NPo-forskning
fra Miljøstyrelsen

B - abstracts

Nitrogen and Phosphorus in Groundwater

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
B - abstracts

Nitrogen and Phosphorus in Groundwater

Project abstracts
of the Danish NPo Research Programme

Miljøministeriet
Miljøstyrelsen

List of Contents

INTRODUCTION

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.

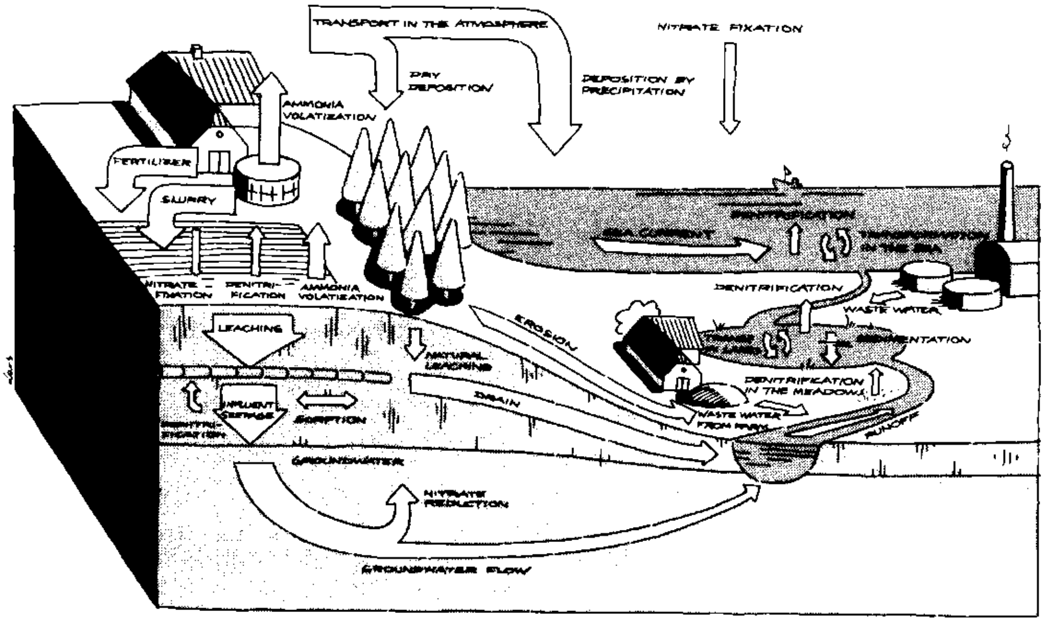

Figure 1.1 Transport and transformation of nitrogen and phosphorus in the environment

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 1.13.

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.

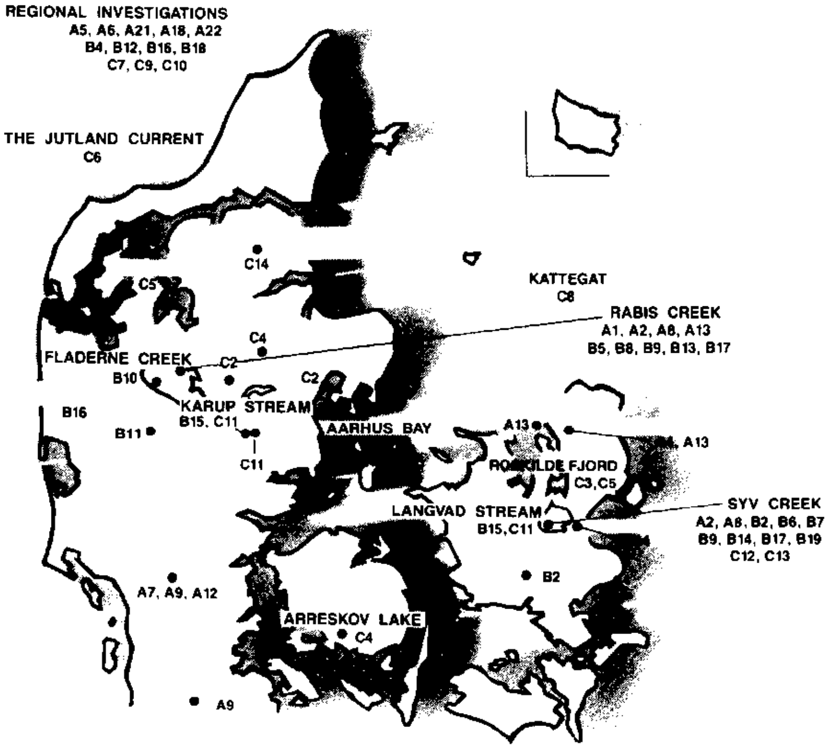

Figure 1.2 Location of the NPo-projects.

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.

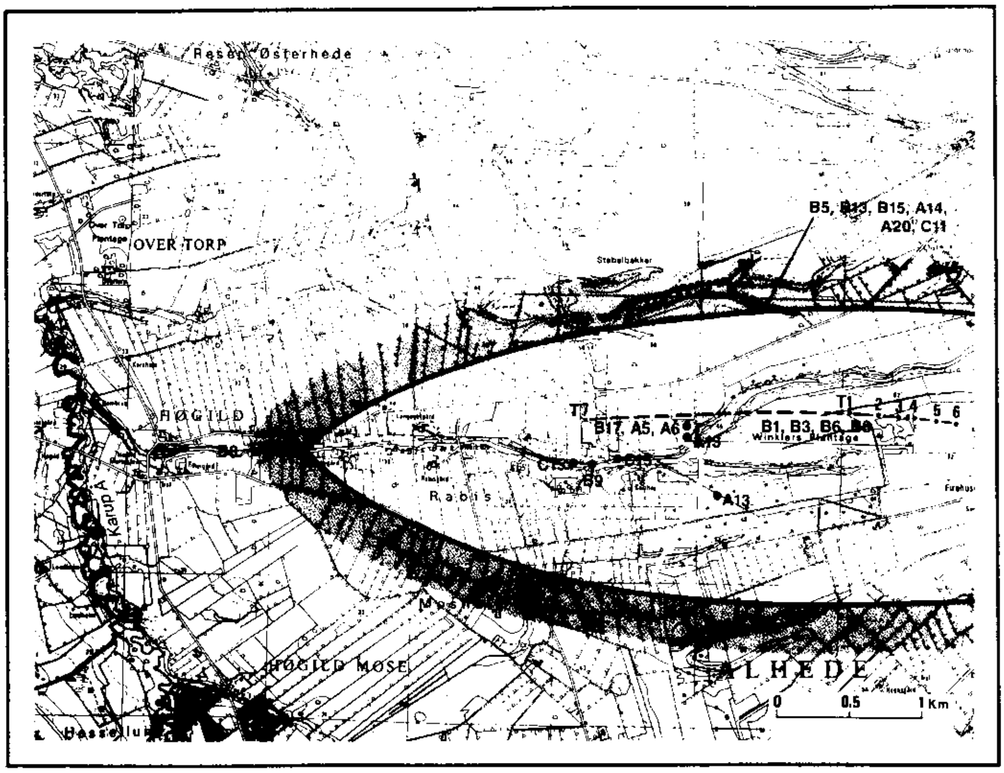

Figure 1.3 The study basin Rabis creek in Jutland.

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.

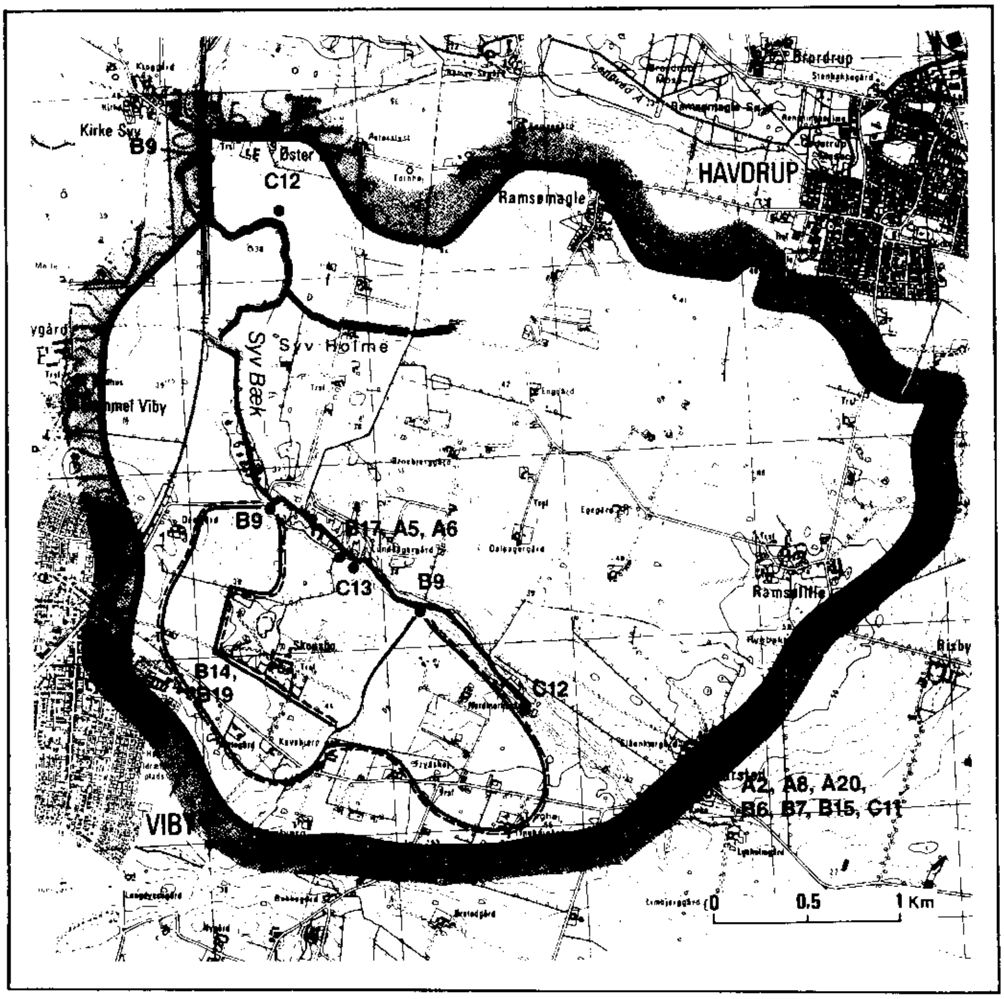

Figure 1.4 The study basin Syv creek on Sealand.

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 B1

Chemical nitrate reduction by Fe(II)compounds

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SUMMARY

Chemical NO_3^- reduction by Fe(II) in presence of Fe silicates (arfvedsonite and augite) was demonstrated at slightly acidic conditions. The NO_3^- reduction by Fe(II) was not mediated by ionic (dissolved) Fe(II) or by the silicate mineral surface per se, but took place only if a precipitation of Fe oxyhydroxide was present on the mineral surface. The importance of Fe oxyhydroxide in catalysis of chemodenitrification was further demonstrated for chemical NO_2^- reduction by Fe(II), which was strongly stimulated by presence of an Fe oxyhydroxide (lepidocrocite); maximum rates were here recorded at slightly alkaline conditions.

Unknown Fe(II)-containing compounds, e.g. mixed-valence Fe(II)-Fe(III) oxyhydroxides ("green rusts"), seemed to support the chemodenitrification process in the in vitro experiments. Such compounds are likely to be present in the subsoils, where chemodenitrification could be significant.

1. INTRODUCTION

In O_2-free layers of subsoils, NO_3^- or NO_2^- may be reduced to nitrogen gases (primarily N_2O and N_2) by denitrification. While bacteria certainly mediate the process, inorganic compounds such as ionic Fe(II) may be reductants in chemical NO_3^- or NO_2^- reduction (chemodenitrification). Ionic Fe(II) appears from dissolution of Fe(II)-containing minerals such as Fe silicates and Fe sulfides in aquifers (Postma and Brockenhuus-Schack, 1987). Chemodenitrification by Fe(II) is not well studied under in situ conditions, however, and there is little information on reaction rates and kinetic control of the process.

In the present study, the catalytic effect of Fe silicates, pyrite and Fe oxyhydroxides on chemical NO_3^- and NO_2^- reduction by Fe(II) was investigated in vitro in O_2-free reactors.

2. MATERIALS AND METHODS

Two O_2-free experimental systems were used: 1. Fluidized bed reactor to study the slow process of chemical NO_3^- reduction by Fe(II), including the catalytic effect of Fe silicates and pyrite. 2. Batch reactor (bulk suspension) to study the rapid process of chemical NO_2^- reduction by Fe(II), including the catalytic effect of Fe oxyhydroxides.

Mineral phases were analyzed for purity and crystallinity by scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis. Specific surface areas of the minerals were determined. The soluble phase was analyzed for Fe(II), NO_3^- and NO_2^- by standard chemical techniques and the gaseous phase for N_2O by gas chromatography. The pH was determined by an electrode inserted in the reactors.

3. RESULTS AND DISCUSSION

1. Chemodenitrification by Fe(II) in presence of Fe silicates.

Dissolution of Fe silicates (arfvedsonite and augite) and chemical NO_3^- reduction were studied under acidic conditions in the fluidized bed reactor. Under O_2-free and strongly acidic conditions (pH 1) arfvedsonite crystals dissolved and released ionic Fe(II) into solution (Postma, 1990). As shown in Fig. 1, however, release of ionic Fe(II) at slightly higher pH (pH 3) resulted in precipitation of Fe oxyhydroxide on the arfvedsonite crystals.

