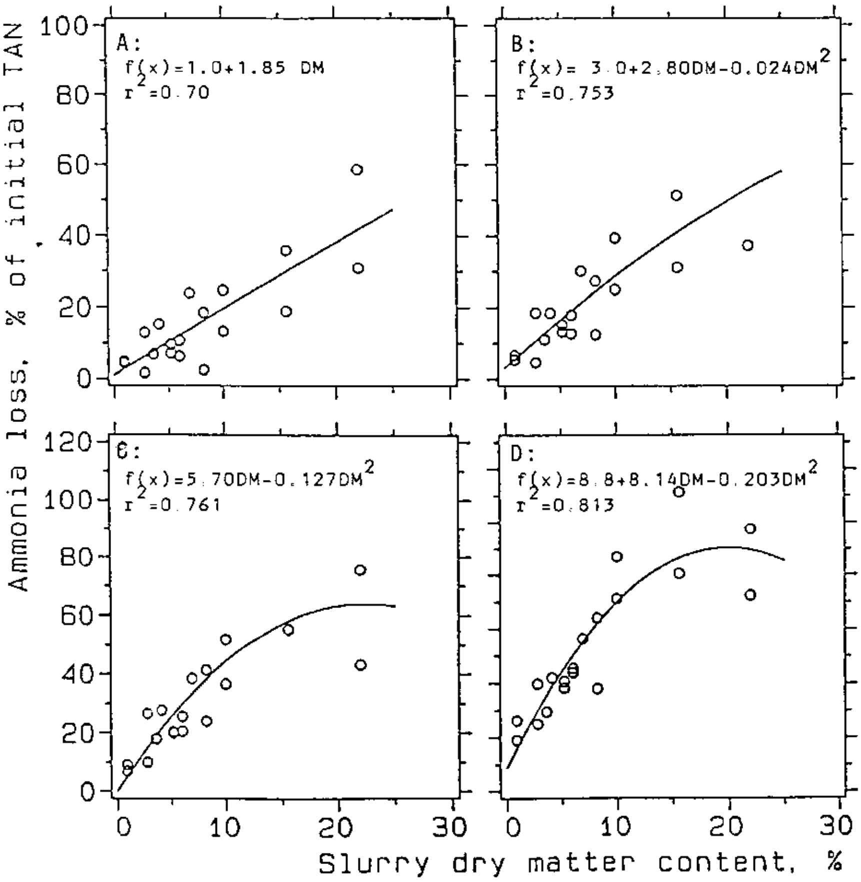


Figure 7. Figur 6. Accumulated ammonia loss related to slurry dry matter content during the periods (A) 0-6 h, (B) 0-12 h, (C) 0-24 h and (D) 0-6 d in percent of TAN in the slurry (Sommer et al., 1991). Slurry pH was 7.1-7.5 and TAN 1.6-3.0 g N/L. Wind speed in metal duct was 2.8-3.8 m/s and temperature 0.5-19.6°C.

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National Agency of Environmental Protection
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The N, P and Organic Matter Research Program 1985-1990

Number A8

Leaching of Plant Nutrients from Cultivated Areas

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SUMMARY

The leaching of N, P, K and organic matter was investigated in areas with ordinary farming.

Leaching of N

There have been large variations in the annual leaching of NO_3-N, on sandy soils ranging from 19 to 154 kg NO_3-N/ha and on clayey soils from 29 to 117 kg NO_3-N/ha. The leaching of total N is estimated to have been 5-30 kg N/ha higher. Especially smaller leachings for grass areas, 20-25 kg NO_3-N/ha, have been found. The leaching of NH_4-N is normally less than 1 kg/ha on mineral soil. Inexpedient use of animal manure can increase the leaching of N significantly.

Leaching of P

The leaching of total P has been calculated to an average of 0.6 and 1.3 kg P/ha annually on sandy and clayey soils respectively, and the quantities of PO_4-P to 0.2 and 0.1 kg/ha. Higher leaching of PO_4-P on sandy soils than on clayey soils is due to higher percolation. Calculated leaching of total P - especially on clayey soils - must be taken with some reservation, however.

Leaching of K

A very high percolation of K has been measured on sandy soils, an average of 72 kg/ha against 8 kg/ha annually on clayey soils. However, the leaching on the investigated sandy soils has probably been higher than normal on sandy soil.

Leaching of organic matter

With the applied analysis frequency the estimation of leached amount of organic matter is uncertain but the leaching has been substantial.

1. INTRODUCTION

Background

The present knowledge of the leaching of plant nutrients from the root zone on cultivated areas in ordinary farming is insufficient. Most of the research carried out so far of leaching from the root zone have been in connection with applying commercial fertilizers. Only few investigations of leaching after supply of animal manure have been carried out in Denmark. The research in this project was therefore mainly carried out in fields where animal manure frequently was supplied.

2. MATERIALS AND METHODS

Research localities

The research have been carried out in areas with ordinary farming in the two NPo-workshop areas near Rabis and Syv. The sandy soil fields near Rabis will in the following be designated S1-S6 and the claysoil fields near Syv designated L1-L4.

Soil-physical analyses

The texture in the plow layer and the plant available water in the root zone on the research localities are shown in Table 1. For sandy soil it is assumed that the root depth is 0.5 m and for clayey soils 1.0 m.

Table 1. Texture of the plow layer and plant available water in the root zone on the research localities.

	Field									
	S1	S2	S3	S4	S5	S6	L1	L2	L3	L4
Humus	4	3	3	3	4	2	2	3	2	2
Clay <0.002 mm	5	4	4	6	7	5	17	13	17	14
Silt 0.002-0.02 mm	10	5	6	7	10	5	19	23	21	13
Fine sand 0.02-0.2 mm	31	14	20	19	29	9	39	40	38	41
Coarse sand 0.2-2.0 mm	50	74	67	65	50	79	23	21	22	30
Available water, mm	114	71	90	90	112	62	152	155	153	140

Analyses of soil water

The chemical composition of the soil water has been determined by taking soil samples whereafter the soil water was extracted in the laboratory. The extracted soil water has been analysed for NO_3-N and in some of the samples also for pH, COD, NH_4-N, total N, PO_4-P, total P and K. Samples which were analysed for NO_3-N only, have been extracted by shaking approx. 100 g soil with 200 ml 1 N KCl whereafter the NO_3-concentration in the "diluted" soil water was determined, and the NO_3-concentration in the soil water was calculated on the basis of the known dilution. In other samples the soil water was extracted by centrifugation.

Sampling frequency

The frequency of sampling for analysis of NO_3-N was adapted to the excess precipitation. I was aimed at taking these samples for every 20 mm excess precipitation. A full analysis programme was carried out twice annually. For total P the analyses were carried out more frequently, however.

Leaching from the root zone

The quantities of nutrients leached have been calculated by multiplying daily percolation with daily concentrations in soil water at a depth of 70-100 cm. Concentrations for days between the sampling have been calculated by linear interpolation between the nearest previous and the following analysis. The percolated water quantities have been calculated on the basis of climate data. Calculation of total N by this method would be very uncertain, however, because of too few analyses compared to NO_3-N and due to the variation of the concentrations of total N. Therefore the leaching of total N was estimated by assuming that the difference in concentrations of NO_3-N and total N for each locality was similar to the average of analyses with a full analysis programme, Table 2, that is approx. 5 mg/l. The amounts calculated in this way is then added to the calculated leaching of NO_3-N which is far more certain because of the frequent sampling.

3. RESULTS

Analysis results

The average solute concentrations for samples taken from a depth of 70-100 cm, where the whole analysis programme has been carried out, are shown in Table 2, in which the research period and the percolation are also shown.

N in soil water

From table 2 it appears that N is mainly found as NO_3-N in the soil water. The quantity of NH_4-N in soil water on mineral soil is minimal under normal circumstances. The difference between NO_3-N + NH_4-N and total N is probably mainly organic N. The average difference between NO_3-N and total N has been approx. 5 mg N/l for most of the localities, for locality L4 only 2.6 mg N/l, however.

Table 2. Research periods, total percolations, mm, and average concentrations for each analysis parameter on the investigated areas. Only analyses where the whole analysis programme has been carried out are included.

Loka- lity	Period	mm	pH	COD	NH_4-N	NO_3-N	Tot-N	PO_4-P	Tot-P	K
				<——			mg/l			——>
S1	apr 87-okt 89	1189	7.4	428	0.110	34.7	39.8	0.031	0.15	12.6
S2	apr 87-apr 90	1590	7.2	513	0.271	14.4	19.2	0.049	0.19	28.1
S3	nov 87-apr 90	1320	7.0	198	0.281	19.6	25.3	0.038	0.14	20.5
S4	nov 87-apr 90	1327	7.3	192	0.173	8.5	13.8	0.120	0.21	8.7
S5	nov 87-apr 90	1374	7.0	305	0.102	9.7	14.5	0.032	0.14	7.1
S6	nov 87-apr 90	1325	7.0	222	0.382	11.7	16.2	0.025	0.18	16.2
L1	nov 87-apr 90	764	7.9	121	0.106	26.4	32.6	0.036	0.36	3.9
L2	nov 87-apr 90	805	8.1	120	0.066	41.8	47.8	0.026	0.34	3.2
L3	nov 87-apr 90	743	8.0	128	0.059	17.6	21.9	0.075	0.27	4.2
L4	nov 87-apr 90	797	7.8	122	0.028	21.5	24.1	0.030	0.24	1.1

Supplementary NO_3-analyses

As mentioned above analyses of NO_3-N were made considerably more often than the other analysis parametres, and the number of total P analyses was somewhat increased compared to the original plan. The course of concentrations of the two analysis parametres in a depth of 70-100 cm on each research area is shown in Figure 1, where also the nutrient quantities supplied by manure and fertilizers and the time of supply are shown.

In the summer of 1987 the NO_3-concentrations were high on the two sandy soils under investigation. The reason for this must be found in the high precipitations that summer with percolation from the root zone as a consequence most of the summer. In case of normal precipitation rates there would only be a little or not any percolation at all in this period. In both areas the NO_3-concentrations were reduced considerably during the autumn. In the other sandy soil areas the sampling was not begun until the end of October 1987. That year a large part of the leaching of NO_3-N had probably taken place before the sampling was started.

On locality S3 and S5 a strong increase of the NO_3-concentrations was found during February and January 1988. In both cases slurry had been spread approx. 4 weeks before the increase of NO_3-concentrations at a depth of 70-100 cm was found. The fast leaching of NO_3-N after the supply of slurry is due to the unusually mild winter with fast nitrification of NH_4-N supplied by slurry as a consequence as well as to the large precipitations in the period.

High variations in P-concentrations

For total P high variations in the concentrations were found and in some cases very high concentrations in single samples.

Variations in PO_4-P

The variation in the concentration of PO_4-P is considerably lower than for total P, and there seems not to be higher concentrations on clay soil than on sandy soil as for total P.

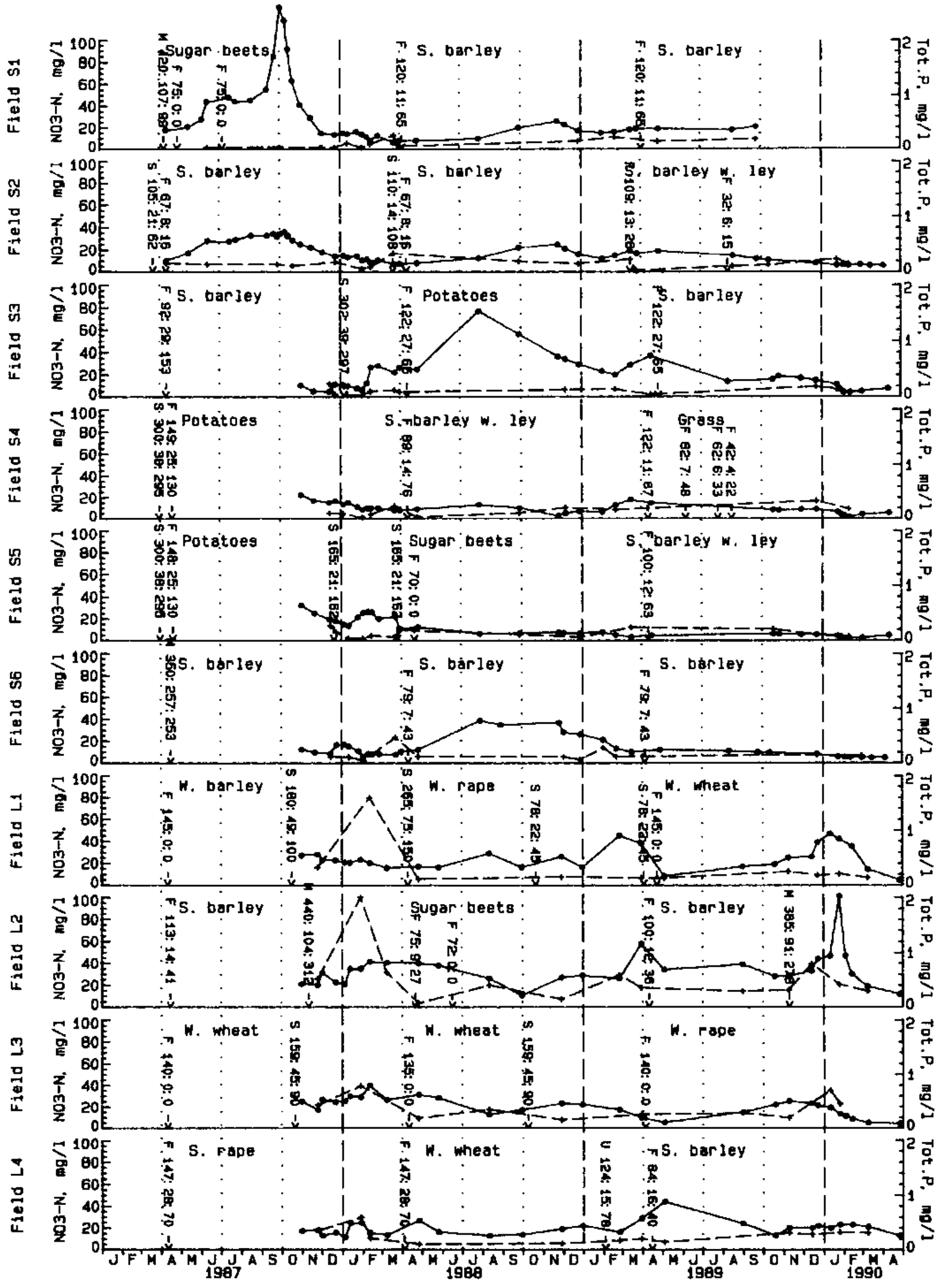

Figure 1. Concentrations of NO_3-N (solid lines) and total P (dotted lines) at a depth of 70-100 cm on the investigated fields. Furthermore crops as well as times for supply of fertilizers (F), manure (M), urine (U) and slurry (S) are shown. Figures indicate supplied nutrients (N:P:K) in kg/ha. For animal manure total N are shown.

Highest K-concentrations on sandy soil

The concentrations of K in the soil water below the root zone are generally higher on the sandy soils than on the clayey soils. There are, however, also large differences between fields with the same type of soil.

Calculated leaching

The calculated annual percolation in mm and leaching of nutrients on each locality are shown in Table 3.

Average NO_3-leaching

The average calculated leaching of NO_3-N for the sandy soil and clay soil areas has been 69 and 66 kg NO_3-N/ha annually, respectively. Undoubtedly, considerable quantities have been leached in the summer and autumn of 1987 before the sampling had begun on the last 8 localities.

Leaching of total N

Estimates of the leaching of total N show an average leaching of total N of 93 kg N/ha and 79 kg N/ha on sandy soils and clayey soils, respectively. As for NO_3-N it must be taken into consideration that very likely there must have been a considerable leaching in the summer and autumn of 1987 on the localities S3-S6 and L1-L4 before the sampling was started. As already stated direct calculation of leaching of total N with the used analysis frequency is uncertain because of high variations in the concentrations.

Leaching of NO_3-N

From Figure 2 it appears that the unusually large precipitations on the sandy soils at Rabis in January and February of 1990 have only caused a limited extra leaching of NO_3-N because this had been leached at that time. On the clayey soils the precipitation and the percolation have been lower in this period, but the leaching of NO_3-N has been significantly higher. NO_3-N is often leached from sandy soils at this time of the year, but not on clayey soils because of higher water content. Here this is further obvious because of higher precipitation on the sandy soils.

Table 3. Crops, annual percolations and leachings from the root zone in the research areas. Furthermore under Ma it is indicated if animal manure was applied to the crop or (in the calculation period) to a following crop. Under C it is indicated if the area was vegetated in the autumn and winter period. The calculation period is, when nothing else is indicated, from 01.05.-30.04.

Loc. Year	Crop	Ma	C	Perc. mm	COD	NH_4-N	NO_3-N	tot.N	PO_4-P	tot.P	K
					<-------------			kg/ha			------------->
S1 87-88	Fodder beets	+	-	727	2050	0.58	138.	175.	0.19	0.29	77.
88-89	Spring barley	-	-	390	837	0.39	75.	95.	0.16	0.64	47.
S2 87-88	Spring barley	+	-	716	2690	2.49	147.	181.	0.41	1.05	217.
88-89	Spring barley	+	-	409	768	0.74	76.	96.	0.23	0.72	104.
89-90	S.barley w.ley	-	+	430	806	0.88	32.	53.	0.25	0.78	115.
S3 87-88 1)	Spring barley	-	-	432	1810	0.08	56.	81.	0.15	0.43	70.
88-89	Potatoes	+	-	417	709	0.81	154.	178.	0.26	0.51	109.
89-90	Spring barley	-	-	473	342	1.26	51.	78.	0.09	0.62	66.
S4 87-88 1)	Potatoes	+	-	434	1550	0.41	55.	78.	0.26	0.42	38.
88-89	S.barley w.ley	-	+	460	682	0.51	47.	71.	0.61	0.71	41.
89-90	Clover grass	-	+	434	458	1.35	25.	48.	0.69	0.99	27.
S5 87-88 1)	Potatoes	+	-	434	1764	0.44	90.	111.	0.17	0.54	41.
88-89	Fodder beets	+	-	484	2114	0.35	28.	51.	0.08	0.66	34.
89-90	S.barley w.ley	-	+	457	530	0.65	19.	41.	0.18	0.49	24.
S6 87-88 1)	Spring barley	+	-	431	1580	0.60	48.	67.	0.13	0.67	71.
88-89	Spring barley	-	-	423	787	1.07	104.	123.	0.14	0.66	68.
89-90	Spring barley	-	-	472	768	2.53	32.	53.	0.11	0.68	73.
L1 87-88 1)	Winter barley	+	+	317	596	0.18	71.	91.	0.12	3.0	15.0
88-89	Winter rape	+	+	170	189	0.10	49.	60.	0.06	0.24	6.1
89-90	Winter wheat	+	+	277	274	0.14	86.	103.	0.11	0.58	11.8
L2 87-88 1)	Spring barley	+	-	318	750	0.10	100.	119.	0.05	3.9	11.1
88-89	Fodder beets	+	-	192	181	0.15	60.	72.	0.04	0.59	5.6
89-90	Spring barley	-	-	294	248	0.23	117.	135.	0.07	1.3	8.5
L3 87-88 1)	Winter wheat	+	+	317	813	0.15	88.	102.	0.29	1.9	11.9
88-89	Winter wheat	+	+	157	152	0.10	29.	36.	0.12	0.30	7.2
89-90	Winter rape	-	+	268	276	0.20	41.	53.	0.21	1.2	11.4
L4 87-88 1)	Spring rape	-	+	318	756	0.09	56.	64.	0.08	1.3	2.9
88-89	Winter wheat	-	-	185	160	0.05	39.	44.	0.06	0.26	2.4
89-90	Spring barley	+	-	294	217	0.10	60.	68.	0.11	0.90	3.3

1) 01.11.1987 - 30.04.1988

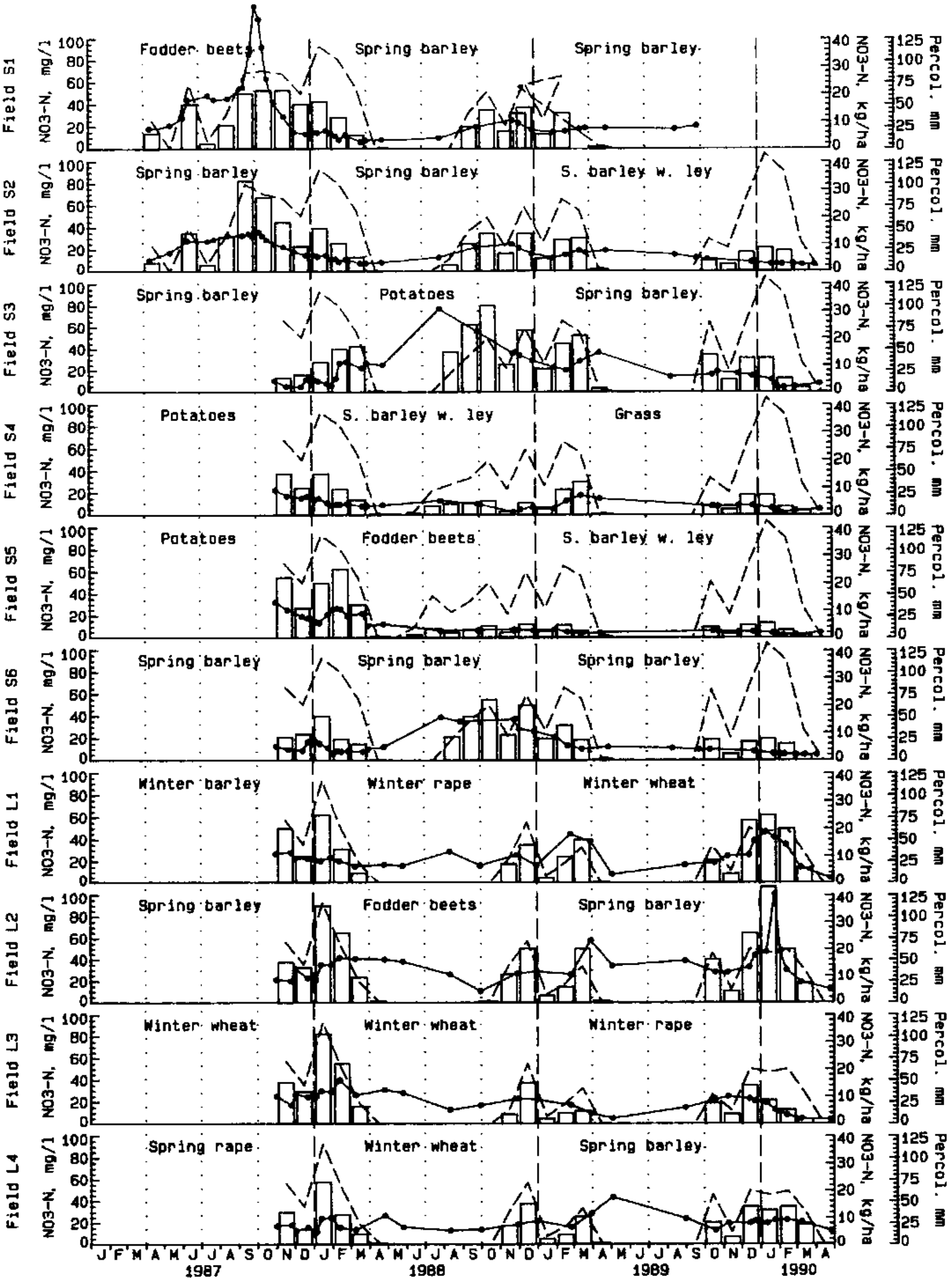

Figure 2. Monthly percolation (dotted lines), leaching of NO_3-N (columns) as well as concentrations of NO_3-N (solid lines) on the research fields.

Lower leaching from grass

The leaching of NO_3-N was clearly lower in areas with an established crop the whole year than in areas where a new crop was sown every year, and by which the area was bare for a period of the year. It seems that crops sown in the autumn on clayey soils have not been so effective in reducing the leaching as grass crops have been on sandy soils.

Leaching of NH_4-N

The leaching of NH_4-N is uncertain with the applied analysis frequency. The leaching has been minimal, however.

Leaching of total P

Leaching of total P has been calculated to an average of 0.6 kg P/ha for sandy soil areas and 1.3 kg P/ha for clayey soil areas, and leaching of PO_4-P to an average of 0.2 and 0.1 kg/ha, respectively. Because of methodology problems the quantities must be taken with some reservation, however.

The higher leaching of PO_4-P on the sandy soil areas is especially due to excess precipitation and higher percolation as a consequence. The reason for higher concentrations of total P and higher variations in this on clay soil than on sandy soil is not known.

Leached K-quantities

The leaching of K has been calculated to an average of 72 kg K/ha and 8 kg K/ha for the sandy soils and the clayey soils, respectively. The leaching on these sandy soils has undoubtedly been higher than what is normal for sandy soils.

Organic matter

The calculated leaching of organic matter estimated by COD is uncertain with the applied analysis frequency. The leaching has been significant, however, and the quantities have clearly been larger on sandy soils than on clayey soils. Since there are not any sufficiently tested methods of extracting soil water for these analyses - as in the case of P, the analyses results must be taken with some reservation.

4. DISCUSSION AND CONCLUSION

Leaching of N

There have been great variations in the leaching of N, in sandy soil areas varying from 19 to 154 kg NO_3-N/ha annually and on clayey soil areas varying from 29 to 117 kg NO_3-N/ha annually. The variation has been higher than in earlier investigations, for instance Simmelsgaard (1985). Especially small leachings of NO_3-N for grass areas, approx. 20-25 kg/ha annually, have been found. Areas, where grassland has been ploughed, have not been included in the relative short research period, but it is well known that the leaching of N can be high after ploughing grass field.

The average leaching of NO_3-N per year has been 69 and 66 kg/ha for the sandy soils and the clayey soil areas, respectively. The annual leaching of total N is estimated at 5-30 kg N/ha higher values than for NO_3-N and highest in case of excess precipitation and percolation. The leaching of NH_4-N has been minimal. When estimating the measured leachings, it must be taken into consideration, however, that there were unusual climatic conditions in the research period, especially larger precipitation and higher winter temperatures than normal.

Leaching of N after supply of manure

In two cases significant leachings of NO_3-N were found on sandy soil immediately after supply of slurry in December and January respectively. It shows that manuring at times which are generally considered as appropriate also can cause an increased leaching of N.

Leaching of P

Because of methodology problems the calculated leaching of P must be taken with some reservation, especially for clayey soils. The leaching of total P has been calculated to an average of 0.6 kg P/ha and 1.3 kg P/ha and the quantities of PO_4-P to 0.2 kg/ha and 0.1 kg/ha for sandy soils and clayey soils, respectively. Higher leaching of PO_4-P on sandy soils is due to higher excess precipitation and percolation.

If compared with PO_4-quantities in drainage water on clayey soils (Pedersen, 1985), there is a good agreement with these, when it is taken into consideration that only a part of the run-off was discharged through drains on these areas.

Leaching of K

The leaching of K has been calculated to an average of 72 kg K/ha and 8.1 kg K/ha for the sandy and clayey soils respectively. The leaching on these sandy soil areas has undoubtedly been higher than normal on sandy soil. The leaching of K has in this way been higher than the net purchase of K on farms in sandy soil areas, which have been calculated earlier (Hansen, 1985, 1986, 1990). In these investigations net purchases of K in sandy soil areas have usually been 40-50 kg K/ha annually. One of the reasons for the higher leaching of K can be that animal manure is not supplied according to K-demands. On these very coarse sandy areas the adsorption capacity is too small to store higher quantities of K, and unnecessary supply of K will often be leached.

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Studies of N-transformation in Arable Soils. N-mineralization, denitrification and N-leaching

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Resumé.

N mineralization, denitrification and N leaching in the root zone were studied in situ in the field experiments on sandy loam soil (Askov) and coarse sandy soil (Jyndevad) during 3 years (1987 - 1990). Pig slurry and inorganic fertilizers were applied to spring barley. Additionally the effect of autumn application of pig slurry to bare soil as well as influence of catch crop on N processes, in the root zone on coarse sandy soil, were studied.

The fertilizers applied as well as type of soil caused variation in N mineralization. Net N mineralization, measured by sequential in situ measurements, totaled 34-179 kg N ha^{-1} yr^{-1} and 80-137 kg N ha^{-1} yr^{-1} for Askov and Jyndevad, respectively.

The results indicated that the amount of nitrogen mineralized influenced the amount of nitrogen leached, which ranged from 27 to 82 kg

NO_3^--N ha^{-1} yr^{-1} and from 18 to 212 kg NO_3^--N ha^{-1} yr^{-1} for Askov and Jyndevad, respectively. Nitrate losses in soils increased after pig slurry treatment. Autumn application of pig slurry to bare sandy soil caused increased leaching of nitrates, reaching 172 kg NO_3^--N ha^{-1} yr^{-1}. The catch crop reduced leaching of nitrate in the root zone of spring barley from 80 to 47 kg NO_3^--N ha^{-1} yr^{-1}.

The denitrification losses totaled about 7 kg N ha^{-1} yr^{-1} on sandy loam soil. The highest denitrification rates were obtained on the sandy loam soil, following the NPK-addition. The average daily rate of denitrification during the March to May, 1989 period was 0.1 kg N ha^{-1}. The yearly losses of N by denitrification on the coarse sandy soil was maximum 1 kg N ha^{-1}.

1. Introduction

Concern about the environment and better utilization of nitrogen has led to a research programme dealing with nitrogen transformation in Danish arable soils.

The main purpose for this project was:

-to quantify the N transformation and N transport in the root zone, dependent on cultivation conditions and on soil type.

-to increase the N utilization especially from slurry and reduce the losses of N to the environment (ground- and surface-water).

The studies included N mineralization, denitrification and N-leaching measured in various cultivation systems, crops, type and application rate of fertilizers and soil types under field conditions.

2. Material and methods.

Experimental sites and treatments.

The field experiments were located at two agricultural experimental stations; Askov - sandy loam soil (62% sand, 25% silt, 11% clay; pH 5.9; organic C 1.3%) and Jyndevad - coarse sandy soil - (87% sand, 6% silt, 4% clay; pH 6.4; organic C 1.7%). Spring barley with or without grass, undersown as catch crop, was treated with various fertilizer types, including application of inorganic fertilizers as well as pig slurry (table 1). Pig slurry was applied at a rate corresponding to approximately 100 kg NH_4^+-N ha^{-1} $year^{-1}$ (Askov and Jyndevad). In addition a half rate of 50 kg NH_4^+-N ha^{-1} $year^{-1}$ in pig slurry was applied to Jyndevad soil. The application rate of inorganic fertilizer was approximately 120 and 133 kg N ha^{-1} for Jyndevad and Askov soil, respectively. The fertilizer contained an equal amount of ammonium and nitrate nitrogen. Unfertilized plots (0N) were included in the experiments; on Askov soil the plots were unfertilized since 1984, on Jyndevad a new unfertilized plot was chosen for the experiments each year, which was fertilized with pig slurry (100 kg NH_4^+-N ha^{-1}) in the previous years, since the experiment was initiated in 1987.

Experimental years (1987-1990) were characterized by considerable amounts of precipitation (836 mm) and warm winters (4°C), with only a few days with below freezing air temperature.

Table 1. Amount and type of fertilizer in the field experiments.

Application rate§ kg N ha^{-1} $year^{-1}$	Fertilizer type and time of application
Crop: spring barley	Catch crop (cc): Rye grass
Sandy loam soil (Askov)	
0 N*	
100 NH_4^+-N(150)§	Pig slurry, spring*
133 N	NPK*
Coarse sandy soil (Jyndevad)	
0 N*	
50 NH_4^+-N(83)	Pig slurry, spring
110 NH_4^+-N(170)	Pig slurry, spring*
110 NH_4^+-N(140)	Pig slurry, autumn*
110 NH_4^+-N(170)	Pig slurry, spring + cc
120 N	NPK*

§Total N applied with pig slurry in parentheses.
*Treatment, where denitrification was measured.

Mineralization.

Measurements of the N mineralization have been carried out using a recently described technique (Raison et al., 1987). The method evaluated changes in pools of inorganic nitrogen in the soils and was based on sequential soil coring and in situ incubation of undisturbed soil cores. Metal tubes were driven into the soil (4.5 cm in diameter and 20 cm in length). The tubes were covered with plastic covers, which prevented N leaching from the incubated soil. The tubes were left for in situ incubations for periods of time ranging from 1 to 4 months. For each period the following measurements were taken for soil mineral-N content: initial in bulk soil (N_i) and final in incubated covered cores (N_c), which enabled the following N changes to be calculated:

$$\text{NET MINERALIZATION} = \text{inorg. } N_c - \text{inorg. } N_i$$

The net mineralization was equal to the actual net mineralization, when denitrification was assumed to be zero, unless otherwise indicated.

Denitrification.

Denitrification loss was estimated by an acetylene inhibition technique modified after Christensen (1985). The soil cores (length = 10 cm, diameter = 3 cm) were collected from each treatment and incubated at actual field temperature, in gas tight 20 l jars, with 10% acetylene. After 24 hours the cores were removed, closed with serum stoppers. Air samples from the cores were taken with 2 hours interval, during a 6 hours period, to determine the linear N_2O evolution rate. Then the rate of N_2O evolution was calculated using 1) Bunsen absorption coefficient for N_2O in water (Tiejde, 1982), 2) the soil water content, 3) the volume of the core and 4) the weight of the soil sample.

N-leaching.

The calculation of N-leaching was based on weekly measurements of nitrate concentration in the soil water at the bottom of the root zone. The soil water was extracted by means of ceramic suction cells placed 100 cm and 80 cm below the surface of Askov and Jyndevad soil, respectively. The water balance in the growing season and in the autumn was based on weekly measurements of soil water contents by means of neutron moderation method, precipitation and evapotranspiration (Simmelsgaard, 1985).

Analysis.

Ammonia and nitrate in soil samples were extracted with 2 M KCl. Nitrate-N and ammonium-N in soil water samples and soil extracts were determined spectrofotometrically with a Technison autoanalyser (Henriksen and Selmer-Olsen, 1970) or by a flow injection system (Giné et al., 1980).

3. Results and discussion.

3.1 N mineralization.

The mean daily rates of mineralization for Askov soil ranged from 0.03 to 3.2 kg N ha^{-1} day^{-1} (Table 2). In periods shortly after pig slurry and NPK application either high mineralization (1988) or immobilization (1989) was observed, which was equivalent to a removal of 1.3 to 4.1 kg N ha^{-1} day^{-1} during the growing season 1989. The reason for this is unclear but may have been partly due to a very low precipitation in 1989, which caused the progressive drying out of soil.

The total amounts of net N mineralized during one year period for Askov soil were 60, 107 and 113 kg N ha^{-1} for unfertilized, pig slurry and NPK fertilized plots, respectively (Table 2). Mineralization rates on unfertilized plots varied during growing season (0.1-0.4 kg N ha^{-1} day^{-1}). Mineralization continued during autumn/winter periods (Fig.1).

The mean daily rates of net mineralization for the Jyndevad soil during a comparable period and comparable treatments ranged from 0.01 to 1.3 kg N ha^{-1} day^{-1} (Table 3). The total amount of N mineralized during one year period was 105, 137 and 82 kg N ha^{-1} for unfertilized, pig slurry (100 kg N) and NPK fertilized plots, respectively (table 3).

The pattern of N mineralization for unfertilized Jyndevad soil showed higher rate at the beginning of growing season (0.8 kg N ha^{-1} day) caused by residual effect of the slurry applied to this plot a year before measurements took place.

Table 2. Daily rates of N mineralization/immobilization and net N mineralized on Askov soil during the experimental years. SE of means (n = 12) in parentheses.

Askov	0 N	Pig slurry 100 N	NPK 133 N
		kg N ha^{-1} day^{-1}	
1987 - 1988			
AUG - SEP	1.0(0.2)	1.9(0.8)	0.8(0.1)
SEP - DEC	0.3(0.03)	0.3(0.04)	0.3(0.01)
DEC - MAR	0.1(0.01)	0.1(0.02)	0.1(0.02)
AUG.87- MAR.88 kg N ha^{-1}	58 (3)	81 (4)	56 (21)
1988 - 1989			
APR - MAY	0.1(0.1)	1.4(1.2)	3.2(1.0)
MAY - AUG	0.3(0.1)	0.6(0.2)	0.1(0.5)
AUG - NOV	0.2(0.02)	0.3(0.1)	0.1(0.04)
NOV - MAR	0.2(0.1)	0.7(0.3)	0.2(0.02)
APR.88- MAR.89 kg N ha^{-1}	63 (4)	179 (51)	147 (39)
1989 - 1990			
APR - MAY	0.03(0.1)	0.03(1.2)	-2.7(1.2)
MAY - JUN	0.4(0.2)	-1.3(0.7)	-4.1(1.4)
AUG - NOV	0.3(0.04)	0.2(0.03)	0.6(0.2)
NOV - MAR	0.2(0.04)	0.1(0.02)	0.2(0.04)
APR.89- MAR.90 kg N ha^{-1}	56 (8)	34 (4)	79 (19)

Net immobilization occurred in Jyndevad soil, which received pig slurry in the autumn to the bare soil, which was equivalent to a removal of 0.01 to 0.4 kg N ha^{-1} day^{-1} during winter period. At the same time nitrate leaching increased 2-3 months later from these plots. Net mineralization for plots with catch crop and plots fertilized with a half dose of pig slurry (50 kg N) was generally lower, although not statistically significant.