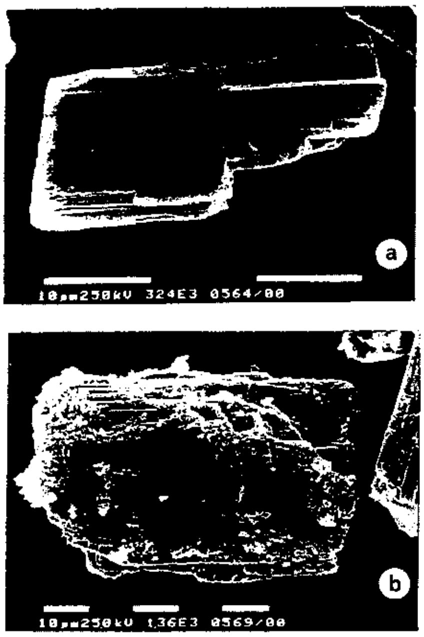

Figure 1. Arfvedsonite crystals without (a) and with (b) precipitation of Fe oxyhydroxide on the surface.

Chemical NO_3^- reduction by Fe(II) was absent at pH 1, but occurred at pH values above 2, when precipitation of Fe oxyhydroxide was found on the silicate mineral. From an experiment initiated at pH 1, Fig. 2 demonstrates that Fe precipitation (consumption of ionic Fe(II) resulting in lower concentration in reactor solution) took place concurrently with an increase of pH to about 2. The formation of Fe oxyhydroxide (occurring after the increase of pH) was observed by SEM analysis during this period. Chemical NO_3^- reduction (consumption of NO_3^- to a lower concentration in reactor solution) occurred after the precipitation of Fe oxyhydroxide. It was concluded that NO_3^- was reduced chemically by an Fe(II)-containing compound formed during the precipitation af Fe oxyhydroxide, rather than by ionic Fe(II) in solution or by the silicate mineral per se.

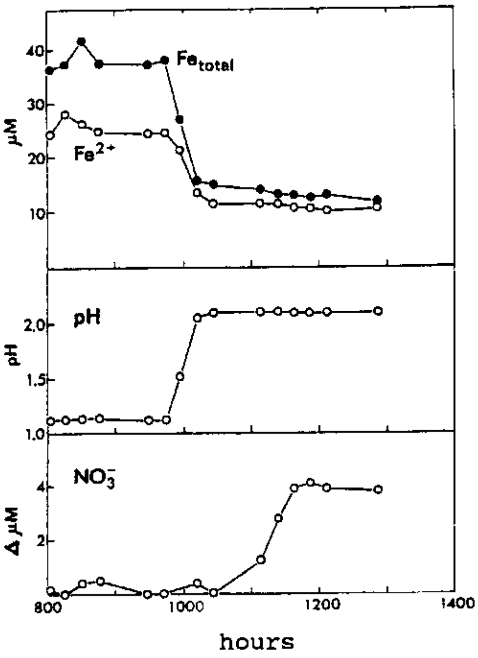

Figure 2. Binding of Fe(II) and release of protons (shown by increase of pH) during precipitation of Fe oxyhydroxide on arfvedsonite crystals in O_2-free fluidized bed reactor (reaction occurs at about 1000 h of incubation). Reduction of NO_3^- (shown by difference of NO_3^- concentrations relative to initial concentration of 15 uM) after Fe oxyhydroxide precipitation (reaction occurring at about 1100 h of incubation).

Similar results were obtained with another silicate mineral, augite, whereas pyrite showed no reactivity under these experimental conditions.

Several experiments were performed in the pH range from about 2 to about 7; the highest rate of NO_3^- reduction by Fe(II) in experiments with Fe silicates was observed at pH 4 (Postma, 1990).

2. Chemodenitrification by Fe(II) in presence of Fe oxyhydroxides:

Chemical NO_2^- reduction by Fe(II) in presence of Fe oxyhydroxide, lepidocrocite (gamma-FeOOH) or ghoetite (alpha-FeOOH), was studied in the batch

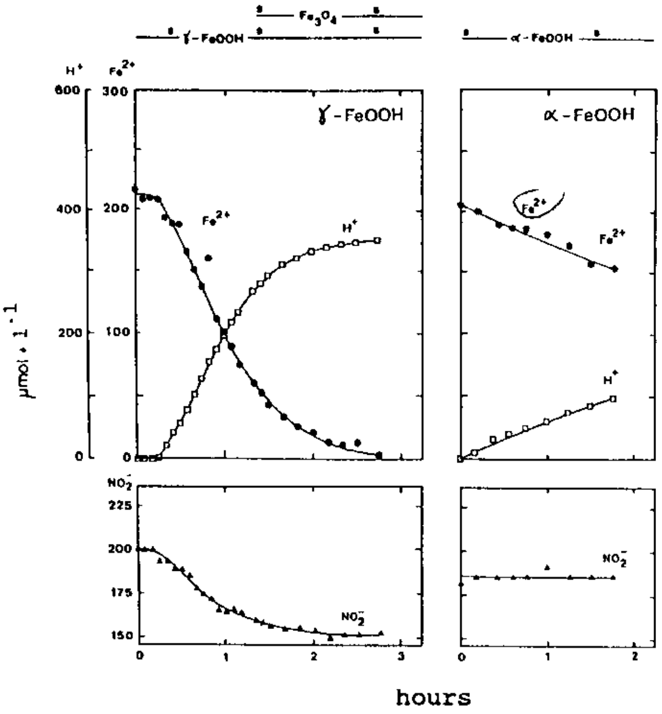

Figure 3. Binding of Fe(II), release of protons, and reduction of NO$_2^-$ during lepidocrocite (left) and ghoetite (right) transformation to magnetite in O$_2$-free batch reactor (controlled pH value of 8). Strong (s) and weak (w) XRD signals for crystalline phases are indicated.

reactor. Experiments were not performed at acidic conditions, where NO$_2^-$ is chemically unstable (self-decomposing).

Figure 3 demonstrates that lepidocrocite transforms into magnetite (Fe$_3$O$_4$) in presence of ionic Fe(II) and slightly alcaline conditions (pH 8). The transformation takes place after binding of Fe(II) to the solid phase and release of protons into solution. A change of the suspension color, from ochre (lepidocrocite) to green-olive ("green rust" ?) and eventually to black (magnetite), could observed during the experiment (Sørensen and Thorling, in press). A similar exchange of ionic Fe(II) and protons was observed in the parallel experiment with ghoetite, but at a slower rate. Green or black coloration, indicating "green rust" or magnetite formation, was not observed by the duration of this experiment.

Chemical NO$_2^-$ reduction took place as soon as binding of Fe(II) to lepidocrocite was initiated (Fig. 3), but was absent in the experiment with ghoetite and in control experiments without Fe oxyhydroxide (only ionic Fe(II) present). It was concluded that NO_2^- can be reduced chemically by an Fe(II)-containing compound formed during the transformation of lepidocrocite into magnetite, rather than by ionic Fe(II) in solution or by lepidocrocite in the solid phase.

Experiments with lepidocrocite, performed at different pH values above 6, showed the highest rate of NO_2^- reduction at pH 8.5 (Sørensen and Thorling, in press).

Chemical NO_3^- reduction by Fe(II) in presence of Fe oxyhydroxides could not be demonstrated in the short-term experiments using the batch reactor, but has been demonstrated earlier at a high temperature of 70°C (Styhr Petersen, 1979).

4. CONCLUSION

Chemical NO_3^- and NO_2^- reduction by Fe(II) is stimulated by the presence of lepidocrocite. The catalysis may be due to the reducing power of Fe(II) in an amorphous or micro-crystalline silicate or mixed-valence oxyhydroxide ("green rust" ?), formed during binding of ionic Fe(II) to lepidocrocite. Chemodenitrification with ionic Fe(II) is slow. Iron silicates and oxyhydroxides could be important catalysts of chemodenitrification, e.g. in the redox transition zone of subsoils (aquifers), where lepidocrocite is commonly found.

5. REFERENCES

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Ministry of the Environment
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Number B2

Nitrate reduction in clayey till

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Abstract

In an area dominated by clayey till the subsoils' ability to reduce nitrate was investigated below beech wood and arable land till a depth of 10-21 m.

In subsoils below wood the nitrate contents (NO_3^-) are below detection limit at all depths, whereas nitrate occurs in measurable quantities in the upper oxidised zone (until c. 3 m) in subsoils under arable land. The NO_3^- reduction is assumed to take place in anaerobic parts of the oxidised zone or at the redox line. Presumably, the reduction is caused by structural ferrous iron (Fe(II)) in the clay minerals.

Below wood and arable land the Fe(II) in the oxidised zone make up 15% and in the reduced zone c. 50% of the total iron content. A leaching of 50 kg N/hectare/year in a period of 80-160 years is calculated to use up the reduction capacity in a 1 m layer of clay.

1. Introduction

Previous investigations of subsoils below arable land have demonstrated that nitrate occurs in considerable amounts in the upper oxidised part, whereas the nitrate content is low in the reduced zone where large amounts of easily accessible ferrous iron occur (Lind & Pedersen, 1976).

Likewise, an investigation of clayey till to a depth of 14 m demonstrated that nitrate was present in the upper oxidised layer, and that the soil layers' ability to reduce nitrate was assumed to be caused by structural ferrous iron in the clay minerals (Ernstsen & Lindgreen, 1985).

The aim of the project was to investigate the nitrate reduction in clayey sediments and the concurrent changes in different chemical components and in clay mineralogy below the root zone in arable land and wood.

2. Materials and methods

2.1 Materials

The investigation was carried out in Sealand in quaternary sediments dominated by clayey till from the Weichsel glaciation, figure 1.

At 4 locations, i.e. two in arable land: Sparresholm (SH) and Ravnsbjerg Løjed (RL) plus two in beech wood: Denderup Vænge (DV) and Storskov (ST), sediments were sampled at approx. 0.5 m intervals to a depth of 10-21 m. The samples were frozen until analysis.

The oxidised reddish brown zone was about 3 m deep under arable land (SH and RL) and forms a relatively well-defined transition (the redox line) to the underlying reduced zone. Below wood (DV and ST) the oxidised zone was deeper, 5-6 m, and the transition to the reduced zone was more diffuse. At SH, RL and DV distinct red and grey mottles were found till a depth of approx. 3 m caused by temporary perched water table (pseudogley).

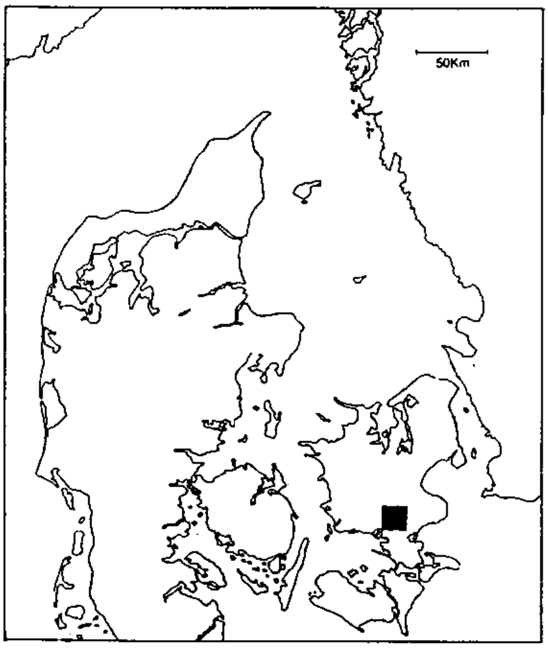

Figure 1. Investigation field in clayey till from the Weichsel glaciation.

The glacial clayey till (to a minimum depth of 2 m) was overlying alternating layers of glacial melt-water sand, and melt-water clay, and clayey till.

In clayey till the content of clay (<2µm) was between 13 and 35%, in glacial melt-water clay 35-55% and in glacial melt-water sand <5%. At SH and RL the pH($CaCl_2$)-value was c. 8 and the calcite content was high (5-30%). At DV and ST acidification processes in the soil had resulted in pH($CaCl_2$)-values of c. 4 to a depth of approx. 2 m. Deeper down the pH($CaCl_2$)-value increased to c. 8 and at the same time the calcite content increased to 5-20%.

The primary content of phosphorus (P) was approx. 400 ppm P (mg P/kg soil) in the clayey sediments and approx. 150 ppm P in sandy sediments. Under wood the vegetation's consumption of the primary content of P could be detected to a depth of 2 m (Ernstsen, 1990).

2.2 Methods

Nitrate was extracted from soil with 2M KCl, exchangeable ammonium was replaced with sodium acetate, pH 8.2 and fixed ammonium was determined after treatment with 5N HF: 1N HCl (Silva and Bremer, 1966).

Easily accessible ferrous iron was determined after extraction into a 3% $AlCl_3$ solution (Lind & Pedersen, 1976). Free Fe oxides were determined by the dithionite/citrate/bicarbonate method (Mehra & Jackson, 1960), and the total contents of iron and manganese in the soil layers were determined by decomposing the sample with HF (Møberg et al., 1988). Different forms of iron were analysed by Mössbauer spectroscopy (Murad, 1988). Phosphorus was extracted into 0.02M sulphuric acid, and organic matter was determined by differential thermal analysis (DTA) with evolved gas analysis (EGA).

The composition of clay minerals (<2 µm) was studied by X-ray diffraction. Calcite was removed by treatment with sodium acetate, pH 5.0. Fine clay (<0.2 µm) and coarse clay (0.2-2 µm) were separated in a continuous-flow centrifuge, and Fe- and Al-oxyhydroxides were removed by the dithionite/bicarbonate/citrate method. Diffractometer mounts were prepared by the pipette method: Mg^{2+}- and K^+-saturated air-dried specimens, Mg^{2+}-saturated glycerol specimens and K^+-saturated specimens heated at 300°C.

3. Results

3.1 Different nitrogen compounds.

Below arable land, SH and RL, nitrate (NO_3^-) occurs in variable quantity in the oxidised zone (max. 3.0 ppm NO3-N; ppm = mg N/kg fine soil), figure 2. At the transition to the reduced zone (the redox line) the content decreases pointedly to below detection limit.

Below wood, DV and ST, the content of NO_3^- is below the detection limit both in the oxidised zone and in the reduced zone, figure 3.

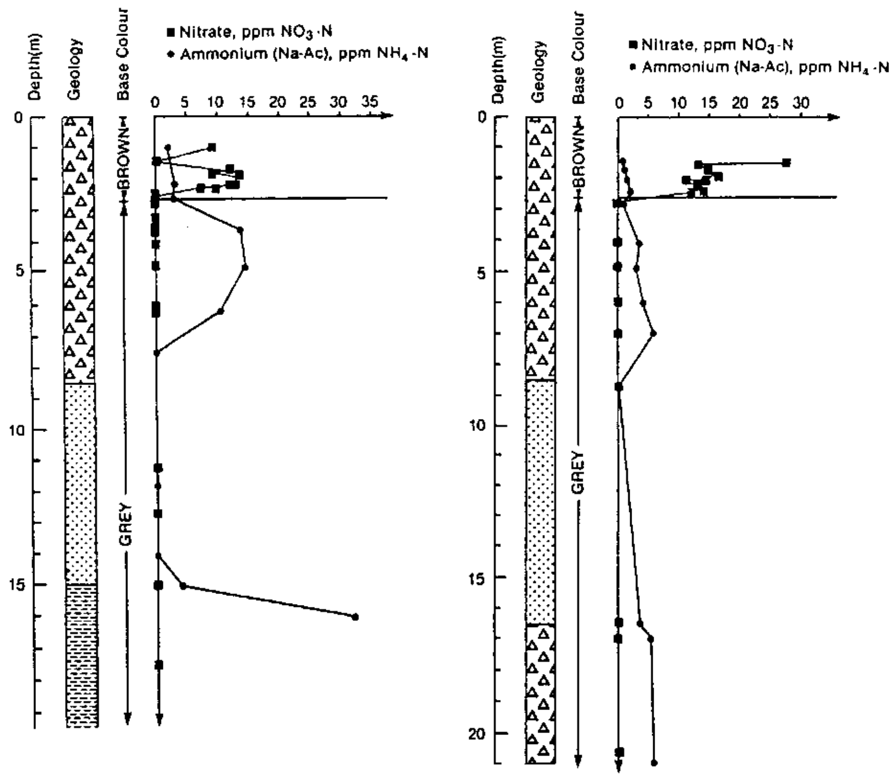

Figure 2. Sparresholm (SH) and Ravnsbjerg Løjed (RL). Nitrate (NO_3^-) and ammonium (NH_4^+) below arable land. △△ : Glacial clayey till, ░ : Glacial melt-water sand, ▤ : Glacial melt-water clay.

Below arable land as well as below wood the content of exchangeable NH_4^+ is relatively low in the oxidised zone. In the reduced zone the quantity of NH4-N increases in the clayey sediments (glacial melt-water clay and clayey till) up to a maximum of 25-30 ppm NH4-N whereas the content stays permanently low in melt-water sand, figures 2 and 3.

Nitrogen in the form of fixed NH_4^+ occurs in much larger quantity than those found as exchangeable NH_4^+ and NO_3^-, table 1. There are no marked differences between the content under arable land and under wood. The distribution seems to depend on the content of clay.

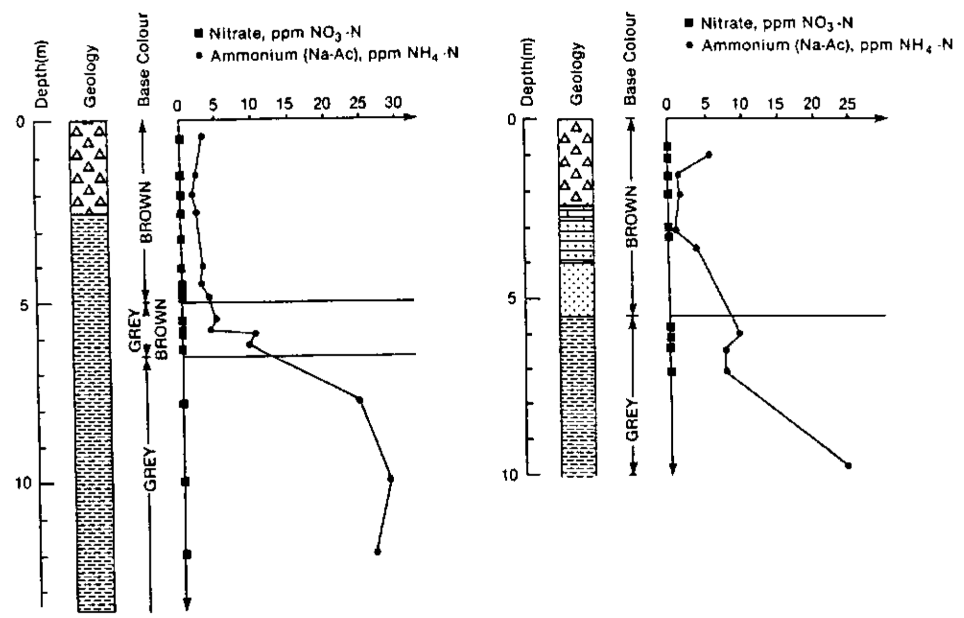

Figure 3. Denderup Vænge (DV) and Storskov (ST). Nitrate (NO_3^-) and ammonium (NH_4^+) below beech wood. △△ : Glacial clayey till, ⋯ : Glacial melt-water sand and silt, ▤ : Glacial melt-water clay, ▦ : Chalk.

3.2 Different iron varieties

The content of easily accessible Fe^{2+} in the oxidised zone is normally less than approx. 10 ppm Fe^{2+} (ppm = mg Fe/kg fine soil), increasing to 11-42 ppm Fe^{2+} in the reduced zone, table 2.

The content of different forms of iron extracted with dithionite-citrate-bicarbonate is higher in the oxidised zone, 0.5-1.5% Fe$_2$O$_3$, than in the reduced zone, 0.1-0.7% Fe$_2$O$_3$, table 3.

Different forms of iron was determined in samples of fine clay (<0.2 µm), coarse clay (0.2-2 µm) and fine soil (<2mm) by Mössbauer spectroscopy.
Ammonium saturated fine clay and coarse clay from arable land were analysed at room temperature, and a few spec-

tra are shown in figure 4. Smaller amounts of iron were found as components at velocities of 6-7 and 8-9 mm/sec. and may be hematite or goethite.

DENDERUP VÆNGE		KCl	Na-Ac	HF:HCl
Depth (m)	Geology	ppm NH_4-N		
2.0	ML	0.6	1.9	150
5.95	DL	5.2	9.2	180
6.24	DL	4.2	9.2	170

STORSKOV		KCl	Na-Ac	HF:HCl
Depth (m)	Geology	ppm NH_4-N		
1.54	ML	0.9	2.0	110
6.04	DL	5.9	9.8	180
9.75	DL	19.5	24.7	220

SPARRESHOLM		KCl	Na-Ac	HF:HCl
Depth (m)	Geology	ppm NH_4-N		
1.0	ML	0.6	2.3	200
2.68	ML	0.5	4.6	160
2.75	ML	1.4	7.3	160
6.23	ML	3.0	10.9	130
16.0	DL	18.0	32.0	210

RAVNSBJERG LØJED		KCl	Na-Ac	HF:HCl
Depth (m)	Geology	ppm NH_4-N		
2.74	ML	0.9	3.1	80
6.0	ML	1.7	4.2	80
21.0	ML	2.4	6.8	50

Table 1. Ammonium extracted into KCl, sodium acetate (Na-Ac), and fixed ammonium (HF:HCl).
Redox line is shown as a double line. ML: Glacial clayey till, DL: Glacial melt-water clay.

The major part of the iron found in these fractions occurs as structural ferrous iron (Fe(II)) and structural ferric iron (Fe(III)) in the clay minerals, figure 4 and table 4. The Fe(II)/(III) ratio changed at the redox line, i.e. from the oxidised zone (2.7 m below surface) to the reduced zone (2.8 m below surface).

Ravnsbjerg Løjed

Depth (m)	Geology	ppm Fe^{2+} (mg/kg)
2.9	ML	5
2.37	ML	2
2.74	ML	11
4.04	ML	15
6.0	ML	27
7.0	ML	26
10.25	DS	17
14.5	DS	17
17.0	ML	19
21.0	ML	15

Sparresholm

Depth (m)	Geology	ppm Fe^{2+} (mg/kg)
1.0	ML	4
2.09	ML	6
2.68	ML	9
3.66	ML	24
4.68	ML	13
6.23	ML	18
7.5	ML	19
11.75	DS	32
15.0	DL	13
17.5	DL	16

Storskov

Depth (m)	Geology	ppm Fe^{2+} (mg/kg)
0.75	ML	<1
1.54	ML	<1
2.04	ML	1
3.04	DV	1
3.61	DV	2
4.5	DS	3
5.8	DL	21
6.04	DL	17
6.32	DL	14
7.11	DL	21
9.75	DL	45

Denderup Vænge

Depth (m)	Geology	ppm Fe^{2+} (mg/kg)
0.5	ML	<1
1.5	ML	1
2.5	ML	<1
4.0	DL	5
4.5	DL	11
4.91	DL	4
5.5	DL	12
5.67	DL	7
6.38	DL	22
7.80	DL	28
10.0	DL	42
12.0	DL	37

Table 2. Easily accessible ferrous iron.
Redox line is shown as a double line, and the transition zone as two double lines. ML: Glacial clayey till, DL: Glacial melt-water clay, DS: Glacial melt-water sand, DV: Alternating thin melt-water beds.

Furthermore, at the same depths, the content of Fe(II) is seen to be generally smaller in fine clay than in coarse clay, table 4.
In samples of fine soil the main part of the total content of iron is found in clay minerals and, furthermore, the changes in distribution of the Fe(II)/Fe(III) ratio are seen at the redox line, table 5.

Changes in structural iron are reflected in the composition of the clay minerals, especially in chlorite which occurs normally in the reduced zone only. Furthermore, the oxidation processes seems to influence the formation of vermiculite, smectite or illite-smectite (Ernstsen, 1990).

Ravnsbjerg Løjed

Depth (m)	Geology	Fe_2O_3 (%)
1.75	ML	-
2.43	ML	0.35
2.60	ML	-
2.67	ML	0.22
2.74	ML	0.16
2.79	ML	0.16
4.82	ML	0.14
6.0	ML	0.12
7.0	ML	0.25
10.25	DS	0.12
19.5	ML	0.13

Sparresholm

Depth (m)	Geology	Fe_2O_3 (%)
1.0	ML	1.27
1.80	ML	1.18
2.09	ML	-
2.29	ML	1.46
2.54	ML	1.02
2.68	ML	2.01
2.75	ML	0.24
2.80	ML	-
15.0	DL	0.69
16.0	DL	0.68
17.5	DL	0.48

Storskov

Depth (m)	Geology	Fe_2O_3 (%)
0.5	ML	0.94
1.04	ML	0.95
1.54	ML	-
2.04	ML	0.87
3.04	DV	0.57
3.61	DV	0.83
4.5	DS	0.24
5.8	DL	0.35
6.04	DL	0.38
6.32	DL	0.32
7.11	DL	0.43
9.75	DL	0.50

Denderup Vænge

Depth (m)	Geology	Fe_2O_3 (%)
0.5	ML	1.83
1.5	ML	0.90
2.5	DL	1.44
4.0	DL	0.83
4.91	DL	1.28
6.58	DL	0.39
7.81	DL	0.48
12.0	DL	0.47

Table 3. Iron extracted into CBD. Redox line is shown as a double line, and the transition zone as two double lines. ML: Glacial clayey till, DL: Glacial melt-water clay, DS: Glacial melt-water sand, DV: Alternating thin melt-water beds.

Sparresholm		Particles <0.2 µm		Particles 0.2-2 µm	
		FeII	FeIII	FeII	FeIII
Depth (m)	Geo-logy	% absorption		% absorption	
1.0	ML	12	88	25	75
2.7	ML	20	80	38	62
2.8	ML	29	71	51	49

Table 4. Structural ferrous iron (Fe(II)) and structural ferric iron (Fe(III)) in ammonium saturated clay from clayey till at Sparresholm.

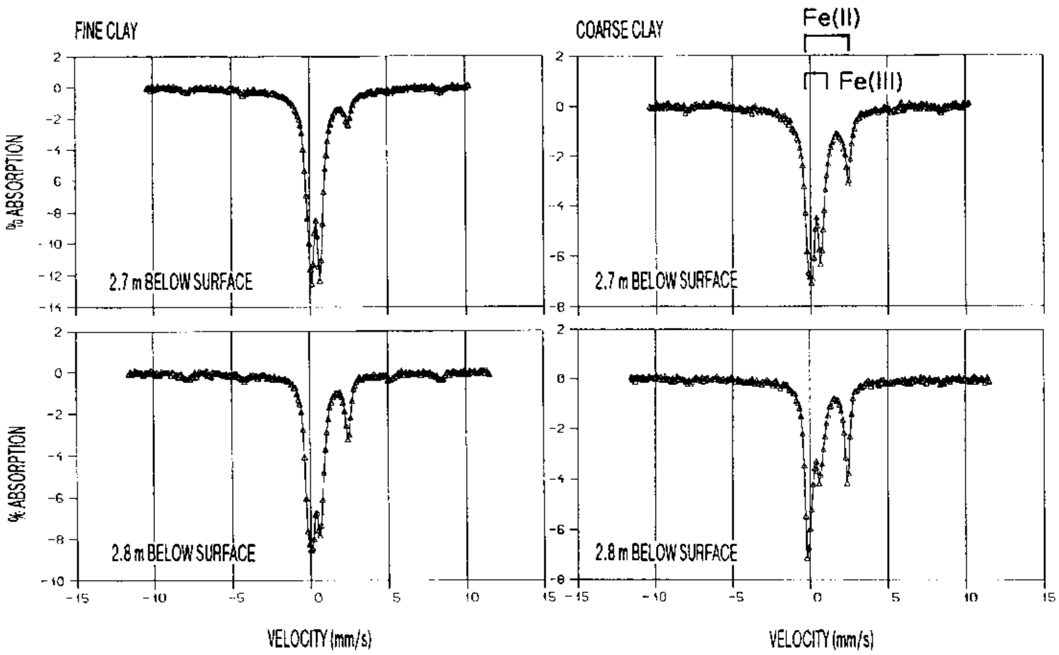

Figure 4. Mössbauer spectra of ammonium saturated clay from clayey till at Sparresholm.