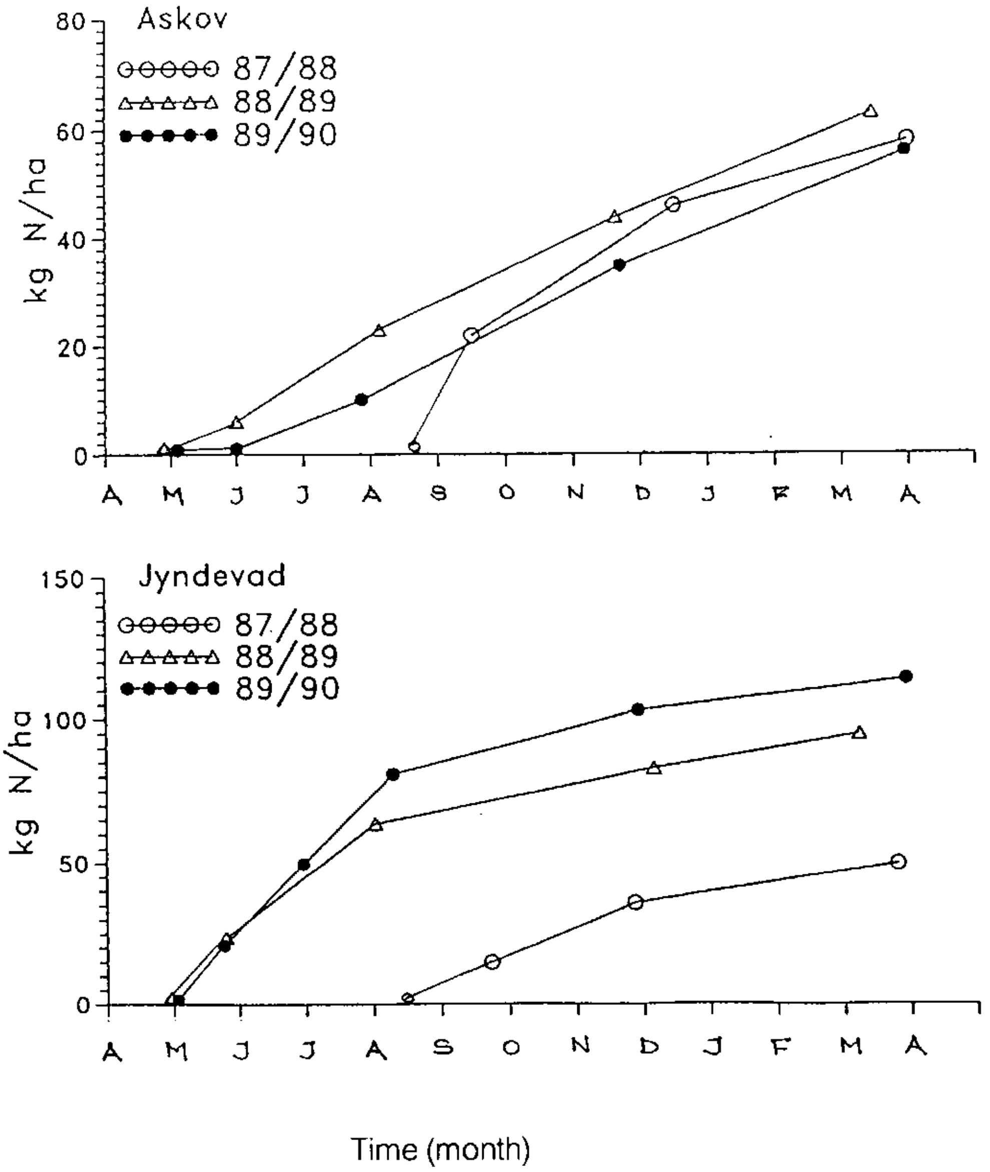

Fig. 1. Pattern of net mineralization in unfertilized (0 N) plots during experimental years on Askov and Jyndevad soils.

Table 3. Daily rates of N mineralization/immobilization and net N mineralized on Jyndevad soil during the experimental years. SE of means (n = 24) in parentheses.

Jyndevad	0 N	PS,S* 50 N	PS,S 100 N	PS,A 100 N	PS,S 100 N + cc	NPK 120 N
			kg N ha^{-1} day^{-1}			
1987 - 1988						
AUG - SEP	0.4 (0)	nd	0.7 (0.1)	nd	0.7 (0.1)	0.5 (0.1)
SEP - NOV	0.3 (0)	nd	0.4 (0)	nd	0.2 (0)	0.2 (0)
NOV - MAR	0.1 (0)	nd	0.2 (0)	nd	0.2 (0)	0.1 (0)
AUG.87- MAR.88 kg N ha^{-1}	50 (2)	nd	68 (3)	nd	59 (4)	50 (2)
1988 - 1989						
APR - MAY	0.6 (0.1)	0.9 (0.8)	0.2 (0.9)	0.4 (0.1)	0.5 (0.8)	nd
MAY - AUG	0.6 (0.1)	0.6 (0.1)	0.4 (0.1)	0.6 (0.1)	0.4 (0.1)	0.5 (0.2)
AUG - DEC	0.2 (0.1)	0.2 (0.1)	0.3 (0.1)	0.2 (0)	0.3 (0.1)	0.2 (0)
DEC - MAR	0.1 (0)	0.1 (0)	nd	-0.4 (0.2)	0.2 (0)	0.2 (0)
APR.88- MAR.89 kg N ha^{-1}	95 (7)	118 (32)	nd	85 (6)	97 (35)	nd
1989 - 1990						
APR - MAY	0.7 (0.1)	-0.1 (0.6)	1.2 (1.5)	0.7 (0.1)	0.01 (0.7)	0.1 (0.5)
MAY - JUN	0.9 (0.1)	0.8 (0.1)	1.3 (0.2)	0.8 (0.1)	0.5 (0.3)	0.7 (0.2)
JUN - AUG	0.8 (0.1)	0.7 (0.1)	0.3 (0.1)	0.6 (0.02)	0.7 (0.1)	0.6 (0)
AUG - NOV	0.2 (0.03)	0.2 (0.03)	0.3 (0.1)	0.2 (0.03)	0.3 (0.04)	0.2 (0.02)
NOV - MAR	0.1 (0.01)	0.1 (0.03)	0.1 (0.03)	-0.01 (0.04)	0.1 (0.02)	0.1 (0.02)
APR.89- MAR.90 kg N ha^{-1}	114 (5)	80 (19)	137 (45)	90 (5)	83 (23)	82 (16)

*Plot names are abbreviated as follows: PS = Pig slurry, S = pig slurry applied in the spring, A = pig slurry applied in the autumn. cc = catch crop. nd = not determined.

3.2 Denitrification.

In Askov soil daily denitrification rates were in range 0.0001-0.1 kg N ha^{-1} day^{-1} (Table 4). In the unfertilized plot no significant differences in denitrification rates were found within each year (Table 4). However significant differences existed between years and periods. In the plot fertilized with 133 kg N ha^{-1} year^{-1} a relatively large loss (0.1 kg N ha^{-1} day^{-1}) was seen in the period from March to May, 1989. This loss was significantly larger than the loss during the same period in 1988. During growing season the denitrification loss was below 0.01 kg N ha^{-1} day^{-1}. During autumn/winter periods denitrification rate increased sporadically to 0.05 kg N ha^{-1} day^{-1}.

Table 4. Daily mean denitrification (kg N ha^{-1} day^{-1}) on Askov soil during 10 periods (1987-1989).

	Treatment		
Year and period	0 N	Pig slurry 100 kg N	NPK 133 kg N
1987			
JUN-AUG	0.0001a*	0.02a	0.01a
AUG-OCT	0.002abc	0.001b	0.01a
OCT-NOV	0.001abc	0.002b	0.012ab
1988			
APR-JUN	0.02cd	0.004ab	0.01a
JUN-SEP	0.01bc	0.005ab	0.004a
SEP-NOV	0.004bc	0.004ab	0.003ac
1989			
MAR-MAJ	0.002abc	0.01a	0.1cd
MAJ-AUG	0.002ab	0.0002c	0.001e
AUG-NOV	0.001abc	0.001cbc	0.001ce
NOV-DEC	0.002abc	0.003ab	0.05a

*Values within the same treatment are significantly different (95% level of probability), when not followed by the same letter.

It should be noted, that the comparison between the means (Table 4) were done on the mean logarithmic rates, and that the method used to convert the logarithmic mean rates into the original scale somehow tends to underestimate the denitrification rates.

No significant differences in denitrification rates were seen in soil fertilized with pig slurry except period June-August, 1987 and May-August, 1989, where N losses in the two periods were 0.02 and 0.0002 kg N ha^{-1} day^{-1}, respectively.

The denitrification losses on the coarse sandy soil were very low (Table 5), less than 1 kg N ha^{-1} year^{-1}. The denitrification losses measured every day, in a period 2 days before autumn application of pig slurry to 6 days after the addition, were very low and in the same range as found in the other periods measured (data not shown).

Table 5. Daily mean denitrification rate (kg N ha^{-1} day^{-1}) in Jyndevad soil during 1988-1989.

	Treatment			
Period	0 N	PS, S* 100 N	PS, A 100 N	NPK 120 N
MAR-MAY	0.001	0.0003	0.002	0.001
MAY-AUG	0.001	0.001	0.001	0.001
AUG-MAR	0.001	0.001	0.001	0.001

* Plots abbreviation as in table 3.

3.3 Nitrate leaching

Assuming the same cultivation (crop, N-fertilizer, etc.) in every experimental year, the differences in nitrate leaching were due to climatic conditions, i.e. temperature and amount and distribution of precipitation.

At both locations the years 1987 - 1990 were characterized by considerable amount of precipitation and warm winters, with only a few days with temperature below freezing point.

For Askov soil the lowest amount of nitrate leached was from the unfertilized treatment (Table 6). In the years 1987-88 and 1988-89 nitrate leaching was highest from the treatment with N-fertilizer. The main reason for this is probably, that this treatment received 133 kg N ha^{-1} in N-fertilizer while the treatment with pig slurry received 100 kg NH_4^+-N ha^{-1}. The nitrate leaching during the last year of experiment in all treatments was very high compared to the first two years. This was probably due to the different climatic conditions.

Table 6. Nitrate leaching on Askov soil during the experimental years.

	MAY.87- MAR.88	MAR.88- MAR.89	MAR.89- MAR.90
		kg N ha^{-1} $year^{-1}$	
0 N	27	23	71
100 N			
Pig slurry, spring	31	40	82
133 NPK	53	50	79
LSD_{95}	ns	1	ns

For Jyndevad soil the nitrate leaching was higher, compared to the same treatments for Askov. This was probably due to a low field capacity on Jyndevad soil, compared to Askov soil.

When judging the nitrates leaching from the unfertilized treatments, one must remember, that at Askov this plot has been unfertilized since 1984, while at Jyndevad this plot has received normal amount of N-fertilizer, since the experiment started. Until the year before measurements took place, Jyndevad plot received 100 kg NH_4^+-N ha^{-1} in pig slurry, in the spring. At Jyndevad the mean nitrate leaching was highest in the treatment with autumn applied slurry and least in the treatment with undersown grass as a catch crop (Table 7). In the treatment, which received 100 kg NH_4^+-N ha^{-1} at the beginning of December, the amount of nitrate leached, corresponded to the amount of applied NH_4^+-N ha^{-1}. Leaching took place during the winter and the following growing season/autumn. In the years, where the autumn applied inorganic nitrogen was not leached before the growing season, the remaining nitrate was leached to the bottom of the root zone. This was concluded, after the next year crop yield was at the same level as from the unfertilized treatment (data not shown).

Table 7. Nitrate leaching on Jyndevad soil during the experimental years.

	MAY.87- MAR.88	MAR.88- MAR.89	MAR.89- MAR.90
	kg N ha^{-1} $year^{-1}$		
0 N	49	55	81
50 N Pig slurry, spring	80	68	76
100 N Pig slurry, spring	110	68	68
100 N Pig slurry, autumn	212[2]	106	198
100 N Pig slurry, spring + catch crop	95	18	28
120 NPK	78	47	65
LSD_{95}	38[1]	21	43

[1]) Treatment, which received slurry in the autumn not included in statistic analysis.
[2]) The experiment started in 1987, and slurry was applied to this plot in spring 1987 instead of autumn 1986.

In the plots which received 100 kg NH_4^+-N ha^{-1} in pig slurry in spring and with grass as a catch crop, the mean nitrate leaching was 47 kg NO_3^--N ha^{-1} $year^{-1}$.

The effect of the catch crop on nitrate leaching was small during the first year of the experiment (Table 7). Due to a long period of rain, the main crop was first harvested in September, and growth of the catch crop became very poor compared to the other experimental years.

During the last two years of experiment the harvest of the main crop took place in August, and the nitrate leaching was 18 and 28 kg NO_3^--N ha^{-1} $year^{-1}$, respectively. This was 50 and 41 kg NO_3^--N ha^{-1} $year^{-1}$ less than the corresponding treatment without catch crop.

The period of investigation has, generally, been characterized by considerable amount of precipitation. Especially the summer 1987 was characterized by a high precipitation, which caused high nitrate leaching, at both Askov and Jyndevad. In the following years there was no nitrate leaching of significance during the summer (data not shown).

4. DISCUSSION AND CONCLUSION

The mineralization of organic N from soil humus, organic fertilizers and plant material is of considerable significance in supplying available N to crops. N mineralization varied depending on soil type and fertilizers applied, and amounted to 34 - 179 and to 80 - 137 kg N ha^{-1} $year^{-1}$ for Askov and Jyndevad, respectively (Table 2 and 3).

In general mineralization takes place within limited temperature ranges, but it may still occur at relatively low temperatures, as 2°C

(Stevenson, 1986). The experimental years were generally characterized by warm winters, with an average temperature 4°C. Net mineralization continued during this period with a stable rate at 0.2 kg N ha^{-1} day^{-1} (Table 2 and 3).

A high availability of both carbon and nitrate throughout the year, especially by addition of pig slurry, was expected to increase the denitrification losses considerably (Maag, 1989). However, denitrification measurements under the actual field temperature and water contents indicated, that only about 7 and 1 kg N ha^{-1} $year^{-1}$ was lost for sandy loam and coarse sandy soil, respectively (Table 4 and 5).

The results indicated the influence of the amount of nitrogen mineralized on the amount of nitrates leached, especially during the winter periods from soil left bare. Yearly leaching amounted from 27 to 212 kg N ha^{-1} (Table 6 and 7). Catch crop reduced essentially leaching of nitrates.

To improve N efficiency in soil and decrease N losses to the environment, high concentration of inorganic N should be avoided, especially in periods, when losses are likely to occur. This requires smaller amounts of fertilizer N as well as a greater contribution of soil N mineralized, as a N source to crop. Furthermore, during periods without crop N uptake, N losses can be reduced through the catch crop. Prolonged crop N uptake, by sowing a catch crop can reduce N losses considerably.

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Simulation of Biomass Production, Nitrogen uptake and Nitrogen Leaching in Spring Barley Crop Production

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Introduction

Objectives

The losses of nitrogen from agricultural arable land to the aquatic environment have increased in many areas, in particular during the recent four decades. Thus great concern has arisen as to how an economically and environmentally sustained agricultural crop production can be developed. The objective of the present study was to develop a mathematical model of the soil plant system to enable simulation of crop production, soil water dynamics and nitrogen dynamics in crop production at various agricultural management practices and strategies. The aim has been a model applicable at field level as a management tool as well as at higher level for administrative and strategic planning purposes. The model which is described in great details elsewhere (Hansen et al., 1990a) is developed for a number of agricultural crops. In this presentation, however, only the main feature and performance of the model applied particularly to barley crop production at various management practices are described.

Model description

Main modules

The model comprises a number of main modules viz. a hydrological model including a submodel for soil water dynamics, a soil temperature model, a soil nitrogen model including a submodel for soil organic matter dynamics, and a crop model including a submodel for nitrogen uptake. The soil part of the model has a one dimensional vertical structure. The soil profile is divided into

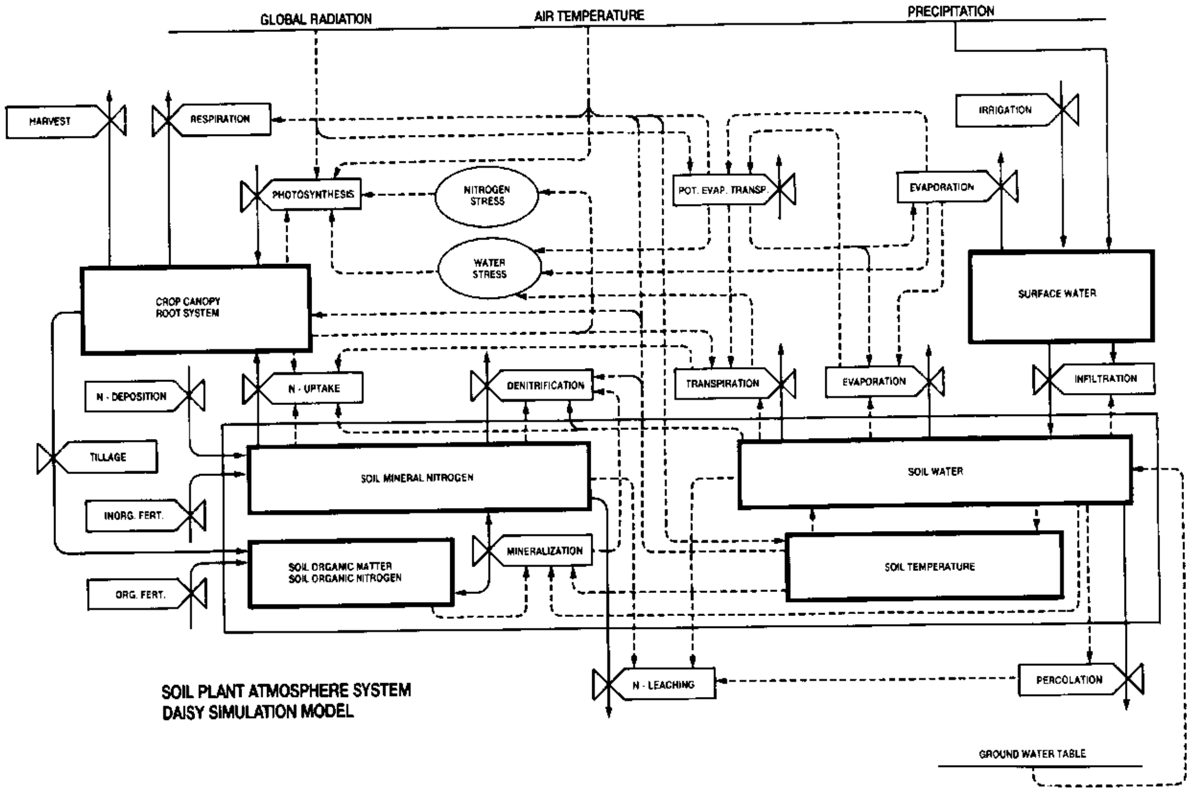

Fig. 1. Relational diagram of the soil plant system. Global radiation, air temperature, and precipitation are driving variables. Rectangles represent system state variables, valve symbols represent processes while ovals represent auxiliary variables. Solid lines represent flows of matter while broken lines represent flows of information.

layers on the basis of physical and chemical soil characteristics. A relational diagram of the overall model is shown in Fig. 1.

Hydrological model

The hydrological processes considered in the model include snow accumulation and melting, interception of precipitation by the crop canopy, evaporation from crop and soil surfaces, infiltration, water uptake by plant roots, transpiration, and vertical movement of water in the soil profile. In the model snow melting is influenced by incident radiation, and soil and air temperatures. Interception is determined by precipitation and by the crop canopy. The soil water dynamics is modelled by Richards equation (Richard, 1931):

Water dynamics

$$C_w \frac{\partial \psi}{\partial t} = \frac{\partial}{\partial z}\left[K_w \frac{\partial \psi}{\partial z} - K_w\right] - S \qquad (1)$$

where C_w is specific water capacity, ψ is soil water pressure potential, K_w is hydraulic conductivity, S is water uptake by plant roots, t is time, and z is soil depth. The vertical flow rate q is given by the Darcy equation:

$$q = - K_w \frac{\partial \psi}{\partial z} + K_w \qquad (2)$$

Water uptake

Modelling of the water uptake by plant roots is based on steady state radial flow to the root surfaces:

$$S = L \frac{\theta_r}{\theta_s} \frac{\int_0^{\psi_s} K_w d\psi - \int_0^{\psi_r} K_w d\psi}{-\frac{1}{2} \ln (r_r^2 \pi L)} \qquad (3)$$

where L is root density, θ_r is soil water content at the root surface, θ_s is soil water content at saturation, ψ_s and ψ_r is soil water

Evapotranspiration

pressure potential of the bulk soil and at the root surface, respectively, and r_r is root radius. The potential evapotranspiration constitutes the upper limit for the considered evaporation and transpiration processes. In the present study the potential evapotranspiration was calculated by using a modified Makkink equation (Makkink, 1957; Hansen, 1984).

Temperature model

The soil temperature is modelled by solving an extended heat flow equation which includes the effect of frost and thaw processes:

$$\frac{\partial\,(C_h T)}{\partial t} - L_f\,\rho_i\,\frac{\partial X_i}{\partial t} = \frac{\partial}{\partial z}\left(K_h\frac{\partial T}{\partial z}\right) - \rho_w\,c_w\,\frac{\partial(Tq)}{\partial z} \qquad (4)$$

where C_h is volumetric heat capacity of soil, T is soil temperature, L_f is latent heat of freezing, ρ_i is density of ice, X_i is volumetric fraction of ice, K_h is thermal conductivity calculated according to de Vries (1963), ρ_w is density of water, and c_w is the specific heat capacity of water. The freezing process induces water flow in the soil as ice formation is assumed to take place in the large soil pores extracting water from small pores resulting in water flow towards the freezing zone (Miller, 1980).

Soil nitrogen model

The transformation and transport processes considered in the model include net mineralization of nitrogen, nitrification, denitrification, nitrogen uptake by plants, and nitrogen leaching from the root zone. It appears that before mineralization can take place the soil organic matter has to be degraded and dissolved in the soil solution. These processes may be considered as the steps determining the turnover rate of soil organic matter (Nielsen et al., 1988). The net mineralization is thus governed by the turnover of organic matter in the soil which conceptually is divided into three main pools viz. dead native soil organic matter (SOM), microbial biomass (BOM), and added organic matter (AOM). Each main pool of organic matter is subdivided into two or three subpools

Organic matter pools

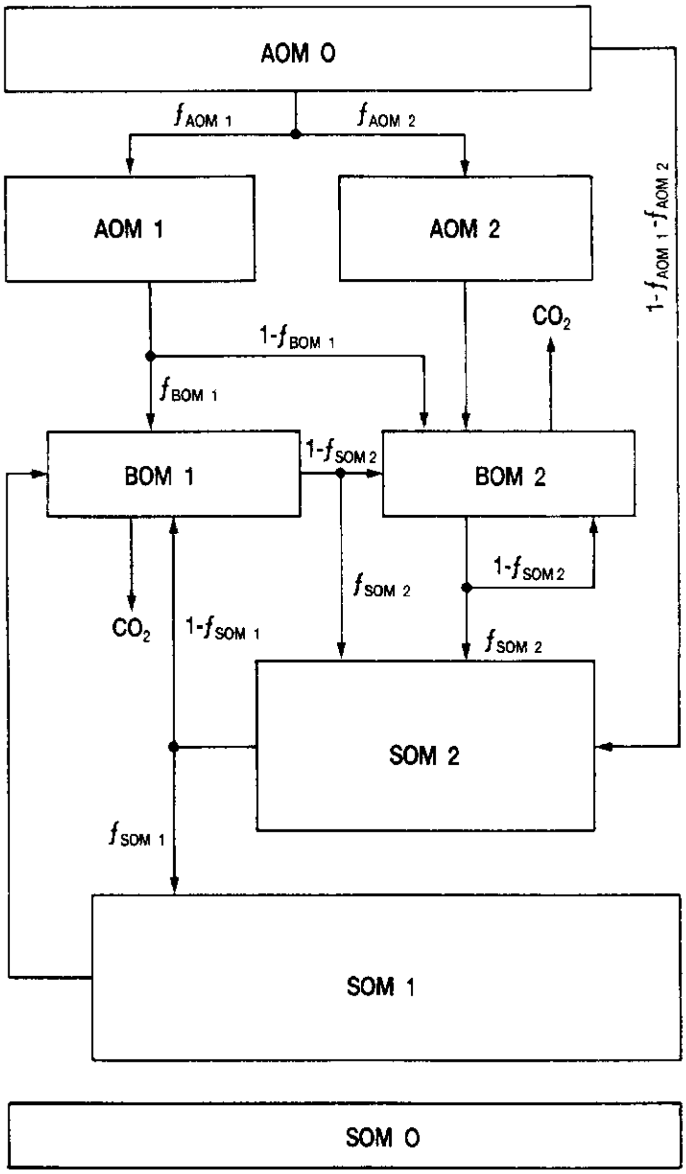

Fig. 2. Pools of organic matter and related partitioning coefficients. AOM: Added organic matter, BOM: Biomass, SOM: Soil organic matter.

Soil organic matter

each one being characterized by a particular carbon nitrogen ratio and by a particular turnover time, Fig. 2. Thus dead native soil organic matter (SOM) is subdivided into three subpools disignated SOM_0, SOM_1, and SOM_2, respectively. The subpool SOM_0 can be neglected as it consists of almost inert organic matter. The rates of decomposition of SOM_1 and SOM_2 are simulated by first order reaction kinetics. The subpool SOM_1 is assumed to consist of chemically stabilized organic matter, i.e. compounds with a chemically structure that imply resistance to biological attack, while the subpool SOM_2 is assumed to consist of organic matter part of which is physically stabilized, i.e. compounds which is protected against biological attact by adsorption to soil colloids or entrapment within soil aggregated (Jenkinson and Rayner, 1977; Veen et al., 1984, 1985).

Microbial biomass

The microbial biomass in the soil which usually accounts for less than 3% of the organic carbon (Eiland, 1985) is subdivided into two subpools designated BOM_1 and BOM_2, respectively, in order to obtain a relatively stable as well as a more dynamic part of the microbial biomass (Veen et al., 1985). The subpool BOM_1 is considered to be the more stable part while subpool BOM_2 is considered to be the more dynamic part of the microbial biomass. Simulation of biomass turnover is based on growth efficiency, maintenance respiration, and death rate coefficients.

Added organic matter

The added organic matter (AOM_0) is organic fertilizers such as farmyard manure, slurry, green crop manure, or crop residues left in the field after harvest. The added organic matter is allocated to the subpools AOM_1, AOM_2 and SOM_2. The subpool AOM_1 is assumed to consist of mainly cell wall material while AOM_2 is assumed to consist of mainly water extractable cell material. The organic matter allocated to the soil subpool SOM_2 is assumed to consist of lignin mainly and other resistant compounds (Veen and Paul, 1981). The subpool AOM_1 is substrate for both BOM_1 and

First order reaction

BOM_2, and decomposes slowly, while AOM_2 which is easy decomposable is substrate for BOM_2 only. The rates of decomposition of AOM_1 and AOM_2 are simulated by first order reaction kinetics.

Abiotic factors

The considered abiotic factors influencing the carbon turnover are soil temperature, and soil water status, and in the case of subpools SOM_1, SOM_2, BOM_1, also clay content. It is assumed that no interaction exists between the effect of the various abiotic factors and that the combined effect is multiplicative. The abiotic function adopted which were derived from various sources in literature (Addiscott, 1983; Anderson, 1979; Cambell et al., 1981; Miller and Johnson, 1964; Orchard and Cook, 1983; Stanford et al., 1973; Stanford and Epstein, 1974; Stott et al., 1986; Sørensen, 1975; Veen and Paul, 1981) are shown in Fig. 3.

Carbon balance

A carbon balance for each pool of organic matter can be established resulting in an expression for the rate of change of carbon dC/dt in each particular pool. As each pool of organic matter is characterized by a particular carbon nitrogen ratio [C/N] an overall organic nitrogen balance can be established resulting in an equation for net mineralization ξ_m of nitrogen:

$$\xi_m = -\sum_i [C/N]_i^{-1} \frac{dC_i}{dt} \tag{5}$$

Mineralization

If net mineralization is negative, i.e. net immobilization occurs, it is assumed that NH_4-N is utilized in preference to NO_3-N by the microbial biomass.

In well aerated arable soils at relative high water content ($1.5 < pF < 2.5$), pH in the range 4-8, and soil temperature higher than 5°C microbial activity is usually limited by the availability of organic carbon and most NH_4-N is biological oxidized to NO_3-N

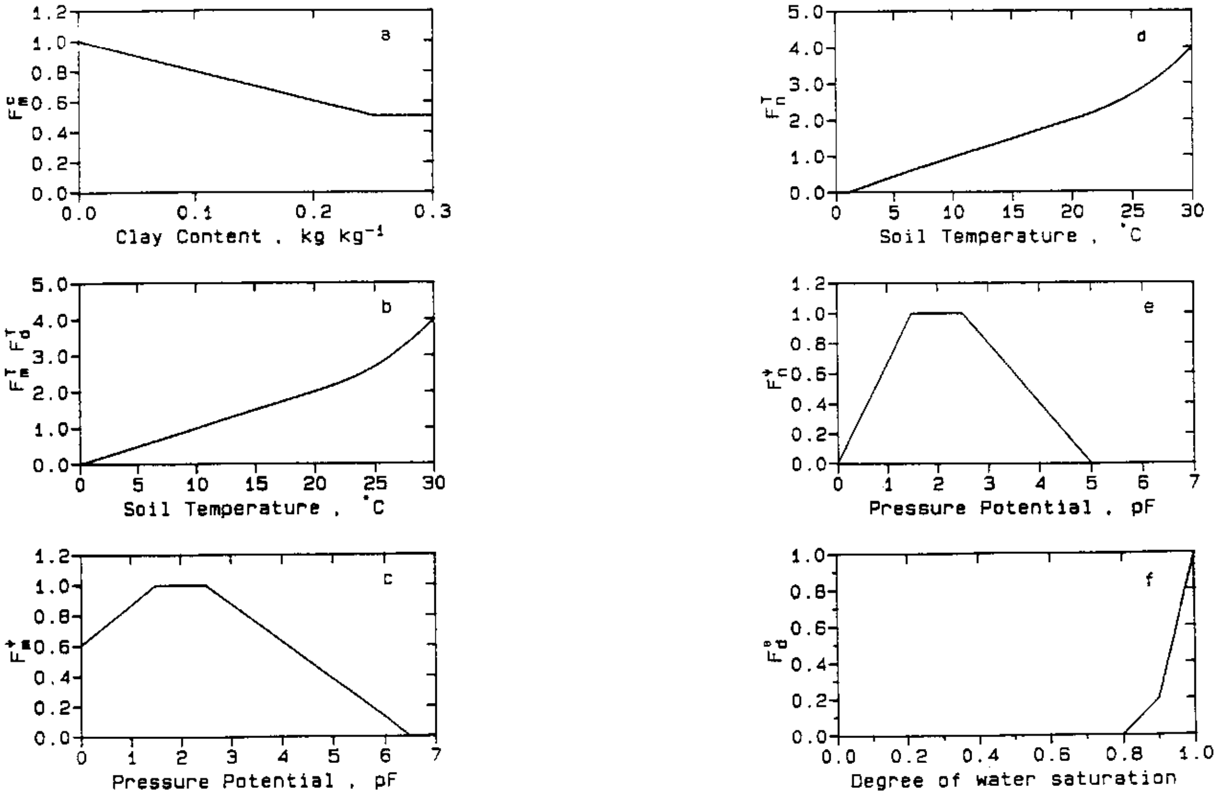

Fig. 3. Abiotic functions applied in the soil nitrogen model. Mineralization (a,b,c), nitrification (d,e) and denitrification (b,f).

as rapidly as it is formed by the process of mineralization. Under such conditions nitrification can be expressed by first order reaction kinetics.

Nitrification

The considered abiotic factors influencing the nitrification are soil temperature and soil water status. It is assumed that no interaction exists between the effect of soil temperature and soil water status, respectively, and that the combined effect is multiplicative. The abiotic functions adopted which were derived from various sources in literature (Flowers and O'Callaghan, 1983; Miller and Johnson, 1964; Reichman et al., 1966; Sabey, 1969) are shown in Fig. 3. As the O_2 concentration in soil solution usually is correlated with temperature and soil water content the effect of O_2 concentration on the nitrification rate is implicitly included in the combined effect of soil temperature and soil water content.

Denitrification

Denitrification is modelled by defining a potential denitrification rate, i.e. the denitrification rate under complete anaerobic conditions. The potential denitrification rate ξ_d^* is assumed to be related to soil temperature and CO_2 evolution rate (Lind, 1980):

$$\xi_d^* = F_d^T \alpha_d^* \xi_{CO_2} \tag{6}$$

where F_d^T is a soil temperature function identical to F_m^T, α_d^* is an impirical constant and ξ_{CO_2} is CO_2 evolution rate. Under partly anaerobic conditions the potential denitrification rate is reduced according to the oxygen status of the soil expressed as a function of soil water content adopted from Rolston et al. (1984), Fig. 3. The actual denitrification rate is either determined as the reduced potential denitrification rate or as the rate at which nitrate in soil is available for denitrification.

Nitrogen uptake

The nitrogen uptake model is based on the concept of a potential nitrogen demand simulated by the crop model, and the availability of nitrogen in the soil for plant uptake, i.e. the rate at which nitrogen can be made available at the root surfaces. The transport of nitrogen from the bulk soil to the root surfaces is based on a number of assumptions. Each root exploit an average effective volume of soil which is assumed to be a cylinder around each root. The radius of this cylinder is assumed to correspond to the average half distance between the roots. It is assumed that nitrogen is transfered to the root surface by mass flow and diffusion and that the concentration - distance profile develops in time in a stepwise manner, and at each timestep it approximates to a steady state profile (Baldwin et al., 1973). In the present model it is assumed that nitrogen uptake equals the nitrogen flux towards the root surface. Based on these assumptions the flux of nitrogen I towards the root surface is calculated:

$$I = \begin{cases} 2\pi Db(\bar{C} - C_r)\left[\dfrac{\beta^2 \ln \beta}{\beta^2 - 1} - ½\right]^{-1} & \alpha = 0 \\ q_r \dfrac{(\beta^2 - 1)\bar{C} - C_r \ln \beta^2}{(\beta^2 - 1) - \ln \beta^2} & \alpha = 2 \\ q_r \dfrac{(\beta^2 - 1)(1 - ½\alpha)\bar{C} - (\beta^{2-\alpha} - 1)C_r}{(\beta^2 - 1)(1 - ½\alpha) - (\beta^{2-\alpha} - 1)} & \text{else} \end{cases} \qquad (7)$$

$$\alpha = \frac{q_r}{2\pi Db}$$

$$\beta = (r_r^2 \pi L)^{-½}$$

where q_r is radial water flow rate, D is the diffusion coefficient, $\bar{C}$ is average concentration in solution, C_r is concentration at root surface, and b is buffer power of soil. If the uptake is limited by the availability of nitrogen then C_r is equal to zero and hence the root acts as a zero sink. In this case total uptake of nitrogen is calculated by integrating I over the entire root system. In the case of ample nitrogen supply the total nitrogen uptake is determined by the potential nitrogen demand. Then total uptake is distributed over the entire root zone by assuming a common value of C_r to exist along the root surfaces of the entire root system. Soil layers in which $\bar{C} < C_r$ are assumed not to contribute to nitrogen uptake. The calculations are performed for both ammonium and nitrate. It is assumed that ammonium is taken up by plant roots in preference to nitrate.

Nitrogen movement

Simulation of the vertical movement of nitrogen is modelled by solving the convection dispersion equation:

$$\frac{\partial(A + \theta C)}{\partial t} = \frac{\partial}{\partial z}\left[\theta D^* \frac{\partial C}{\partial z} - qC\right] + \Phi \qquad (8)$$

where A is adsorbed nitrogen, D* is the dispersion coefficient, C is the bulk concentration of nitrogen in solution, and Φ is a sink source term. The convection dispersion equation is solved for ammonium as well as for nitrate. In the case of ammonium the relation between adsorbed and dissolved ammonium is described by an adsorption desorption isotherm derived from Schouwenberg and Schuffelen (1963), while in the case of nitrate adsorption is considered insignificant. The sink source term for ammonium and nitrate $\Phi_{NH_4^+}$ and $\Phi_{NO_3^-}$, respectively, in the convection dispersion equation integrates the transformation and transfer processes of ammonium and nitrate, respectively:

$$\Phi_{NH_4^+} = \xi_m + \xi_{f,NH_4^+} - \xi_{u,NH_4^+} - \xi_n \qquad (9)$$

$$\Phi_{NO_3^-} = \xi_n + \xi_{f,NO_3^-} - \xi_{u,NO_3^-} - \xi_d \qquad (10)$$

where ξ_m, ξ_n and ξ_d is net mineralization, nitrification, and denitrification, respectively, while ξ_{f,NH_4^+}, ξ_{f,NO_3^-}, and ξ_{u,NH_4^+}, ξ_{u,NO_3^-} are fertilizer input and root uptake of NH_4^+-N and NO_3^--N, respectively. It is noted that $\bar{C}$ in equation (7) corresponds to C in equation (8).

Crop model

In the present model a crop is considered to consist of two parts viz. shoot and root. The shoot is characterized by dry matter content and leaf area index, while the root system is characterized by dry matter content, rooting depth and root density. The crop model is based on the thermal unit concept which imply that crop development from emergence to harvest can be described in terms of temperature sum. Plant emergence and leaf area index at the early stage of crop canopy development are simulated solely as functions of temperature sum while leaf area index L_{ai} at later stages of crop canopy development is simulated as of function of both temperature sum and accumulated amounts of shoot dry matter:

$$L_{ai} = \begin{cases} 20\ W_s & \Sigma T_a \le 450 \\ 20\left[1 - \dfrac{3.0(\Sigma T_a - 450)}{(\Sigma T_a - 450) + 1450}\right] W_s & \Sigma T_a > 450 \end{cases} \tag{11}$$

Leaf area index

where W_s is the accumulated amount of shoot dry matter, and ΣT_a is the temperature sum calculated from emergence.

Simulation of crop dry matter production is based on calculation of daily gross canopy photosynthesis, partitioning of assimilates between shoot and root, and respiration of shoot and root, respectively.

Gross photosynthesis

The calculation of gross canopy photosynthesis is based on the assumptions that gross leaf photosynthesis can be described by a single light response curve (Goudrian and Laar, 1978) and that the light distribution within the crop canopy can be described by Beer's law. The daily gross canopy photosynthesis $F_{g,1}$ is calculated as:

$$F_{g,1} = f^{-1} \varepsilon S_a \tag{12}$$

$$\varepsilon = 0.15 - \left[0.158 - 0.094 \frac{L_{ai}}{L_{ai} + 3} \right] \frac{S_a}{S_a + 7.8 \cdot 10^6} \tag{13}$$

$$S_a = (1 - A_v)(1 - \exp(-K L_{ai}))\, \alpha_v S_i \tag{14}$$

where f is the energy content of carbohydrates, ϵ is radiation conversion efficiency coefficient, S_a is absorbed photosynthetically active radiation (PAR), A_v is the reflection coefficient of crop canopy, K is the extinction coefficient of crop canopy, S_i is global radiation, and α_v is the fraction of photosynthetically active radiation in the global radiation. Corresponding values of ϵ, L_{ai} and S_a were obtained by applying the basic assumptions on crop canopies with various values of L_{ai} for days with various radiation patterns, and integrating the gross leaf photosynthesis over space and time. Equation (13) is the result of a parametrization of the relation between ϵ, L_{ai} and S_a

Assimilation partitioning

The assimilate partitioning between shoot and root is considered as a function of temperature sum: Thus the function of assimilates allocated to shoot γ_s is estimated as:

$$\gamma_s = \begin{cases} 0.4 + 0.45 \dfrac{\Sigma T_a}{800} & \Sigma T_a < 800 \\ 0.85 & \Sigma T_a \geq 800 \end{cases} \tag{15}$$

Respiration

The fraction of assimilates allocated to root γ_r is equal to 1-γ_s. The respiration is assumed to include growth respiration as well as a temperature dependent maintenance respiration (McCree, 1970). Thus the daily growth of shoot ΔW_s is calculated as:

$$\Delta W_s = Y_s (\gamma_s F_g - r_{m,s} W_s) \tag{16}$$

where Y_s is the assimilate conversion coefficient, and $r_{m,s}$ is the temperatur dependent ($Q_{10} = 2$) maintenance respiration coefficient. Calculation of daily root growth is performed by analogy to the corresponding calculation of daily shoot growth.