Sparresholm		Particles <2 mm	
		FeII	FeIII
Depth (m)	Geo-logy	% absorption	
2.4	ML	29	71
4.2	ML	47	53
6.3	ML	44	56

Ravnsbjerg Løjed		Particles <2 mm	
		FeII	FeIII
Depth (m)	Geo-logy	% absorption	
1.8	ML	16	84
2.7	ML	44	56
4.8	ML	48	52

Denderup Vænge		Particles <2 mm	
		FeII	FeIII
Depth (m)	Geo-logy	% absorption	
3.3	DL	14	86
4.8	DL	15	85
7.7	DL	41	59

Table 5. Structural ferrous iron (Fe(II)) and structural ferric iron (Fe(III)) in fine soil (<2 mm). Redox line is shown as a double line. ML: Glacial clayey till, DL: Glacial melt-water clay.

3.3 Organic matter and manganese

Regardless of the land use, the content of organic matter make up a maximum of 0.4% C and seems to be determined by the clay contents of the layers, and in view of this the contents in the oxidised zone and in the reduced zone are broadly alike, table 6.

Ravnsbjerg Løjed

Depth (m)	Geology	C (%)
1.74	ML	<0.1
2.60	ML	0.1
2.67	ML	0.1
2.74	ML	0.3
6.0	ML	0.1
19.5	ML	0.1

Sparresholm

Depth (m)	Geology	C (%)
1.0	ML	0.2
2.29	ML	0.3
2.54	ML	0.3
2.68	ML	0.4
2.75	ML	0.3
4.75	ML	0.3
17.0	DL	0.4

Storskov

Depth (m)	Geology	C (%)
0.5	ML	0.1
2.04	ML	0.1
3.61	DV	0.1
4.5	DS	<0.1
5.8	DL	0.3
7.11	DL	0.3

Denderup Vænge

Depth (m)	Geology	C (%)
0.5	ML	0.2
2.5	DL	0.1
4.91	DL	0.2
6.38	DL	0.3
7.81	DL	0.3

Table 6. Organic matter (C). Redox line is shown as a double line, and the transition zone as two double lines. ML: Glacial clayey till, DL: Glacial melt-water clay, DS: Glacial melt-water sand, DV: Alternating thin melt-water beds.

Under arable land, at SH, the amount of manganese is seen to vary between 0.7-0.8% MnO_2 in both the oxidised and in the reduced zone (Ernstsen, 1990).

4. Discussion and conclusions

In an area dominated by clayey till and with different nitrogen impact (arable land and wood) the distribution of different nitrogen compounds, forms of iron and clay mineralogy was investigated.

The limit between the oxidised zone and the reduced zone (the redox line), i.e. at approx. 3 m below surface under arable land and at 5-6 m below surface under wood, visualises the changes in the redox conditions in the subsoil, and this limit has proved to be very important for the distribution of different chemical and clay mineralogical parameters.

Below arable land NO_3^- occurs only in the oxidised zone where, by the way, the distribution seems to depend on both variations in the nitrate concentration in the percolating water and the redox conditions. At the redox line the content of nitrate decreases distinctly to below the detection limit. Under the root zone the reduction is assumed to be attached primarily to the redox line and in anaerobic parts of the oxidised zone. Corresponding results has been obtained at other Danish investigations in clayey till (Ernstsen et al., 1990). Below wood without N-application the nitrate content is below detection limit in all levels.

Exchangeable ammonium (NH_4^+) occurs mainly in the reduced zone. The amount of exchangeable ammonium make up 1-15% of the amount found in the soil layers as fixed ammonium.

Under the root zone the amount of nitrogen in fixed ammonium exceeds the amount found in the form of nitrate and exchangeable ammonium. Probably, fixed ammonium forms a primary content in the sediments.

Different redox conditions are also reflected in the distribution of different forms of iron. Easily accessible ferrous iron occurs mainly in the reduced zone where it makes up a rather small amount (up to a maximum of 50 ppm) compared to the amount of structural ferrous iron in the clay minerals (1-2%).

Free iron oxidehydroxides, primarily presumed to be formed by oxidation of structural ferrous iron outside the crystal structure, occur mainly as coatings in the oxidised zone.

The main part of the iron in the clay sediments consists of structural ferrous iron (Fe(II)) and structural ferric iron (Fe(III)). The Fe(II)/Fe(III) ratio is changed at the redox line. Fe(II) makes up approx. 15% Fe(II) in the oxidised zone and approx. 50% Fe(II) in the reduced zone. This applies to arable land as well as to wood. The composition of the clay minerals is influenced by the Fe(II)/Fe(III) ratio.

In this investigation it has been possible to prove the result of the nitrate reduction processes. The process course has not yet been described in detail but it implies both chemical reactions and microbiological processes (Ernstsen, 1990).
Manganese and organic matter are assumed to participate in the nitrate reduction to a smal extent. Therefore, the ferrous iron capacity has been used in the calculation of the soil layers' ability to remove nitrate.
The part of the soil layers' total iron content which is presumed to be active at different processes, including nitrate reduction, has been calculated as the ferrous iron capacity of the soil layers, table 7.
Below arable land and wood the quantity of active ferrous iron is assumed to be 25% which corresponds with the difference between Fe(II) in the reduced zone and the oxidised zone. The total content of iron in the soil layers was calculated to an average of 3% Fe for SH, 1.9% Fe for RL and 3.6% Fe for DV. The volume weight of the soil is assumed to be 1.6.

	Capacity of ferrous iron per m^3	
	g	mol
Sparresholm	12000	210
Ravnsbjerg Løjed	7600	140
Denderup Vænge	15600	280

Table 7. Capacity of ferrous iron.

The nitrate reduction process is assumed to take place according to the equation below:

$$5Fe^{2+} + NO_3^- + 12H_2 \text{--->} 5Fe(OH)_3 + 0.5N_2 + 9H^+$$

On an annual nitrate leaching of 50 kg N/hectare (0.355 mol/m^2) the capacity at SH will be used up in a 0.8 cm thick layer, which corresponds to approx. 120 years per metre clay layer. At RL the capacity is 1.2 cm/year, and at DV 0.6 cm/year.

Therefore, intensive farming with application of large quantities of nitrogen seems to play a relatively modest role for the oxidation of ferrous iron in clay layers in comparison to the oxidation processes, which have taken place in the last 10-15,000 years, in arable land as well as in wood.

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Nitrate Reduction and Solid Organic Carbon in Aquifer Materials

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Abstract

A new term called Total Reduction Capacity (TRC) is introduced to quantify the total amount of reduced compounds in aquifer materials analytically. By applying the method to 48 aquifer samples from Rabis Creek it is shown that TRC is mainly attributed to organic carbon in the sediment. A distinct increase of TRC was observed at and below the oxidation-reduction front. Oxygen and nitrate were present above the oxidation-reduction front but disappeared in the front, indicating TRC to be an important bulk parameter in controlling nitrate concentrations in groundwater.

In simple batch experiments only biological nitrate reduction was seen, and the reduction was not correlated with the TRC content or the oxidation status of the sediment. No increase of sulfate concentration was seen during the batch experiment, indicating that nitrate reduction caused by oxidation of reduced sulfur compounds was not a significant process. Increasing contents of inorganic carbon in batch with significant nitrate reduction pointed at solid organics in the aquifer material as the major nitrate reducing component.

Introduction

The contamination of groundwater by nitrate found in many countries has lead to increasing interest in natural processes in aquifer materials lowering the nitrate concentration in the groundwater.

In top soils the main mechanism for reducing nitrate is denitrification, i.e. microbial reduction of nitrate to nitrogen gas by organic matter oxidation. In the early studies of nitrate reduction in deep soil profiles by Lind and Pedersen (1976b) both the number of nitrate reducing bacteria and the amount of organic matter was expected to be too low to support microbiological nitrate reduction, and nitrate reduction by chemical oxidation of ferrous iron was considered to be the major oxidation-reduction process. The reaction can be expressed in the form:

$$5Fe^{2+} + NO_3^- + 12H_2O \rightarrow 5Fe(OH)_3 + 1/2N_2 + 9H^+ \qquad (1)$$

showing that reduction of 1 mg NO_3^--N requires approximately 20 mg of ferrous iron. Based on Lind and Pedersen (1976a) the amount of available ferrous iron in sandy Danish aquifer material is roughly estimated to 0.05 %, which according to Equation 1 indicates that 40 g of aquifer material is needed to reduce 1 mg of NO_3^--N.

Recently a significant microbial activity has been documented in groundwater and aquifer material (see e.g. Ghiorse and Wilson (1988)). Consequently, microbiological nitrate reduction processes seems feasible in groundwater and aquifer material if other reduced compounds than ferrous iron are present.

Oxidation of reduced sulfur compounds as thiosulfate, sulfur and hydrogen sulfide are known to support nitrate reduction through the activity of the bacteria *Thiobacillus denitrificans* (Vishniac (1975)). Kölle et al. (1983) proposed nitrate reduction in groundwater by the oxidation of iron sulfides (e.g. pyrite, FeS_2) through the process

$$\begin{aligned} &5/14FeS_2 + NO_3^- + 2/7H^+ \rightarrow \\ &\qquad 5/7SO_4^{2-} + 5/14Fe^{2+} + 1/2N_2 + 1/7H_2O \end{aligned} \qquad (2)$$

showing that 1.6 mg of FeS_2 is required to reduce 1 mg of NO_3^--N. Pyrite has been found in the level of 1-2 % in association with lignite in a number of aquifers, but in most aquifers the amount of available reduced sulfur compounds is believed to be approximately 0.01 % which according to Equation 2 indicates that 16 g of aquifer material is needed to reduce 1 mg of NO_3^--N.

Recently nitrate reduction by microbial oxidation of organic matter (denitrification) has gained interest with respect to aquifer material (Leuchs (1985), Trudell et al. (1986), Morris et al. (1988), Starr and Gillham (1989)). The denitrification process may be represented by the reaction

$$5/4CH_2O + NO_3^- + H^+ \rightarrow 5/4CO_2 + 1/2N_2 + 7/4H_2O \qquad (3)$$

where CH_2O indicates solid organics in aquifer materials. According to Equation 3 approximately 1.1 mg of organic C is required to reduce 1 mg of NO_3^--N. Organic C may be found dissolved in groundwater in concentrations from approximately 1 to 10 mg C/l and as solid organic C in aquifer material. In coarse grained aquifers the content of solid organic C is supposed to be in the range 0.005 to 0.5 %. Both dissolved and solid organic C may potentially act as electron donor for denitrification, but from the amounts given it can be estimated, that the main theoretical capacity for denitrification must be attributed to the solid organic C. Assuming a content of 0.05 % organic C is available for denitrification in an aquifer material, Equation 3 indicates that 2.2 g of aquifer material is required to for denitrification of 1 mg NO_3^--N.

Based on the processes and estimated nitrate reduction capacities presented above it is assumed, that both the oxidation of reduced sulfur compounds and solid organic C can contribute significantly to nitrate reduction in sandy aquifer material, whereas nitrate reduction through the oxidation of ferrous iron is believed to be insignificant.

This study was initiated to (i) determine the Total Reduction Capacity (TRC) of sandy aquifer materials from different soil profiles, (ii) correlate the TRC of the aquifer materials to their content of Total Organic Carbon (TOC) and Total Reduced Sulfur (TRS), and (iii) determine whether nitrate reduction as observed from simple lab-incubation experiments could be assigned to oxidation of organic C or reduced sulfur compounds.

Materials and methods

Aquifer materials and groundwater were sampled by The Geological Survey of Denmark at the NPo-research area at Rabis Creek and at the plantation of Mangehøj, both located in the western part of Jutland. In this study approximately 70 wet and 50 freeze dried samples of aquifer material from eight 30-35 m deep profiles at Rabis Creek and 50 wet samples from a 62 m deep profile at Mangehøj are included. All wet samples were dried at 105 °C and sieved < 2 mm.

Incubation experiments

Incubation of aquifer materials were performed as simple batch experiments in brown glass bottles with polypropylene screw tops. 5 to 50 g of aquifer material from selected depths were weighted into series of 15 bottles. The bottles were filled with water low in oxygen, containing nitrate (approximately 6.5 mg NO_3^--N/l), inorganic pH-buffer (pH = 7.1, total alkalinity 2.0 meq/l), glucose (5 mg/l) and inoculum and incubated at 20 °C. pH, total alkalinity and concentration of nitrate, nitrite and sulfate were then followed as a function of incubation time by harvesting 1-2 bottles each time step. To control the incubation method and the involved materials a parallel series were performed without aquifer material. 3 bottles from each series were sterilized by autoclavation 2 days after setup to make it possible to separate chemical and biological nitrate reduction.

Addition of pH-buffer was required to maintain a neutral and relatively constant pH throughout the experiment, especially in aquifer samples from the oxidized part of the Rabis Creek profiles. Glucose was added to obtain anaerobic conditions in the bottles immediately after the incubation was started. If there was no oxygen in the bottles, glucose was used only for nitrate reduction, and the glucose could then account for the reduction of a maximum of 1.9 mg NO_3^--N/l. As the aquifer materials were freeze dried or dried at 105 °C it was decided to inoculate the water to ensure a homogeneous biological activity in all batches. The inoculum was composed of a mixture of pretreated waste water, extracts from top soils and a culture of sulfide oxidizing and nitrate reducing bacteria (probably *Thiobacillus denitrificans*).

Chemical water analysis in incubation experiments

Water samples from the incubation experiments were analyzed for pH, total alkalinity, nitrate, nitrite and sulfate. pH was measured with a Radiometer Research pH Meter PHM 64 and a combination electrode. Total alkalinity (TAL) was determined by connecting a Radiometer Autoburette ABU 11 to the pH Meter and titrating with 0.05 N sulfuric acid to pH 4.5. Nitrate, nitrite and sulfate analysis was performed on a Technicon AutoAnalyzer. Nitrate and nitrite was determined by methods based on modifications of procedures from Technicon Corporation (1969). Sulfate was determined by the methylthymol blue method described in APHA (1985).

Oxygen and nitrate in groundwater

Dissolved oxygen and nitrate in groundwater samples from Rabis Creek were determined by The Geological Survey of Denmark (refer to Kristiansen et al. (1990)).

Total Reduction Capacity

A new and more sensitive term called Total Reduction Capacity (TRC) is introduced to determine the content of reduced species (e.g. reduced iron, reduced sulfur compounds and organic carbon) in aquifer materials. TRC was measured with a modification of a procedure originally developed for determination of organic carbon in topsoils by Mebuis (1960). Five to ten grams of the aquifer material samples were treated with 9.5 ml of a digestion solution for one hour at 140°C in Pyrex 26 x 200 mm glass tubes with plastic screw tops with PTFE cap liners on an electric heating block. The digestion solution was 0.04 N potassium dichromate in 60 % (w/w) sulfuric acid with silver sulfate as catalyst. The residual dichromate was determined after cooling and dilution by titration with a 0.1 N ferrous ammonium sulfate solution and with Ferroin as an oxidation-reduction indicator. All TRC results are given in milliequivalents of electrons/kg.

Total Organic Carbon and Total Reduced Sulfur

Total Organic Carbon (TOC) and Total Reduced Sulfur (TRS) in the aquifer materials was determined by The Geological Survey of Denmark on the freeze dried samples (refer to Kristiansen et al. (1990)).

Expected relationship between TOC, TRS and TRC

The determined TRC-values are believed to be caused only by the oxidation of TOC and TRS in the aquifer materials, and the TRC may be expressed as

$$\text{TRC (meq/kg)} = a \cdot \text{TOC (\%)} + b \cdot \text{TRS (\%)} + c \qquad (4)$$

where *a* and *b* are constants representing the composition of organic matter and reduced sulfur, respectively, and *c* ideally equals zero.

Based on the assumptions that the average oxidation state of organic carbon in aquifer materials is similar to the average oxidation state of organic carbon in soils (approximately zero), and that the organic carbon is oxidized to the oxidation state +4 (corresponding to CO_2) in the TRC analysis, the magnitude of *a* can be estimated to 3333 meq/% TOC.

The oxidation state of reduced sulfur in aquifer materials may vary from -2 (corresponding to FeS) to zero (corresponding to elemental S). Assuming reduced sulfur to be oxidized to the oxidation state +6 (corresponding to SO_4^{2-}) in the TRC analysis, the magnitude of *b* can be estimated to vary between 1875-2500 meq/% TRS.

Results

Correlation of TRC with TOC and TRS

Results from the TOC and TRS analysis performed by The Geological Survey of Denmark on 50 freeze dried samples of aquifer materials were compared with the determined TRC-values. The average content of TOC, TRS and TRC were

Table 1: Linear regression analysis on TRC versus TOC and TRS for 48 samples of aquifer material from Rabis Creek (TRC in meq/kg, TOC and TRS in %).

Model 1:	TRC	= $a \cdot TOC + b \cdot TRS + c$			
Estimated parameters:	a	= 2970	±	194	***
	b	= 1581	±	632	**
	c	= − 79	±	20	***
	R^2	= 0.86			
Model 2:	TRC	= $a \cdot TOC + c$			
Estimated parameters:	a	= 3072	±	201	***
	c	= − 69	±	21	***
	R^2	= 0.84			

0.09±0.05 %, 0.013±0.015 and 211±167 meq/kg, respectively, showing that the main part of TRC was attributed to TOC. In a preliminary statistical analysis TOC and TRS were found to be independent. Only 48 samples are included in the linear regression analysis shown in Table 1, while two of the samples had extremely high TOC- (approximately 0.7 %) and TRC-values (> 1000 meq/kg) due to a considerable content of lignite. The statistical analysis shows a significant correlation between TOC, TRS and TRC (Model 1), and the observed TOC- and TRS-coefficients are close to the expected values. As a consequence of the fact, that TOC was the main contributor to TRC, it was, however, not surprising to find an equivalent correlation when TRS was excluded from the statistical analysis (Model 2). Figure 1 shows a scatterplot of TRC versus TOC and the estimated regression line for the 48 samples under investigation. The estimated TOC-coefficient is again close to the expected value.

In a parallel test TRC-values determined on a number of aquifer samples before and after drying at 105°C were compared, and it was found that drying did not affect TRC. Unfortunately, it was not possible directly to compare TRC-values determined on freeze dried samples and samples dried at 105°C, while there were no coincident samples, but generally no difference in TRC-levels were seen in the two treatments.

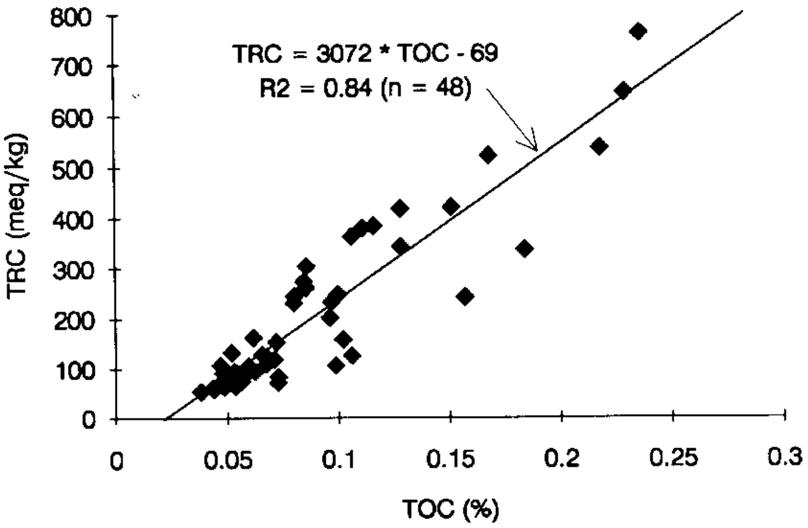

Figure 1: TRC versus TOC for 48 samples of aquifer material from 8 profiles at Rabis Creek.

TRC-profiles

In Figure 2 a TRC-profile of the aquifer materials from Mangehøj is shown. TRC is low (< 30 meq/kg) throughout most of the profile, but both in the top and in the bottom of the profile the TRC-level is much higher (> 500 meq/kg). The higher TRC-level at the top of the profile is due to organic matter in the root zone, whereas the higher level at the bottom is a result of a considerable content of lignite. The change in TRC at the depth of 58 m represents the transition from the oxidized to the reduced zone of the profile (the oxidation-reduction front). At the same depth a distinct change in color of the sediment from red to grey was observed.

In Figure 3 TRC-profiles of aquifer materials taken at the boreholes T2, T3 and T8 at Rabis Creek are shown together with the respective concentration profiles of dissolved oxygen and nitrate in groundwater. As in the profile from Mangehøj the observed increase in TRC could be used to locate the oxidation-reduction front. Generally, TRC is < 150 meq/kg in the oxidized part of the aquifer and > 150 meq/kg in the reduced part. The color of the sediment changed from mainly red

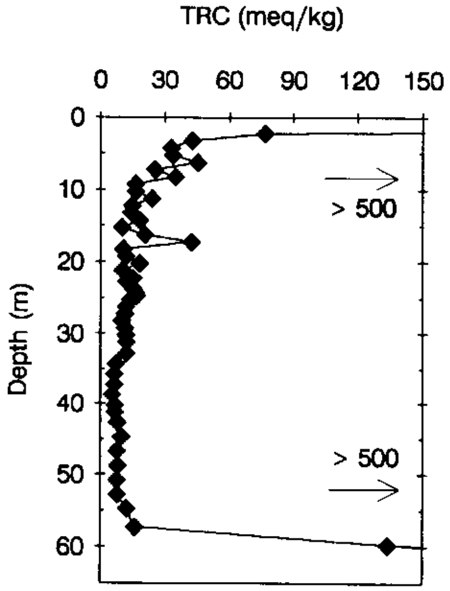

Figure 2: TRC-profile from the borehole at Mangehøj.

to grey at the oxidation-reduction front as seen in the Mangehøj profile. Both in T2 and T3 thin strata with significant contents of lignite leading to very high TRC-values were seen at approximately 30 m depth.

Comparison of the oxygen and nitrate concentrations found in groundwater with the TRC-profiles in Figure 3 shows that oxygen and nitrate is present above the oxidation-reduction front while both compounds disappear completely in the front zone. According to Postma and Boesen (1990) the disapperance of oxygen and nitrate cannot be explained only by dilution with oxygen and nitrate free water in the aquifer. The reduction of oxygen and nitrate at the oxidation-reduction front may then be attributed to the oxidation of reduced compounds leading to decreasing TRC-content of the sediment and a depression of the oxidation-reduction front.

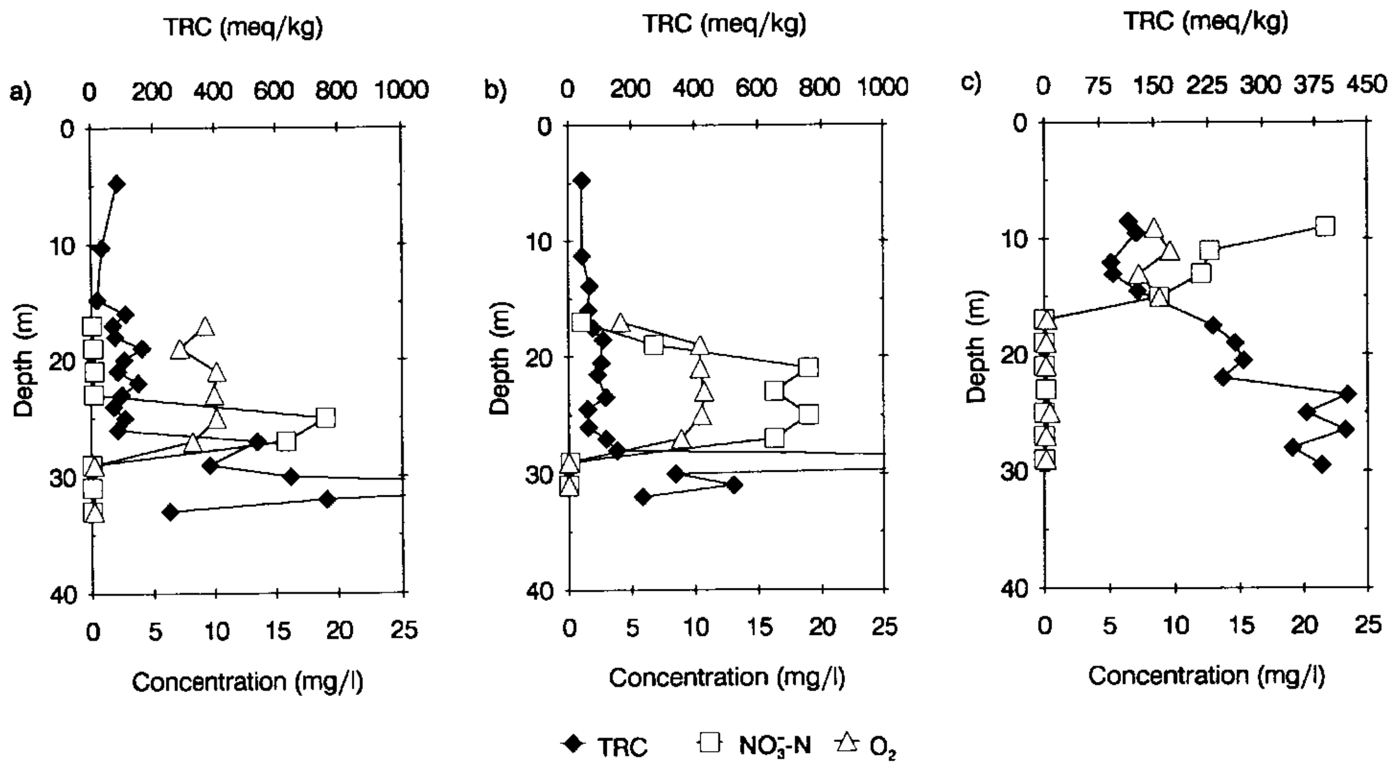

Figure 3: Vertical profiles of O_2 and NO_3^--N concentrations in groundwater and of TRC of sediment at the boreholes T2, T3 and T8 at Rabis Creek.