Root penetration

Root penetration is assumed to take place if a daily net root growth ΔW_r occurs, if the soil temperature is above 4°C, and if the actual rooting depth d_r is less than the maximum rooting depth allowed in the particular soil considered. Daily root penetration Δd_r is calculated in accordance with Jacobsen (1976) as:

$$\Delta d_r = 0.25 (T_s - 4{,}0) \tag{17}$$

where T_s is the soil temperature at the actual rooting depth d_r. The distribution of root density L in the soil profile is described in accordance with Gerwitz and Page (1974). In order to establish the root density distribution it is assumed that the total root lengh is proportional to the accumulated amount of root dry matter and that the root density at the rooting depth d_r is 0.01 cm cm^{-3}.

Root density

Water limited crop production

The gross canopy photosynthesis may be limited due to water and/or nitrogen deficiency. The gross canopy photosynthesis under conditions of water deficiency $F_{g,2}$ is calculated as:

$$F_{g,2} = F_{g,1} \frac{E_{a,c}}{E_{p,c}} \tag{18}$$

where $E_{a,c}$ is actual crop evapotranspiration and $E_{p,c}$ is potential crop evapotranspiration. The gross canopy photosynthesis under conditions of nitrogen deficiency $F_{g,3}$ is calculated as:

$$F_{g,3} = F_{g,2} \frac{N_c - N_c^o}{N_c^a - N_c^o} \tag{19}$$

Nitrogen limited crop production

where N_c, N_c^o and N_c^a is the amount of nitrogen in the crop at the actual nitrogen supply, at extremely low nitrogen supply, and at just ample nitrogen supply, respectively. The daily potential nitrogen demand ΔN_u^p is calculated as

$$\Delta N_u^p = N_c^p - N_c \tag{20}$$

where N_c^p is the potential amount of nitrogen in the crop. The nitrogen concentrations corresponding to N_c^p, N_c^a, and N_c^o, respectively, assumed to be functions of temperature sum are illustrated in Fig. 4 for the two parts of the crop viz. shoot and root. At harvest the crop nitrogen is distributed between root and shoot by using equation (21):

$$C_r = 0.9 \sqrt{C_s} \tag{21}$$

Nitrogen concentrations in shoot and root

where C_r and C_s is nitrogen concentration in per cent in root and shoot dry matter, respectively. The parts of the crop which is not removed at harvest e.g. stuble and root are allocated to the appropriate pools of organic matter in the soil.

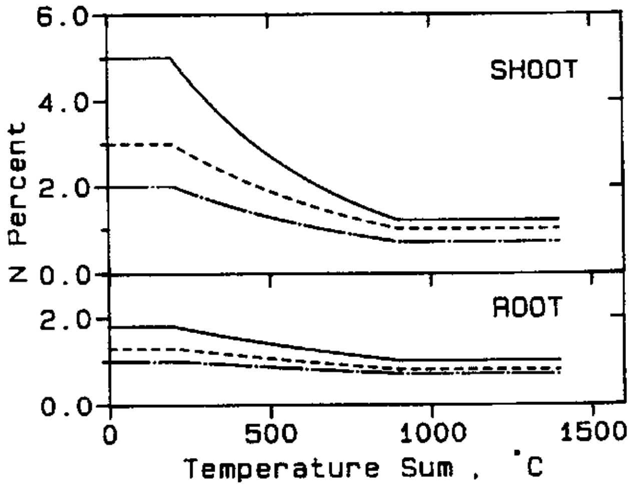

Fig. 4. Nitrogen concentrations in spring barley as function of temperature sum at potential nitrogen content (solid line), content at just ample nitrogen supply (dashed line), and content at extremely low nitrogen supply (dash dotted line).

Model validation

Experimental data set

The experimental data set used in the present validation has been described in detail by Lind et al. (1990) and Djurhuus (1990). The data were obtained in field experiments 1987-1988 and 1988-1989 with spring barley grown at various nitrogen fertilizer treatments on two locations, Askov and Jyndevad, Table 1.

Experimental treatments

The application rate of mineral fertilizer nitrogen was 133 and 120 kg N ha^{-1} for Askov and Jyndevad, respectively. Pig slurry was applied at a rate corresponding to an application rate of 100 kg N ha^{-1} as ammonium. It is noted that Jyndevad plot 4 received double application rate of pig slurry in 1987 as pig slurry was applied in the spring as well as in the autumn.

Table 1 Experimental treatments available for model validation.

Treatment	Askov	Jyndevad
No fertilizer	Plot 1	Plot 6
Pig slurry, autumn[1)]	–	Plot 5
Pig slurry, autumn[2)]	–	Plot 4
Pig slurry, spring	Plot 4	Plot 3
Pig slurry, spring[3)]	–	Plot 2
Mineral fertilizer	Plot 8	Plot 1

[1)] With undersown catch crop; [2)] In 1987 also spring application; [3)] Half application rate.

Model parameters

The required hydraulic properties in terms of soil water characteristic and unsaturated hydraulic conductivity functions were derived from the experimental data set. Thermal properties of the soil were calculated according to de Vries (1963). The experimental data on carbon content of the soil were used in the initialization of the soil nitrogen model.

Initialization

The soil water profiles and the soil nitrogen profiles, respectively, were initialized by using the first set of measurements obtained from the experimental data set. Model parameters used in the present simulations were obtained from Hansen et al. (1990). The driving variables, i.e. daily values of global radiation, air temperature, and precipitation, required to run the model for the present purpose were provided by Olesen (1990). In the present study validation on biomass production, nitrogen uptake, and nitrogen leaching has been considered. Validation on soil water dynamics and other aspects of soil nitrogen dynamics has been described elsewhere (Hansen et al. 1990a,b).

Driving variables

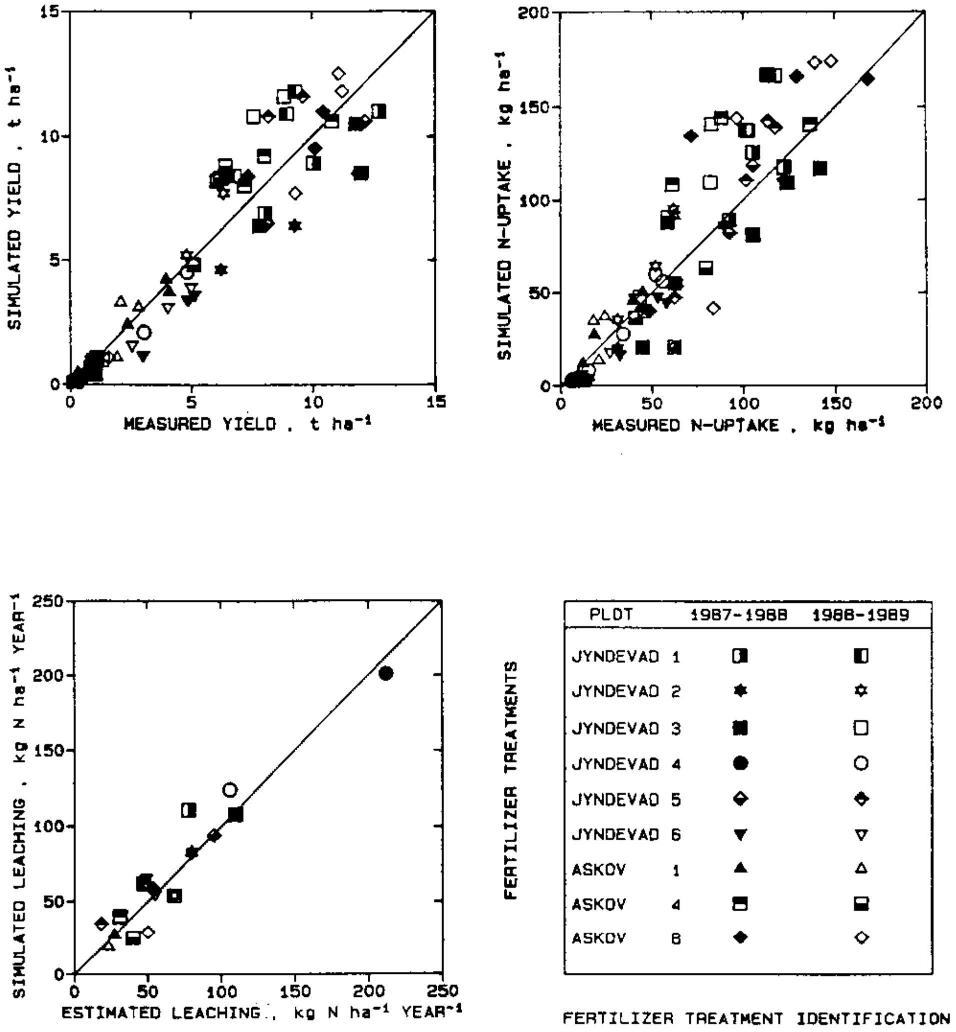

Fig. 5. Relations between experimental and simulated values of biomass production (crop yield), nitrogen uptake, and nitrogen leaching.

Biomass production

Measured and simulated values of biomass production and nitrogen uptake are shown in Fig. 5. The data points are almost evenly distributed around the 1:1 line although it appears that the model tends to slightly underestimate biomass production and nitrogen uptake during the first part of the growing season, whereas later in the growing season the model tends to slightly overestimate the nitrogen uptake. However, it should be realized that the experimental data are subject to statistical uncertainty and that the present crop model does not take into account any possible detrimental effects other than those caused by soil water and soil nitrogen deficiency.

Nitrogen leaching

Estimated and simulated values of nitrogen leaching are shown in Fig. 5. The estimated values of nitrogen leaching were obtained as accumulated values of the product of estimated water discharge and nitrate nitrogen concentration at the lower boundary of the soil profile considered. This method is most reliable at low concentration gradients in the profile and at low rates of water discharge. The data points are almost evenly distributed around the 1:1 line. In general the agreement between estimated and simulated values of nitrogen leaching is considered satisfactory. It is noted in particular that even in the extreme case of double application rate of pig slurry to Jyndevad soil plot 4 1987 the model predicts exellently the subsequent high value of nitrogen leaching.

Model application

Cropping system

The model can be used to simulate the effect of various cropping systems, various irrigation and fertilization strategies, and management operations including soil tillage and crop residue management on crop production and the dynamics of water, carbon, and nitrogen in the soil including loss of nitrogen by leaching processes. In the present study the effects of straw incorporation in soil as compared to straw removal from the field was simulated for twenty consecutive years of barley crop production.

Straw incorporation

Two soil types which are described elsewhere (Lind et al. 1990) were considered viz. Askov soil (sandy loam) and Jyndevad soil (coarse sand) while levels of annual fertilization considered were 60, 90, and 120 kg N ha^{-1}. System characterization and model parameters used in the simulations were as in the case of model validation exept hydraulic functions which for the Jyndevad soil were derived from Hansen et al. (1986). The period considered was 1966-1986 for which driving variables measured at Askov were provided by Olesen (1990).

Crop production

For the Jyndevad soil which has only a small content of available water making the crop production very much dependent on precipitation in the growing season big variations in crop production occurred from year to year due mainly to limited water supply in several years, while for the Askov soil with a relatively high content of available water crop production was more stable over the years considered, Fig. 6. In the Askov soil straw incorporation reduced dry matter production in the first year at the application of 60 and 90 kg N ha^{-1}, whereas in most other cases straw incorporation in soil increased the dry matter production.

Soil nitrogen balance

During the twenty years considered the soils were increasingly exhausted for nitrogen. However, in all cases the straw incorporation delayed the nitrogen exhaustion of the soil, Fig. 6. For the Askov soil the average annual nitrogen exhaustion of the soil was 20 and 34 kg N ha^{-1} with straw incorporation and straw removal, respectively. These simulation results are in good agreement with experimental results obtained by Christensen (1990). The corresponding values for the Jyndevad soil were 38 and 46 kg N ha^{-1}, respectively. Nitrogen fertilizer application appeared to have only minor effect on nitrogen exhaustion of the soil.

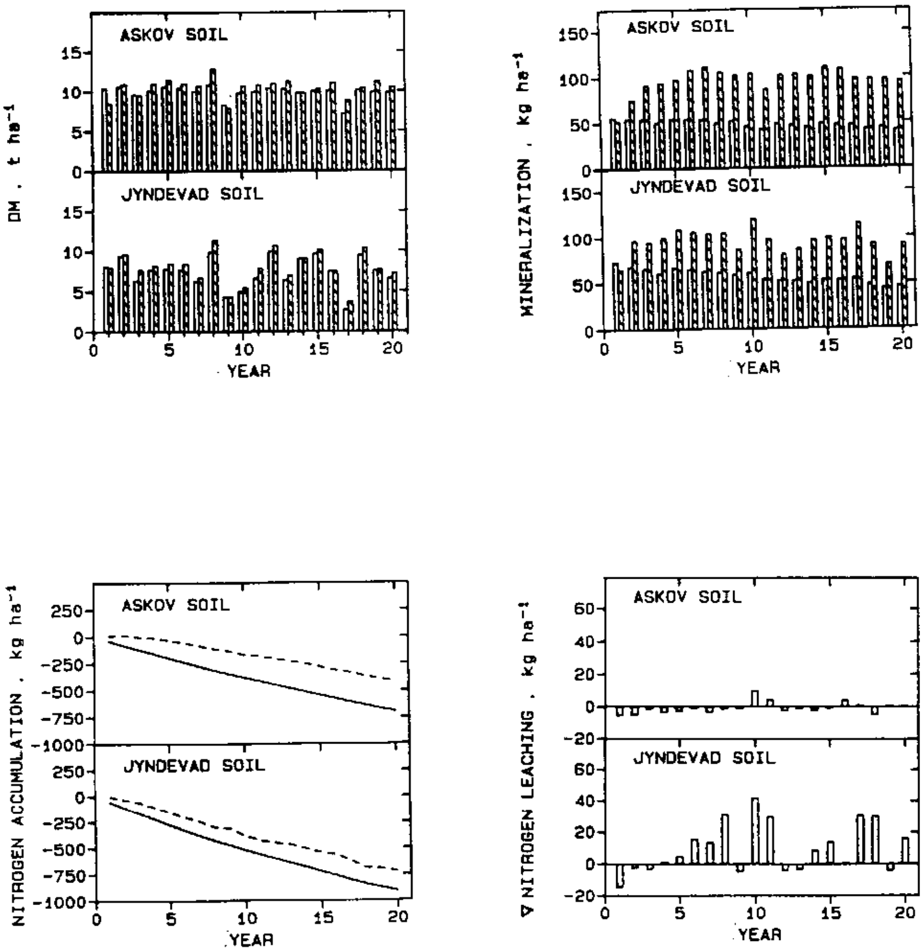

Fig. 5. Crop yield, nitrogen accumulation in soil, mineralization of nitrogen, and the effect of straw incorporation on nitrogen leaching simulated for 20 consecutive years of barley crop production. Straw incorporation (hatched columns, broken lines), straw removed (open columns, solid lines).

Mineralization

For both soils it appears that at all levels of nitrogen fertilization the net mineralization of nitrogen in the first year after straw incorporation was highest when the straw was removed from the field which can be attributed to an initial immobilization effect of straw incorporation. However, from the second year the net mineralization of nitrogen was highest in all cases when straw was incorporated in soil.

The simulated increases due to straw incorporation of net mineralization of nitrogen in the period of nitrogen uptake by spring barley are shown in Table 2. For the Jyndevad soil it appears that the increase of net mineralization of nitrogen in that particular period increases from ca. 10 kg N ha^{-1} in year 1 to about 20 kg N ha^{-1} in year 20. The corresponding values for the Askov soil are about 4 and 25 kg N ha^{-1}, respectively. The results indicate that after few years, straw incorporation would decrease the annual demand of nitrogen fertilizer application with about 20 kg N ha^{-1} in a continuous spring barley cropping system.

Table 2. Simulated increases in net mineralization of nitrogen, kg N ha^{-1}, in the period April 1. - July 15. due to straw incorporation.

Year	Soil	Nitrogen fertilizer, kg N ha^{-1}		
No.	JB No.	60	90	120
Year 1	1	10	9	16
Year 2	1	15	17	17
Year 10	1	14	18	18
Year 20	1	18	22	24
Year 1	6	4	4	5
Year 2	6	10	18	24
Year 10	6	20	26	28
Year 20	6	21	25	28

Nitrogen leaching

According to the simulation results it appears that leaching of nitrogen during the first year after straw incorporation may be reduced by up to 10 and 20 kg N ha^{-1} in Askov soil and Jyndevad soil, respectively, due to straw incorporation, Fig. 6. However, after some years depending on soil type and level of nitrogen fertilizer application this descrease is changed to an increase in nitrogen leaching due to increased net mineralization og nitrogen resulting from incorporation of straw.

Summary

Model description

A dynamic simulation model for the soil plant system has been developed and described. The model includes a number of main modules viz. a hydrological model including a submodel for soil water dynamics, a soil temperature model, a soil nitrogen model including a submodel for soil organic matter dynamics, and a crop model including a submodel for nitrogen uptake. The soil part of the model has a one demensional vertical structure. The soil profile is divided into layers on the basis of physical and chemical soil characteristics. The model enables simulation of biomass production, soil water dynamics, and nitrogen dynamics in crop production at various agricultural management practices and strategies.

Model validation

In the present study the simulation model was used to simulate biomass production, nitrogen uptake, and nitrogen leaching in spring barley crop production at two locations at various levels of nitrogen fertilization. The model was validated by comparing simulated values with experimental data. It is concluded that the overall performance of the model is satisfactory although some minor adjustments of the model may prove to be necessary.

Model application

An example of model application is given by simulation of effects of straw incorporation in soil during twenty consecutive years of barley crop production as compared to removal of straw from the field. For the two soils considered the results show

that the soil nitrogen balance is negative in nitrogen fertilizer based long term barley crop production,

that the nitrogen exhaustion of the soil is decreased by straw incorporation,

that the annual net mineralization of nitrogen increased considerably after some years of straw incorporation,

that net mineralization in the growth season is increased by up to 20 kg N ha^{-1} after some years of straw incorporation,

that nitrogen leaching during the first year after straw incorporation may be reduced by up to 20 kg N ha^{-1} as a result of straw incorporation, and

that depending on soil type and nitrogen fertilizer application rate the annual nitrogen leaching may increase after some years of straw incorporation.

Acknowledgement

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Determination of Ammonia Emission by use of Passive Flux Samplers

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ABSTRACT

Test of a new type of passive flux sampler for determination of NH_3 emission

A new type of passive sampler for determination of ammonia fluxes from land surfaces was tested in a micrometeorological mass balance method. The flux sampler consists of 2 glass tubes, each with a length of 10 cm and an internal diameter of 0.7 cm. The two glass tubes are connected in series with each other and with a thin stainless steel disc, having a 1 mm hole in the centre. The inner surface of the glass tubes are coated with oxalic acid.

The method with passive flux samplers was compared to a reference method which uses acid traps, pumps, flow meters, anemometers and a data logger. The comparison of the two methods was carried out on a circular plot with a radius of 15 m. Emission of ammonia was achieved by placing 140 beakers containing an $(NH_4)_2SO_4/NaHCO_3$ solution with an initial pH around 9 on the experimental area.

Recommendation of passive flux samplers

The results show that the passive flux samplers can be used in a micrometeorological mass balance method to give accurate determinations of the vertical flux density of ammonia from a circular field. The passive flux samplers make pumps, flow meters and anemometers unnecessary and ammonia loss can be determined easily and cheaply without the requirement of large labour force which is needed in the reference method.

1. INTRODUCTION

Uncertain estimates of ammonia emission from agricultural activities

Estimates of ammonia emission from agricultural activities are still very uncertain. In order to improve the estimates there is a great need for data on ammonia volatilization from manure stores and from manure and fertilizers applied to the surface of agricultural land. Furthermore, very few results are available on the emission of ammonia from the foliage of agricultural crops.

Conventional methods have disadvantages

Ammonia volatilization is strongly influenced by air temperature and wind speed. The frequently used chamber technique alters the micro-climatic conditions and may give incorrect estimates of ammonia emission (Ferm, 1983; Ferguson et. al. 1988). Instead, micrometeorological techniques have to be used because they do not disturb the environmental conditions which influence ammonia volatilization (Denmead 1983; Black et al. 1985).

Micrometeorological measurements based on energy balance methods or aerodynamic methods require extensive and uniform land areas. Such requirements are not necessary in micrometeorological measurements based on mass balance (Denmead 1983). In the mass balance approach, the flux of the gas into the atmosphere from a treated area of limited upwind extent is equated with the rate at which the gas is carried by the wind across a vertical plane at the downwind edge. No special form of the wind speed profile or correction for thermal instability is required. Micrometeorological mass balance methods are thus suitable for measuring ammonia emissions from smaller plots. However, in their convential form they are very labour demanding and still have the disadvantages associated with requirements of instrumentation for measurements of aerial NH_3-concentration and wind speed (see e.g. Ryden and McNeill, 1984) .

Advantages of passive flux samplers

In order to simplify micrometeorological mass-balance measurements Ferm (1986) developed a simple technique based on passive flux samplers for ammonia. This technique has several potential advantages:

- easy to operate
- low labour requirements
- ammonia emission can be integrated over long time periods
- wind speed and wind direction measurements are not required
- electricical power is not needed

Principle of passive flux samplers

The passive flux samplers collect ammonia in an amount that is proportional to the product of the ammonia concentration and the wind speed component along the sampler (Ferm 1986). Thus, the collected amount of ammonia is proportional to the integrated horizontal ammonia flux through a fixed vertical surface. By adding the ammonia flux from the experimental area through four directions at right angles to each other and subtracting the corresponding fluxes into the plot from the surroundings, the horizontal net flux of ammonia from the plot can be estimated. Knowing the horizontal net flux of ammonia in several heights above the plot, the ammonia volatilization from the plot (the vertical flux density of ammonia) can subsequently be calculated.

Test of passive flux samplers

The passive flux samplers have been tested in wind-tunnel experiments under laboratory conditions (Ferm 1986). Under field conditions they have so far only been used in one single case in which NH_3-volatilization from surface applied slurry was measured (Ferm and Christensen 1987). However, the method has never been tested against a conventional, accepted micrometeorological technique. Such a test was the purpose of the present investigations.

2. MATERIALS AND METHODS

Ammonia source

The experimental area consisted in experiment 1 of a square with a sidelength of 21 m. In the rest of the experiments, the experimental area was a circle with an area of 707 m^2 (radius 15 m). The ammonia source consisted of 140 flat beakers (diameter 15 cm, height 3 cm), containing a $(NH_4)_2SO_4$ solution. The experiments were started by adding a $NaHCO_3$ solution to the beakers. The total volume of solution was 0.5 ℓ with a NH_4^+ concentration about 1 M. The pH of the NH_4^+/HCO_3^- solution was initially 8.5-9.0 and dropped during the experiments to around 8.0 (Tab. 2).

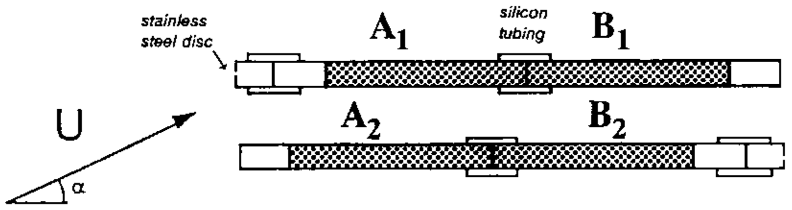
2.1 Mass-balance method with passive flux samplers

Description of passive flux sampler

The passive flux sampler consisted of two glass tubes coated internally with oxalic acid (Fig. 1, hatched part). The oxalic acid coating was made by sucking methanol containing 3% oxalic acid up into each glass tube. After draining of the methanol solution the tubes were dried with ammonia free air. The tubes were closed immediately after drying.

Each glass tube was 100 mm long with an inner and outer diameter of 7 and 10 mm, respectively. Two glass tubes were connected by means of a small piece of silicon tubing (Fig. 1). To each pair of glass tubes was furthermore connected a stainless steel disc (thickness 0.5 mm in Experiments 1, 2, 3, and 4 and 0.05 mm in experiments 5 and 6) with a hole (diameter 1 mm) in the centre. The disc was glued onto a 10 mm long glass tube that was connected to the the two oxalic acid coated glass tubed by use of a piece of silicon tubing (Fig. 1).

The purpose of the stainless steel disc was to decrease the wind speed inside the tubes in order to achieve a low friction resistance and a high NH_3 collection efficiency. The wind speed inside the tubes will be approximately proportional to the wind speed outside the tube multiplied with the cosine of the angle between the wind direction and the tube axis (Fig. 1). Tubes and stainless steel discs were manufactured by Mikrolab Aarhus A/S, Axel Kiers Vej 34, DK-8270 Hoejbjerg, Denmark.



$$\frac{(A_1+A_2)}{2\cdot\pi\cdot r^2\cdot 0.7} \approx \int_{t_1}^{t_2} U\cdot\cos\cdot\alpha\cdot[NH_3]\cdot dt$$

Fig. 1. Passive NH_3 flux samplers. *NH_3 is collected in tubes A_1 and A_2 but not in B_1 and B_2 when wind direction and wind speed is represented by the vector U. Tubes A_1 and A_2 collect the same amount of NH_3 if α is 0°. When α increases, the amount of NH_3 collected by A_1 decreases more rapidly with α than does cos(α), while A_2 collects and amount of NH_3 that decreases more slowly with α than does cos(α) (Ferm 1986). However, the average amount of NH_3 collected by the two tubes as a function of α corresponds approximately to cos(α). Thus, the NH_3 flux through a plane perpendicular to the longitudinal axis of the samplers can be determined.*

Field measurements with passive flux samplers

The passive flux samplers were at the start of the experimental period mounted in four heights (75, 150, 225, and 300 cm) on 4 masts placed at right angles to each other on the periphery of the circular experimental area. Two flux samplers were mounted in each height, one with the stainless steel disc towards the experimental area, the other having the disc towards the surroundings. Ammonia coming from the experimental area was thus collected through the stainless steel disc in the first flux sampler and through the open end of the second. Conversely, ammonia from the surroundings was collected through the open end of the first sampler and through the disc of the second. At the end of the 9 hour exposure period the flux samplers were taken down from the masts and closed with plastic caps. In the laboratory, the glass tubes were eluated with 3 ml deionized water. The ammonium concentration in the leachate was analysed by use of a Flow Injection Analyzer.

Calculation of horizontal ammonia flux

The horizontal flux of ammonia (F_{hz}, μg NH_3-N m^{-2} s^{-1}) through two flux samplers facing same direction was calculated on basis of the following equation:

$$F_{hz} = \frac{A_1 + A_2}{2 \cdot \Pi \cdot r_d^2 \cdot K \cdot \Delta t} \qquad (1)$$

where A_1 and A_2 is the amount of ammonia in the two glass tubes facing same direction (see e.g. A_1 and A_2 in Fig. 1), r_d is the radius of the hole in the stainless steel disc (0.5 mm), Δt is the time between the start and the conclusion of the measurement, and K is a correction factor (K = 0.7). The correction factor was determined in wind tunnel experiments (Ferm 1986). The factor is less than 1 because the stainless steel disc creates some turbulence that reduces the wind speed.

Calculation of vertical ammonia flux

The vertical net-flux of ammonia from the experimental area (F_v) was calculated using the following equation:

$$F_v = \frac{1}{2 \cdot r} \sum_{h=1}^{h=4} \sum_{m=1}^{m=4} (F_{hz,p} - F_{hz,s}) \Delta h \qquad (2)$$

where $F_{hz,p}$ and $F_{hz,s}$ is the horizontal flux from the experimental area and surroundings, respectively, in each height of measurement

(h) at each mast (m), Δh is the height interval represented by each set of the four sets of flux samplers (Δh = 1.125 m for flux samplers in 0.75 m height, and Δh = 0.75 m for flux samplers in 1.5, 2.25 and 3 m height), r is the radius of the experimental plot (15 m), corresponding to half of the fetch (the effective stretch the wind has passed over the experimental area).

That the effective stretch is equal to 2r can be derived from Fig. 2. Two pairs of flux samplers receive air that has passed a stretch of $2r \cdot \cos\alpha + 2r \cdot \sin\alpha$ over the experimental plot (see bold arrows in Fig. 2). The stretch thus varies between 2r and 2.83r when α varies between 0° and 45°. However, the flux is not only proportional to the NH_3 concentration (here assumed to be proportional to the stretch travelled above the source) but also to the cosine of the angle between the wind direction and the longitudinal axis of the samplers (Fig. 1). Accordingly, the effective fetch will be the sum of the products $2r \cdot \cos^2\alpha$ and $2r \cdot \sin\alpha \cdot \cos(90\text{-}\alpha)$ which is equal to 2r.

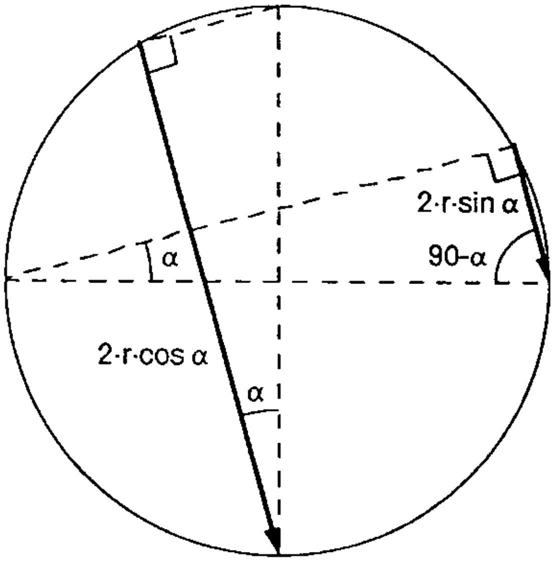


Fig. 2. *Graphical presentation of the representativeness of the four masts surrounding a circular plot. Further explanation of the Figure is given in the text.*

2.2 Reference method

Reference method uses ammonia traps, anemometers, pumps, flow meters, and a data logger

The downwind mast, placed in the centre of the experimental area, was equipped with ammonia traps placed at 25, 50, 75, 110, 150, 225, and 375 cm above the soil surface. A mast with four air temperature sensors (Rotronic MP100TST-010) at 100, 150, 200, and 300 cm above soil surface, and 7 anemometers (Vector Instruments A101M) at 25, 50, 75, 110, 150, 225, and 375 cm above soil surface, was placed 1 m from the central mast. The signals from the air temperature sensors and from the anemometers was recorded by a data logger (Cambell CR10/WP). Two masts with an ammonia trap at 100, 200, and 300 cm above soil surface were placed at the upwind edge of the experimental area.

Conventional ammonia trap

The NH_3 trap consisted of a 100 ml test tube with a bottle head supporting a gas dispersion tube. The traps contained 60 ml 0.05 M H_2SO_4. The air flow through the trap was 8 l min^{-1} provided by a Neuberger membrane pump. The traps were changed every 3rd hour. The concentration of ammonium in the traps was measured spectrophotometrically by use of an autoanalyzer.

Calculation of ammonia flux densities

The horizontal flux of ammonia in each height of measurement was calculated as the product of wind speed and mean atmospheric concentration of ammonia. The ammonia loss from the experimental area (the vertical flux of ammonia) was calculated using the following equation (Denmead 1983; Ryden & McNeill 1984):

$$F_v \hat{=} \frac{1}{r} \int_{z_0}^{z_p} (\overline{uc} - \overline{uc_b}) dz \qquad (3)$$

Mean wind speed (u) and mean atmospheric NH_3 concentration (c) in the 3-hour periods of measurement were used in the calculations of F_v. In Eq. 3, r is the radius of the circular experimental plot (15 m), c_b is the mean background concentration of NH_3, z_p is the height at which the concentration of ammonia has decreased to its background value (i.e. the height of profile development), and z_0 is the height at which wind speed has fallen to zero.

3. RESULTS AND DISCUSSION

Ammonia emission measured with passive flux samplers

The horizontal flux of ammonia determined with the new type of passive flux samplers is shown in Table 1. The highest NH_3-flux from the experimental plot was in all cases observed at the masts placed on the downwind edge of the plot. As an example, a high horizontal NH_3-flux from the experimental plot to the surroundings ($F_{hz,p}$) was observed on the eastern and southern mast in experiment 1 (Table 1) in which the prevailing wind direction was north-western (Table 2). Conversely, the horizontal NH_3-flux from the surroundings to the experimental plot was highest at the upwind edge of the plot.

The horizontal net-flux of NH_3 ($\Sigma F_{hz,p} - \Sigma F_{hz,s}$ in Table 1) decreased in all of the experiments linearly with the logarithm of height (z):

Exp. 1: $\Sigma F_{hz,p} - \Sigma F_{hz,s} = -80.3 \ln(z) + 84.5$ $\quad r^2=0.91$

Exp. 2: $\Sigma F_{hz,p} - \Sigma F_{hz,s} = -10.6 \ln(z) + 13.6$ $\quad r^2=0.94$

Exp. 3: $\Sigma F_{hz,p} - \Sigma F_{hz,s} = -38.0 \ln(z) + 48.1$ $\quad r^2=0.97$

Exp. 4: $\Sigma F_{hz,p} - \Sigma F_{hz,s} = -32.8 \ln(z) + 34.4$ $\quad r^2=0.95$

Exp. 5: $\Sigma F_{hz,p} - \Sigma F_{hz,s} = -160.0 \ln(z) + 165.0$ $\quad r^2=0.94$

Exp. 6: $\Sigma F_{hz,p} - \Sigma F_{hz,s} = -150.5 \ln(z) + 167.0$ $\quad r^2=0.96$

The relationship between horizontal net-fluxes of NH_3 in 0.75, 1.5, 2.25 and 3 m height above the experimental plot as determined by passive flux samplers and the reference method is shown in Fig. 3. There was a strong linear relationship between the horizontal NH_3 flux densities measured by the two methods (Fig. 3, $F^{net}_{flux\ samplers} = 2 + 2.7F^{net}_{ref}$).

Table 1. Horizontal NH_3 fluxes from the experimental plot ($F_{hz,p}$) and from the surroundings ($F_{hz,s}$) as a function of mast and height.

		Flux, µg NH_3-N m^{-2} s^{-1}								Net flux*
		North		East		South		West		ΣF_{hzp}-ΣF_{hzs}
Exp.	Height	$F_{hz,p}$	$F_{hz,s}$	$F_{hz,p}$	$F_{hz,s}$	$F_{hz,p}$	$F_{hz,r}$	$F_{hz,p}$	$F_{hz,s}$	
1	300	0	6.8	13.6	0	17.0	7.7	3.4	11.7	7.8
1	225	2.5	4.9	21.9	5.9	17.6	5.8	0.9	7.7	18.6
1	150	0	11.7	39.5	7.7	24.4	5.9	0	8.3	30.3
1	75	2.5	17.0	92.6	8.3	65.7	4.3	5.9	18.5	118.6
2	300	0	1.5	1.5	0.9	5.7	1.5	1.5	0.9	3.9
2	225	0.9	2.5	3.4	1.5	4.3	1.5	1.5	1.5	3.1
2	150	0	1.5	1.5	0	6.8	0.9	4.3	1.5	8.7
2	75	0.9	1.5	0	1.5	12.7	0.9	7.7	0	17.4
3	300	3.4	6.8	6.8	8.3	17.6	8.3	13.6	9.3	8.7
3	225	10.8	10.8	5.9	4.9	15.1	10.2	20.1	8.3	17.7
3	150	6.8	4.3	4.9	6.8	12.7	5.9	29.3	9.3	27.4
3	75	0.9	10.2	4.9	5.9	22.8	4.9	65.7	11.7	61.6
4	300	15.1	11.7	16.1	4.9	6.8	9.3	8.3	21.0	-0.6
4	225	8.3	10.2	15.1	4.9	6.8	7.7	4.9	9.3	3.0
4	150	10.8	6.8	26.9	8.3	8.3	4.9	10.8	10.2	26.6
4	75	4.9	11.7	48.8	6.8	14.2	6.8	7.7	8.3	42.0
5	300	15.1	18.5	34.6	6.8	12.7	19.4	5.9	9.3	14.3
5	225	11.7	18.5	38.0	16.1	23.5	12.7	4.9	9.3	21.5
5	150	14.2	17.6	56.5	2.5	37.0	14.2	7.7	9.3	71.8
5	75	11.7	13.6	128.1	3.4	112.0	4.9	8.3	10.2	228.0
6	300	13.6	15.1	39.5	7.7	9.3	10.8	5.9	26.9	7.8
6	225	21.0	14.2	54.0	10.8	19.4	15.1	10.2	10.8	53.7
6	150	11.7	24.4	107.7	4.3	14.2	10.8	15.1	29.3	79.9
6	75	16.0	14.2	225.6	10.2	29.3	14.2	3.4	14.2	221.5

* µg NH_3-N m^{-2} s^{-1}

Comparison of horizontal NH_3 fluxes

It is noted that the slope of the regression line should not be 1 because of a difference in the fetch (the stretch the wind passes above the source) between the two methods: The reference method is based on measurements of the horizontal flux in the centre of the experimental plot while the new method is based on measurements of the horizontal flux across the periphery of the plot. The stretch the wind passes above the plot in the new method varies between 2r and 2.83r when α varies between 0° and 45° (see

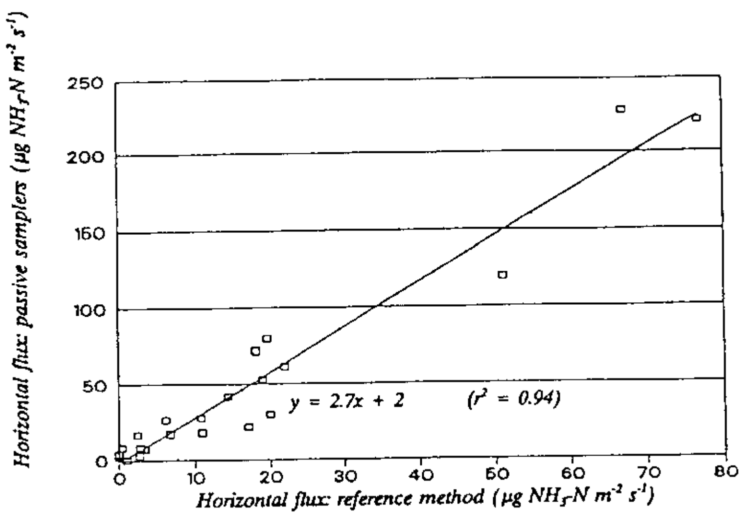


Fig. 3. *Relationship between horizontal flux densities of ammonia measured by a micrometeorological method with a new type of passive flux samplers and a conventional micrometeorological method with acid traps (reference method).*

Fig. 2 and text). However, since the flux is not only proportional to the NH_3 concentration (here assumed to be proportional to the stretch the wind passes above the source) but also to the cosine of the angle between the wind direction and the longitudinal axis of the samplers (Fig. 1) the effective fetch should be equal to 2r (see Fig. 2 and Text). In spite of this fact, the slope of the regression line in Fig. 3 was somewhat higher than 2 (2.7 with a standard deviation of 0.15), while the intercept was not significantly different from 0 (2 with a standard deviation of 2.8). The high slope is mainly due to the results obtained with the flux samplers in 75 cm height in experiments 5 and 6, i.e. the two experiments in which the thickness of the stainless steel disc was reduced to 0.05 mm. Exclusion of these data from the regression analysis reduces the slope to 2.3 ± 0.15. We do not think, however, that the overestimation of the fluxes in Experiments 5 and 6 was due to a systematic error introduced by reducing the thickness of the stainless steel disc. Other things may have been involved. For example, some beakers with NH_4^+ /HCO_3^- solution may have been to close to a flux sampler, thus affecting the results in a non representative way. If a too thick disc is used there may be a risk for a too low air flow inside the glass tubes when the air has to make a bend in the hole as would be the the case when the wind direction is oblique to the axis of the sampler.