Batch experiments

Generally a considerable variation were observed with respect to nitrate and nitrite concentrations between batches in the time series. Nitrate reduction and nitrite were only observed in unsterilized batches indicating that nitrogen transformations were caused by biological activity. To examine the progress of the nitrate reduction all determined nitrate and nitrite concentrations were converted to nitrogenous oxidation equivalents ($Oxeq_{(NO_3^- + NO_2^-)}$):

$$Oxeq_{(NO_3^- + NO_2^-)} \text{ (meq/l)} = 5/14 \cdot NO_3^- \text{ (mg N/l)} + 3/14 \cdot NO_2^- \text{ (mg N/l)}$$

In Figure 4 the time course of $Oxeq_{(NO_3^- + NO_2^-)}$ and sulfate is shown in both sterilized and unsterilized batches for the control series without aquifer material and for two series with aquifer material. From the control series it can be seen that the glucose added initially primarily has been used to reduce oxygen, and that the oxidation of glucose has been completed within the two days before sterilization, as the content of $Oxeq_{(NO_3^- + NO_2^-)}$ corresponds to the initial nitrate concentration (6.5 mg NO_3^--N/l = 2.3 meq/l of $Oxeq_{(NO_3^- + NO_2^-)}$) throughout the experiment in both sterilized and unsterilized batches. The fact that $Oxeq_{(NO_3^- + NO_2^-)}$ is unchanged throughout the experiment in the unsterilized batch without aquifer material indicates that the plastic screw caps do not act as electron acceptors.

Except for presence of aquifer material the setup conditions were the same as in the control series for all other batch series. By comparing the series with aquifer material with the control series the reduction of $Oxeq_{(NO_3^- + NO_2^-)}$ caused by reduced compounds in the sediment (i.e. TRC) could be isolated. Generally, the extend and rate of $Oxeq_{(NO_3^- + NO_2^-)}$ reduction was not associated with the TRC content or the oxidation status of the sediment, or the amount of TRC added with the sediment. Reduction of $Oxeq_{(NO_3^- + NO_2^-)}$ was mainly seen in aquifer materials that had been freeze dried before incubation and the reduction rate decreased significantly after the first month of incubation indicating that the freeze drying treatment had made some of the TRC available as electron acceptors for nitrate reduction.

No increase in sulfate concentration were observed in batch series with significant nitrate reduction indicating that oxidation of reduced sulfur compounds are not

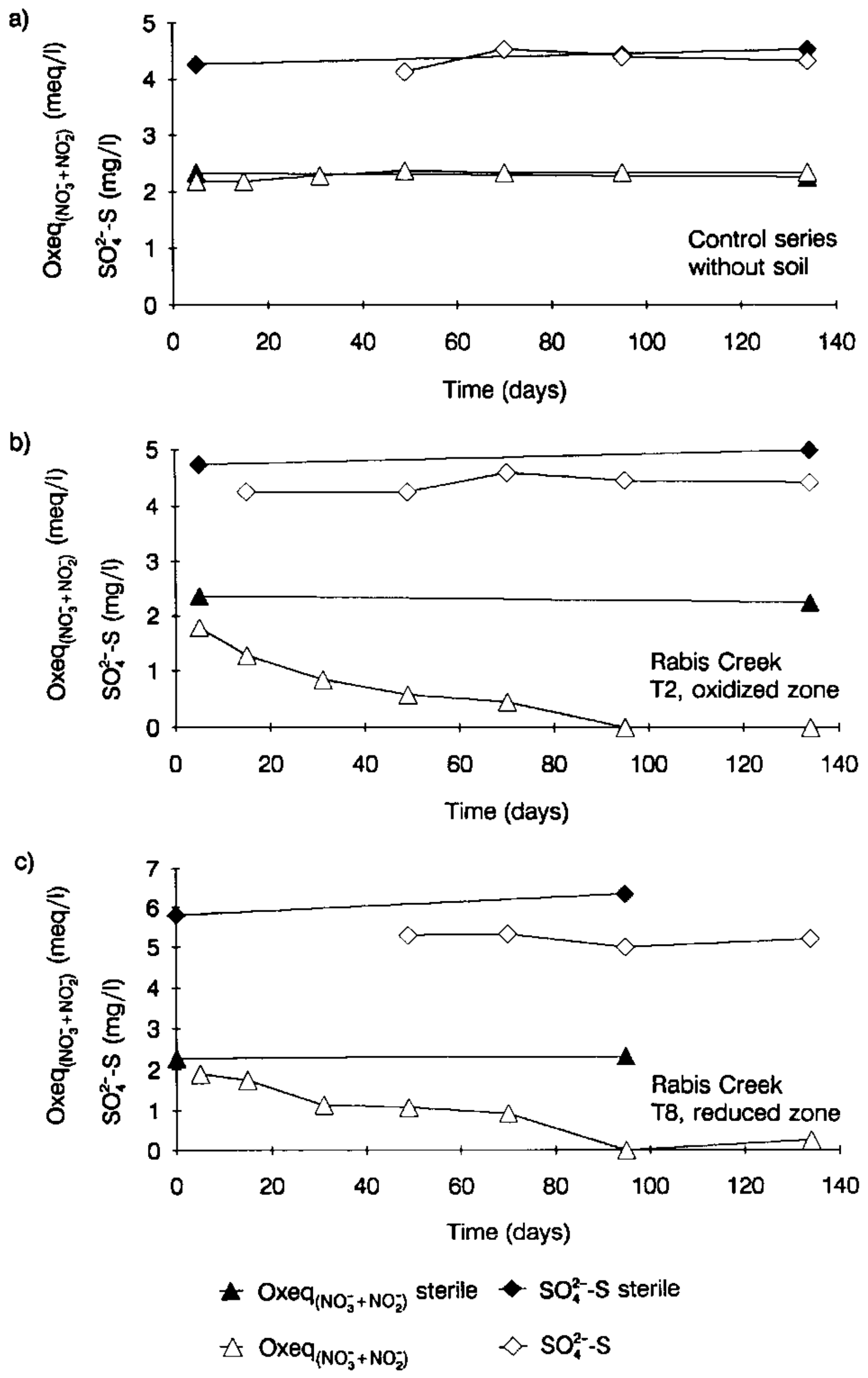

Figure 4: Time course of oxidation equivalents ($Oxeq_{(NO_3^-+NO_2^-)}$) and sulfate in sterilized and unsterilized batch series.

a significant contributor to nitrate reduction, since this process according to Equation 2 would result in a release of approximately 1.6 mg SO_4^{2-}-S/mg NO_3^--N reduced.

If the observed nitrate reduction was attributed to oxidation of organic matter, this process would according to Equation 3 result in a release of inorganic carbon (TIC) of approximately 0.09 mmol TIC/mg NO_3^--N reduced. Based on the determined pH and total alkalinity the amount of TIC released in each batch were calculated. For each batch the calculated TIC release is shown as a function of the observed nitrate reduction in Figure 5, and in spite of a considerable variation, some correlation between released TIC and nitrate reduction is seen. This points to solid organic carbon in the aquifer material as the major nitrate reducing component in the batch experiments carried out.

Discussion and conclusion

Based on the observed correlation between TOC, TRS and TRC it seems reasonable to use TRC as a simple and inexpensive measure of the reduced compounds in aquifer materials. TRC may be detected as low as 5 meq kg^{-1} with fair precision. This detection limit, assuming that all the reduction capacity is due only to solid organic carbon, corresponds to a sediment content of less than 0.002 % C. Such a low content of solid organic carbon is according to Powell et al. (1989) very difficult, if at all possible, to determine analytically by direct analysis. In this study, the major contributing component of the TRC was found to be organic carbon.

The comparison of oxygen and nitrate concentration profiles with TRC profiles from the Rabis Creek area has shown, that oxygen and nitrate are present above the TRC-determined oxidation-reduction front while both compounds disappear completely in the front zone. Pedersen et al. (1990) has presented similar observations in profiles from another Danish sandy aquifer. According to these observations, the performed characterization of the sediment in terms of TRC profiles shows that TRC seems to be an important bulk parameter in controlling the oxygen and nitrate concentration in the profiles. However, as a consequence of the very strong chemical oxidation conditions used in the TRC-determination

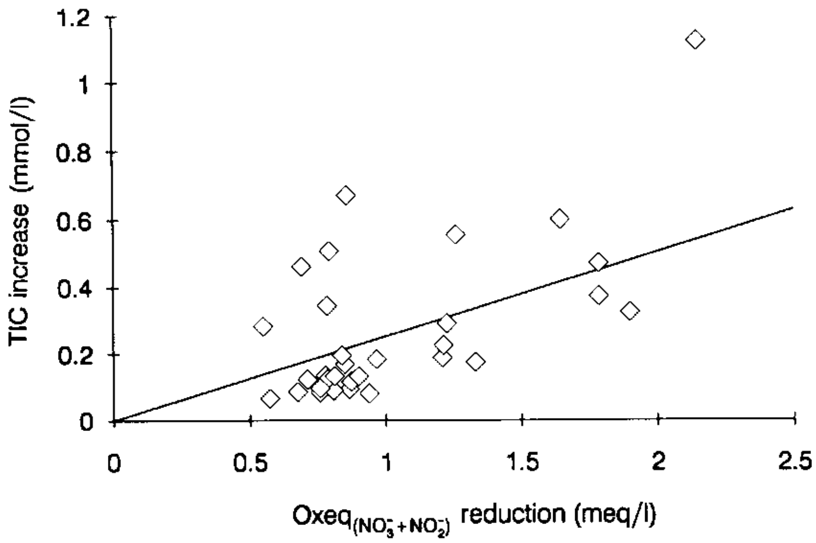

Figure 5: Increase of TIC as a function of observed nitrate reduction in batch series with aquifer material from Rabis Creek. The line represents the expected TIC-increase according to Equation 3.

and the fact that reduction capacity is still present in the oxidized zone, it is obvious that TRC is not a measure of reduction capacity immidiately available for natural chemical and biological processes.

In the batch experiments only biological nitrate reduction was seen, and the extend and rate of reduction was not associated with the TRC content or the oxidation status of the sediment, or the amount of TRC added with the sediment. However, freeze drying of the sediment before incubation may have made parts of the TRC available for oxidation, hiding the original characteristics of the sediment.

No increase of sulfate concentration was seen during the experiment, and the nitrate reduction caused by oxidation of reduced sulfur compounds indicated by the field investigations by Postma and Boesen (1990), could not be repeated in the lab-experiments. On the contrary, increasing contents of inorganic carbon in batches with significant nitrate reduction rather points to solid organic carbon in the aquifer material as the major nitrate reducing component.

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Number B4

Nitrate and Phosphate in Danish Aquifers

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Summary

Nitrate and phosphate in Danish aquifers

This report describes an investigation of nitrate- and phosphate concentration in ground water and drinking water from 20 important aquifers in Denmark. The investigation is based on existing data registers and databases at the Geological Survey of Denmark and the Institute for Applied Geology, Technical University of Denmark.

High nitrate in phreatic aquifers

Low nitrate content in confined aquifers

The study shows that the nitrate content is particularly high in phreatic aquifers without covering clay layers. In confined aquifers protected by thick clay layers the nitrate content is significantly lower. Locally high nitrate concentrations are found in deep confined aquifers due to insufficiant well head protection. However, the extent of contamination is limited and in none of the investigated aquifers a hindrance for drinking water supply. No correlation is found between aquifer lithology and nitrate concentration.

The water treatment on Danish waterworks does not include nitrate removal at present. Simple oxidation and filtering are the most common treatment. Small amounts of nitrate in drinking water, therefore, can arise from oxidation of ammonia. In general, however, nitrate concentration in drinking water is a good indicator of the nitrate concentration in ground water.

Phosphate concentrations in ground water in general are low compared to present standards for drinking water. In deeper wells there is a tendency to lower concentration than in shallow wells. Analyses from dug wells show a significantly higher phosphate contents. This indicate that phosphate in ground water is primarily restricted to shallow aquifers and due to local contamination.

Phosphate in drinking water rarely above permissible value

By the common drinking water treatment the phosphate content normally will be reduced. Drinking water concentrations reflect therefore both the ground water character and the water treatment. Phosphate content (P-total) above the standard for drinking water (0.15 mg/l) is found in appx. 1% of the examined analyses. The range 0.01-0.05 mg/l is the most frequently represented.

1. Introduction

This report is a contribution to the Danish NPo-research programme on environmental effects of Nitrogen, Phosphorus and Organic matter.

Purpose of investigation

The object of this investigation is to study the nitrate- and phosphate concentrations in some important Danish aquifers and illustrate the quality of drinking water applied from these aquifers. More than 95% of the drinking water supply in Denmark is based on ground water from aquifers in depths from 0 to 100 metres. The most important aquifers are:

Danish aquifers

- senonian chalk
- danien limestone
- selandien limestone
- miocene quartz sand
- quaternary glaciofluvialtile sand and gravel.

The aquifers are of different age and lithology, and are found in different depths. Furthermore, the aquifers are covered by sediments of different thickness and lithology.

These factors influences the nitrate- and phosphate content of the ground water. Other important factors are the hydrological conditions and the technical standards of the waterworks and wells. The most serious contaminations are found in shallow wells located near dunghills and sewers. Also in wells with inadequate wellhead protection local contamination occurs.

Waterworks

There are appx. 3000 waterworks in Denmark. The most common water treatment is oxidations and subsequent filtering. This treatment does not affect the nitrate content, but small amounts of nitrate can occur from oxidation of reduced ground water containing ammonium. In general the drinking water data are valuable as indicators for the nitrate contents in ground water. This is not the case for phosphate, as the water treatment normally will reduce the phosphate content due to oxidation formation of ferri-phosphate. In oxidated ground water only small amounts of phosphate are to be expected. In reduced ground water a certain phosphate content is expected.

The drinking water database, therefore, is not very suitable for studying phosphate in ground water.

2. Material and Methods

2.1 Ground water

Mapping of nitrate and phosphate in Danish aquifers are done on the basis of lithological and water quality data from geological and geochemical databases at the Geological Survey of Denmark. The geological database contains well data from water supply wells reported by the drillers supplied with sample descriptions and geological interpretations. The geochemical database contains reported analyses from samples generally taken in connection with well development. Time series of water quality data from single wells are generally not available.

Geological and geochemical databases

The amount of data in both databases are large although uneven distributed in the different areas. Detailed informations about the number of analyses from the different areas are found in (Kelstrup and Nielsen, 1989). Reduction in data have been done in cases of doubthful lithological description, and in cases where the analyse values are given in terms like trace, greater than and less than.

Representativity

The observation point in this survey is the water supply well, which have been performed for practical purpose and not scientific purpose. This implies for wells in a water table aquifer, that the the screened part is placed in the lower third of the aquifer. A water sample, therefore, may represent the nitrate free part of the aquifer or a mixture of water from different levels of the aquifer. Thus the analyses have a tendency to give too low values.

Influence from technical standard

In Denmark it is common that the well head, pump and other technical installations are placed in a so called well pit often with leaky bottom and sides. In clayey areas, it is common in the winter season to find intermittent saturated conditions around the well pits with the consequence that surface water may have direct access through the casing to the aquifers. In a well-cum-bore well situation an even more hazardeous situation occur when the well head are placed below the water table in the old dugged wells.

Situations as those discribed above are probably the reason why a relatively high nitrate content can be found in areas, where the aquifers are confined and below thick layers of clay.

The amount of water supply wells performed in old wells (the well-cum-bore well situation) may in some areas reach 30% of the total number of wells. For these reasons nitrate data from data from drilled wells in old dugged wells, as well as from dugged wells, are shown for comparison with data for the selected aquifers, fig. 1. The twenty aquifers, which are chosen to describe the nitrate situation, are selected with regard to geographical and lithological spreading, see fig. 1 and 2.

The above mentioned aquifers have been analysed for nitrate content by means of three different diagrams for each aquifer. That is a nitrate-frequency diagram, 5 year mean diagram and a clay -thickness diagram (Kelstrup and Nielsen, 1989). Finally, a conclusive diagram has been prepared, fig. 1.

Nitrate frequency diagram

The nitrate frequency diagram shows for each aquifer the percentage number of analyses distributed in concentration classes of 5 mg/l. Furthermore, location, total number of analyses, mean year of sampling, spreading and mean depth are indicated on the diagram.

5 year mean

The 5 year mean diagram shows for each aquifer the

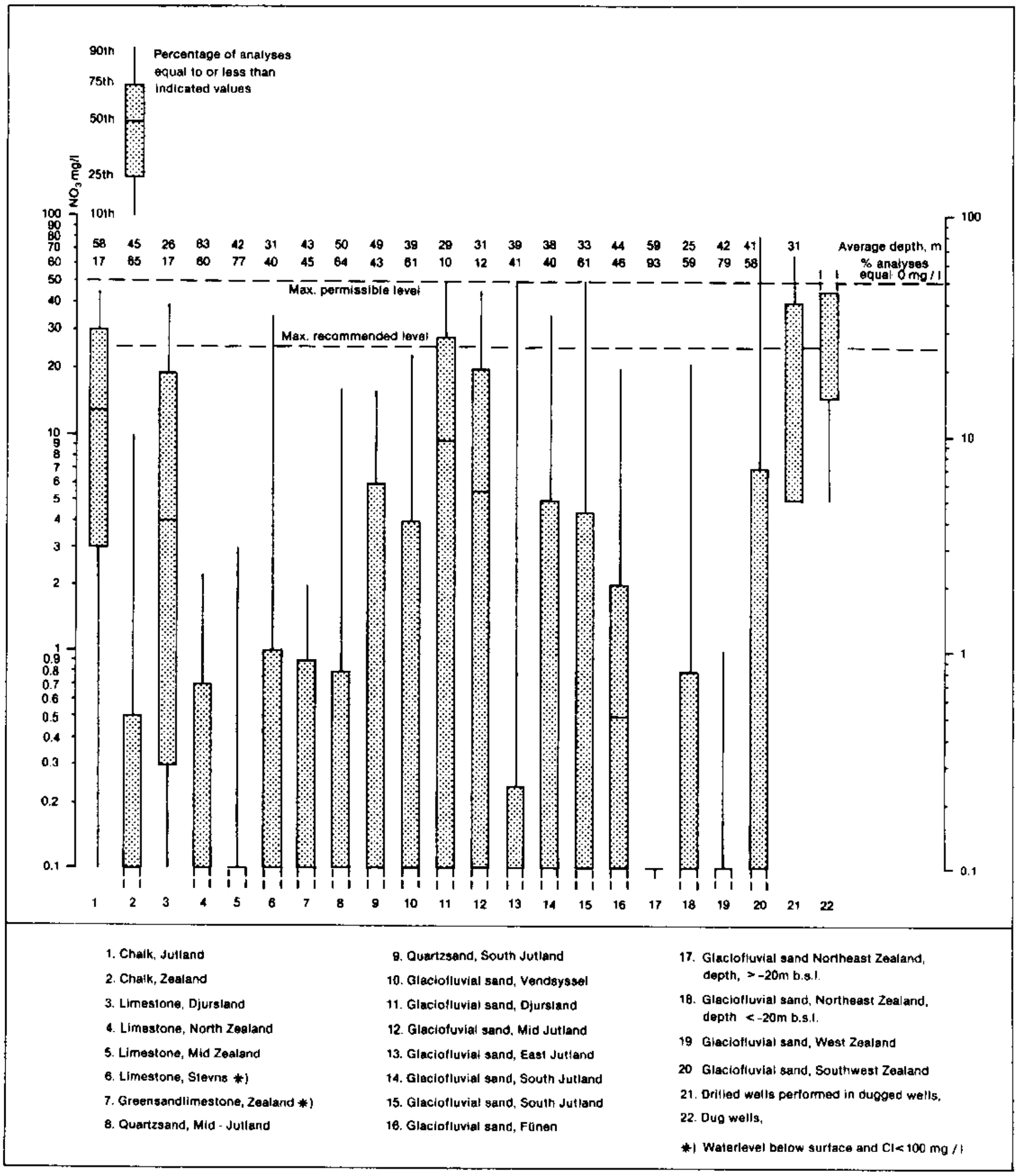

Fig. 1. Nitrate concentrations in Danish aquifers.

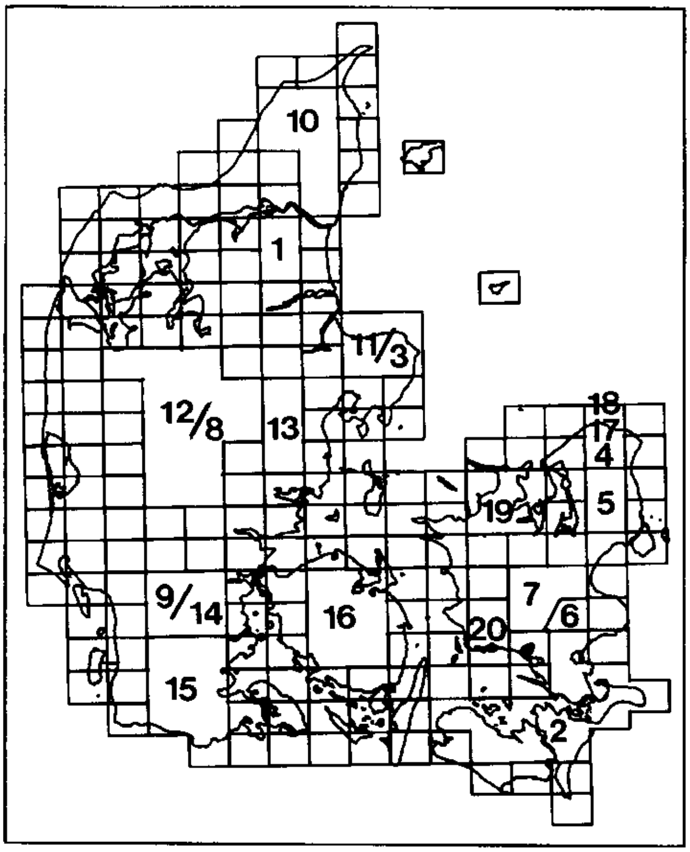

Fig. 2 Selected Danish aquifers
Numbers refer to the aquifers on Fig.1.

diagram

mean concentration of 5 year interval classes. Furthermore number of analyses are shown in each 5 year interval, the mean thickness of covering clay layers and the mean deapth. Finally are shown location and total number of analyses.

Clay thickness diagram

The clay thickness diagram shows the nitrate concentration versus thickness of covering clay and silt layers above the screened interval.

Conclusive diagram

The conclusive diagram, fig. 1. shows the nitrate concentration for each aquifer corresponding to the 10%, 25%, 50%, 75% and 90% quantiles, mean deapths of sampling and number of analyses with 0 mg/l nitrate.

Phosphate

The phosphate situation is not described for each aquifer, but for the whole country.

2.2 Drinking water

The Institute for Applied Geology, Technical University of Denmark, has for the National Agency for Environmental Protection established a national database for drinking water supply (Overgaard, 1986 and Overgaard et al., 1990).

Drinking water database

The database contains information for appx. 3000 waterworks covering 99% of the drinking water supply in the country. The database contains a total of appx. 70.000 chemical control analyses - each of 1 to 20 chemical parameters.

The database system is PC-based and it is runned on a standard PC with MS-DOS. With a minimum effort it is possible to create regional outlines for drinking water quality, for instance nitrate concentrations for a given period. Furthermore, it is possible to print or calculate trends for a given chemical parameter.

In this project waterworks from the selected 20 regions have been chosen for further analyses. For these waterworks the productive aquifers have been defined and only waterworks using one aquifer are accepted for this investigation. A total of 501 waterworks are fulfilling these criteria.

For each of the 20 regions the mean-value for 1985-87 nitrate and total-P are calculated for every water work. The nitrate values are plotted on geographical maps, where the mean concentrations are graduated in 4 ranges.

A trend analyses for nitrate has been carried out for waterworks fulfilling the following criteria:

- mean nitraconc. greater or equal to 5 mg/l
- at least 8 analyses available in the period 1980-89.

The results of this trend-analyses are shown in a table.

3. Results

3.1 Nitrate in ground water

Aquifers in senion chalk

Aquifers in chalk (No. 1 and 2 and fig. 1 and 2) Two aquifers have been investigated, one situated in Northern Jutland (1), and one in Southern Zealand, Lolland-Falster and Moen (2).
The aquifer in Jutland is phreatic as well as confined with great variability in thickness of covering clay layers. The Zealandic aquifer are confined and covered with thick clay-layers. In both aquifers are found a correlation between the thickness of clay layers and nitrate content. The difference in thickness of clay-layers causes a difference in nitrate content. In Jutland 75% of the analyses are below 30 mg/l, the median value 12 mg/l, the same values for the Zealandic chalk aquifer are 0,5 mg/l and below 0,1 mg/l.

Aquifers, danian limestone

Aquifers in danian limestone (No. 3, 4, 5 and 6 on figs. 1 and 2).
The aquifer in Djursland (3) have phreatic conditions with thin to lacking cover layers or confined conditions with covering clay layers less than 10 m. The aquifer in north eastern Zealand (4) are confined below thick clay layers and at least two overlying sand aquifers. The aquifer in Middle Zealand (5) are confined with thin covering clay layers and one overlying sand aquifer. Finally, the aquifer on Stevns (6) are confined with thin covering clay layers in the eastern part with increasing thickness towards west.

In all 4 aquifers a connection with thick clay layers and low nitrate content and vice versa have been established. Some exceptions occur especially in Middle Zealand and on Stevns, probably due to insufficient well head protection.

The nitrate concentration in the ground water from the four areas shows a significant correspondence with depth to aquifer and thickness of clay layers.

In Djursland 90% of the analyses are below 40 mg/l nitrate, 75% below 19 mg/l, the median value is 4 mg/l. The aquifers in north eastern Zealand and on Stevns show almost identical results with 75% of the analyses below 0,7 and 0,9 mg/l and median values below 0,1 mg/l. In the aquifer in Middle Zealand 75% of the analyses are below 0,1 mg/l.

Aquifer, selandien limestone

Aquifers in selandian limestone (No. 7 in figs. 1 and 2)
The aquifers are confined with thick cover layers of clay, which generally gives good protection to the aquifer. Exceptionally high nitrate values are attributed to insufficient well head protection. 75% of the analyses are below 0,85% mg/l nitrate with a median value below 0,1 mg/l.

Aquifers, miocene quartzsand

Aquifers in miocene quartz sand (No. 8 and 9 in figs. 1 and 2)
Aquifers in quartzsand are represented from 2 areas, one from Mid-Jutland (8) and are from Southern Jutland (9).
The aquifers are confined and have similar depths. In the aquifer material layers of mica clay and lignite occur. These rocktypes are not aquifers, but have a content of organic matter and pyrite, which generally are regarded to have nitrate reducing capacities.

The thickness of covering clay layers varies and may be missing, so a hydraulic contact to the overlying water table aquifers (No. 12 and 14) on figs. 1 and 2) may be established. Nitrate free water is found in connection with clayey cover layers, where the clay layers are missing high nitrate values may be found.

The 75% quantile from the Mid-Jutland area are 0,8% mg/l compared with 6 mg/l in the southern area (fig. 1). The median value in both areas is 0,1 mg/l.

Aquifers, glaciofluviatile sand and gravel

Aquifers in glaciofluviatile sand and gravel from 11 areas have been investigated, 4 of these are phreatic and 7 confined.

Phreatic aquifers

The phreatic aquifers are all situated in Jutland (No. 11, 12, 14 and 15 on figs. 1 and 2). The aquifers are mainly found in Weichselian outwash plains, although Saalian and Weichselian till deposits in some areas are included.