Table 2. Mean wind speed, air temperature, air humidity and wind direction 1 m above the soil surface.

Parameter	Experiment					
	1	2	3	4	5	6
Wind speed, m s^{-1}	4.1	1.1	1.9	2.4	3.7	4.3
Air temperature, °C	14.5	4.3	9.6	12.1	17.4	16.3
Air humidity, %	65	70	49	47	72	67
Wind direction	NW	NE	NE	W	NW	W
Initial pH	8.6	8.5	8.6	8.3	8.9	9.1
Final pH	8.0	-	8.4	8.0	8.0	8.2

Comparison of vertical NH_3 flux densities

The results for vertical flux densities of ammonia determined using the passive flux samplers and the reference method is given in Tab. 3. There was a strong linear relationship between the vertical flux densities of ammonia measured by the passive flux samplers and the reference method ($F_{\text{flux samplers}} = 0.6 + 0.97F_{\text{ref}}$, $r^2 = 0.88$).

Amount of ammonia lost from the source

The amount of NH_3 volatilized from the beakers with NH_4^+/HCO_3^- solution varied from 171 mg NH_3-N per beaker in the experiment with lowest NH_3-emission to 3240 mg NH_3-N per beaker in the experiment with the highest NH_3 emission. Expressed per unit land area these NH_3 losses correspond to a NH_3-N flux between 1.1 and 20.0 μg NH_3-N m^{-2} s^{-1} (Tab. 3). The highest losses af NH_3 took place in experiment 6, in which air temperature wind speed, and initial pH were relatively high (Tab. 2). Ammonia volatilization from aqueous solutions increases exponentially with temperature (Vlek and Stumpe 1978). The lost amount of NH_3-N relative to the initial amount of NH_4^+-N in the beakers varied from about 40% in experiment 6 to only 3% in experiment 2.

Table 3. Comparison of vertical NH_3 flux densities as measured by (1) loss of NH_3 from beakers with NH_4^+/HCO_3^- solution, (2) reference method and (3) passive flux samplers.

Exp.	NH_3 loss from beakers $\mu g\ NH_3N\ m^{-2}\ s^{-1}$	Reference method	Passive flux samplers
		Vertical NH_3 flux, $\mu g\ NH_3\text{-}N\ m^{-2}\ s^{-1}$	
1	11.7 ± 0.8	10.8	8.3
2	1.1 ± 0.4	0.6	1.0
3	8.3 ± 0.8	3.1	3.6
4	6.1 ± 0.6	2.2	2.2
5	19.4 ± 1.9	8.6	11.2
6	20 ± 1.4	10.8	11.9

Part of the ammonia lost from the source was absorbed by the soil

The NH_3 emission measured with the two micro-meteorological methods was somewhat smaller than the amount of NH_3 lost from the source. The difference was most likely caused by absorption of NH_3 to the soil surface. The NH_3 absorption was greatest in experiments 2 and 3 which were carried out in spring on a ploughed field with moist soil while experiment 1 was carried out on a stubble field with a relatively dry surface. Closely above the beakers there was a detectable odour of NH_3. This means that the concentration of NH_3 in the air just above the beakers was at least 50 mg m^{-3} (Jones 1973). Calculated on basis of this concentration, a deposition of e.g. 8 $\mu g\ NH_3\text{-}N\ m^{-2}\ s^{-1}$ (difference between 20 and 12 $\mu g\ NH_3\text{-}N\ m^{-2}\ s^{-1}$; Table 3, Exp. 6) would require a deposition velocity of only 0.02 cm s^{-1}. This is a very low value compared to e.g. velocities of 1 to 2 cm s^{-1} measured for dry deposition of NH_3 on vegetation (Duyzer et al. 1987).

4. CONCLUSION

Passive flux samplers can be recommended

The passive flux samplers can be used in a micrometeorological mass balance method to give accurate determinations of the vertical flux density of ammonia from a circular field. The passive flux samplers make pumps, flow meters and anemometers unnecessary and ammonia loss can be determined easily and cheaply without the requirement of large labour force which is needed in the reference method.

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Ammonia Volatilization from Slurry Tanks with Different Surface Coverings

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SUMMARY

Ammonia volatilization losses from slurry tanks was studied during a winter-spring and a summer period. The loss rate was simultaneously measured from eight tanks with a wind-tunnel system, giving a posibility to relate the reduction in ammonia loss by different surface layers. Convective transport of ammonium to the surface layers due to stirring or temperature gradients in the slurry increased ammonia losses substantially. In winter-spring (7.3°C) ammonia losses was half the losses during summer (16.9°C), due to lower temperatures. Surface crustings reduced ammonia losses to 20% of the losses from stirred slurry. In the winter-spring experiment it was shown that a layer of chopped straw (15 cm) could replace a surface crusting layer. Ammonia losses from slurry covered by rape oil, leca stone, sphagnum peat and floating foil was low.

1. INTRODUCTION

mmonia losses reduces the efficiency of manure for plant production

Gaseous loss of ammonia from animal manure reduces the efficiency of the animal manure for plant production. The emission of ammonia from animal manures is the greatest source of atmospheric ammonia in Europe (Buijsman et al., 1987). The deposition of ammonia or ammonium may detrimentally affect nitrogen-limited natural ecosystems (Roelofs, 1986).

Ammonia can be lost by volatilization from stables, manure storages, during appplication of manure, and from applied manure (Kruse et al., 1989, Ryden et al., 1987). It is generally believed that there is no further loss of ammonia after incorporation of manure in the soil.

Little is known about ammonia loss rates from manure storages. In model calculations the losses of ammonia from storage and stables was assumed to be 10% (Buijsman et al., 1987). This figure represents an average of very variable ammonia losses (Ryden et al., 1987; Muck & Steenhuis, 1982).

Knowledge of ammonia losses from slurry storages is needed

More knowledge is needed of ammonia loss from storages under various conditions, to be able to decide wether the losses are of importance or not. The advisory services will then be able to select the cheapest and most effective methods to reduce the ammonia loss.

Ammonia loss from slurry tanks was examined with a wind tunnel system during a winter and a summer period. The effect of different surface coverings was determined simultaneously.

2. MATERIAL AND METHODS

2.1 Treatments

Ammonia volatilization from 8 slurry tanks ($2.6\ m^2$) with different surface coverings was studied

Ammonia losses from slurry tanks with 8 different surface coverings were examined (Table 1). The slurry which was stirred once every week was assumed to be a control having no surface covering. The surface crustings of straw residues on the unstirred slurry were concidered to be one treatment. The other five treatments were surface coverings consisting of respectively raw rapeoil, sphagnum peat, chopped straw, floating foil and lecastone (floating granules of montmorillonitic clay). One slurry tank had a wodden cover.

Table 1. Surface coverings of the slurry and characteristics of the surface crustings.

Surface covering		Surface crusting			
		dec. 1989-june 1990		july-sept. 1990	
Type	Thickness,cm	Thicknes, cm	% DM	Thickness, cm	% DM
Rape oil	0.9	3.5	15.3	1.0-2.0	19.5
Sphagnum peat	9.0	1.0-4.0	11.2	0	0
Stirring, weekly		0.5-1.0*	12.9	0	0
Chopped straw	17.0	0	0	0	0
Surface crusting		0	0	7.0	12.5
Floating foil		0	0	0	0
Leca stone	9.0	0	0	0	0
Wodden lid	2.0	5.0	11.7	0	0

* Crusting was reestablished within one or two days after stirring.

Ammonia losses were measured during a winter-spring and a summer period

The experimental trials in the period from December 1989 to June 1990 and July to September 1990 were concidered to be a winter-spring and a summer experiment, respectively.

During winter-spring no surface crusting layer developed on the unstirred slurry

During the winter-spring experiment no surface crusting developed. Therefore in the summer experiment, material was taken from the crusting layer of the slurry in the tank of the neighbour farm, and spread on the surface of the slurry in the experimental slurry tank.

2.2 Slurry and slurry analysis

TAN content (Total Ammoniacal Nitrogen=ammonium+ammonia) of the slurry was determined by direct distillation of ammonia with MgO, collection of ammonia in boric acid-indicator solution and titration with standard HCl solution. Total-N were analysed using the Kjeldahl method and a Tecator kjeltec Auto 1030 analyzer. Dry matter content (DM) was determined gravimetrically upon oven drying at 80°C and slurry bulk pH with a standard electrode (Radiometer).

Cattle slurry from a neighbour farm was used for the experiments

The slurry was taken from a slurry tank of a neighbour farm in December 1989 and stored in the tank of the experimental station until use. Table two gives characteristics of the cattle slurry and the amount of slurry in the tanks during the two experimental periods. The differences in total-N, TAN and pH, is probably due to microbial activity during the storage period of half a year at the experimental station.

During the experiments total-N and TAN in the unstirred slurry tank was determined 10, 20, 50 and 100 cm below slurry surface. After the experiment total-N and TAN was also determined at 150 cm.

Table 2. Amount of added slurry and characteristics of the cattle slurries.

Experimental period	Amount m^3/tank	Total-N g N/l	TAN* g N/l	pH	Dry matter %
21.12.89- 15.06.90	4.13	5.15	2.47	7.5	5.92
6.07.90 2.09.90	4.00	4.06	2.59	7.7	5.92

2.3 Ammonia loss measurements

Ammonia losses were measured with 8 windtunnels simultaneously

The ammonia losses were measured using a wind-tunnel system like the one described by Lockyer (1984) and Christensen & Sommer (1989). Eight wind-tunnels each consisted of an inverted transparent polycarbonate box-shaped shell (40 cm high, 100 cm wide and 310 cm long), attached to the shell was a circular metal duct (470 cm long and diameter 40 cm), housing a fan driven by an electric powered engine. The rectangular shells was covering each of the eight slurry tanks, which was 90 cm wide , 289 cm long and 165 cm deep (area 2.601 m^2). The metal ducts was equipped with vane anemometer heads measuring wind speed. Two of the metal ducts were equippped with thermocouple sensors. Signals from the sensors were scanned at 1 minute intervals and stored as hourly means on a data logger.

NH_3-concentrations was first measured with an ammonia monitor and later with gas washing

After passing the experimental plot and the vane anemometer, the air stream was sampled in front of the fan through NH_3-impermeable teflonpipes (FEP teflon). From the 1. of February to the 1. of April 1990 the am-bottles

monia concentrations were periodically measured with an ammonia monitor (Thermo Electron Model 14 AA). From the 1. of April 1990 ammonia was trapped in 250 ml absorption flasks fitted with a sintered glass distribution tube through which pumps (ASF 7010 Z) were drawing the air at 4 l/min. The flasks contained 100 ml of 0.01 M H_3PO_4. Ammonia in the air was trapped in the phosphoric acid and subsequently determined colorimetrically by the indophenol reaction.

From 1. of February to 15. of June 1990 ammonia concentrations was measured periodically

During the period 1. of April to 7. of June 1990 there was only one set of gas absorptions flasks and pumps available. Therefore, ammonia loss could only be determined from one slurry tank pr. day. From the 7th of June 1990 ammonia concentrations from all wind-tunnels and the background ammonia concentrations at the inlet of the tunnels were determined simultaneously with nine sets of absorptions flasks and pumps.

The estimated ammonia loss rate did not change the 1. of April 1990, when the ammonia monitor was replaced by gas absorption flasks (Fig. 2). Indicating that the two systems for measuring ammonia concentrations gave similar results.

The ammonia collection period was 24 h during four days after a weekly stirring of the slurry in the tank with no surface covering (Tabel 1), during the rest of the week the ammonia collection period was 72 h.

Background ammonia concentrations was subtracted to give net ammonia losses

For a given period , background ammonia concentrations were subtracted from those obtained for treated plots. Ammonia loss was calculated multiplying the net-ammonia concentration with the air flow and ammonia collection period.

2.4 Meteorological data

Data recorded at the climate station situated 30 m from the slurry tanks were used to provide temperature measurerements for periods of datalogger malfunctions. Air temperature was measured at a height of 20 cm in a standard screen (Olesen, 1988). An intercallibration showed that tunnel temperature was gererally 1-2°C higher than air temperatures measured at a height of 20 cm (Figure 1). Temperatures were not adjusted for the discrepancy.

Air temperatures from a climate station could be used

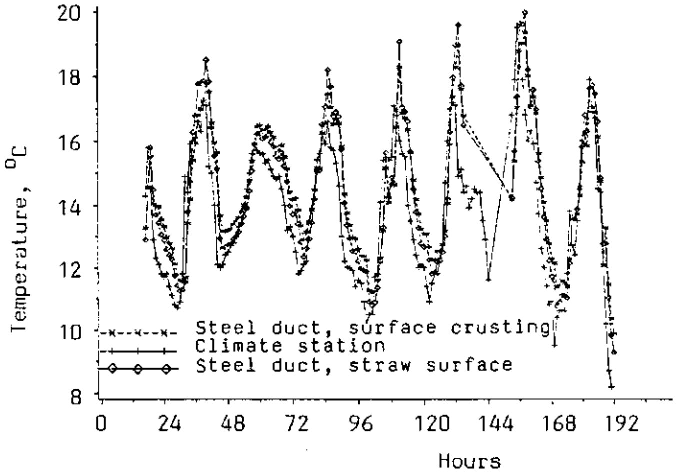

Figure 1. Hourly mean air temperature measured in the metal duct of the wind tunnel covering the straw and untreated slurry and at the climate station (height 20 cm).

3 RESULTS

Air temperatures were 7.3 and 16.9°C during the period of winter-spring and summer, respectively

Mean air temperature was 7.3°C and 16.9°C during the winter-spring and summer, respectively (Table 3). During the winter-spring experiment the mean daily air temperature increased from about 2°C to 14°C. During the summer experiment temperatur increased from about 13°C the 6. of June to 24°C the 12. of July, and decreased to 15°C at the end of the experiment. The measured mean wind speed during the two periods was 3.3 and 3.5 m/s, respectively (Tabel 3).

High ammonia losses were observed due to stirring of the slurry

During the winter-spring period ammonia loss was only measured periodically, the daily ammonia loss rate is therefore presented as a monthly mean. Consequently no peaks in ammonia loss rate can be seen due to stirring of the slurry (Fig. 2). During the summer experiment there was a peak in ammonia loss rate after stirring (Fig. 3). Two to four days after stirring the loss rate had fallen to the values determined the day before stirring took place.

Table 3. Wind speed measured in the metal duct and mean air temperature during the experiments (1 S.D. in brackets).

Experimental period	Wind speed m/s	Air temperature °C
21.12.89- 15.06.90	3.3 (1.2)	7.3* (4.2)
6.07.90 2.09.90	3.5 (0.2)	16.9 (4.2)

*Measured at the climate station (20 cm).

From the tank with surface crusting ammonia loss rate decreased during the summer experiment. In the winter experiment no surface crusting developed and the ammonia loss rate increased during the experimental period.

The seven surface coverings reduced ammonia volatilization

In both experiments surface covering with rape oil, chopped straw, leca stone and sphagnum peat reduced the ammonia loss rate compared to that from stirred slurry (Fig. 2 and 3). The loss rates were more or less constant during the winter-spring experiment (Fig. 2), but decreased during the summer experiment (Fig. 3). The only exception from this pattern was the ammonia loss from the rape oil covering, where loss rate increased during the summer (Fig. 3), due to developping cracs in the rape oil layer. In the summer and winther experiment ammonia loss rates from slurry covered with floating foil and a wodden lid was small.

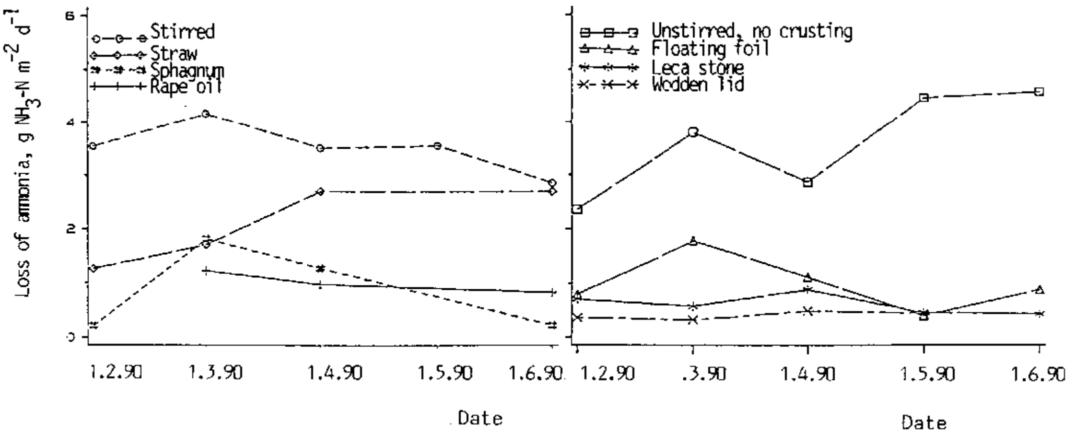

Figure 2. Daily ammonia loss rate from slurry tanks during the winter-spring experiment.

During both experiments the TAN concentrations in the surface layers of the unstirred slurry was smaller than in the bottom layers. One exception was a short period in March 1990 in which TAN concentrations in the surface increased (Fig. 4).

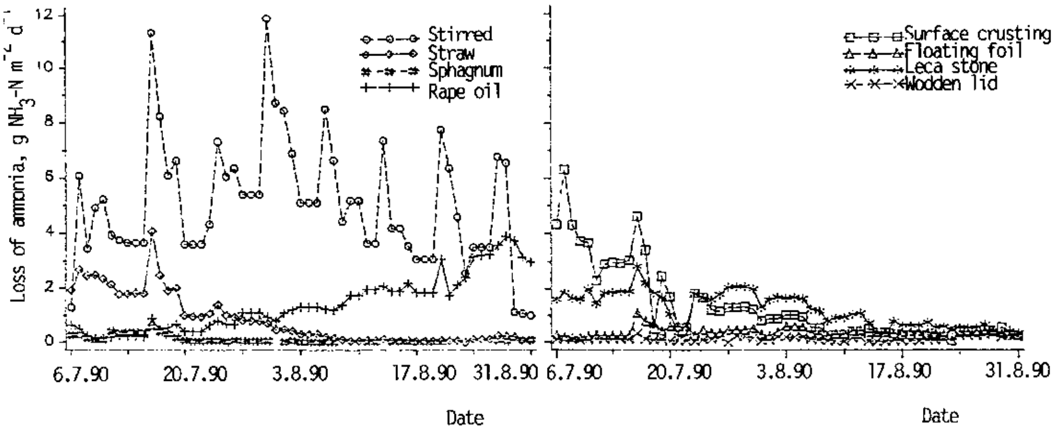

Figure 3. Daily ammonia loss rate from slurry tanks during the summer experiment.

Halfyear ammonia loss rates were calculated

To enable a comparison of the losses during the two experiments, halfyear ammonia loss was calculated (Table 4). The halfyear ammonia loss during the winter-spring expriment was calculated by multiplying the mean daily ammonia loss rate measured from February to June 1990 with 180 days. The daily loss of ammonia seemed to fluctuate around a constant level after 1-1½ month of storage. By calculating the halfyear ammonia loss in a summer period, it was therefore assumed that the average daily loss rate of the last two weeks was an estimate of the daily loss rate for the next four months. From the stirred slurry the losses thus calculated was smallest during the winter-spring experiment (Table 4). From the unstirred slurry with no surface crusting losses was the same as the losses from the stirred slurry. Ammonia losses from slurry with surface treatments was substantially smaller than from the stirred slurry.

4 DISCUSSION

The system was adjusted to relatively high wind speeds to deminish the effect of boundary layers

It was assumed that the ammonia loss rate was unaffected by small differences in wind speed, if the wind speed in the tunnels were high. The main reason for this is that the gas phase resistance (boundary layer) is small at high wind speeds (Sommer et al., 1991). The wind speed in the tunnels were high, and the ammonia loss rate measured in the 8 windtunnels is therefore comparable, even if there was small differences in the wind speed.

Ammonia losses is linear related to TAN concentrations in the surface layers

The rate of ammonia loss depends on the concentration of atmospheric ammonia at the slurry surface. This concentration is linearly related to TAN concentrations in surface of the slurry at constant pH, temperature and wind velocity (Vlek & Stumpe, 1978). Therefore the ammonia loss rate was very high from the stirred slurry (Fig. 2 and 3) as TAN was readily transferred by convection to the surface layer . The stirring of the slurry resulted in a peak in the ammonia loss rate on the day, when the slurry was stirred (Fig. 3). After stirring the period with high ammonia losses will result in a reduction in the TAN concentrations in the surface layers, which will cauce declining ammonia loss rates with time.

Table 4. Accumulated halfyear ammonia loss from 8 slurry tanks with different covering.

Type	Dec. 1989-June 1990		Juli-Sept. 1990	
	kg NH_3-N m^2		kg NH_3-N m^2	
	pr. halfyear	in p.c.*	pr. halfyear	in p.c.*
Stirring, weekly	0.66	100	1.34	100
Surface crusting**	0.63	95	0.24	18
Chopped straw	0.30	45	0.14	10
Rape oil	0.18	27	0.56	42
Leca stone	0.12	18	0.25	19
Sphagnum peat	0.11	17	0.01	1
Floating foil	0.18	27	0.09	7
Wodden lid	0.08	12	0.05	4

* In p. c. of ammonia loss from the stirred slurry.

** During the winter-spring experiment no surface crusting developed.

rom stirred slurry the
alfyear ammonia loss
vere 0.66 and 1.34 kg
H_3-N/m^2 during winter-
spring and summer respec-
ively

In the summer experiment ammonia loss from the stirred slurry was declining throughout the periods, probably due to a decrease in pH and TAN concentrations of the surface layers of the slurry. The halfyear ammonia loss was 0.66 kg NH_3-N/m^2 and 1.34 kg NH_3-N/m^2 in the winter and summer experiment, respectively. Similar ammonia loss rates was found by Bode (1990). From the unstirred slurry with no surface crusting layer ammonia loss was similar to the loss from the stirred slurry. The ammonia loss rate from the unstirred slurry increased in March (Fig. 2). This is partly a result of convective transport of TAN, increasing the TAN concentration in the surface layer (Fig. 4), and partly due to air temperature increasing in March and April 1990 .

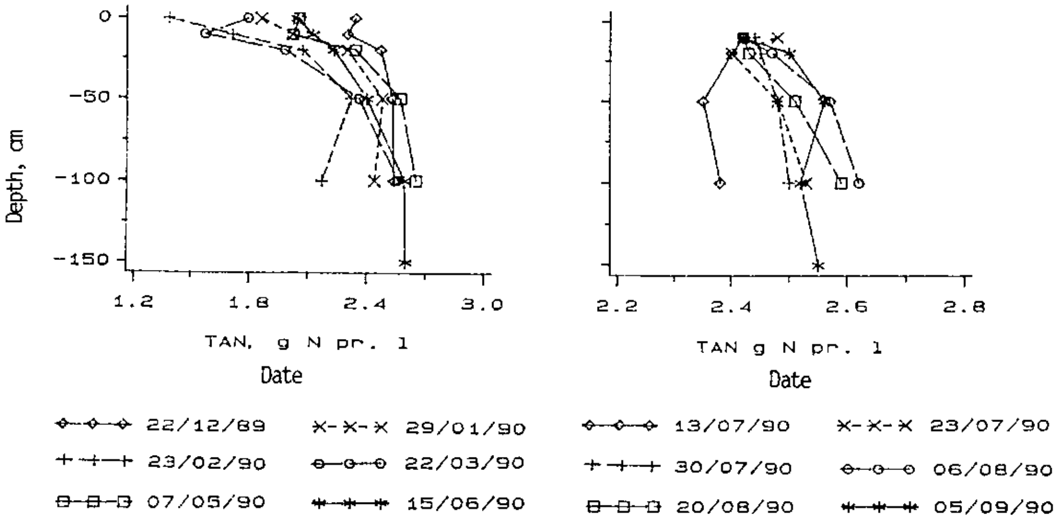

Figure 4. TAN concentration in diffents depth of unstirred slurry with no surface crusting during the winter-spring and summer experiments.

The surface coverings are creating immoveable layers in the air above the slurry and in the surface of the slurry, which is decreasing the ammonia losses

Surface crustings, sphagnum peat, chopped straw and leca stone is creating an immoveable air layer above the slurry surface. Through this layer ammonia has to be transported slowly by diffusion, whereby the concentration of atmospheric ammonia at the slurry surface will increase. High atmospheric ammonia concentrations is limiting the loss of ammonia from the slurry to the air layer above the slurry. Submerged material from the surface layer will limit convective transport in the surface layer of the slurry and TAN must be transported slowly by diffusion to the air-slurry interface (Muck and Steenhuis, 1982). The two diffusion barriers developed in and over the slurry decreased ammonia loss rate to between 1 and 45% of the loss rate from the stirred slurry (Tabel 4). In the study of Bode (1990) the ammonia loss was reduced to 73% whith natural crust formation and 29% from slurry on which crusts formation was improved by mixing chopped straw in the slurry. Natural crust formation was limited in the experiments of Bode (1990), therefore the effect of natural crust was lower than in the present study. From at buttom loaded manure storage, ammonia loss was 3-8% of the nitrogen compared to 29-39% from a top loaded storage due to the effect of diffusion barrieres (Muck et al. 1984).

Bubbles and cracks in the rape oil covering resulted in small ammonia losses

A surface layer of rape oil is reducing ammonia volatilization as TAN is not soluble in oil. Therefore ammonia is not transported through the oil to the air. In the winter-spring experiment gas bubbles, however, penetrated the rape oil covering giving small ammonia loss throughout the period (Fig. 2). In the summer experiment cracks developed in the oil layer as the oil was partly absorbed by the surface crusting and dried out. Therefore ammonia loss rate increased during the experimental period (Fig. 3). The rape oil reduced ammonia loss to 27% of the loss from stirred slurry in winter and 42% in summer.

Ammonia loss from the slurry covered with floating foil and a lid was reduced to between 4 and 27% of the ammonia loss from the stirred slurry. Gas was collected under the floating foil, which therefore was vauled in the center. This resulted in the formation of a slit between the foil and the sides of the slurry tank giving rise to minor losses of ammonia.

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Changes in Nutrient Dynamics in Marginal Agricultural Land

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<u>Résumé.</u>

The changes in nutrient dynamics, with primary reference to nitrogen, was followed over a three year period in marginal farming land. In this field experiment a cropping system was compared to more extensively grown grassland plots, as well as to natural heath-vegetation on undisturbed soils.

It was found that the change from crop rotation to grassland or fallow field did not have any significant effect on the nitrogen mineralisation. Losses due to denitrification was low, - below 1 kg N ha^{-1} $year^{-1}$, whereas the symbiotic nitrogen fixation could contribute significantly to the nitrogen input. In a pure stand of legumes approximately 120 kg N ha^{-1} $year^{-1}$ was fixed.

The change from normal agricultural practice had an almost immediate effect on the leaching of nitrogen from the root zone. The leaching declined from 50 - 60 kg N ha^{-1} $year^{-1}$ to only 8 kg N ha^{-1} in the fertilised grazed plot and to less than 5 kg N ha^{-1} in the uncultivated green fallow plot.

The decline in nitrogen leaching could be measured to a depth of 3 m at St. Lyngby and to 9 m at Rabis. The concentration of nitrate under grass dropped from 35 - 8 mg NO_3-N l^{-1} during the measuring period.

The leaching of PO_4-P showed the same trends as in the case of nitrogen. The change to grassland reduced the leaching of P to about 1/10 during the investigation period.

1. Introduction.

From experiments performed at experimental farms, where the experimental conditions are well controlled, a relatively good knowledge exsists about leaching of nitrogen from agricultural soils. In case of actual agricultural practices, only few studies have been carried out to asses the leaching of nitrogen. Similarly, very few investigations have been carried out on extensively grown soils and on marginal farming land.

The purpose of this investigation was primarily to follow the leaching of nitrogen and other nutrients in sandy soils which immediately before the start of this project were taken out of the normal agricultural practice. For comparison, measurements were carried out also in a field, which was still managed in a traditional way, and in a reference soil with a natural Calluna-vegetation only recieving nutrients through precipitation.

2. Materials and methods.

2.1. Localities.

Five localities, all on sandy soils, were selected for the experiments (Fig. 1).

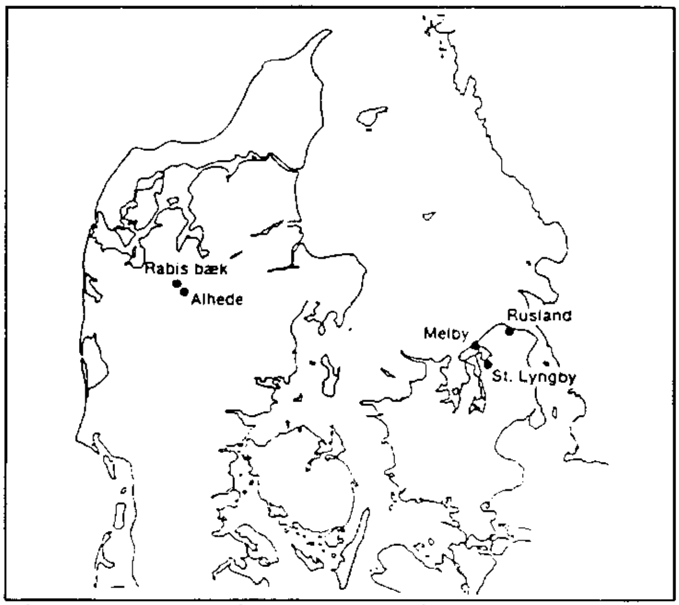

Figure 1. Location of experimental areas.

2.2. Management.

Alhede and Melby are two localities which have not been used for agricultural purposes, and at both places the vegetation was dominated by heather (Calluna vulgaris L.).

Rusland was taken out of agriculture in 1945, and the vegetation was dominated by grasses, lichenes and bushes (Sarothamnus scoparius L.).

Rabis and St. Lyngby were both agricultural land until 1987, when the soils were sown with a mixture of grasses and yellow medick (Medicago lupulina L.). The St. Lyngby locality was studied more intensively than the others, and the following treatments were established:

- black fallow,
- green fallow,
- unfertilised and grazed,
- fertilised and grazed

- traditional agricultural practice.

2.3. Measurements.

At the locality at St. Lyngby, which was studied more intensively than the others, a number of different measurements and analyses were conducted.

Developments in the vegetation after sowing the grass/legume-mixture was followed by measuring the plant biomass. The plant material from the biomass measurements was divided into two fractions: leguminous plants and non-leguminous plants.

The microbial cycle of nitrogen in the upper layer (0 - 20 cm) of the soil was studied by measuring the biological nitrogen fixation, N-mineralisation, nitrification and denitrification. The nitrogen fixation was measured using the acetylene reduction teqhnique. In the presence of the enzyme nitrogenase acetylene (C_2H_2) is reduced to ethylene (C_2H_4), which can be measured on gaschromatograph.

Denitrification was measured using the acetylene inhibition method. In the presence of acetylen the reduction of N_2O to N_2 is inhibited, and the production of N_2O represents the total denitrification.

N-mineralisation and nitrification in the upper 20 cm soil was measured using the so-called in situ method, where also the plant uptake plus N-leaching from the upper 20 cm soil layer is measured (Debosz and Vinther, 1989).

Different equipments were installed to collect precipitation and soil water (Fig. 2). Series of suction cups (teflon) as well as lysimeters with a diameter of 20 cm were installed under the root zone at a depth of 90 cm. Soil water from the suction cups and per-

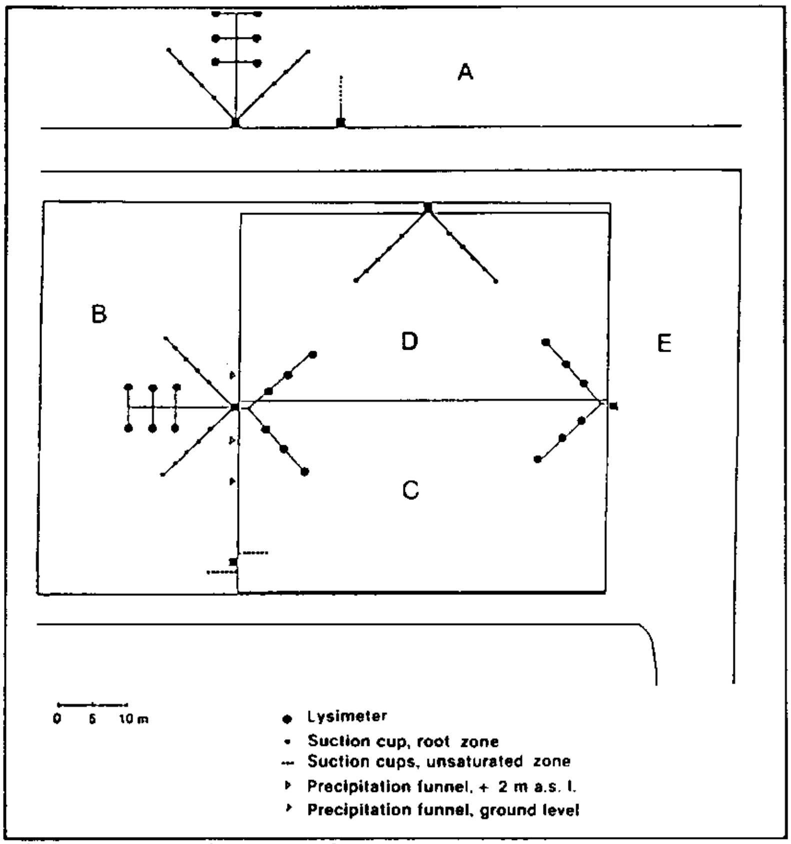

Figure 2. Equipments installed at St. Lyngby. A = crop rotation, B = green fallow, C = unfertilised and grazed, D = fertilised and grazed, E = black fallow.

colates from the lysimeters were collected through plastic tubes. Three series of suction cups (teflon) were installed in the unsaturated zone at depths until 9 m. These cups were exposed to a low pressure from a vacuum pump, so that soil water was collected continuously. The soil water and percolates were analysed for pH, NO_3-N, NH_4-N, dissolved inorganic P, total P, Cl^-, SO_4^-, Na^{++}, K^+, Ca^{++} and Mg^{++}.

For further details on measurements, see Christensen et al. (1990).

2.4. Water balance.

A water balance model EVACROP was used in order to calculate the leaching of nitrogen and phosphorous. EVACROP calculates actual evaporation from the root zone and infiltration at the depth of 1 m (Olesen & Heidmann, 1990). Input parameters for the model are daily values of global radiation, temperature and precipitation. Leaching from the root zone is based on calculations with EVACROP and ion concentrations in soil water isolated with suction cups (St. Lyngby) or percolate (Melby, Rusland and Rabis).

3. Results.

3.1. Microbial N-transformation in the root zone.

In the period from August 1987 to August 1988 the in situ method was used on the fallow treatment. The area was ploughed in the spring 1987, and the vegetation was very

Tabel 1. N-mineralisation, nitrification and plant uptake + leaching from the upper 20 cm soil layer, kg N ha^{-1}.

	Black fallow	Green fallow	Crop rotation
	Aug. 1987 - Aug. 1988		
N-mineralisation	85	58	
Nitrification	71	38	
Plant + uptake leaching.	85	42	
		May 1988 - May 1990	
N-mineralisation		128	199
Nitrification		94	207
Plant uptake + leaching		131	286

sparse during the first year. Therefore it isassumed that most of the nitrogen mineralised during this period (Table 1) has been leached below the measuring depth (20 cm) and further down under the root zone. Unfortunately, no measurements of the actual leach-ing took place in this plot.

Losses of nitrogen from the upper soil layer due to denitrification was found to be negligible, - less than 1 kg N ha^{-1} $year^{-1}$.

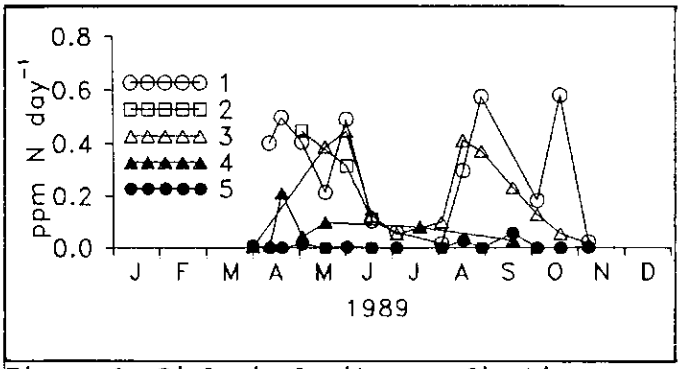

Figure 3. Biological nitrogen fixation activity. 1 = mostly legumenous plants, 5 = no legumes.

The biological nitrogen fixation was estimated from measurements of the nitrogenase activity in samples with varying amounts of leguminous plants (Fig. 3), combined with measurements of the relative distribution of leguminous plant biomass. In a pure stand of legumes approximately 120 kg N ha^{-1} was fixed anually from the atmosphere, whereas only 1 - 2 kg N ha^{-1} was fixed by free living bacteria. The number of legumes in the field was greatly affected by the treatments (Table 2).

The highest legume plant biomass was found in the unfertilised treatment, where sheep kept the competing grasses down. Based on measurements of the acetylene reduction (Fig. 3) and on the distribution of legumes (Table 2), the biological nitrogen fixation in 1988 was estimated to 37, 39 and 30 kg N ha^{-1} in the green fallow, unfertilised grazed and fertilised grazed plots respectively. The corresponding figures in 1989 was 6, 18 and 7 kg N ha^{-1}.

Table 2. Relative distribution of legumes.

Date	Green fallow	Unfertilised and grazed	Fertilised and grazed
June 1988	46	46	58
Aug 1988	13	27	13
Sept 1989	0	25	1
Jan 1990	3	40	1

3.2. Nitrate concentration in the root zone.

The change from normal agricultural practice to permanent grass had an almost immediate effect on the concentration of NO_3-N in the root zone (Fig. 4).
Already in the first winter after the sowing of the grass the NO_3-concentration dropped to about 1 ppm or 1/10 of the concentration in the agricultural field. The NO_3-concentration in the test field which recieved fertiliser and was grazed by sheep was measured only in the period from September 1989 to April 1990. Here the concentration was around 5 ppm which means that the grass was not able to take up all the added nitrogen.

3.3. Leaching from the root zone.

Based on calculations with the water balance model EVACROP and on nitrate concentrations in soil water measured with suction cups (Fig. 4) leaching of nitrogen from the root

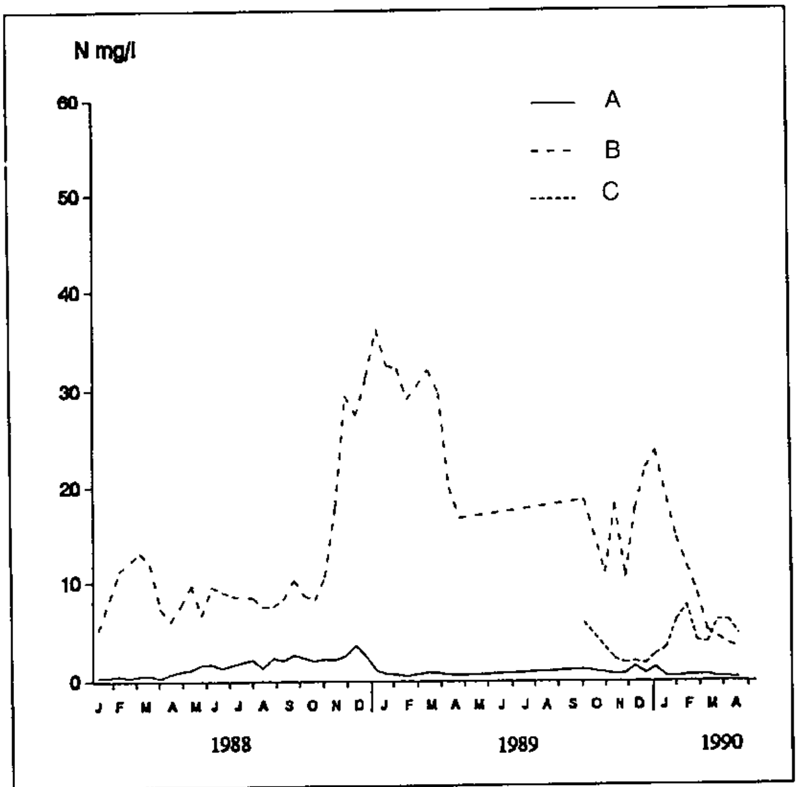

Figure 4. NO3-N-koncentration at the depth of 90 cm in St. Lyngby. A = green fallow, B = crop rotation and C = fertilised and grazed.

zone is calculated and shown in Fig. 5. In both winter periods the mean temperature was above normal. The winter of 88/89 was rather dry with a net precipitation of 206 mm, whereas the winter of 89/90 was wet with a net precipitation of 277 mm.

In spite of the high infiltration in 89/90, the leaching was only 44 kg N ha^{-1}, compared to 60 kg N ha^{-1} in 88/89. One explanation of this discrepancy could be that the growing season of 1988 was very dry with drought symptoms in the barley. Under these conditions the crop was not able to take up nitrogen, and the nitrogen left in the soil during the summer and early autumn was leached out

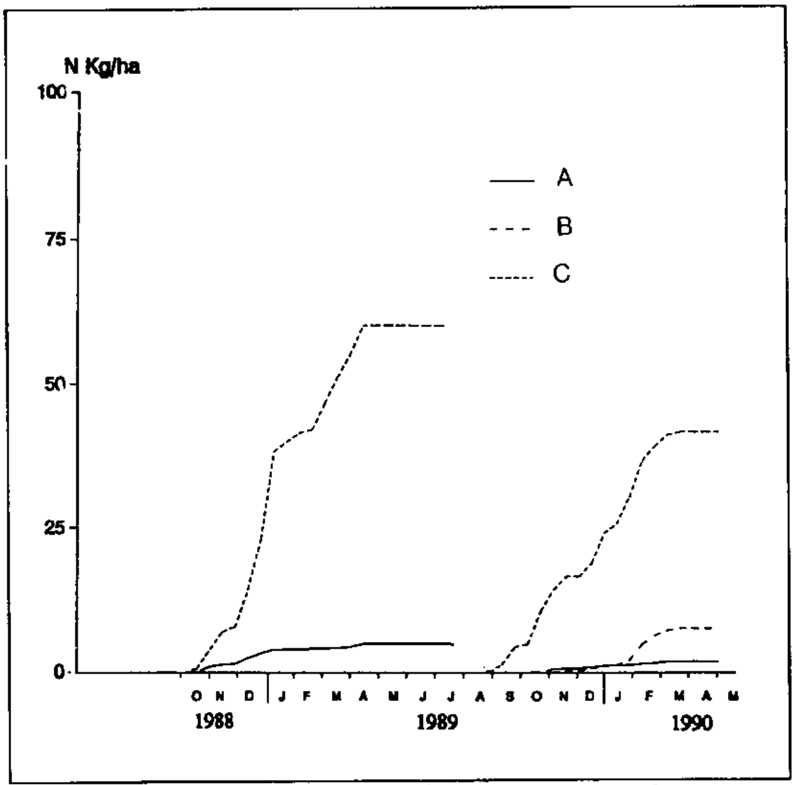

Figure 5. Accumulated leaching of NO_3-N and NH_4-N at St. Lyngby. A = green fallow, B = fertilised and grazed, C = crop rotation.

during the late autumn.

In 1989 the fertilised grass recieved 200 kg N ha^{-1} as calcium-ammonium-nitrate and only 8 kg N ha^{-1} was leached out during the following winter.

The leaching of nitrogen from the root zone at Melby, Rusland and Rabis (Fig. 6) was very low with maximum values of 5 kg N ha^{-1} $year^{-1}$.

The leaching of PO_4-P shows the same trends as in the case of nitrogen. Sowing of grass reduced the leaching of P to about 1/10 during the investigation period. Only the agricultural field recieved P, as NPK, during this period, namely 34 kg ha^{-1} in 1989 and 18 kg ha^{-1} in 1990.

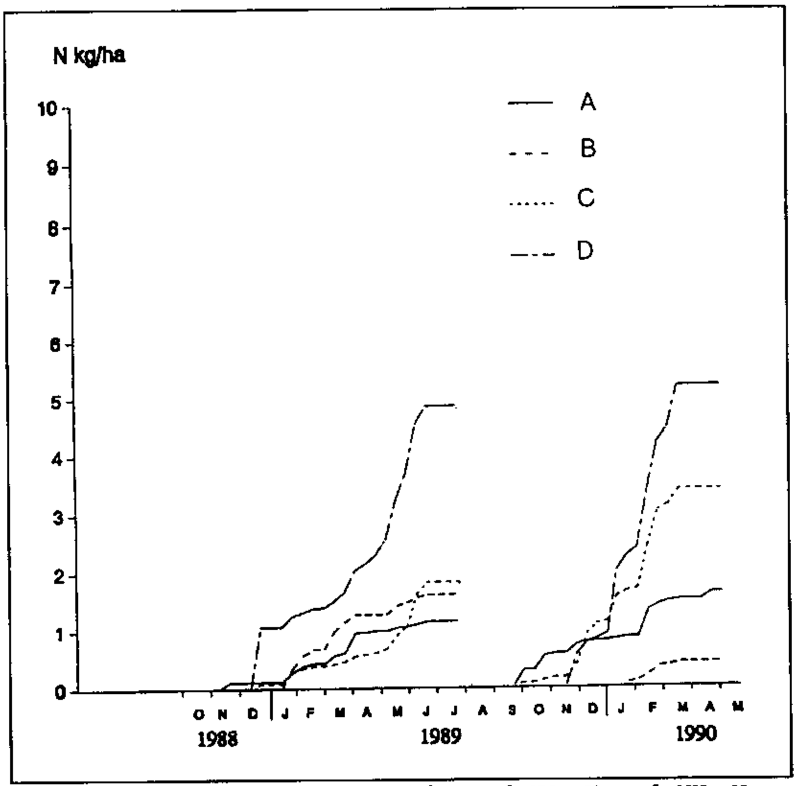

Figure 6. Accumulated leaching of NO_3-N and NH_4-N at Melby (A), Rusland (B), Alhede (C) and Rabis (D).

3.4. Leaching to groundwater.

Measurements of nitrate concentrations under the root zone at St. Lyngby and at Rabis started about one and a half year after the grass was sown. By then the grass was well established and had decreased the nitrate concentration in the root zone considerably at St. Lyngby (see previous chapters). During the investigation period these effects could be seen also at greater depths (Fig. 8). About one year after establishment of the grass the nitrate concentration had reached a

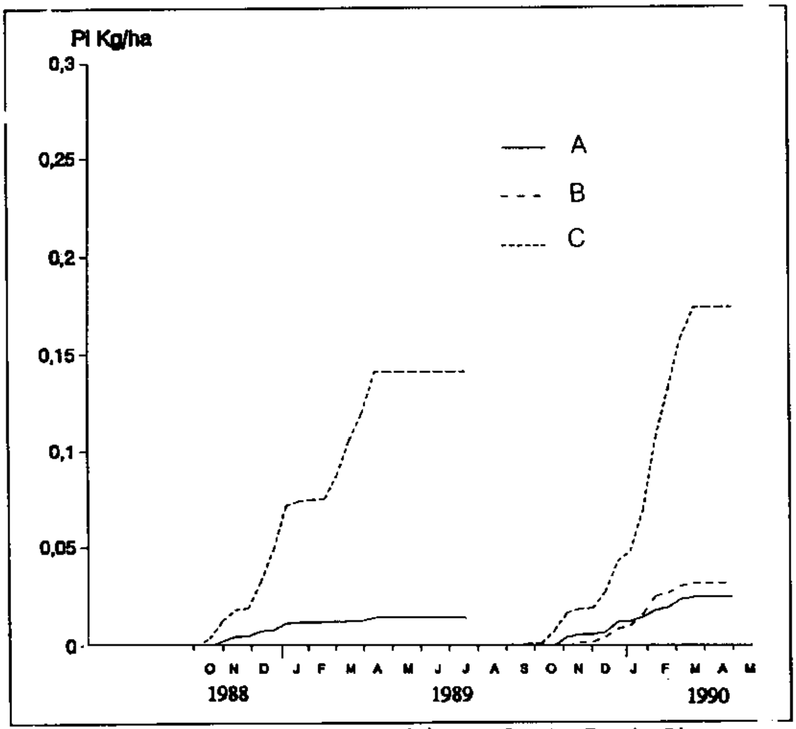

Figure 7. Accumulated leaching of PO_4-P at St. Lyngby. A = green fallow, B = fertilized and grazed, C = crop rotation.

low level at 0.9 and 1.9 m. At 2.9 m the effect of the grass could be followed during the measuring period where the concentration dropped from 35 to 8 mg NO_3-N l^{-1}. At greater depths the concentration was not affected during the period.

At the Rabis locality the concentration of nitrate was decreasing generally throughout the measuring period (Fig. 9). Still one and a half year after the sowing of the grass a relatively high concentration of nitrate was measured in the depth of 2 m, but already during the winter of 88/89 this concentration was reduced to about half the amount. Also at 3 m the nitrate concentration was relatively high, and mainly, it was the leaching of this nitrate which caused a significant increase in the nitrate concentration at 5 m in April 1988.

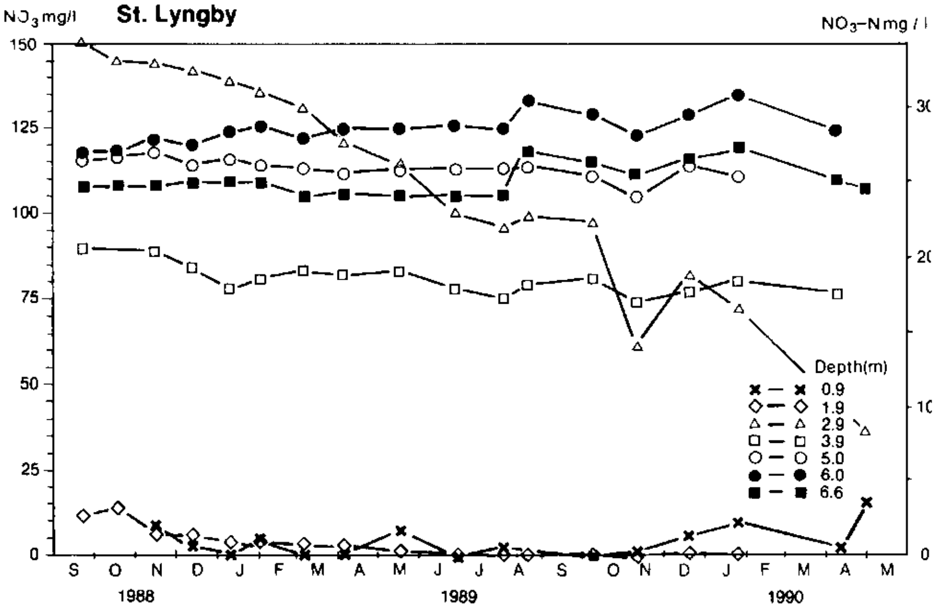

Figure 8. Concentrations of NO_3-N at different depths under green fallow at St. Lyngby.

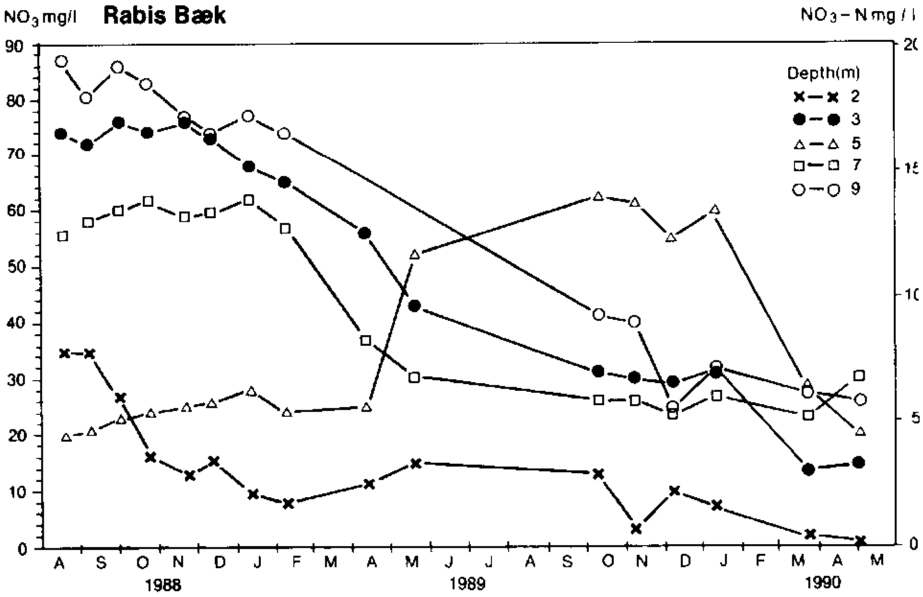

Figure 9. Concentration of NO_3-N at different depths under green fallow at Rabis.

4. Discussion and conclusions.

Measurements of the microbial nitrogen transformation in the upper soil layer (0 - 20 cm) showed that neither the change from a crop rotation to fallow nor the change to grassland had any significant effect on the nitrogen mineralisation. Approximately 100 kg N ha^{-1} was mineralised annually. Evidence of underestimation of the nitrogen mineralisation when using the in situ technique in plant covered fields has been discussed (Debosz & Vinther, 1989). Losses of nitrogen due to denitrification was found to be very low, less than 1 kg N ha-1 year-1. This is in accordance with field measurements on other Danish coarse sandy soils (Andersen et al., 1983; Lind et al., 1990; Jacobsen & Vinther, 1990).

Input of nitrogen through symbiotic nitrogen fixation can be considerable depending on the amount of leguminous plants in the field. In the present investigation it was found that approximately 120 kg N ha^{-1} was fixed annually in a pure stand of yellow medick compared to less than 2 kg N ha^{-1} where no legumes were present. These results correspond fairly well with earlier reports where LaRue & Patterson (1981) estimated the nitrogen fixation in a clover-crop in North Ireland to be 268 kg N^{-1} $year^{-1}$, Frame & Newbold (1986) found 74 - 280 kg N ha^{-1} $year^{-1}$ in a clover crop in Great Britain, and Wivstad et al. (1987) found 242-319 kg N ha^{-1} $year^{-1}$ in an alfalfa-crop in Sweden.

The leaching of nitrogen from natural ecosystems have been measured only in few investigations. In a forest in Western Denmark Bille-Hansen & Hovman (1989) found a leaching of 0.5 to 1 kg N ha^{-1} $year^{-1}$. Matzner & Ulrich

(1980) found that 2 kg N ha^{-1} $year^{-1}$ was leached from a heath area in Germany, which corresponds very well to the 2-3 kg N ha^{-1} $year^{-1}$ found in the present investigation.
In a lysimeter experiment Søegaard (1988) found N-leaching from a grass and clover-grass crop ranging from 8 - 56 kg N ha^{-1} $year^{-1}$. In a coarse sandy soil Simmelsgaard (1985) measured 45 kg N ha^{-1} $year^{-1}$ leached under a grass crop. In the present investigation a change from crop rotation to permanent grass reduced the leaching from 45-60 kg N ha^{-1} $year^{-1}$ to 2-5 kg N ha^{-1} in the unfertilised grass. Even after application of 200 kg N ha^{-1} $year^{-1}$, only 8 kg N ha^{-1} was leached.
This immediate reduction in the N-leaching as a result of changing from crop rotation to permanent grass could be registered in the deeper soil layers as well. Three years after changing the agricultural practice(May 1990), the nitrate concentration had dropped to below 10 mg NO_3-N l^{-1} at all depths at Rabis. In the beginning of the period (Aug. 1988) the concentration at 9 m's depth was 20 mg NO_3-N l^{-1}.
In the plot still under cultivation at St. Lyngby, a rather low nitrate concentration was measured at 7.7 m's depth. Whether this was due to nitrate reduction (chemical or microbial) or to other factors could not be demonstrated in the present investigation.

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Ammonia Emission from Barley Plants
Field investigations 1989 and 1990

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ABSTRACT

The exchange of ammonia between the atmosphere and the canopy of spring barley crops growing at three levels of nitrogen application was studied for two years by use of micrometeorological techniques. Ammonia was volatilized from the aerial plant parts in the period between ear emergence and maturity. The volatilization took place in the daytime, not in the nighttime. The total loss of NH_3 amounted in both years to ½-1½ kg NH_3-N ha^{-1}.

The experimental years were characterized by very favorable conditions for grain dry matter formation and for reutilization of nitrogen mobilized from leaves and stems. Consequently, a very high part of the nitrogen in the mature plants was located in grain dry matter (80-84% in 1989; 74-80% in 1990). The efficient reutilization of nitrogen may have reduced the volatilization of ammonia.

1. INTRODUCTION

Background for research on ammonia volatilization from plants

Results from field experiments 1982-1984 with barley showed that 5 to 40 kg nitrogen ha^{-1} was lost from the aerial plant parts in the period between ear emergence and maturity (Schjørring et al. 1989). The greatest losses of nitrogen had taken place from plants with a low nitrogen harvest index (ratio between grain-N content and total plant-N content at maturity). It was suggested that the losses were partly due to nitrogen volatilization from the shoots.

Volatilization of ammonia from plant surfaces has been demonstrated in growth chamber experiments (Farquhar et al. 1980, O'Deen & Porter 1986, Parton et al. 1988, Schjørring 1990). Under field conditions, Harper et al. (1987) found a total loss of about 15 kg NH_3-N ha^{-1} from a wheat crop.

Ammonia volatilization from plants is measured under field conditions in Denmark

The objective of the present experiments were:

- to investigate the exchange of ammonia between barley crops and the atmosphere.
- to relate the ammonia exchange to the rate of nitrogen application and the dynamics of nitrogen in the plants.

2. MATERIALS AND METHODS

2.1 Experimental area

Experimental area and treatments

The experimental area was located on a morainic sandy loam just outside Copenhagen, Denmark. Spring barley (Hordeum vulgare L. cv. Corgi) was grown at three levels of nitrogen (NH_4NO_3) application: 40 kg N ha^{-1} (low), 120 kg N ha^{-1} (optimum) and 160 kg N ha^{-1} (high). In each nitrogen level, 4 replicates of 4 m^2 micro plots were treated with ^{15}N-enriched fertilizer (about 5% as $^{15}NH_4{}^{15}NO_3$) in order to follow uptake and translocation of fertilizer derived N in the plants.

2.2 Measurements of NH_3 emission

Micrometeorological methods do not affect the microclimate

The exchange of ammonia between a plant canopy and the atmosphere is most conveniently studied by use of micrometeorological techniques because these do not disturb the microclimate in the crop (Denmead 1983).

Description of method used in 1989 (aerodynamic method)

In 1989 the measurements of ammonia emission were based on determinations of equilibrium profiles of windspeed and NH_3-concentration in the atmospheric surface layer above the crop (aerodynamic method). The experimental area consisted of three separate fields with from 0.8 to 3.5 ha. Windspeed, temperature and NH_3-concentration were measured at six heights above the crop canopy and at 2 heights within the canopy. Corrections of windspeed and NH_3-concentration profiles for thermic instability were carried out according to Paulson (1970). The vertical ammonia flux, F_v (μg NH_3-N m^{-2} s^{-1}) above the exchange surface was calculated as:

$$F_v \hat{=} k^2 \alpha c^* \qquad (1)$$

where k = von Karmans constant (0.40), α = slope of the corrected logarithmic windspeed profile (m s^{-1}), and c^* = slope of the corrected logarithmic NH_3-concentration profile (μg NH_3-N m^{-3}).

Description of method used in 1990 (mass balance method)

The requirement of extensive land areas could not be accomplished in 1990. Therefore, a mass balance method was used instead of the aerodynamic method. In the mass balance technique, the vertical NH_3-flux is calculated from differences in the amount of ammonia transported across the windward boundary and the centre of an experimental area.

The experimental plots were established as circles with a radius of 25 m and a mutual distance of 30 m in a field of 3.5 ha. Nitrogen was not applied to the barley plants growing between the circles. Windspeed and NH_3-concentration were measured in 8 heights in the centre of the circles and in 3 heights at the windward boundary. The vertical ammonia flux, F_v was calculated as (Ryden & McNeill 1984):

$$F_v \hat{=} \frac{1}{x} \int_{z_o}^{z_p} (\overline{uc} - \overline{uc_b}) dz \tag{2}$$

where x = radius of the experimental circle (m), u = windspeed (m s^{-1}), c = atmospheric ammonia concentration in the centre (μg NH_3-N m^{-3}), c_b= ammonia concentration at the windward boundary (μg NH_3-N m^{-3}), z = height above zero plane displacement (m), z_p= height at which c equals c_b (m), z_o= height at which windspeed falls to zero (m).

Atmospheric NH_3-concentration

The atmospheric NH_3-concentration in the different heights in and above the crop canopy was measured by drawing air through 250 ml Drechsel gas washing bottles containing 100 ml of 0.05 M H_2SO_4. The air flow through each trap was 8 l min^{-1}. After a given period of measurement (typically 9^{00}-18^{00}), the ammonia concentration in the H_2SO_4-solution was determined spectrophotometrically.

No ammonia emission from the soil surface

The eventuality of ammonia emission from the soil surface was checked by placing small beakers containg a NH_3 absorbing liquid (ammoniumnickelsulphate with 5 ppm methyl red) on the soil surface. The beakers were placed underneath an overturned plastic pot pressed 1 cm down into the soil. After 4 days, the content of NH_3 was determined by titration. Ammonia was not in any case liberated in detectable amounts from the soil surface.

2.3 Sampling of plant material

Crop nitrogen dynamics

Plants were harvested twice each week throughout the experimental period. After the plants were cut off they were put into a cooling bag and quickly transported to a cold store (4°C) where they were subsampled and divided into the following 7 fractions: ear, flag leaf, two upper leaves, two middle leaves, lower leaves, stems and shoots without ears. These fractions were subsequently analysed for nitrate, ammonium, amides, amino acids and total nitrogen in order to relate the ammonia exchange to the nitrogen dynamics in the plants. Furthermore, the activity of glutamine synthetase and glutamate synthase, two key enzymes in the nitrogen metabolism, was determined in some of the fractions.

Analysis of plant material

The plants not divided into fractions were used for determination of the time course of dry matter yield and total crop N content. Inside the micro-plots applied ^{15}N-labelled fertilizer, 15 plants were taken at each sampling time. Only data for total-N content and ^{15}N-enrichment are included in the present paper. Total-N was determined by a Carlo Erba EA 1108 elementary analyzer and ^{15}N by a mass spectrometer (Tracermass Stable Isotope Analyzer, Europa Scientific).

3. RESULTS

3.1 Ammonia emission 1989

Ammonia volatilization took place about and after ear emergence

Ammonia emission during the day period is shown in Fig. 1. The NH_3-emission started during stem elongation (early in June, about 40 days after seedling emergence). The highest values for NH_3 emission were measured about and after ear emergence, which took place in the last part of june (58 to 65 days after seedling emergence). This period coincides with senescence-induced protein degradation and intensive nitrogen re-mobilization from the vegetative plant parts (leaves and stem). The NH_3 emission declined during the end of the grain filling period as the plants reached full maturity. On some occasions, plants in the 40 N and 120 N treatments, but not plants in the 160 N treatment, apparently absorbed ammonia from the air (negative emissions in Figs 1). During the night period, no ammonia was emitted (Fig. 2).

No ammonia emission during nighttine

The total loss of ammonia amounted to ½ - 1½ kg NH_3-N ha^{-1}

The total amount of ammonia lost from the aerial plant parts in 1989 was ½ to 1½ kg NH_3-N ha^{-1} (Table 1). Plants in the high-N treatment (160 kg N ha^{-1}) lost most ammonia. The grain yield was not significantly different at the three levels of nitrogen application while grain protein content (grain nitrogen x 6.25) increased with increasing rate of nitrogen application (Table 1). About 80% of the nitrogen content of the mature plants was present in grain dry matter. This is a quite high nitrogen harvest index (Table 1).

High grain yield and nitrogen harvest index

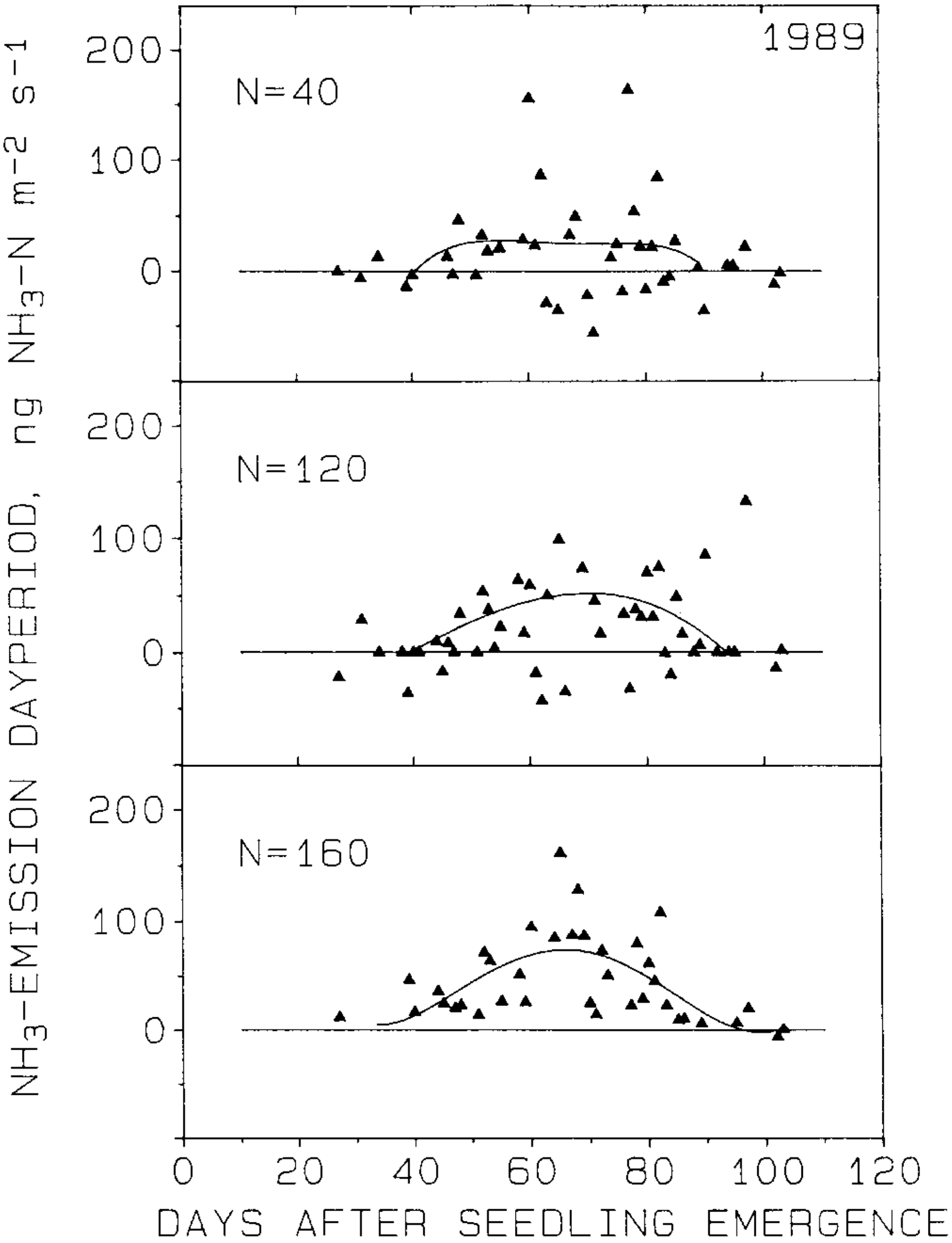

Figure 1. Daytime ammonia emission from the canopy of barley crops growing at three different levels of nitrogen application (40, 120 and 160 kg N ha^{-1}, respectively) in 1989. Curves show 4th order polynomia fitted to the experimental data by minimizing least squares deviation. Ear emergence took place between 58 and 65 days after seedling emergence.

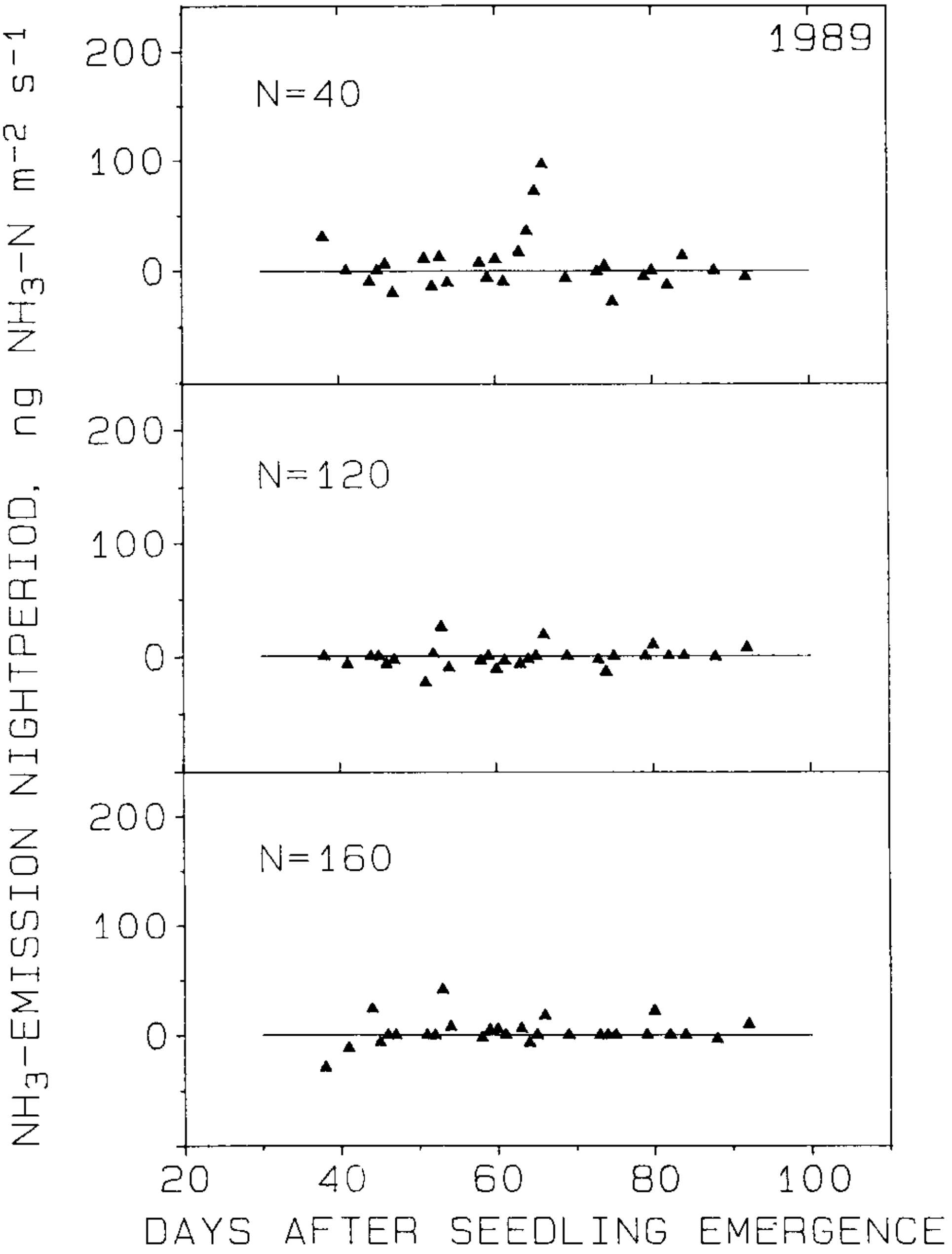

Figure 2. Nighttime ammonia emission from the canopy of barley crops growing at three different levels of nitrogen application (40, 120 and 160 kg N ha^{-1}, respectively) in 1989. Ear emergence took place between 58 and 65 days after seedling emergence.

No loss of ^{15}N-labelled nitrogen

In accordance with the small losses of ammonia measured in 1989, no losses of fertilizer derived nitrogen (^{15}N-labelled) from the aerial plant parts were observed in the period between ear emergence and maturity (Fig. 3).

Table 1. Total ammonia loss, nitrogen harvest index, grain yield and grain protein content of spring barley applied 40, 120 and 160 kg N ha^{-1}, respectively, in 1989. Data for nitrogen harvest index, grain yield, and grain protein content are mean values ± 95% confidence limits (n = 8). Ammonia loss was calculated by integration of 4th order polynomia fitted to the experimental data by minimizing least squares deviation (Fig. 1).

	Nitrogen application (kg ha^{-1})		
	40 N	120 N	160 N
Ammonia loss (kg NH_3-N ha^{-1})	0.6	0.7	1.3
Nitrogen harvest index (%)	84 ± 2	80 ± 3	80 ± 3
Grain yield* (hkg ha^{-1})	64 ± 5	62 ± 7	63 ± 8
Grain protein content (%)	9.8 ±0.5	12.6 ±1.1	13.7 ±0.8

* 15% water content

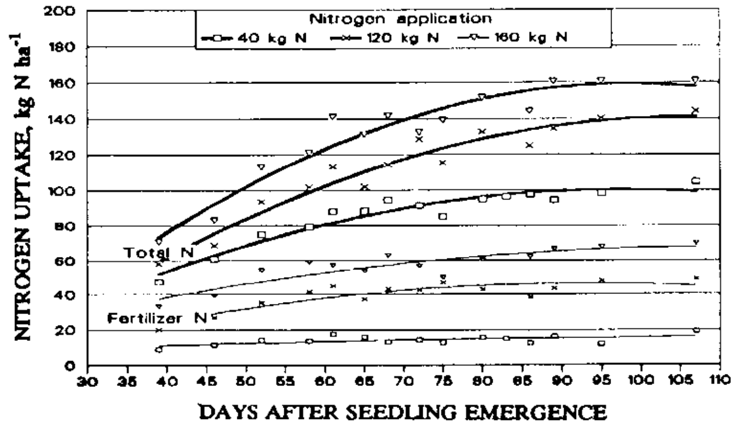

Figure 3. Time course of total nitrogen uptake and of fertilizer derived nitrogen (^{15}N-labelled) uptake in barley growing at 3 levels of nitrogen application in 1989.

High atmospheric NH_3 concentration within the high-N canopies

Mean values of the atmospheric NH_3 concentration in different heights within and above the crop canopy during the period between ear emergence and end of grain filling are given in Table 2. In the treatments receiving 120 and 160 kg N ha^{-1}, the mean NH_3 concentration within the crop canopy was significantly ($P = 0.05$) higher than the NH_3 concentration above the canopy. Since ammonia was not in any case released from the soil, the rise in atmospheric NH_3 concentration within the crop canopy must have been due to ammonia released from the plant surfaces. The mean atmospheric NH_3 concentration in the 120 and 160 N canopy was also higher than that within the 40 N canopy (Table 2).

Table 2. Mean atmospheric ammonia concentrations (µg NH_3-N m^{-3} air) in 2 heights above and 2 heights within the crop canopy in 1989. Mean values ± 95% confidence limits for the period between June the 23rd and July the 15th (62 to 85 days after germination).

Height above soil surface*	Nitrogen application (kg ha^{-1}) 40 N	120 N	160 N
250 cm	1.5 ± 0.6	1.8 ± 0.5	2.0 ± 0.7
150 cm	1.8 ± 0.6	1.7 ± 0.5	2.0 ± 0.6
35 cm	1.9 ± 0.6	2.8 ± 0.9	2.8 ± 0.6
15 cm	1.5 ± 0.7	3.9 ± 0.8	3.9 ± 0.8

* Canopy height was ca. 70 cm

3.2 Ammonia emission 1990

Lower ammonia losses in 1990 than in 1989

Ammonia emissions in 1990 were lower than those in 1989 (compare Tabs 1 and 3). Plants applied 120 kg N ha^{-1} lost most ammonia in 1990 (Table 3). The plant stand in the 160 kg N ha^{-1} treatment developed rather heterogenous. This may explain the lower grain yield in this nitrogen treatment compared to the 120 kg N ha^{-1} treatment. The heterogenous plant stand may also to some extent be the reason for the very small ammonia emission observed at 160 kg N ha^{-1}. Nitrogen harvest indexes were 3-6% lower in 1990 than in 1989. This was mainly due to a slightly lower grain protein content in 1990 than in 1989 (compare Tabs 1 and 3). The nitrogen harvest index decreased with increasing rate of nitrogen application.

Just as in 1989, ammonia only volatilized during the day period in 1990 (Figs 4 and 5). The highest rates of ammonia emission were observed around the time of ear emergence and later on in the grain filling period (fig. 4).

Table 3. Total ammonia loss, nitrogen harvest index, grain yield and grain protein content of spring barley applied 40, 120 and 160 kg N ha^{-1}, respectively, in 1990. Data for nitrogen harvest index, grain yield, and grain protein content are mean values ± 95% confidence limits (n = 8). Ammonia loss was calculated by integration of 4th order polynomia fitted to the experimental data by minimizing least squares deviation (Fig. 4).

	Nitrogen application (kg ha^{-1})		
	40 N	120 N	160 N
Ammonia loss (kg NH_3-N ha^{-1})	0.4	0.9	0.2
Nitrogen harvest index (%)	80 ± 1	77 ± 3	74 ± 2
Grain yield* (hkg ha^{-1})	63 ± 7	80 ± 9	75 ± 9
Grain protein content (%)	8.6 ±0.4	11.0 ±0.6	12.6 ±0.9

* 15% water content

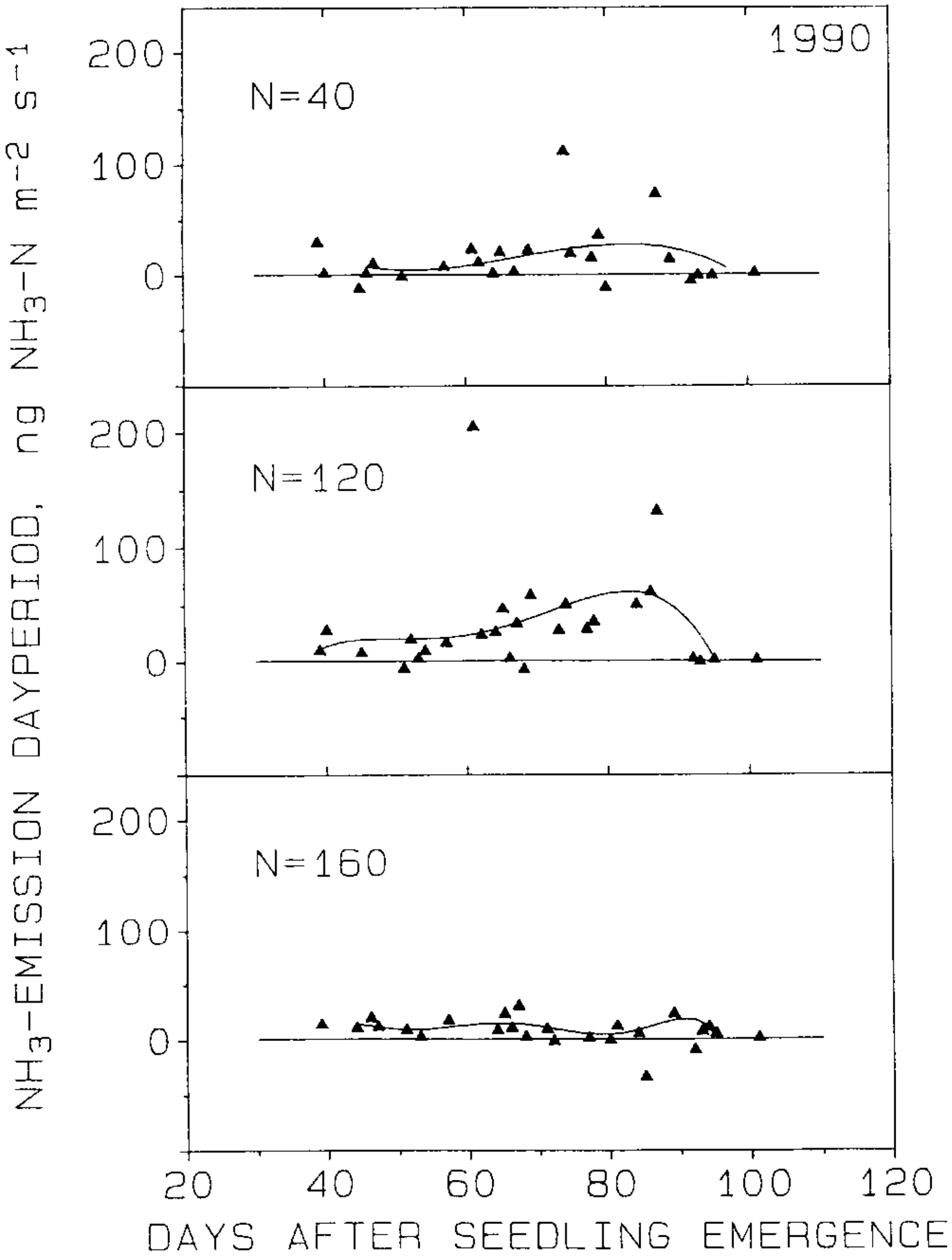

Figure 4. Daytime ammonia emission from the canopy of barley crops growing at three different levels of nitrogen application (40, 120 and 160 kg N ha^{-1}, respectively) in 1990. Curves show 4th order polynomia fitted to the experimental data by minimizing least squares deviation. Ear emergence took place between 58 and 65 days after seedling emergence.

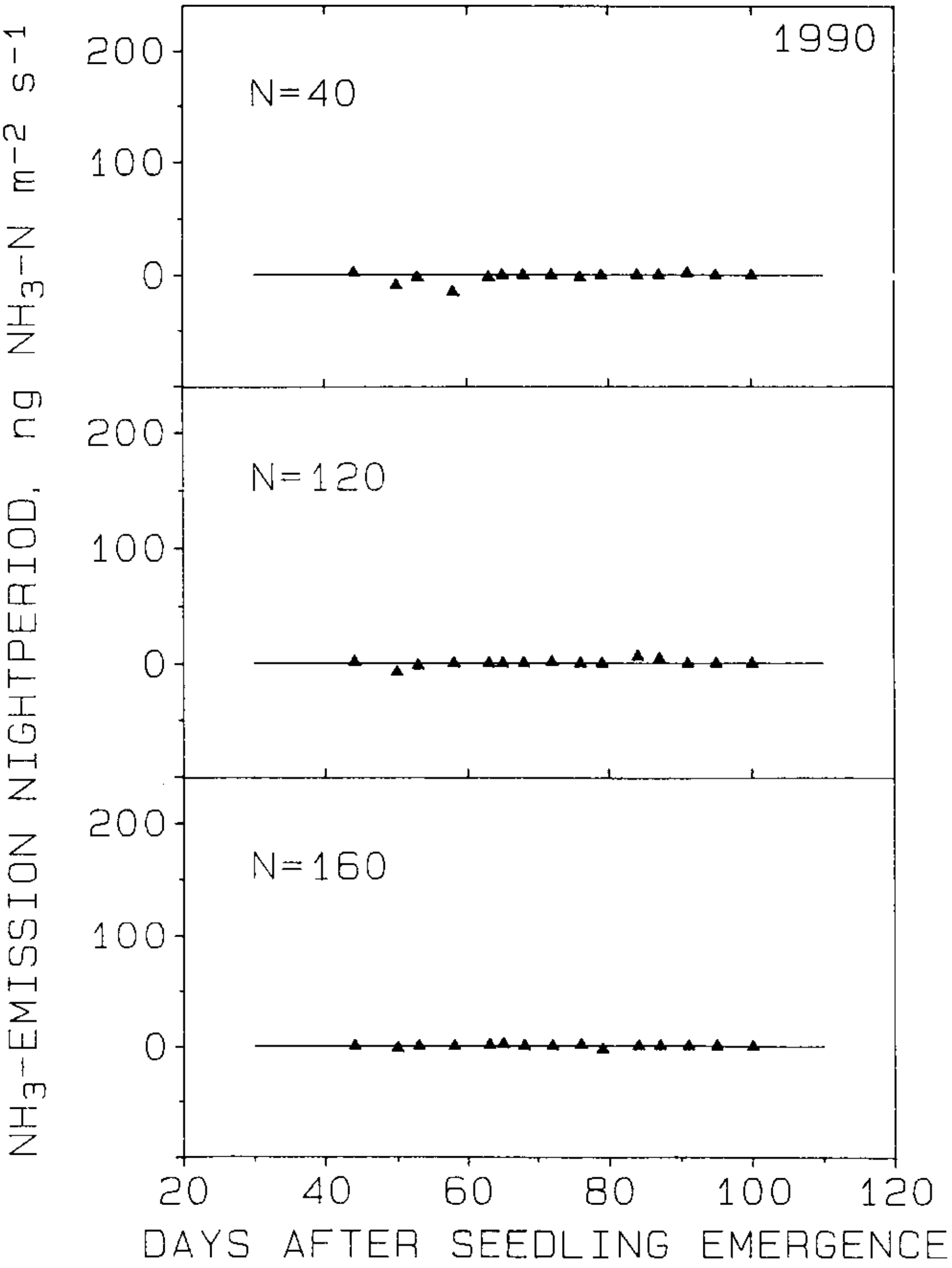

Figure 5. Nighttime ammonia emission from the canopy of barley crops growing at three different levels of nitrogen application (40, 120 and 160 kg N ha^{-1}, respectively) in 1990. Ear emergence took place between 58 and 65 days after seedling emergence.

No loss of fertilizer derived (^{15}N-labelled) nitrogen in 1990

In accordance with the small losses of ammonia measured in 1990, no decline in either fertilizer derived nitrogen (^{15}N-labelled) or in total N content of the above-ground plant parts was observed in the period between ear emergence and maturity (Figs 6 and 7).

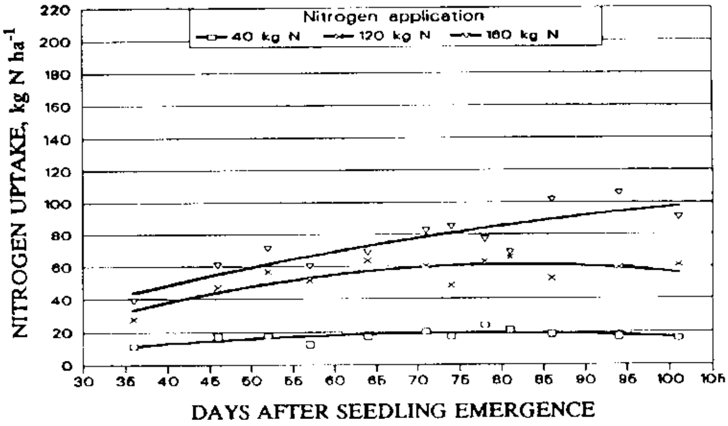

Figure 6. Time course of fertilizer derived nitrogen (^{15}N-labelled) uptake in barley growing at 3 levels of nitrogen application in 1990.

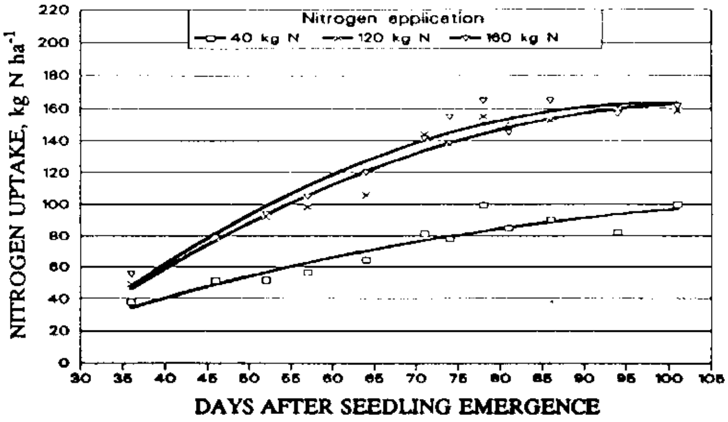

Figure 7. Time course of total nitrogen uptake in barley growing at 3 levels of nitrogen application in 1990.

4. DISCUSSION AND CONCLUSION

Plants emitted NH_3 in both years

The lost ammounts of ammonia were small

The total loss of ammonia from the aerial plant parts of spring barley was ½ to 1½ kg NH_3-N ha^{-1} in both of the experimental years. Compared to the amount of ammonia lost from manure, which on average is estimated to be about 45 kg NH_3-N ha^{-1} of agricultural land in Denmark (Miljøstyrelsen 1984), it must be concluded that ammonia emission from barley plants was an insignificant pathway of nitrogen loss in the two experimental years.

Favourable conditions for remobilization and re-utilization of nitrogen may have reduced the loss of ammonia

Both years were characterized by very favourable growth conditions. Consequently, high grain yields and effective depositon in the grain of nitrogen mobilized from vegetative plant parts was achieved. This resulted in high nitrogen harvest indexes (80-84% in 1989; 74-80% in 1990) and may have reduced the ammonia emission in the two years. Losses of more than 10 kg N ha^{-1} of fertilizer derived nitrogen from the aerial parts of spring barley plants in the period between ear emergence and maturity were observed by Schjørring et al. (1989) but only when the nitrogen harvest index at maturity became less than 63%; plants having a nitrogen harvest index above 68% had only lost insignificant amounts of fertilizer derived nitrogen.

Continuous production of ammonia in nitrogen metabolism

Balance between ammonia producing and consuming processes

Nitrogen liberated during senescence induced protein degradation in leaves and stem is a very important source for grain protein formation. In cereal grasses, 50 to 80% of the nitrogen present in reproductive plant parts at anthesis may be retranslocated to the ear (Dalling et al. 1976; Harper et al. 1987). Before being exported to the ear, amino acids liberated during protein breakdown in senescing leaves are converted to transport amino acids and amides. During this conversion of amino acids, NH_3/NH_4^+ is released as an intermediate (Dalling et al. 1976; Simpson & Dalling 1981). Even very low concentrations of NH_3/NH_4^+ may have phytotoxic effects, so NH_3/NH_4^+ are rapidly reassimilated in the glutamate synthase/glutamin synthetase cycle (GS/GOGAT-cycle) (Miflin & Lea 1976; Joy 1988). If the release of NH_3/NH_4^+ exceeds the assimilation capacity, accumulation of toxic levels of NH_3/NH_4^+ in the leaf tissue may be prevented by release of NH_3 through the stomata. Stomata are only open in the light which may explain why ammonia emission did not occur during the nighttime.

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Microbial Biomass in the Rhizosphere

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SUMMARY

Barley plants in a loamy sand (Askov Research Station, Denmark) accumulated a larger microbial biomass in the rhizosphere (rhizoplane and surrounding few mm of soil) compared to the bulk soil. This was apparently due to exudation from plant roots, resulting in higher availability of organic substrate in the rhizosphere. The accumulation of N in the microbial biomass was relatively small compared to fertilizer input, however, and the great importance of the microorganisms in plant growth and efficiency of fertilizer use was due to their role in N cycling, rather than N storage.

1. INTRODUCTION

The roots of living plants comprise an important source of substrate for growth of microorganisms. In the rhizosphere, exudation of low-N substrates (carbohydrates and carboxylic acids) may explain why microorganisms are dependent on inorganic N sources (NH_4^+ and NO_3^-) for assimilation and growth.

The growth of microorganisms in the rhizosphere could result in a transient accumulation (storage) of N after fertilization in spring. If so, not only the competition for N between plants and microorganisms, but also important processes of NO_3^- loss (denitrification, runoff, etc.) could be affected.

The purpose of the present study was therefore to investigate if a significant, temporary accumulation of fertilizer NO_3^- took place in the rhizosphere of growing barley plants in spring.

2. MATERIALS AND METHODS

The experimental site at Askov Research Station was a sandy loam, in which barley seeds (April 20, 1990; 180 kg/ha) and KNO_3^- fertilizer (April 30, 1990; 100 kg N/ha) were introduced according to standard practice.

At several occasions in April, May and June, undisturbed soil cores were taken to the laboratory for analysis. Storage took place at 5°C until the next day.

A dissection technique, by which small soil samples (about 0.1-0.2 g) could be carefully removed from the undisturbed cores was developed. A binocular microscope served for visual inspection of the sampling depth and distance from the roots. Larger pieces of root material in the samples was removed. The subsamples were immediately transferred to closed glass vials to prevent water loss.
Some of the samples were used for analysis of NO_3^- and NH_4^+ concentrations; extraction in 2 M KCl solution (1 h, room temp.) was followed by centrifugation and analysis by colorimetry (flow injection).

Other samples were used for determination of microbial biomass by a chloroform-fumigation procedure (Brookes et al., 1985 a,b). Fumigation in the chloroform-saturated atmosphere in the vials was chosen to be of 3 days duration, followed by extraction in 2 M KCl solution (1 h, room temp.). After centrifugation, the samples were analyzed for amino-bound N (ninhydrin-reactive N) according to Moore and Stein (1954) as a measure of microbial organic N (biomass).

3. RESULTS

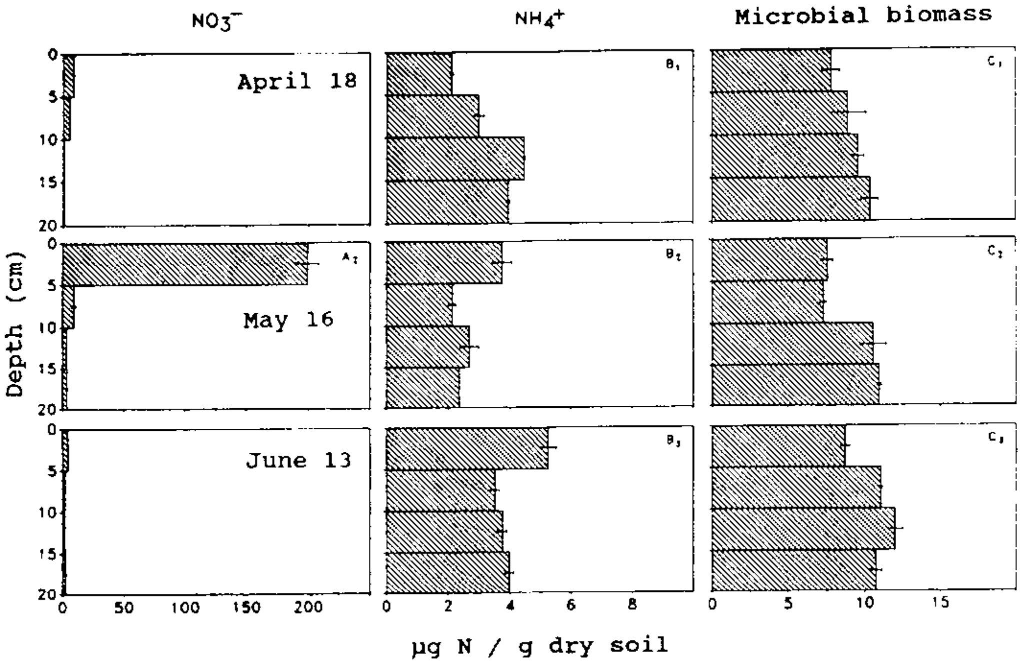

Figure 1. Depth profiles of NO$_3^-$, NH$_4^+$ and microbial biomass contents in soil without barley plants. Standard deviations are indicated (3 soil cores).

Figure 1 shows profiles of NO$_3^-$ and NH$_4^+$ concentrations together with the distribution of microbial biomass in soil without plants (control) on April 18 (before NO$_3^-$ fertilization), and on May 16 and June 13 (after NO$_3^-$ fertilization). It may be noticed that all fertilizer NO$_3^-$ was present in the upper few cm of soil and was removed within 1-2 months after fertilization. Figure 1 also demonstrates that NH$_4^+$ concentrations and microbial biomass distributions in the soil without plants were not affected by the application of fertilizer NO_3 .

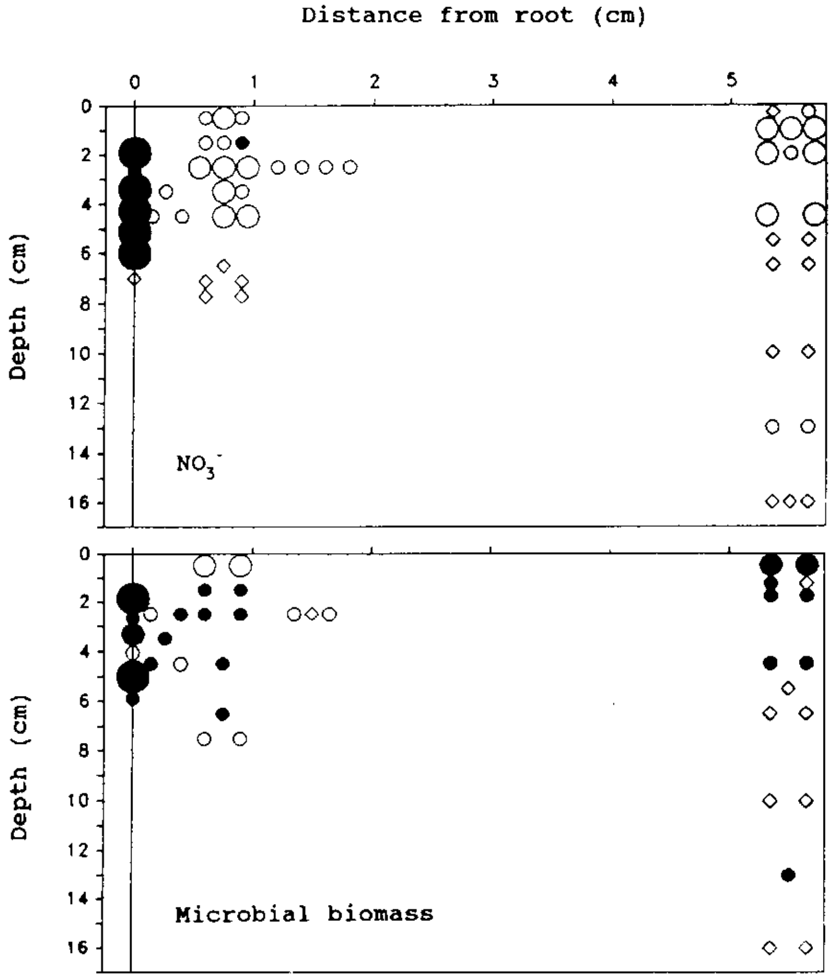

Figure 2. Distribution of NO_3^- concentrations (upper diagram) and microbial biomass content (lower diagram) on June 13 in soil with barley plants. Data points are placed according to soil depth and distance from reference root (indicated by vertical line). The symbols indicate relative difference from values measured in the bulk soil without plants (○: 0-50 % smaller, ◯ : 50-100 % smaller, ● : 0-100 % larger, ● : 100-200 % larger, ⬤ : >200 % larger, ◇: not significantly different).

Figure 2 shows the distribution of NO_3^- concentrations and microbial biomass on June 16, when the fertilizer NO_3^- had been consumed by

plant uptake, denitrification etc. The symbols of Fig. 2 indicate relatively high or low values (compared to bulk soil) determined at different depths and distances from an "idealized" root surface (see figure legend). Relatively high NO_3^- concentrations and contents of microbial biomass were observed close to the root surface, while samples taken only a few mm away from the root surface had values similar to those from the bulk soil.
Assuming that the subsamples taken close to the root were not significantly influenced by tissue fragments and thus overestimating the true contents of NO_3^- and microbial biomass in the rhizosphere, the results indicate that no significant buildup of microbial biomass occur as a result of the NO_3^- fertilization, except perhaps at very short distance from the root.

4. DISCUSSION

The study could not demonstrate any seasonal variation in microbial biomass content in the bulk soil without barley plants. It was concluded that NO_3^- fertilization had no direct effect on microbial biomass content in the bulk soil.

In contrast, there was apparently a higher content of microbial biomass in the rhizosphere (root surface or soil within a few mm from the root surface) after NO_3^- fertilization. However, this was probably due to exudation of organic carbon substrate from the plant roots and thus a result of higher availability of organic carbon and better conditions for microbial growth in the root zone. It was unlikely that NO_3^- fertilization was directly stimulating microbial growth in the rhizosphere.

Further studies of microbial biomass and N transformations in the root zone should incorporate the important regulatory mechanism exerted by exudation of organic substrate from the roots.

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Analysis of the composition of Soil Water - a comparison of Methods

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ABSTRACT.

A comparison of chemical analyses of soil water, taken from suction cups, minilysimeters centrifuged or extracted from soil samples, has been performed. Test over short time intervals showed considerable disagreements between the methods concerning some parameters. The analyses of NO_3-N demonstrate a insignificant deviation between the sampling methods, apart from cases with high groundwater table. The tested minilysimeters showed some deviation in nitrate contents. In the first case the deviations may be generated by sampling soil water from the soil stratum below the suction cups mainly. The tested lysimeters may affect the flow pattern of the soil water and cause time dependent delay in concentration, which shows up in short time series while on annual base is of minor importance. For NH_4-N, PO_4-P and Tot-P considerable problems were determined regarding the methods in use. The analyses of K has in most cases proved consistence between the individual methods, with exception of the ceramic suction cups, which tends to absorbed most of the NH_4-N, PO_4-P, Tot-P and K. Present study did not evaluate if the soil water sampled was representative to the infiltrating water in the field.

1. INTRODUCTION

In order to calculate the leaching of plant nutrients from the root zone, it is essential to determine the concentrations of nutrients in the soil water.
Sampling of soil water from the unsaturated zone may be achieved in different ways. In this project four different methods have been compared:

1. Sampling by suction cups
2. Sampling by minilysimeters
3. Centrifugation of soil samples
4. Extraction of soil samples.

Using the methods 1 and 2 water samples for chemical analyses are obtained directly. By method 3 and 4 soil samples are taken and soil liquid is extracted in the laboratory. Using method 3 the soil water is centrifuged out of the sample, whereas additional liquid (1 N KCl) must be added to the soil sample to get excessive liquid for analyses when method 4 is chosen. The original concentration is then calculated on the basis of the diluted solution ratio.

2. MATERIAL AND METHODS

The sampling methods have been compared by synchronously sampling on 5 locations twice during the period February-April 1990. For more details, see Hansen et al. (1991).

Due to the spatial variation in the field several soil water samples are collected, and mixed together to one common sample prior to the analysis. In present study the analyses

have been carried out on single samples, enable statistic calculations.
Further, it is assumed, that the values are normal distributed, although this has not been tested. In case of high variation and/or low number of analyses, calculation of the standard deviation was not processed.

Table 1. The soil type and sampling depth at the test sites. The sampling period is shown for the lysimeters and the suction cups, and the number of single samples for the different methods.

Locality	Type of soil	Depth m	Collec. period	Lysi-meters	Suction cups	Soil samples
Fladerne	Coarse sand	1.0	1 month	6	4	16
St. Lyngby	Clayey sand	1.0	2 weeks	6	10	16
Askov	Sandy clay	1.0	3 days		12	16
Rønhave	Sandy clay	1.0	2 days		57	16
Gøderup	Peat	0.3	2 days		12	16

The minilysimeter used at Fladerne is of box type (30 * 40 * 20) cm. The lysimeters were buried with the bottom in a depth of 1 m. The soil column was drained by a 40 cm hanging water column (Jacobsen et al. 1990).
At St. Lyngby lysimeters is cylindric with a diameter of 20 cm and a height of 50 cm. The bottom of the lysimeters were placed in 90 cm.b.s. The soil column was drained at the bottom by a hanging wick system of 25 cm (Christensen et al. 1990).

At Fladerne, St. Lyngby and Gøderup teflon cups were used, while ceramic cups were installed at Askov and Rønhave.

The analysis programme included NO_3-N, NH_4-N, PO_4-P, Tot-P, K, Cl and SO_4, except for method 4 in which only NO_3-N was analyzed. However, the complete analysis programme has not been carried out in all cases.

The soil samples were stored at -20 °C from sampling until the analyzing. The water samples from Fladerne have been kept cooled at 8 °C until analyses. All other water samples have been kept frozen, until the analysis were carried out.

3. RESULTS.

In most cases no significant difference between the KCl, the centrifugation and the suction cup method has been detected for nitrate analyses, Fig. 1. However, at Fladerne and St. Lyngby, there seems to be a non-systematic deviations between the methods, although a slight tendency of higher NO_3 concentrations on clayey soil with the centrifugation method may be indicated. The results of the lysimeters differ from the other methods.

For NH_4-N there is inconsistency between all the compared methods. Obviously, methodological problems accounts for most of the discrepancy, as determination NH_4-N in soil water is quite complicated.

Consistence was acquired between analyses of PO_4-P, Tot-P and K at Fladerne and St. Lyngby, from the teflon cups and the centrifugation methods taking the variation between the single samples into consideration. Nevertheless, there is a tendency to lower concentrations of Tot-P and K for suction cups. At Askov and Rønhave, where the ceramic suction cups were used, the concentrations have been clearly lower in the suction cups, probably because these elements are absorbed by the suction cups. However, other factors may also influence the concentration. The lysimeters

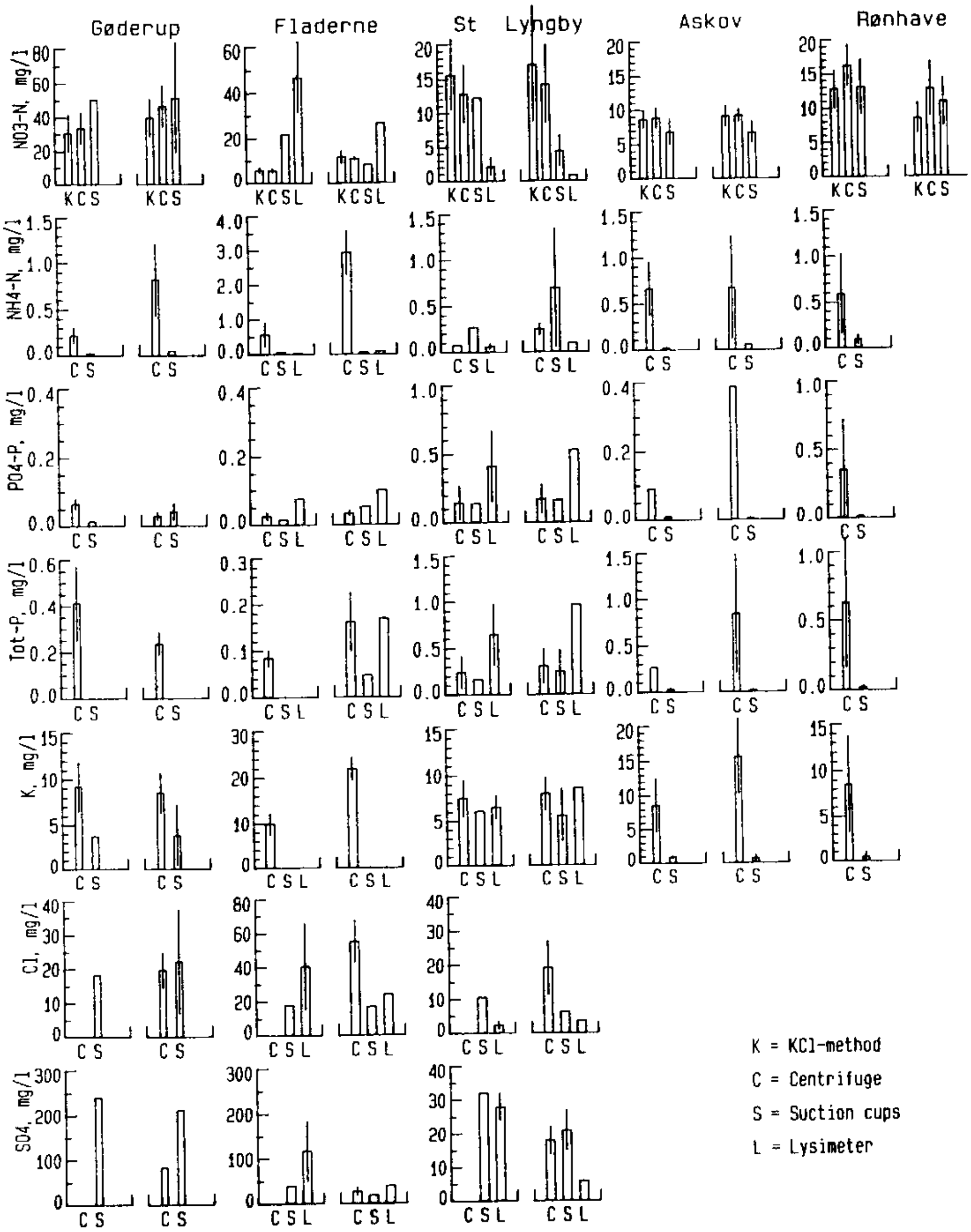

Figure 1. Revue of the analysis. The coulumns denote the average concentrations, and the vertical lines indicate the standard deviation, when estimated. The results from the first sampling date are shown to the left, the second to the right in the subfigures.

showed diverging results for these elements, except for K.
Analyses of Cl showed considerable deviations between the suction cup and the centrifugation methods at Fladerne and St. Lyngby, but good agrement at Gøderup. No significant difference between the sampling methods was determined for SO_4, however, at Gøderup, SO_4 demonstrates a variations between the individual samples, and the standard deviations have not been estimated.

Some divergence between the suction cups and the soil samples with respect to NO_3-N and Cl were detected at Fladerne and St. Lyngby. At both locations a rather good agreement for NO_3-N was found in the first sampling, but a considerable difference in the second. Cl showed a difference in both sampling. An explanation may be the high ground water level at the time of sampling. In such cases a considerable part of water derives from the soil stratum below the suction cup, due to the increasing hydraulic conductivity with depth. This problem is substantial for sandy soils but minor for clayey soils. Naturally this also affects other elements than NO_3-N and Cl. If the composition in the soil water does not vary with depth, this will of course be of no importance.

The lysimeters have in most cases shown a composition of soil water, which deviates from the other methods of sampling. One of the reasons is, that the lysimeters have affected the flow pattern of the soil water. When mounting such lysimeters the capillary contact to the underground is disrupted and the drainage of the soil water becomes different in and outside the lysimeters at the same depth. The water content in the lysimeters may also be different from the outside, which may introduce a time delay in water movement. Consequently, the time dependent change in the composition of the soil water may occur.

Measurements over long time periods (≈1 year) with suction cups and lysimeters showed, however, comparative leaching values for a number of substances with a typical deviation of 10-30%, Christensen et al (1991).

Centrifugation of soil samples extracts water from a part of the pore system dependent of applied force. By increasing the centrifugal force the soil drainage is increased and still smaller pores are drained. To investigate, the importance of the centrifugation speed to the composition of the extracted soil water, a sample from Rønhave was centrifuged at 3 different speeds, Table 2. For most elements no significant differences were found. The concentration of K seems to increase by increasing gravitational force, but the difference is small compared to the uncertainties of the sampling.

Table 2. The concentrations (mg/l) in soil water extracted at different gravitational force.

G*)	pF	NO_3-N	NH_4-N	PO_4-P	Tot-P	K
300	2.5	12.0	0.21	0.002	0.04	3.0
1000	3.0	12.0	0.22	0.002	0.11	3.2
3000	3.5	13.0	0.23	0.001	0.09	3.5

*) Gravitational force

4. CONCLUSIONS.

Four different methods for obtaining soil water from the unsaturated zone for chemical analyses have been compared. In several cases significant deviations between the nutrient concentration were detected.

The ceramic suction cups, used at Rønhave and Askov, are only suitable for elements, as NO_3-N and probably Cl and SO_4, which are not adsorbed by the cups. Elements as NH_4-N, PO_4-P, Tot-P and K are adsorbed by these suction cups. Suction cups of teflon, on the contrary, are usable for these substances.

Water extraction by suction cups seems to be a problem, if the groundwater level is near to the suction cups. In such cases it is expected, that the suction cups foremost extract water from the soil below the suction cups. It is due to the fact that the water content and the hydraulic conductivity, in such cases increase with the depth.

For NO_3-N there is a tendency, that the centrifugation method shows higher concentrations than the KCl method. For NH_4-N the centrifugation method in almost all cases have shown higher concentrations compared with the other sampling methods. The reasons are not known, but may be due to the pre-treatment and freezing of the soil samples prior to the centrifugation.

In well drained soil profiles with a low groundwater level a substantial part of the infiltration water will bypass lysimeters of the tested types caused by changed potential gradients. A high groundwater level may introduce a better drainage inside lysimeters than in the soil adjacent to the lysimeters. This could result in higher infiltration ratio into the lysimeters. Consequently, the water volume sampled in the lysimeter is not usable as an estimate of the infiltration. Determination of the infiltration must be calculated by modelling the water balance or detected by the use of another methods.

The tests have shown that in a number of cases there are considerable problems in determining the concentrations of plant nutrients in soil water. All analysed elements has a high spatial variability in the concentrations in the soil. Consequently, it is necessary to take a considerable number of samples to achieve a fairly accurate average estimation of the concentrations of the soil water. Additionally, there is a difference in the spatial variability for the different elements and between different locations.

In present study it has been examined, if the tested sampling methods produce comparable results, but the project did not include investigations of the methods to obtain representative analysis of the seeping soil water. Neither has it been examined, if the handling of the soil samples when sampling or freezing and thawing before extraction of soil water, affects the composition of soil water or if freezing of the water samples before analysis affects the analysis results.

5. LITERATURE.

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Atmospheric Deposition of Nitrogen Compounds in Denmark

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Abstract

Detailed emission inventories were made for ammonia and nitrogen oxides for Denmark. These inventories were used in a statistical atmospheric transport model to calculate the deposition for Denmark and surrounding sea areas. The calculated nitrogen deposition was about 2000 kg N km^{-2} a^{-1} for the land area of Denmark and about 1000 kg N km^{-2} a^{-1} for the Kattegat sea area. About 57% of the total nitrogen deposition in the land area of Denmark comes from Danish sources. For the Kattegat area this is only about 35%.

1. Introduction

Why are nitrogen components important?

Nitrogen components are important components because they act as fertilizers. A high atmospheric input of nitrogen components to ecosystems may lead to a change in the composition of the vegetation, cause imbalances in the nutrient supply of plants, which may have unfortunate effects such as premature shedding of needles (Nilsson and Grennfelt, 1988; Roelofs et al., 1985). Moreover, it may lead to acidification of the soil.

Nitrogen is a controlling factor for the growth of algae in the Danish coastal waters. High loads of nitrogen components in sea areas can therefore lead to algal blooming, and then to an oxygen deficit after degradation of the algae which have sunk to the bottom. This oxygen deficit causes the deaths of fish and benthic organisms. These effects on the ecosystems are the main reasons for establishing the extensive Danish research programmes "NPo" and "Marine Research Programme '90" for studying the nitrogen cycle. About 30%

of the nitrogen input to Danish coastal waters originates from the atmosphere (Richardson and Ærtebjerg, 1991).

Definitions groups of components

The main nitrogen components which can act as fertilizers are ammonia (NH_3) and its reaction product ammonium (NH_4^+), and nitrogen oxides (NO_x = NO + NO_2) and their reaction products NO_3t (= nitric acid (HNO_3) + nitrate aerosol (NO_3^- aerosol)). In this paper the sum of NH_3 and NH_4^+ is called NH_x, the sum of NO_x and NO_3t is called NO_y, and the sum of all these nitrogen components is called "total N".

Why using a model?

NH_3 and NO_x are emitted from low-level sources, which due to atmospheric mixing results in a rapid decrease with distance in ground level concentration and deposition. As there are many scattered sources in Denmark, the concentrations of these components show a large spatial variability. In order to properly measure the concentration patterns over the country it would be necessary to set up thousands of stations. However, his would simply cost too much money. Therefore a combined approach was chosen, in which the patterns are modelled and a limited number of measurements are used to validate the model results.

Why is the TREND model used?

Within the framework of the "Marine Research Programme '90", a photochemical transport model will be developed in which several processes will be incorporated in detail. Due to limitations in the computing time, this model will have a spatial resolution of 25x25 km^2 or larger. To get a first impression of the concentrations patterns, the statistical atmospheric transport model TREND, developed at the National Institute of Public Health and Environmental Protection (RIVM), the Netherlands (Van Jaarsveld and

Onderdelinden, 1991; Asman and Van Jaarsveld, 1990), was applied. The TREND model has the advantage that it is possible to use it with a very detailed spatial resolution (in this case 5x5 km^2), but it has the disadvantage that the same meteorology is used for the whole modelling area, including dry and wet deposition velocities. This implies that model deposition velocities are the same for forests and sea areas, which is a severe distortion. Nevertheless, the model is able to give a reliable first-order estimate of the annually averaged concentration patterns.

In the following sections the atmospheric processes for nitrogen components are discussed as well as their inclusion in the TREND model. The TREND model as adapted for NH_x is described in detail by Asman and Van Jaarsveld (1990). Detailed information on the computations of N deposition in Denmark are given by Asman (1990c) and Asman and Runge (1991).

2. Emission

As NH_4^+ and NO_3t are not emitted in significant quantities, almost all NH_4^+ and NO_3t found in the atmosphere originate from emission of NH_3 respectively NO_x. The present authors constructed NH_3 and NO_x emission inventories for Denmark with a high spatial resolution, as such inventories did not exist beforehand.

NH_3

For NH_3 this was done by using information on the number of animals in every municipality ("kommune" in Danish) and on the consumption of fertilizers for each province ("amt" in Danish). The emissions were then distributed over a 1x1 km^2 grid by applying information from an equally

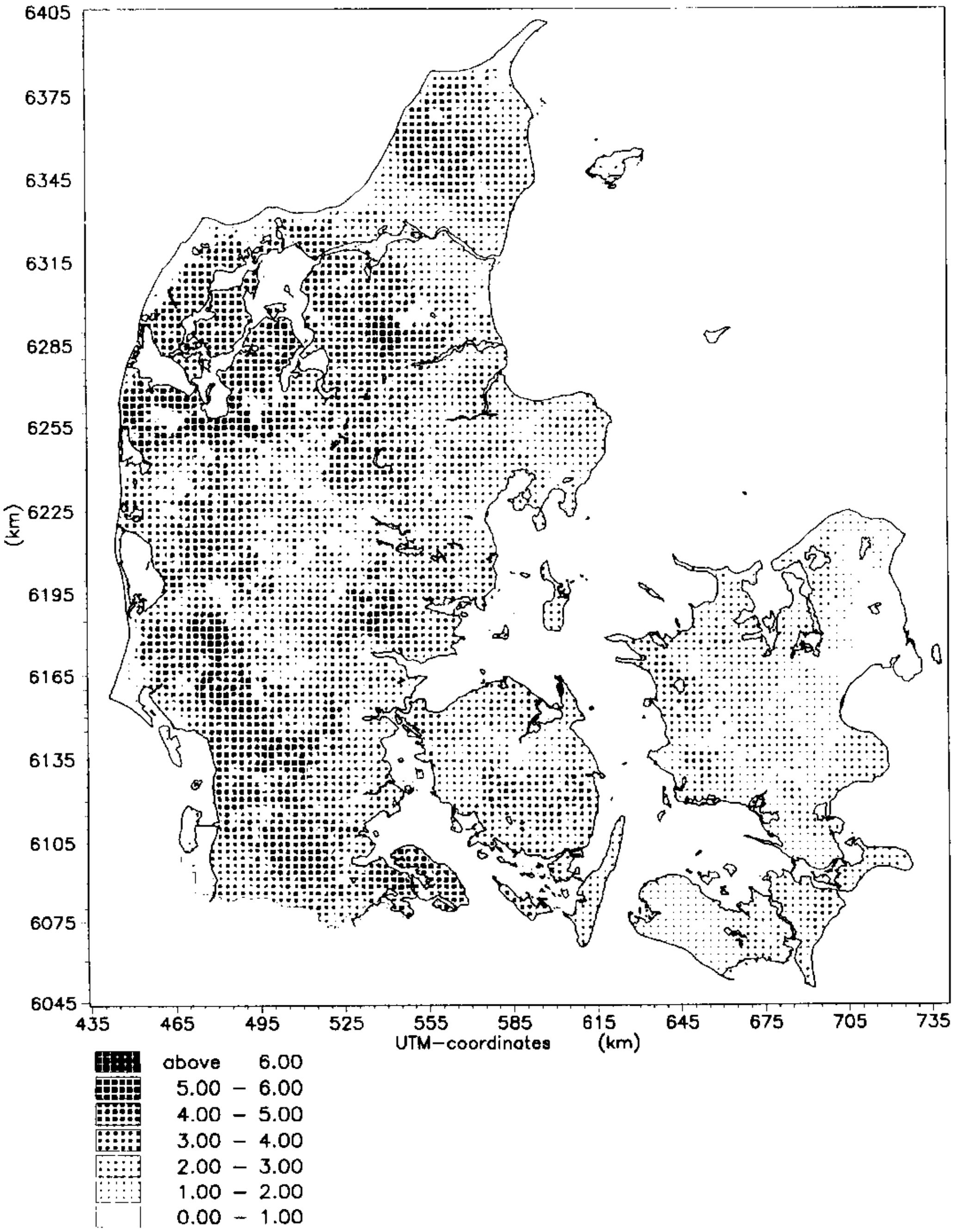

Figure 1. Emission density of NH_3 in Denmark (tonne N km^{-2} a^{-1}).

detailed gridded land-use map for Denmark (Runge and Asman, 1989).

Table 1. NH_3 emission in Denmark (tonne N a^{-1}).

Category	Emission
Cattle	54148
Pigs	36108
Poultry	4018
Horses	328
Sheep and goats1)	110
Fertilizer incl. NH_3	23536
Other*	4398
Total	122646

1)Cats, deer, dogs, foxes, human beings and mink

Table 2. NO_x emission in Denmark (tonne N a^{-1}).

Category	Emission
Domestic heating	2264
Energy generation1)	3924
Industrial combustion	3876
Industrial production	1226
Road traffic	30975
Maritime vessels	7405
Large point sources	39765
Total	89435

1)Excluding large point sources

NO_x

For NO_x an emission inventory with a very coarse spatial resolution had been made by Risø National Laboratory. The NO_x emissions from large point sources (mainly power stations), heating and industrial processes were taken from this inventory, and was distributed over the 1x1 km^2 by using information from the land-use map. Detailed information on the spatial distribution of the traffic density obtained from the Road Data Laboratory in Denmark ("Vejdatalaboratoriet", 1990) was used to compute the NO_x emissions caused by motor vehicles. Figures 1-3 show the spatial distribution of the emissions, and Tables 1 and 2 give an overview of the contributions of different source categories to these emissions (Asman, 1990a; Runge et al., 1991).

European emissions

The concentration patterns over Denmark are not determined by Danish sources alone. It was therefore necessary to include European emissions in the calculations. NH_3 emissions on a 75x75 km^2 grid of Asman (1990b) ,and NO_x emissions of EMEP redistributed over a 75x75 km^2 grid, were used.

The NH_3 emission density (e.g. given in tonne N km^{-2} a^{-1}) in Denmark is the third largest in Europe, but the NO_x emission density is relatively low compared to other countries.
The uncertainties in the emissions of both components are at least 30-40%.

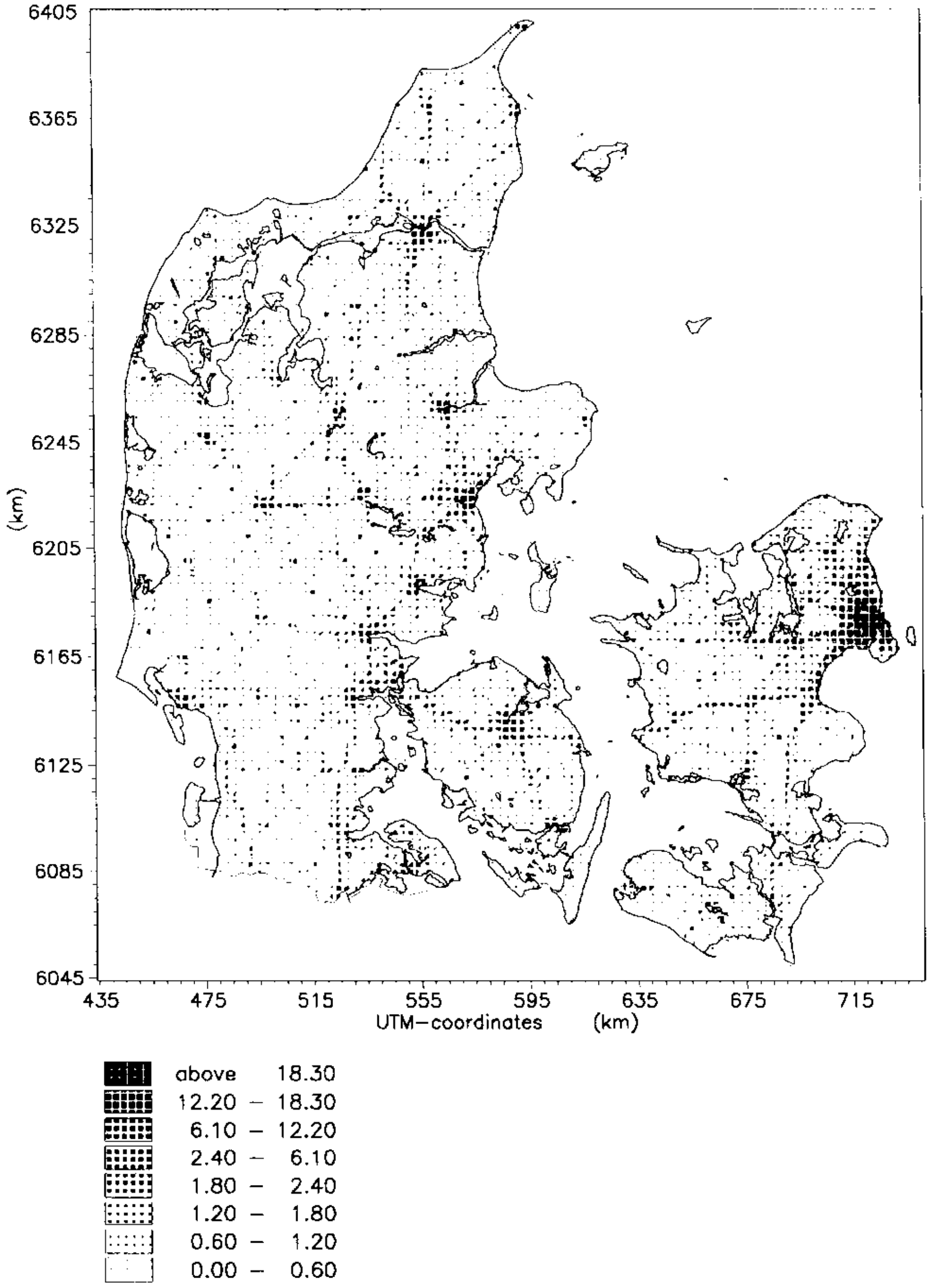

Figure 2. Emission density of NO_x from area sources in Denmark (tonne N km^{-2} a^{-1}).

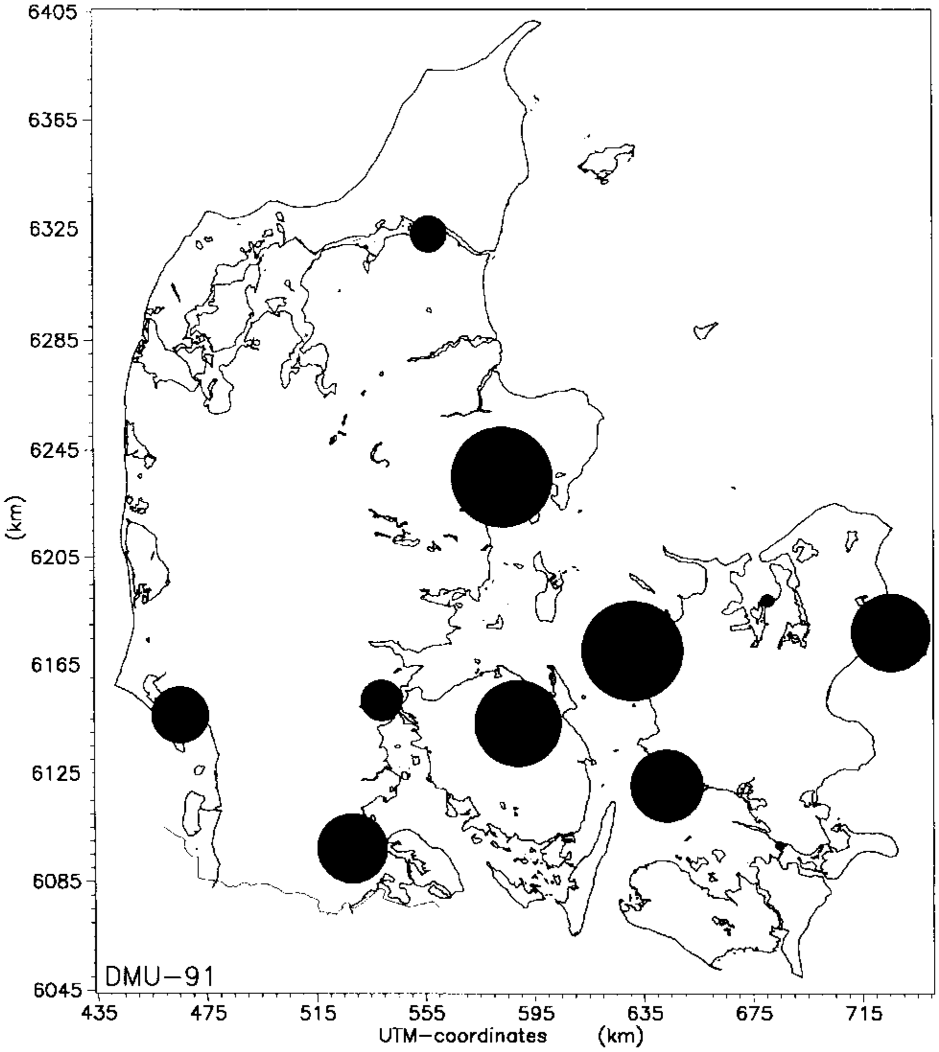

Figure 3. NO_x emissions from major Danish point sources. The diameter of the circle show the relative magnitude of the source.

3. Dry deposition

For modelling purposes dry deposition is conceptually thought to take place through three resistances in a series.

Resistances for transport

The aerodynamic resistance r_a describes the resistance due to turbulent diffusion of material from the atmosphere to a very shallow (about 1 mm) layer near the earth's surface. The aerodynamic resistance increases with height and is therefore usually given for a reference height (1 m). The laminar boundary layer resistance r_b describes the resistance due to molecular diffusion (of gases) or Brownian diffusion (of particles) through the very shallow laminar layer near the surface. The surface resistance r_c describes the ability of the surface to receive the airborne material.

In the model r_a is in the model calculated using meteorological measurements (turbulence), r_b using both meteorological measurements and the properties of the depositing components and r_c using the properties of the depositing components and those of the surface. The values of r_a used in the model are representative for surfaces covered by grass or low vegetation, but not for very rough surfaces as forests.

Dry deposition velocities

The relation of the resistances (s m^{-1}) to the dry deposition velocity v_d (m s^{-1}) is

$$v_d = (r_a + r_b + r_c)^{-1} \ .$$

In the model not one, average value of v_d is used, but different values for different classes of meteorological conditions.

The flux of any material to the surface, F (mol m^{-2} s^{-1}), is given by

$$F = v_d . c \ ,$$

where c is the concentration in the air at 1 m height (mol m^{-3}).

Table 3 shows the average dry deposition velocities computed by the model. They have been weighted by atmospheric concentrations and frequencies of meteorological classes.

NH_x components

The values for NH_3 and NH_4^+ aerosol were based on Duyzer et al. (1987) and Duyzer et al. (1989). A somewhat higher value for r_c was used for NH_3 to take into account that during part of a year deposition to agricultural surfaces will be insignificant, because emission occurs.

NO_y components

The dry deposition velocities for NO and NO_2 are different. These for HNO_3 and NO_3^- aerosol are different too. But due to the setup of the TREND model it is not possible to take these differences into account. Therefore a mean dry deposition velocity weighted by atmospheric concentrations for NO_x and NO_3t should be used. This is quite tricky as the mean NO/NO_2 ratio and HNO_3/NO_3^- aerosol ratio are not known over longer periods for representative stations in Denmark. In lack of better information, the ratios for the Netherlands, 0.54 respectively 0.2 were chosen for Denmark too. The resulting mean deposition velocities are presented in Table 3.

Table 3. Parameter values used in the model.

Dry deposition velocity NH_3	1.2×10^{-2} m s^{-1}
Dry deposition velocity NH_4^+	1.4×10^{-3} m s^{-1}
Dry deposition velocity NO_x	1.8×10^{-3} m s^{-1}
Dry deposition velocity NO_3t	6.7×10^{-3} m s^{-1}
Scavenging coefficient NH_3 *	1×10^6
Scavenging coefficient NH_4^+ *	1×10^6
Scavenging coefficient NO_x *	1×10^4
Scavenging coefficient NO_3t *	1×10^6
Pseudo-first order reaction rate NH_3 to NH_4^+	8.0×10^{-5} s^{-1}
Pseudo-first order reaction rate NO_x to NO_3t	8.4×10^{-6} s^{-1}

* (precipitation/air), close to the source only below cloud scavenging according to Janssen and Ten Brink (1985).

4. Wet deposition

In the TREND model the removal rate of the components by precipitation scavenging is a function of the distance from the source. Under precipitative conditions, scavenging near the source occurs below the cloud base, while at larger distances it occurs both within and under the cloud system. Thus we deal with two different scavenging rates.

In- and below-cloud scavenging

The so-called scavenging coefficient (s^{-1}) is used to describe the scavenging rate. Close to the sources the value of the scavenging coefficient used in the TREND model is based on the results of the below-cloud scavenging model of Janssen and Ten Brink (1985). At distances > 30 km, in-cloud scavenging is the most important scavenging process and the effect of both in-cloud and below-cloud scavenging is described by an overall scavenging coefficient L_0 (s^{-1}):

$L_0 = S.R/H$

where:
S is the scavenging ratio, i.e. the ratio between the concentration in precipitation and that in air (mol/mol),
R is the rainfall rate (m s^{-1}), and
H is the mixing height (m).

Intermittent nature of precipitation

Contrary to dry deposition, wet deposition takes place only during part of the time. In nature, wet deposition occurs intermittently, contrary to dry deposition, which occurs continuously. As the TREND model is a statistical model, an effective overall scavenging coefficient is used, which should provide the same total removal of a component over long time spans as the real scavenging coefficient for only precipitative periods.

Table 3 shows the overall scavenging ratio for the nitrogen components. Apart from NO_x, the nitrogen components are removed effectively by precipitation. The removal rate at a precipitation rate of 1 mm h^{-1} is of the order of 70% h^{-1}.

5. Reaction

NH_3

Under Western-European conditions most NH_3 reacts with sulphuric acid (H_2SO_4) to form NH_4^+ containing aerosol. This is a one-way reaction and the aerosol does not evaporate again. A minor part will react with gaseous HNO_3 and gaseous hydrochloric acid (HCl) to NH_4^+ containing aerosols, but only if the concentrations of gases is high enough. All these reactions have been combined in the TREND model into a single pseudo-first order reaction for the reaction of NH_3 to NH_4^+ (Table 3; Erisman et al., 1988).

NO_x

The major part of NO_x is emitted as NO which subsequently reacts to NO_2. The reaction is determined by a chain of reactions in which e.g. ozone, hydrocarbons and solar radiation play a role. But in the model, NO and NO_2 are not treated separately.

During daytime, NO_2 reacts with OH radicals to HNO_3. During nighttime, NO_2 also reacts to HNO_3 by another chain of reactions. HNO_3 is adsorbed by aerosols, leading to the formation of NO_3^- aerosol. In the TREND model HNO_3 and NO_3^- aerosol are not treated separately. The reactions are combined in the TREND model leading to a pseudo-first order reaction rate for the reaction of NO_x to NO_3t (Table 3).

Pseudo-first order reaction rates

The TREND model allows only one pseudo-first order reaction rate for the reaction of one precursor to one reaction product. It therefore looks as if the reactions in the model are independent of the presence of other components. This is, however, not true as the value of the reaction rate implicitely is determined by the presence of other components.

In Table 3 it can been seen that the pseudo-first order reaction rate of NH_3 to NH_4^+ is rather high and is 10 times as high as that of reaction of NO to NO_2. Therefore most of the NH_3 in Denmark originates from Danish sources, whereas a substantial fraction of the NO_x in Denmark comes from foreign sources. A secondary cause for this difference is that while the emission density of NH_3 is higher in Denmark than in neighbouring countries, for NO_x the opposite is true.

Setup of the statistical model

The model is a statistical atmospheric transport model. The dispersion is described by a Gaussian plume formulation including dry and wet deposition and a pseudo-first order reaction. To make the model more efficient, instead of computing concentrations for each hour of the time period under consideration, computations are made only for a limited number of meteorological classes which are thereafter weighted according to their frequency . Among the discretizations, a total of 12 wind-direction sectors and 6 atmospheric stability classes are distinguished. All other variables are kept constant, this implies that in the model no spatial variation of e.g. dry deposition velocities is accounted for.

It is assumed that the plume is reflected only once at the earth's surface and at the top of the atmospheric boundary layer. Moreover, it is assumed that at large distances from the source the plume is distributed vertically homogeneously over the whole boundary layer, with the exception of a surface layer, in which the plume is affected by dry deposition. The model takes into account the wind variation with height and the mixing height variation with time.

Meteorological statistics used

In lack of detailed meteorological statistics for Denmark, 10 year averages for the Netherlands have been used for the runs of the TREND model. Subsequently meteorological statistics for Denmark have been supplied. They are not significanly different from the Dutch statistics, except that the wind velocity at 10 m height is somewhat higher in Denmark. Therefore, using Danish statistics would only lead to slightly different results, which are insignificant compared to the uncertainties in the emissions.

7. Modelled versus measured results

Model results were compared with already existing measurements (Grundahl and Hansen, 1990; Hovmand, 1990; Rasmussen, 1988), which had the disadvantage that the location of the sites could not be chosen to optimally check the model results. For NH_3 no good set of measurements for verification was available. In the case of NO_x there were only NO_2 measurements available and no NO measurements. As it was assumed that most of the NO_x in Denmark is in the form of NO_2, modelled NO_x concentrations were compared with NO_2 measurements alone.

Concentrations

In Asman (1990c) and Asman and Runge (1991) modelled values are compared with measured values. For NO_x there are too few stations to draw any certain conclusions on the correlation between modelled and measured results, but the model seems to estimate the magnitude of the concentrations rather well. For NH_4^+ aerosol and NO_3t good correlations between modelled and measured values are obtained, but the model seems to to underestimate the concentrations somewhat (20%). However, the underestimation is less than the uncertainty in the emissions.

Wet depositions

For the wet deposition of NH_x and NO_y the correlation between modelled and measured values is not good, and the wet deposition of NO_y is significantly underestimated, even considering the uncertainties in the emissions. The measured wet deposition of NH_x in agricultural areas was reduced with 25% before comparing it with model results, in order to detract the additional dry deposition to the bulk sampler, which had been used for the measurements (Grundahl and Hansen, 1990). For NO_y a similar effect was found, but based on a very limited number of measurements and it was therefore decided not to correspondingly correct the wet deposition of NO_y.

8. Results and discussion

Figures 4-6 show the patterns of computed N concentrations and depositions over Denmark and surroundings. Tables 4 and 5 show the average concentrations and depositions for the land area of Denmark and the Kattegat sea area (between Denmark and Sweden).

Percentage NH_x from Danish sources

It appears that about 75% of the total NH_x deposition in the land area of Denmark originates from Danish NH_3 emissions, whereas for the Kattegat area this is only 53%. The difference is caused by the fact that the NH_3 concentration and thereby the dry deposition of NH_x is much lower in the Kattegat area because there exist, at least in the model, no NH_3 sources in this area. For both the land area of Denmark and the Kattegat less than half of the NH_4^+ aerosol concentration and less than half of the wet deposition of NH_x originates from Danish sources.

Percentage NO_y from Danish sources

The model estimates that in Denmark only about 21% of the total NO_y deposition comes from Danish sources. For the Kattegat this is 18%. Less than half of the NO_x concentration in the air over Denmark originates from Danish sources. The contribution from Sweden to the Kattegat seems in the case of for NH_x and NO_y to be of minor importance. The contribution of Germany, especially to the sea areas south of Denmark is large, for NH_x as well as for NO_y. For the land area of Denmark dry deposition is more important than wet deposition, while for the Kattegat the opposite is true. For Denmark the contribution

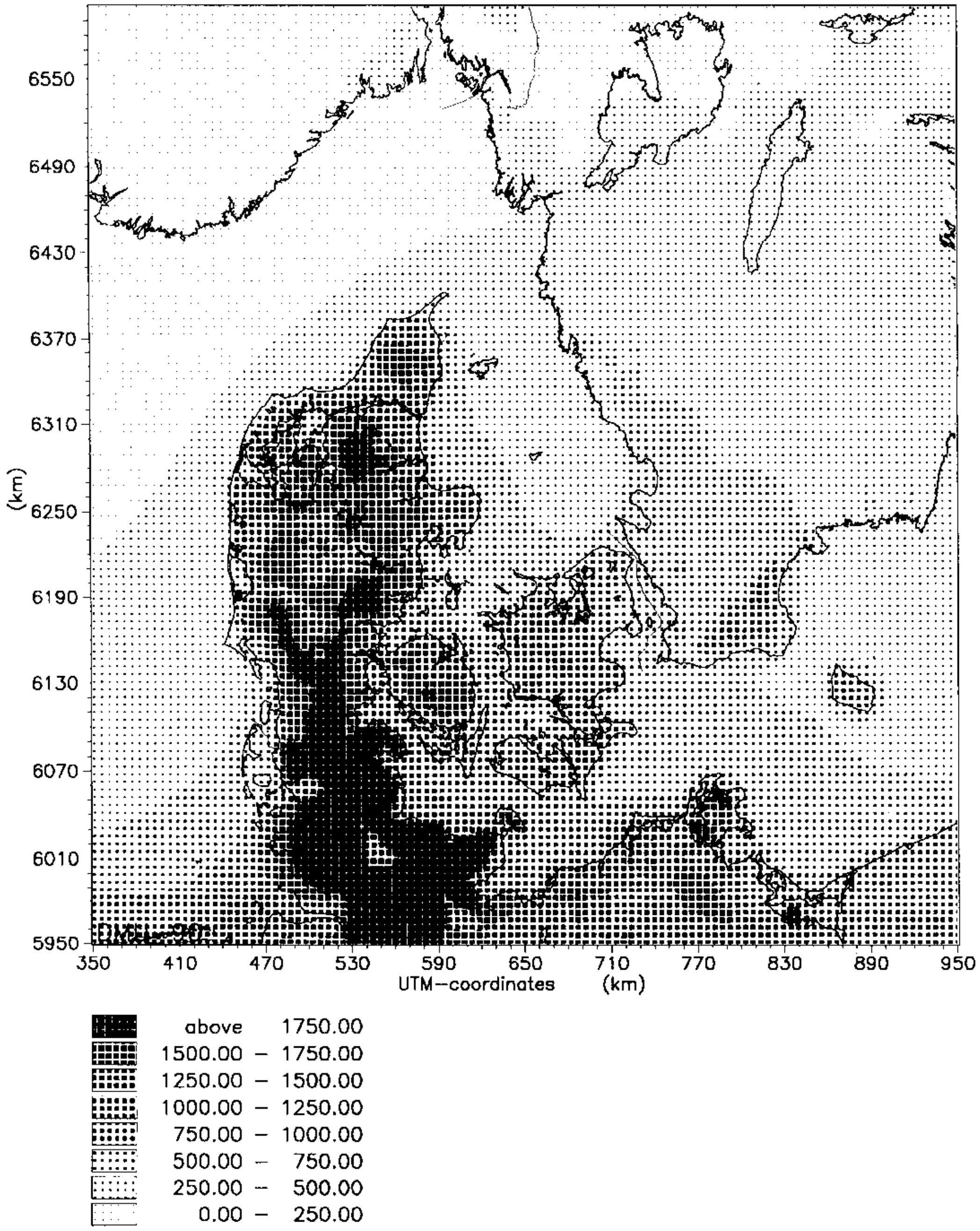

Figure 4. Total deposition of NH_x (kg N km^{-2} a^{-1}).

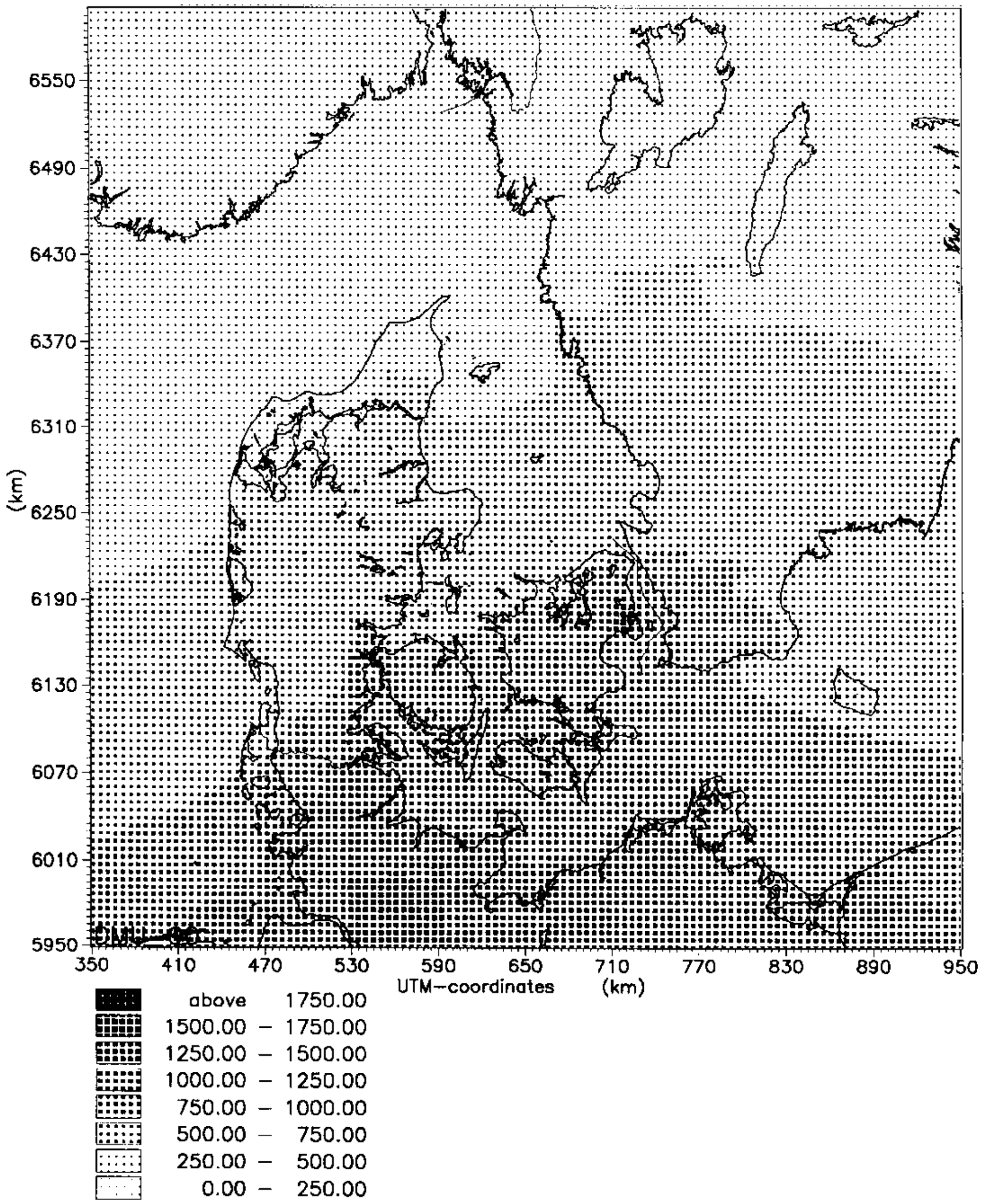

Figure 5. Total deposition of NO_y (kg N km^{-2} a^{-1}).

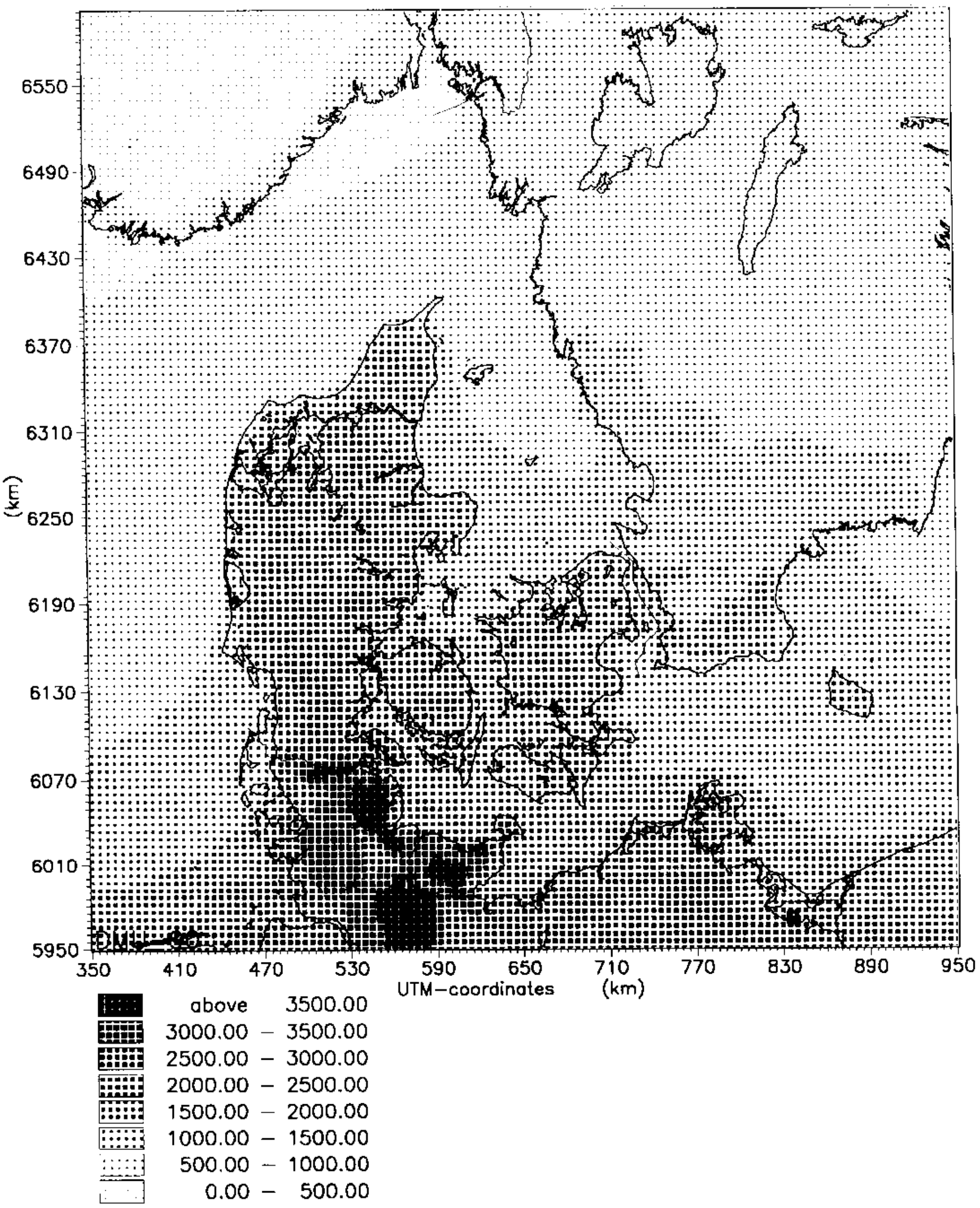

Figure 6. Total deposition of N (kg km^{-2} a^{-1}).

Table 4. Contribution of different countries to NH_x, NO_y and total N deposition to the land area of Denmark and percentage of the total N deposition caused by these countries.

	NH_x			NO_y			N			
	(kg N km^{-2} a^{-1})			(kg N km^{-2} a^{-1})			(kg N km^{-2} a^{-1})			
	dry	wet	total	dry	wet	total	dry	wet	total	%
Denmark	800	228	1028	121	23	144	921	251	1172	57
France	2	17	19	15	23	38	17	40	57	3
Germany	54	136	190	127	108	235	181	244	425	21
Netherl	7	41	48	23	26	50	30	67	98	5
Norway	1	2	2	4	2	7	5	4	9	0
Poland	4	10	14	12	6	18	16	16	32	2
Sweden	5	4	9	18	4	22	23	8	31	1
UK	4	30	33	51	68	119	55	98	152	7
Other	7	28	36	27	29	56	34	55	92	4
Total	883	497	1380	398	291	689	1281	788	2069	100

Table 5. Contribution of different countries to NH_x, NO_y and total N deposition to the Kattegat area and percentage of the total N deposition caused by these countries.

	NH_x			NO_y			N			
	(kg N km^{-2} a^{-1})			(kg N km^{-2} a^{-1})			(kg N km^{-2} a^{-1})			
	dry	wet	total	dry	wet	total	dry	wet	total	%
Denmark	102	161	263	65	34	98	167	195	361	35
France	1	11	12	11	17	28	12	28	40	4
Germany	16	79	95	81	87	169	97	166	264	26
Netherl	3	26	29	15	20	35	18	46	64	6
Norway	1	2	3	6	4	10	7	6	13	1
Poland	4	10	14	10	7	17	14	17	31	3
Sweden	15	9	23	36	7	43	51	16	66	6
UK	2	22	24	39	54	93	41	76	117	11
Other	6	23	29	23	25	48	29	48	77	8
Total	150	342	492	286	255	541	436	597	1033	100

from NH_x to the total N deposition is more important than that from NO_y. For the Kattegat area the opposite is true.

Fate of the Danish emissions

The model predicts that 37% of the Danish NH_3 emission is deposited as NH_x in Denmark. The rest is exported, mainly in the form of NH_4^+ aerosol. Of the Danish NO_x emission only 8% is deposited as NO_y in Denmark. This difference between NH_x and NO_y can be explained partly by differences in the properties of the components involved and partly by the fact that part of the NO_x is released from high sources, which does not lead to a high dry deposition close to the source as is the case for NH_3.

Total N deposition

The modelled total N deposition is about 2000 kg N km^{-2} a^{-1} for Denmark and about 1000 kg N km^{-2} a^{-1} for the Kattegat.

A reduction of the Danish NH_3 emission will lead to a significant reduction of the total NH_x deposition to Denmark and to the Kattegat. A reduction of the Danish NO_x emission will not have a large impact on the NO_y deposition to Denmark and to the Kattegat.

Concentrations and depositions of N components have been computed for all Danish provinces and 12 other sea areas around Denmark, but the results from these computations are not presented here.

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We are very grateful to the Institute of Public Health and Environmental Protection (RIVM), Bilthoven, the Netherlands for placing the TREND model at our disposal. Special thanks go to Hans van Jaarsveld (RIVM) for his help in adapting the model for Denmark. Risø National Laboratory placed an emission inventory for NO_x for Denmark at our disposal, which we could use to make the detailed inventory used in the model calculations. Lisbeth Stenfalk (NERI) made a userfriendly plotting programme, which was extensively used. Nicky Brown (NERI) is gratefully acknowledged for correcting the English.

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Number A19

N-transformation in Soils amended with Digested Pig Slurry

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Resumé

Anaerobically
digested
pig slurry

Nitrogen (N) mineralization and significance of denitrification in soils amended with anaerobically digested pig slurry and untreated (raw) pig slurry were studied in laboratory experiments.

Soils amended with both types of pig slurry, at a rate of 120 mg NH_4^+-N kg^{-1} soil, equivalent to 50 T slurry per hectare, were incubated aerobically (59 days), at moisture near field capacity, at 10° and 20°C.

Potentially
available N

Significantly more mineral-N (mainly nitrate) was produced in soils amended with digested pig slurry (133-140 mg N kg^{-1} soil). These increases may partly have been related to higher ammonium content and lower available carbon content in the soils amended with digested slurry.

Denitrification did not cause a significant loss of N during incubation.

1. INTRODUCTION

Anaerobic digested slurry

During anaerobic production of biogas from pig slurry a large fraction of the organic material in the slurry is decomposed (Table 1). The digested slurry is more resistant to decomposition, as the BOD_5 (Biological Oxygen Demand) decreases to 80-90% of its original value. This is caused by the degradation of easily available carbon compounds during digestion, with only the lignin fraction left intact (Asmus et al.,1988).

Table 1. Composition of pig slurry a) before and b) after anaerobic digestion and c) changing during the process (%).

Reference		Dry matter	Total N	NH_4^+-N	BOD_5	Liquid fraction Tot.C	Liquid fraction Tot.N	Cellulose	Hemicellulose	Lignin
						kg m^{-3}				
Asmus et al. 1988	a)	85	4.3	2.1	13.3			11	70.5	5
	b)	53	4.3	3.1	2.8			7	0.3	5
	c)	-38%	0	+48%	-79%			-36%	-99%	0
Larsen 1986	a)	81	7.3	4.7						
	b)	64	7.3	5.7						
	c)	-21%	0	+21%						
Koriath et al. 1985	a)	32	2.6	1.3	15.2					
	b)	27	2.6	2.1	1.2					
	c)	-16%	0	+62%	-92%					
This study	a)	41	6.6	5.3		5.6	4.8			
	b)	32	6.6	5.5		4.3	4.5			
	c)	-22%	0	+4%		-23%	-6%			

Anaerobic digestion leads to a decrease in organic C and N compounds and to an increase in the content of NH_4^+-N (Table 1).

When used as a N source, slurry often results in large N losses. Parts of the N is lost through volatilization, denitrification and leaching (Lind et al., 1990; Thompson, 1989; Ørtenblad et al., 1990).

Estimation of mineralization of nitrogen (production of NH_4^+-N + NO_3^--N) or nitrification (production of NO_3^--N) are valuable for assessing the nutrient status of slurry and for predicting the amount of nitrogen likely to be made available for crop growth by mineralization.

Available N

Available N may be predicted by determination of inorganic N produced in soil during incubation under aerobic conditions, for various times (Debosz et al., 1987).

The purpose of this work was to compare the effect of anaerobically digested pig slurry with raw pig slurry on nitrogen availability and denitrification losses in agricultural soils, during aerobic incubation.

2. MATERIALS AND METHODS

Soils and slurry.

The three soils selected (see Table 2), were sampled from 0-20 cm, dried to 9% (W/W) water, sieved (<2 mm), and stored at 2°C in polyethylene containers, until the beginning of the incubation.

Type of slurry

Pig slurry was obtained from the experimental digester of Karl Kamp Inc. in Nr. Åby. Some information on composition of the slurry are given in Table 1.

Table 2. Characteristics of soils used for incubation experiments. Partly after Heidmann (1989 a and b).

Parameter		Askov	Ødum	Foulum
Soil type[1]		Sandy loam	Sandy loam	Coarse sandy loam
Initial mineral-N content (mg N kg^{-1})	NH_4^+-N	1.5	0.5	0.8
	NO_3^--N	18.6	10.6	25.4
pH ($CaCl_2$)		6.6	6.7	6.2
Total N (g kg^{-1})		1.2	1.6	1.6
Organic C (g kg^{-1})		13	18	19
Bulk density (g cm^{-3})		1.6	1.4	1.5
Sand (63-2000µ) %		62	74	80
Clay (<2µ) %		11	9	8
Water content (%)		16[2]	21[3]	18[3]

1- According to Soil Survey Staff after Nielsen and Møberg (1984 and 1985).

2- equivalent to 85% of field capacity.

3- equivalent to 100% of field capacity.

Incubation Experiment.

Laboratory experiment was carried out for 59 days and included two types of pig slurry (anaerobically digested and undigested-raw slurry), and two incubation temperatures (10 and 20°C). Soils were treated with 120 mg NH_4^+-N kg^{-1} in slurry, equivalent to 50 T slurry per hectare. Untreated controls were also included. Sufficient water was added to bring the soils almost to field capacity (Table 2). The fine soil was mixed thoroughly, subdivided into portions of about 50 g and each portion was placed in a plastic tube, 6 cm high, 2,5 cm wide. Samples were compacted gently to a bulk density very close to in situ conditions. To reduce water losses during incubation the tubes were placed in glass jars. The amount of water lost from soil samples during incubation was measured gravimetrically at 7-d intervals and was replaced, if it was > 1 ml.

Acetylene inhibition

At day 0, 2, 4, 7, 17, 31 and 59, six tubes from each treatment were transferred to six glass jars, fitted with two serum stoppers, for gas sampling. Half of these jars received 6% acetylene (n=3), the others none (n=3). The jars without acetylene were used for CO_2 determination. The jars with acetylene were used for measurement of N_2O production (denitrification) (Lind et al., 1990).

Mineral N

At various intervals (see above) 3 samples from each treatment were extracted with 2N KCl (1:2). The extracts were analyzed for nitrate and ammonium.

Chemical analysis for nitrate, ammonium and carbon

Nitrate and ammonium were determined spectrophotometrically, after extraction with 2 M KCl (1:2), C determination in pig slurry was performed on the liquid fraction of the slurry, which was separated by centrifugation. Total soluble C was determined using a Dohrmann DC 180 Carbon Analyzer. The water content was determined gravimetrically by drying the soil at 105°C for 24 hours.

All statistical analysis were performed using the Statistical Analysis System SAS (1989).

Mean nitrate- and ammonium-concentrations were calculated for each combination of day, temperature and slurry type.

Statistical analysis

Due to the log normal distribution exhibited by the denitrification measurements mean log denitrification rates were calculated and were subsequently used in the statistical test. Means were tested for significant differences with the GLM program of the SAS system.

The mean denitrification rates were calculated from the mean log denitrification rates using the exponential function.

3. RESULTS

3.1. N and C mineralization

Experiment was performed on three agricultural soils, which did not differ substantially in texture and contents of organic N and C; two sandy loam and one coarse sandy loam soil. It could be shown, that the N-transformation in soil was more influenced by the kind of pig slurry used than by the soil type.

In Fig. 1 the evolution of total inorganic N, NH_4^+-N and NO_3^--N during incubation of sandy loam soil (Ødum) at 20°C was shown.

Untreated pig slurry

Addition of raw pig slurry (120 mg NH_4^+-N kg^{-1} soil) to sandy loam (Ødum soil) resulted in an immediate consumption of NH_4^+-N and at the same time a long decline in total inorganic N in the soil (Fig. 1A). Only a small amount of NH_4^+-N was detected in this soil after 30 days of incubation. Raw pig slurry addition was followed by a continuous production of NO_3^--N during the whole incubation period.

Digested pig slurry

Addition of anaerobically digested pig slurry (120 mg NH_4^+-N kg^{-1} soil) to sandy loam (Ødum) soil at 20°C resulted in a less effective consumption of NH_4^+-N, compared to the other treatment and caused a short decline in total inorganic N in the soil (Fig. 1B). This short immobilization of NH_4^+-N was followed by continuous increase in nitrification rate, which led to accumulation of high amounts of NO_3^--N at the end of incubation period.

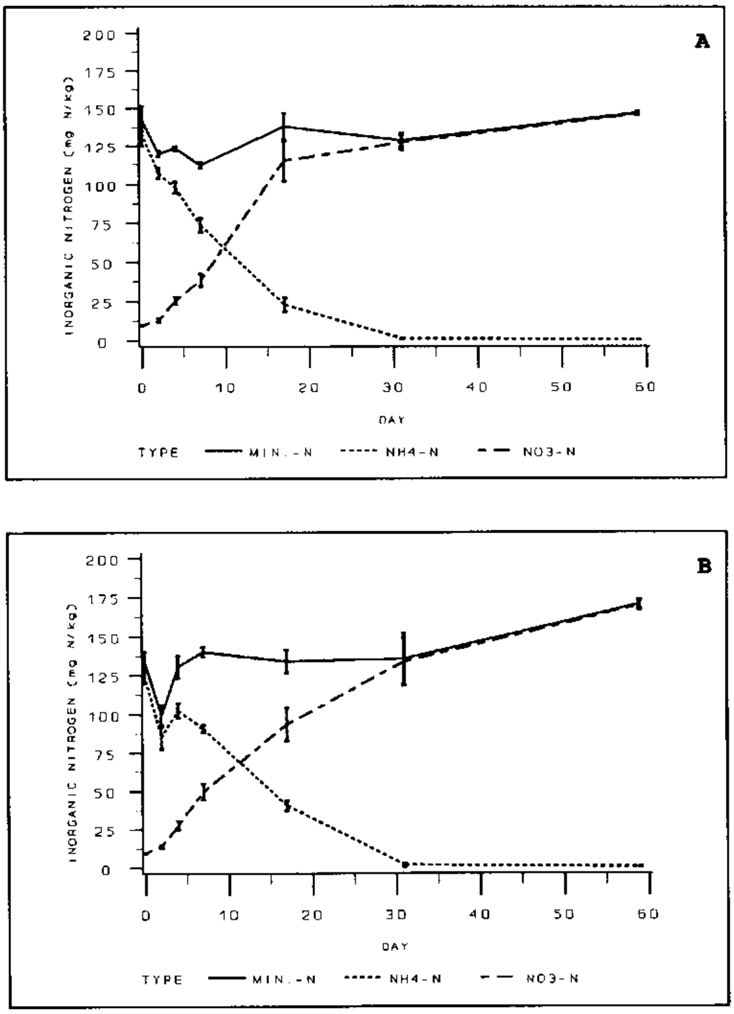

Fig. 1. Evolution of total inorganic N, NH_4^+-N and NO_3^--N as influenced by A) raw pig slurry B) digested pig slurry amendment (120 mg NH_4^+-N kg^{-1} soil) to Ødum soil incubated at 20°C. Bars show standard deviation.

Type of soil

To compare the effect of digested pig slurry with raw pig slurry on nitrogen available in soil and lost by denitrification, the means of the three soils studied were taken into consideration (Table 3). Substantial amounts of nitrate were produced in all treatments after 59 days of incubation (Table 3). Anaerobically digested pig slurry significantly increased nitrate produced in soil, compared with raw pig slurry.

Nitrogen added in raw pig slurry was significantly less nitrified, 92 and 94%, at 10° and 20°C, respectively, than that added in digested pig slurry, 106 and 116%, at 10° and 20°C, respectively.

Table 3. Effect of type of pig slurry added (120 mg NH_4^+-N kg^{-1} soil) to soil[#] on formation of nitrate-N, C-mineralization and denitrification losses after 59 days of incubation, at 10° and 20°C.

Temperature	Pig slurry type	Increase in NO_3^--N[§] during incubation	Total CO_2-C evolved	Total N_2O production
		mg N kg^{-1} soil	mg C kg^{-1} soil	mg N kg^{-1} soil
10°C	Raw	107a*	163a	0.09a
	Digested	130b	163a	0.03a
20°C	Raw	105a	277a	0.4a
	Digested	144b	222b	0.04b

Mean of three soils

§ Increase in NO_3^--N was estimated by subtracting the amount of NO_3^--N produced by soil alone from that produced by soil + added pig slurry.

* Within each temperature series the values in each column are significantly different (95% level of probability), when not followed by the same letter.

C-mineralization

C-mineralization in soil incubated with anaerobically digested pig slurry and raw pig slurry was measured by CO_2 evolution.
The total amounts of C mineralized were highest from soil amended with raw pig slurry and incubated at 20°C (table 3).

3.2 Denitrification

Total denitrification loss

During the incubation time only small denitrification losses could be measured. The total loss during 59 days of incubation at 20°C was estimated to 0.4 and 0.04 mg N kg^{-1} in soil amended with raw and digested pig slurry, respectively. The estimated loss in soil incubated 59 days at 10°C with raw and digested pig slurry was 0.09 and 0.03 mg N kg^{-1}, respectively.

4. DISCUSSION AND CONCLUSION

Anaerobic digestion of pig slurry

Anaerobic digestion of pig slurry removed 23% of the carbon in the liquid fraction and a part of the organic nitrogen was mineralized to ammonium. These transformations may influence the fertilizing value of pig slurry in the soil.

In the case studied the anaerobic digestion was obviously of poor efficiency in increasing the amount of NH_4^+-N in the pig slurry used (4%), in contrast to findings of Larsen (1986), Asmus et al. (1988) and Koriath et al. (1985), who found increases of NH_4^+-N in the range from 21% to 60%.

Mineralization

Laboratory study showed, that soils amended with raw pig slurry immobilized nitrogen, whereas in soils amended with digested pig slurry net mineralization prevailed. The pattern of immobilization and mineralization observed here was similar to that reported by Chaussod et al. (1986) and Ørtenblad et al. (1990).

Chaussod et al. (1986) found, that raw pig slurry immobilized nitrogen and depressed crop yields in pot experiments, whereas application of digested pig slurry did not result in such net immobilization and depressive effect.

Fertilizing effect

Anaerobic digestion improves the fertilizing value of pig slurry, but in field experiments fertilizing effect of digested slurry was only slightly better than that of undigested slurry (Larsen, 1986 and Vetter et al., 1987).

Gaseous losses

Following application of pig slurry to soil gaseous nitrogen losses can occur. The major process involved is ammonia (NH_3) volatilization and possibly denitrification.

The amount of ammonia volatilization from pig slurry applied to soil depends on the chemical characteristics of the slurry (pH, NH_4^+-N and dry matter), as well as application method, and physical and chemical characteristics of soil.

Ammonia volatilization

Experiments have shown, that high pH, NH_4^+-N and dry matter content in slurry leads to large volatilization losses (Nelson, 1982; Sommer and Christensen, 1989). In a field experiment, where ammonia volatilization from raw and digested pig slurry applied to soil has been compared, no difference in volatilization was found (Sommer and Christensen, 1990), probably reflecting, that anaerobic digestion did not change the content of ammonium. At the same time slurry incorporation methods were more important for volatilization losses than slurry processing (Sommer and Christensen, 1990; Vetter et al., 1987).

In the present experiment a part of the ammonia applied with the pig slurry may have volatilized during the incubation, but this loss was probably very small, as the slurry was immediately incorporated into the soil.
Compared to the losses due to volatilization, denitrification losses are generally much lower.

Denitrification losses

In our study only a minor part of nitrogen added in the slurry was denitrified during the incubation period, equivalent to 0.03-0.3% of added NH_4^+-N.
The reason for the low denitrification losses was probably the low soil water content, which is known to be very important (Tiedje, 1989). At a soil moisture lower than field capacity N losses, by reduction of NO_3^-, were hardly important. In an earlier study Lind et al. (1990) found, that the denitrification rate at 125% FC was 100 times the rate at 100% FC.

Nitrate influence

Another factor, that could have retarded denitrification, was the nitrate concentration in the soil (Thompson, 1989).
The small denitrification activity in this study could not be caused by exhaustion of nitrate, as the concentration was steadily increasing during the course of incubation.
These results suggest, that the low production of N_2O was due to factors other than low NO_3-

content, possibly the scarcity of anaerobic sites or available C.

The difference in N-mineralization and denitrification, in soil amended with raw or digested pig slurry, can be explained by the differences in chemical composition between the two types of slurry used. Only the most resistant fractions of the organic material could be found after anaerobic digestion (Table 1).

Available carbon

This means, that during digestion the amount of easily available carbon in the digested slurry is lowered. This is also substantiated by the large decrease in BOD_5 after digestion (Asmus at al., 1988).

In our study less CO_2 was produced from soil amended with digested pig slurry. The lower content of mineralizable carbon (available C) in soil amended with anaerobically digested slurry was closely related to lower carbon content in the liquid fraction, after digestion of the slurry.

Easily available carbon in soil and pig slurry had an important effect on such processes as mineralization - immobilization and denitrification in soil (deCatanzaro and Beauchamp, 1985); Reinertsen et al., 1989; Stanford et al., 1975).

Temperature

In the soils examined a clear relationship was seen between increasing temperature and increasing mineralization and denitrification rates, as also noted by others (Keeney et al., 1979; Lind et al., 1990 and Vinther, 1990). The average temperature coefficient during incubation showed for nitrification a weak temperature response Q_{10} = 1.3, for C mineralization more commonly observed value $Q_{10} = 2$, while denitrification responded more vigorously, but only at the beginning of incubation, $Q_{10} = 4$.

Conclusion

The biological method, based on aerobic incubation, at a constant water potential (100% FC) and temperature indicated, that potentially more available N (mostly nitrate) was mineralized from anaerobically digested pig slurry than from raw slurry. The three soils studied showed a similar pattern of mineralization, which was influenced by the type of pig slurry used, especially its organic C composition, and the incubation temperature. Denitrification losses were low during the first few days of incubation and negligible in the last period of incubation.

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Simulation of Nitrogen Losses using the SOILN Model

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Summary

A soil nitrogen model (SOILN) coupled to a soil water and heat model (SOIL) was used to simulate nitrogen losses from four arable fields in Denmark. The fields were cropped and managed according to conventional farming practices including the application of manure. Two of the fields were located in the middle of Jylland on sandy soils (Rabis), whereas the other two were located in Sjaelland on sandy loam soils (Syv). Model parameterization was based on 3-years of data (1987-90) from the field sites and on previous applications of the model. Simulated nitrate concentrations in the soil solution were compared with corresponding measured values. Mean simulated nitrate leaching from the different fields varied between 49 and 91 kg N ha^{-1} $year^{-1}$.

Various measures to reduce nitrate leaching, involving changes in management practices, were also simulated. A major criterium for these measures was that they should not lead to any changes in crop production levels (N-uptake). Nitrate leaching was reduced by 11%, 31%, 42% and 70% in the four fields by reducing the amount of commercial fertilizer applied and by altering the timing of manure application. Changing from spring crops to winter crops resulted in a reduction in nitrate leaching by 32%, 47%, 53% and 70% respectively. By introducing catch crops, in combination with a reduction in commercial fertilizer rates and a change in the timing of manure application, leaching was reduced by 64%, 65%, 70% and 70%. Corresponding nitrate leaching values in this case were 30, 17, 27 and 20 kg N ha^{-1} $year^{-1}$. Introducing a catch crop in these cropping systems resulted in an increased buildup of soil organic nitrogen. Incorporation of straw and changing from liquid to solid manure were also simulated, but had less pronounced effects on nitrate leaching.

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Farming Practices in some Danish Catchment Areas in 1983 and 1989

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SUMMARY

Purpose	The farming practices in 7 small catchment areas were mapped in 1983-84 and again in 1989 in order to illustrate changes in fertilizer and cropland use and live-stock concentrations.
Live-stock	During both periods, live-stock concentrations within these areas have been approx. 20% larger than the national average mostly due to larger herds of dairy cattle.
Cropland use	The total area with spring sown crops has been reduced by 10% in favour of an 8% increase in winter sown crops. Total area alloted to legumes had increased from 2% in 1983-84 to 7% in 1989. The total area alloted to other crops remained unchanged.
Use of Fertilizer	The total N-consumption in the form of chemical fertilizers decreased from 132 kg/ha in 1983-84 to 129 kg/ha in 1989 due to the increase in total area alloted to legumes. There are large variations in fertilizer application rates from field to field. Application rates greater than optimum are often due to inexpedient application of manure. The discord between the supply and demand of N was reduced during the period.
Manure	Manure storage capacity had increased but was still insufficient in 1989. The increased storage capacity seems to have had limited influence on a timelier application.

1. INTRODUCTION

Previous investigations

Farming practices within watersheds have been studied previously in connection with investigations of nutrient loads on streams (Hansen & Sommer, 1987). Data collection about the farming practices of 173 farms having a total area of 5000 ha within 7 watersheds and a variety of soil types occurred in 1983 or 1984. In order to illustrate changes in farming practices such as fertilizer use, storage capacity and facilities and time of application for manure, the investigation was repeated in 1989.

2. MATERIALS AND METHODS

Methods

In collecting data, all farms within the study areas were visited. Because participation in the study was voluntary, the data was not complete, yet average response was approx. 90%.

Nutrient levels for fields on which manure has been spread have been calculated using standards for nutrient levels provided by the Agricultural Information Office (LIK, 1989). Effective N applied in the form of manure has been calculated from values provided by LIK (1990).

3. RESULTS

Farms investigated

Table 1 summarizes the size of the study areas, the number of farms and the size of each farm. The studies in both 1983-84 and 1989 comprised approx. 5000 ha representing approx. 0.18% of the agricultural area in Denmark. The size of the farms during both periods were similar to the national average.

Table 1. Total area, number of farms participating in the investigation and farm size.

	1983-84	1989
Total area, ha	5067	4962
Number of farms	173	146
ha per farm	29.3	34.0

Live-stock

The average live-stock concentration in 1983-84 was 1.28 and in 1989 1.03 Animal Equivalents, AE (One AE one dairy cow). The AE has been calculated according to the National Agency of Environmental Protection (Miljøministeriet, 1988). Approximately 70% of the live-stock was dairy cattle while the remainder was primarily swine. Live-stock concentrations were at both times approx. 20% larger than the national average due to larger herds of dairy cattle.

Live-stock distribution

A classification of agricultural areas by live-stock concentrations is shown in Figure 1A. It can be seen that in 1983-84 16% and in 1989 20% of the farms had no live-stock. At the same time, the area with live-stock concentrations larger than 2.0 AE/ha was reduced from 20% to 7% of the cultivated area. The area with live-stock concentrations between 0.5-1.5 AE/ha was increased from 35% in 1983-84 to 45% in 1989. In effect there has been a more balanced distribution of live-stock from 1983-84 to 1989.

Cropland use

Crop distribution for cultivated areas seperated into major groups are shown in Figure 1B. Cultivated areas with spring cereal grains and spring rape have been reduced, whereas both winter cereal grains and winter rape have had an increase of 8-10 % of the cultivated area within the same period. The area with legumes has increased from 2% to 7%.

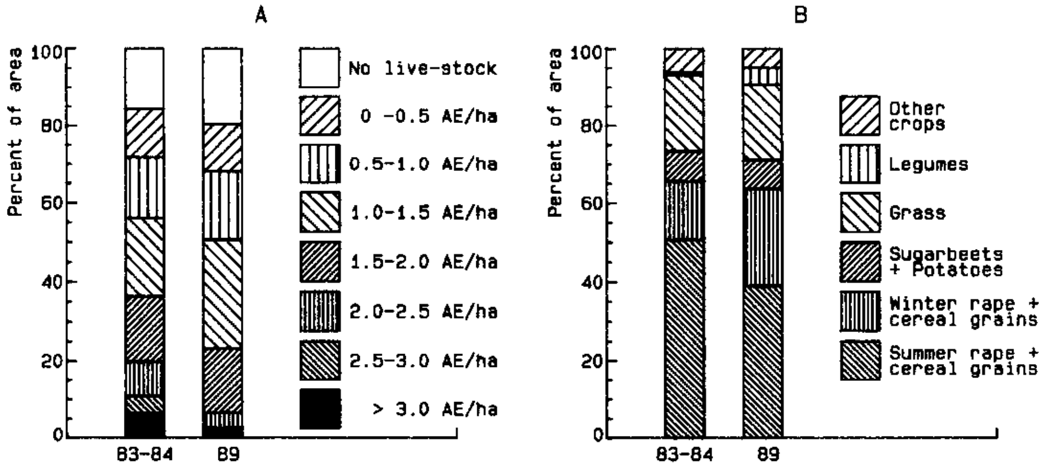


Figure 1. Distribution of agricultural areas by live-stock concentrations for individual farms (A) and distribution of crops on the cultivated areas (B).

Fertilizer use

Average fertilizer consumption for the study areas is shown in Table 2. N-demand calculated according to Hansen (1990) for a defined combination of crops was 162 kg/ha in 1983-84 and 158 kg/ha in 1989. There was relatively good agreement between average N-supply and N-demand.

Table 2. Average fertilizer consumption and effective N-supply for the investigated watersheds. Values in parentheses are national averages.

	1983-84			1989		
	N	P	K	N	P	K
Manure	137(102)	23(18)	118(84)	105(89)	19(17)	87(71)
Chem.Fertilizer	132(136)	16(17)	42(43)	129(135)	13(14)	45(44)
Total	269(238)	39(35)	160(127)	234(224)	32(31)	132(115)
Effective N	159			157		

Chemical fertilizer consumption within the study areas in relation to N has been a little less than the national average while the consumption of P and K was similar. Due to larger live-stock concentrations and correspondingly large quantities of manure, the total amount of fertilizer being applied has been greater than the national average.

Variation in N-supply

Although the agreement between the N-supply and N-demand has been good, there have been large variations for many of the fields. Variations in N-supply to a variety of crops can be seen in figure 2. As the N-demand varies from field to field, the relation supplied N/N-demand has been used. Those areas supplied with substantially more N than necessary were commonly those receiving manure. In almost all of the examples where the N-supply was 40-50 % greater than the N-demand, the inexpedient application of manure has been the problem. Discord between N-supply and N-demand has been reduced considerably from 1983-84 to 1989, yet there was still significant disagreement within many of the fields.

Storage capacity for manure

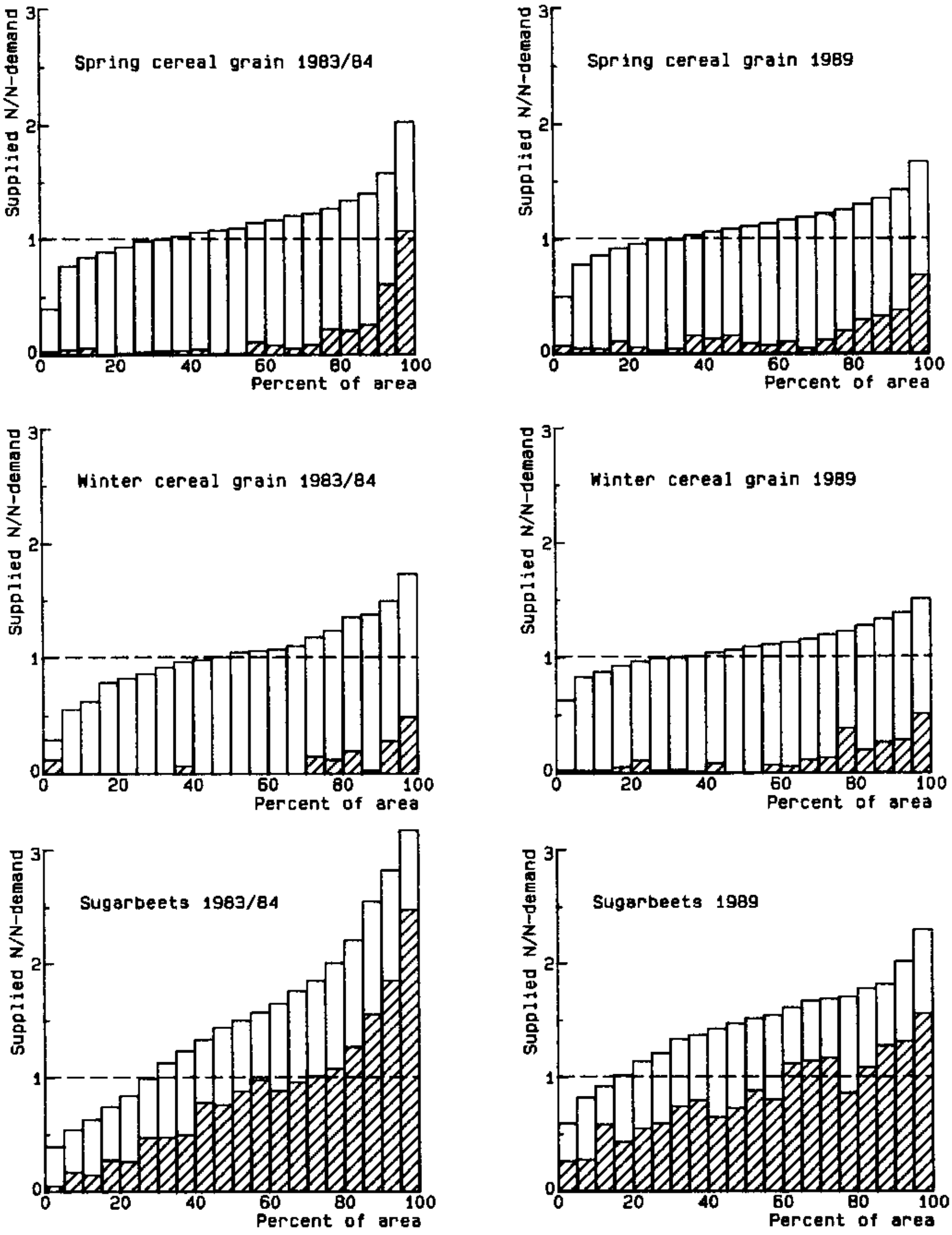
Estimates of manure storage capacity are shown in Figure 3A. As can be seen, storage capacity has generally improved, especially for urine and slurry although in 1989, it was still insufficient in some instances. The increased storage capacity seems to have had little influence on the timeliness of manure application, Figure 3B.

Collection of manure heap runoff

The data collected from the sandy areas during investigations in 1983-84 show that approx. 25% of the runoff from manure heaps had been collected. In 1989 practically all, approx. 98 %, runoff from manure heaps had been collected.

Silage crops

The proportion of grass silage which had not been pre-dried and for which runoff had not been collected was reduced from 18 % of the total grass silage in 1983-84 to 8 % in 1989. Grass was made into silage from approx. 12% of the cultivated area in 1983-84 and 9 % in 1989.



Spring cereal grain 1983/84

Spring cereal grain 1989

Winter cereal grain 1983/84

Winter cereal grain 1989

Sugarbeets 1983/84

Sugarbeets 1989

Figure 2. Variations in the relationship of supplied N/N-demand for spring cereal grains, winter cereal grains and sugarbeets in 1983-84 and 1989. The cross-hatched portion of the column represents the effective supply of N from manure, and the remaining (no cross-hatch) portion of the column represents the supply of N from chemical fertilizer.

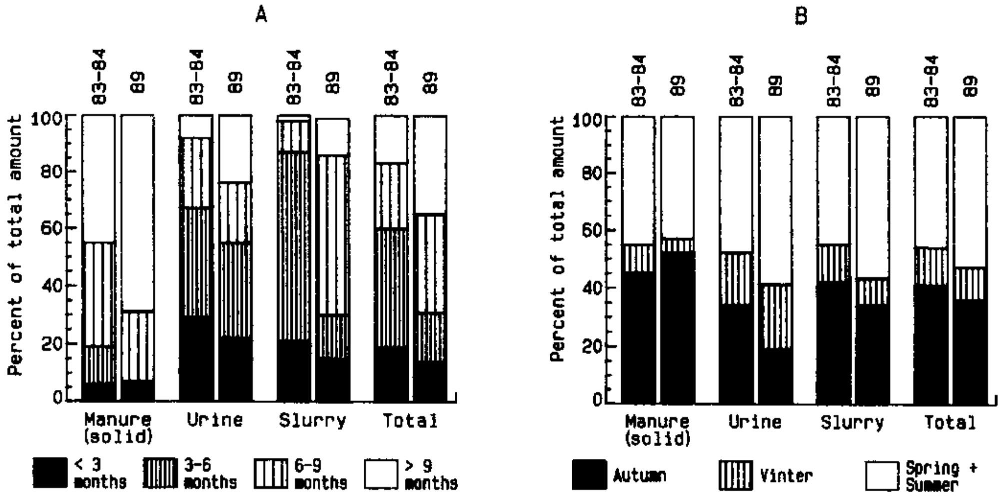


Figure 3. Summary of manure storage capacity (A) and time of application (B).

Purchase and sale of products

Elementary nutrient values for purchased feed, sold vegetable products and sold animal products have been calculated according to Koefoed & Hansen (1990). The calculated nutrient levels per ha cultivated area are shown along with purchases of chemical fertilizers and net purchases of nutrients in Table 3. Net purchase refers to the difference between nutrient content of the purchased and sold products.

Table 3. Net purchases of nutrients, kg per ha, cultivated area.

	1983-84			1989		
	N	P	K	N	P	K
Chemical fertilizer	132	16	42	128	13	45
Manure	3	1	2	8	2	8
Feed	73	14	20	82	16	23
Total purchace	208	31	64	218	30	76
Vegetable products	28	5	12	60	10	26
Animal products	38	8	7	29	6	5
Manure	0	0	0	4	1	4
Total sale	66	13	19	93	17	35
Net purchase	142	18	45	125	13	40

Nutrient purchases in the form of chemical fertilizer

In most instances, the greatest proportion of nutrients were purchased in the form of chemical fertilizer, yet an average of approx. 1/3 of nutrients were purchased in the form of feed. There was a significantly greater purchase of N, P and K than was sold in the form of different products.

Net purchase

Net purchases of N, P and K were, on the average, reduced by 10-20% from 1983-84 to 1989. For N, the most important factor in reduction has been an increase in the total cultivated area with peas in that N-fixation by legumes has not been taken into account. It must also be assumed that the reduction in live-stock concentrations have had a direct effect on the reduction in net purchases of N as there is a significant loss of N fra manure. Reduction in net purchases of P and K has primarily been due to increased sales of vegetable products though some of the reduction in P purchases was owed to the overaal reduction in chemical fertilizers.

Transfer of surplus manure between farms had increased significantly from 1983-84 to 1989 which can be seen from the increased nutrient levels of purchased and sold manure.

4.DISCUSSION AND CONCLUSION

Live-stock

The average reduction of dairy cattle in the areas during the period has been 23 % while that for swine has been approx. 12 %. Dairy herds were at both times approx. 30 % larger than the national average. Swine herds were approx. 10 % larger than the national average in 1983-84 and was equal to the national average in 1989.

Cropland use

The total cultivated area with spring sown crops having a short growing season (spring cereal grains and spring rape) were reduced during the period by approx. 10 %. The areas with winter cereal grains and winter rape were simultaneously increased concurring with the national average. The areas with legumes increased from 2% in 1983-84 to 7% in 1989 in contrast to the respective increase of 1% and 4% on a national basis.

Consumption of

Consumption of chemical fertilizers has been reduced, on the average, from 132 kg N/ha in 1983-84 to 129 kg N/ha in 1989 in comparison reductions on a national basis of 136 and 135 kg N/ha, respectively. The reduction in N consumption has been due primarily to changes in the use of croplands.

Variation in N-supply

Discrepancies between N-supply and N-demand have been noted for a significant portion of the study area, yet it can also be noted that these discrepancies have been greatly reduced from 1983-84 to 1989. Those areas which received only chemical fertilizer generally showed small differences in the N-supply and N-demand. The largest differences were notably seen on those areas and crops on which manure was inexpediently applied.

Storage capacity for manure

The storage capacity for manure had increased, yet was still insufficient by 1989 for a large part of the manure. The increased storage capacity seems to have little influence on the timeliness of manure application.

Silage storage

Storage capacity for silage had improved from 1983-84. Approximately half of the runoff from sugarbeet top silage was still not being collected in 1989.

Net purchase of nutrients

The net purchase of plant nutrients is the difference between nutrient content of the purchased and the sold products. There is a significant net purchase of both N, P and K which along with the amount supplied by rainfall and N-fixation by legumes is either lost and/or accumulated on the individual farms. Previous studies (Hansen & Sommer, 1987) indicate that surplus P is primarily accumulated in the plow layer and that K leaches below the plow layer and accumulates and/or leaches below the root-zone.

5. LITTERATURE

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I forbindelse med NPo-forskningsprogrammet er transport og omsætning af kvælstof og fosfor i jorden og i luften undersøgt. Korte engelske sammendrag beskriver de enkelte forskningsprojekter.

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Nitrogen processes in Danish agricultural soils have been studied in the comprehensive NPo Research Programme. Abstracts of projects on the application and transformation of fertilizers, slurry and manure are presented with special emphasis on nitrate leakage from the rootzone and ammonia volatilization from manure and slurry.

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