For the aquifers in Djursland (11) and Mid-Jutland (12) the 75% quantile are 28-20 mg/l nitrate with a median value of 10-6 mg/l and 50-45% of the analyses above the maximum permissible value of 50 mg/l. In the more southern situated aquifers the 75% quantile are 5-4 mg/l and the median value 0,1 mg/l and with 35-50% of the analyses are above 50 mg/l. The lower values in the southern Jutland are reflected in a relatively higher amount of clay in the cover layers and greater depths to the aquifers.

Confined aquifers

Confined aquifers are found in Vendsyssel, Eastern Jutland, the island of Funen, and on Zealand with surrounding island (No. 10, 13, 16, 17, 18, 19 and 20 in fig. 1 and 2). The aquifers are covered by thick layers of clayey till and often secundary aquifers. The 75% quantile are between 7-0,1 mg/l and median values are between 0,5-0,1 mg/l.

Well-cum-bore well

For comparison with the above given figures similar data are given for well-cum-bore wells and dug wells (No. 21 and 22 in fig. 1). For well-cum-bore wells are found that the 75% quantile is 40 mg/l and for dugged wells are the median value 45 mg/l.

3.2 Nitrate in drinking water

Nitrate in
drinking water
1985-87

The main results of the investigation of nitrate in drinking water for the selected aquifers are illustrated for the selected ranges for the period 1985-87:

0,5	mg NO3/l	59%
5-25	"	27%
25-50	"	12%
50	"	2%

The nitrate content show considerable variations from area to area, which reflects partly the different aquifer and partly different hydrogeological conditions in the same aquifers.

Nitrate in lime-
stone aquifers

Chalk- and limestone aquifers (No. 1-7 on fig.2 and fig.3). The nitrate content is significantly higher in the area south of Aalborg (1) and in in Djursland (3) than in the other areas. In these two areas the aquifers are covered by glacial deposits of highly variable thickness and composition and, locally, the aquifers are phreatic and not covered by younger sediments. In the other areas the aquifers are covered by glacial tills o moderate to considerable thickness. These significant geological differences are assumed to be the cause of the observed variation in the nitrate concentration from area to area.

Nitrate in
aquifers, Jutland

Aquifers of sand, Jutland (No. 8-15, fig. 2, 4, and 5). A considerable number of waterworks with elevated nitrate concentration is found - in the

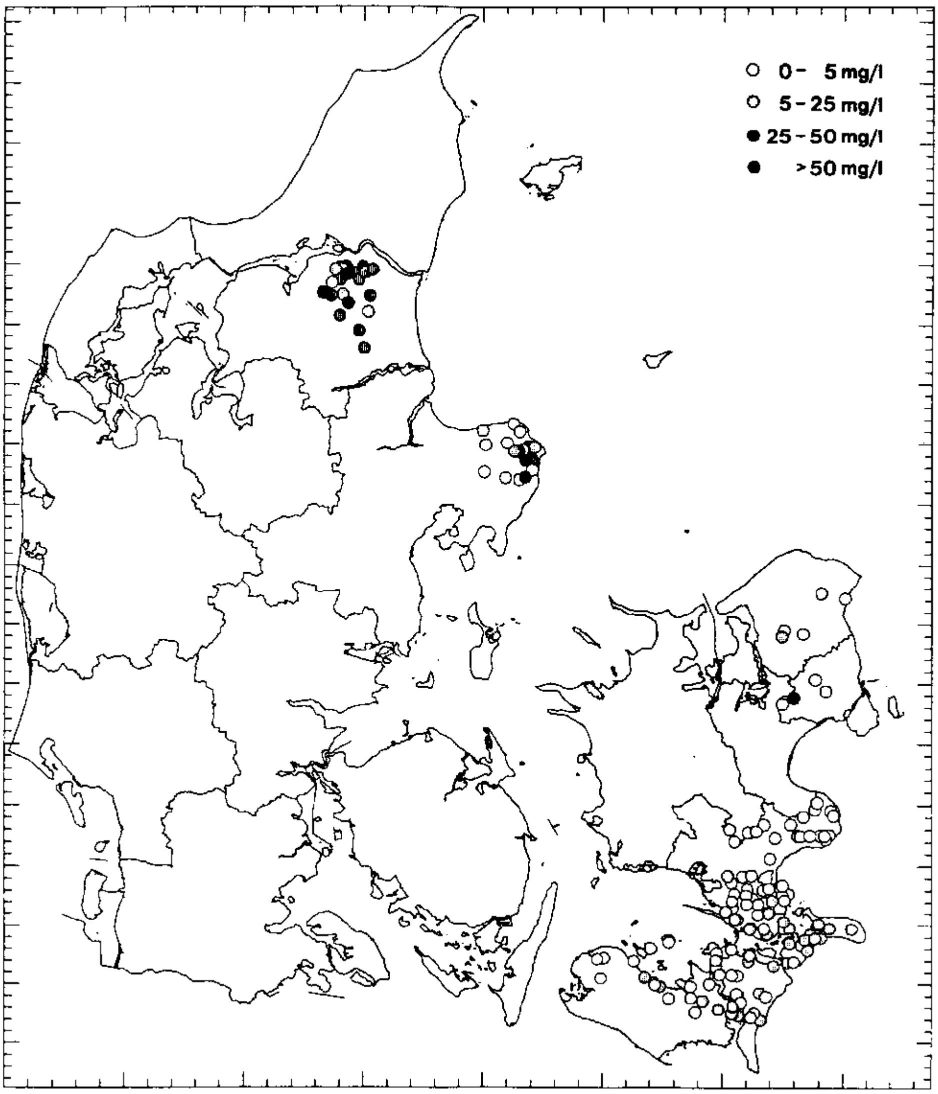

Fig. 3 Nitrate in drinking water from Senonian chalk and Danian limestone.

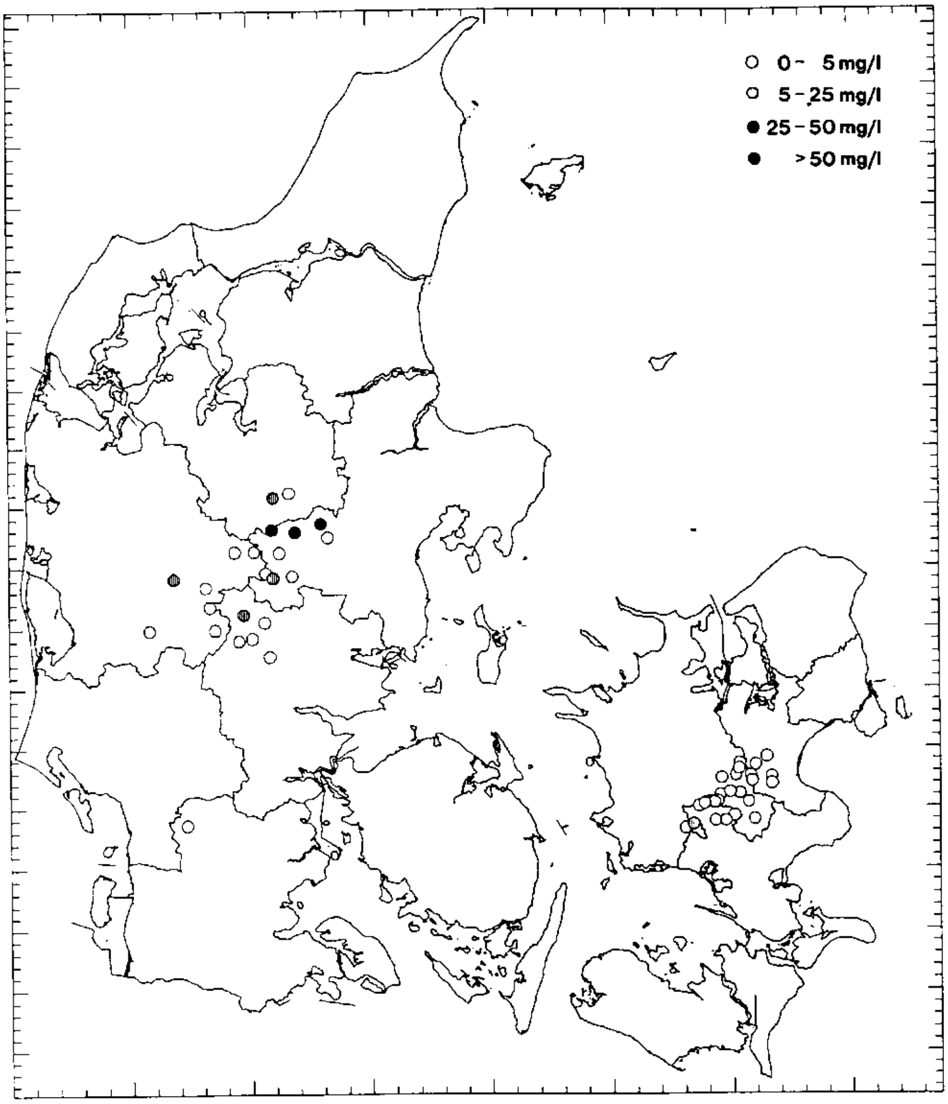

Fig. 4 Nitrate in drinking water from Selandian limestone and miocene quartzsand.

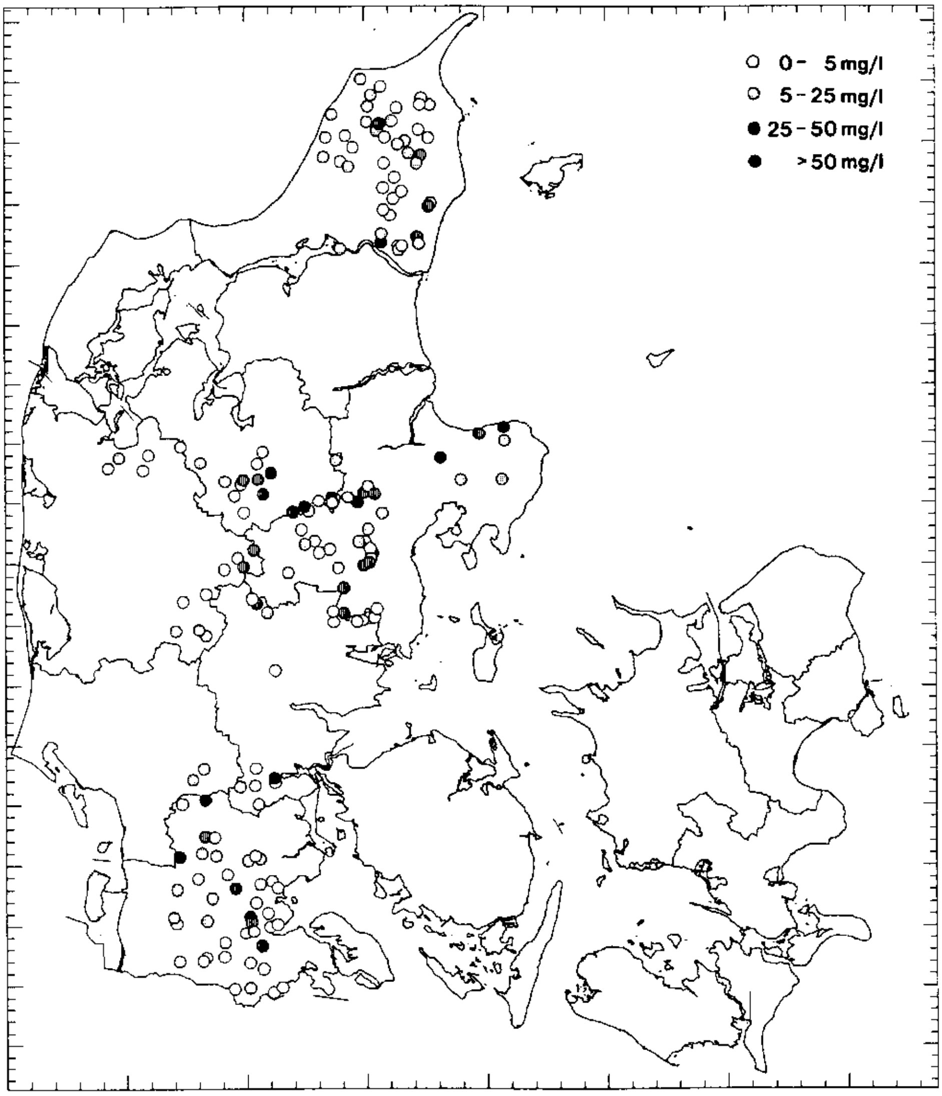

Fig. 5 Nitrate in drinking water from glaciofluviatile sand aquifers, Jutland.

areas 41% to 100% of the waterworks
works have a mean nitrate concentration greater than 5 mg/l. 12% - 60% of the waterworks exceed a nitrate concentration of 25 mg/l.

In area 10 and 13 the aquifers are in general confined. In the other areas the aquifers are commonly phreatic where the covering layer of glacial tills are missing or of limited thickness.

Nitrate in sand aquifers, Funen and Zealand

Aquifers of glaciofluviatile sand, aquifers, Funen and Zealand (No. 16-20, fig. 2 and 6)
The nitrate content in general is low. Only 4 of the 106 waterworks in the areas have a nitrate concentration greater than 25 mg/l.
In general the sand aquifers are confined and covered by considerable layers of tills, and the nitrate vulnerability is therefore assumed to be low.

3.3 Phosphate in ground water

The phosphate concentration have been surveyed for wells from all aquifers in Denmark for the following screen intervals: 0-15 m; 15-30 m, below 30 m, for well-cum-bore well, and for dugged wells. There has not been found any great difference in the 5 situations. For the first 4 situations 60% of the analyses show values below 0,1 mg/l, and for the dugged wells 33% of the analyses are below 0,1 mg/l. No correlation between phosphate and nitrate concentration are found.

Phosphate in drinking water

Phosphate concentrations are registered for 445 waterworks in the investigated areas. 1,8% of the waterworks exceed the drinking water guide level of 0,15 mg/l (total-P). 17% of the waterworks show

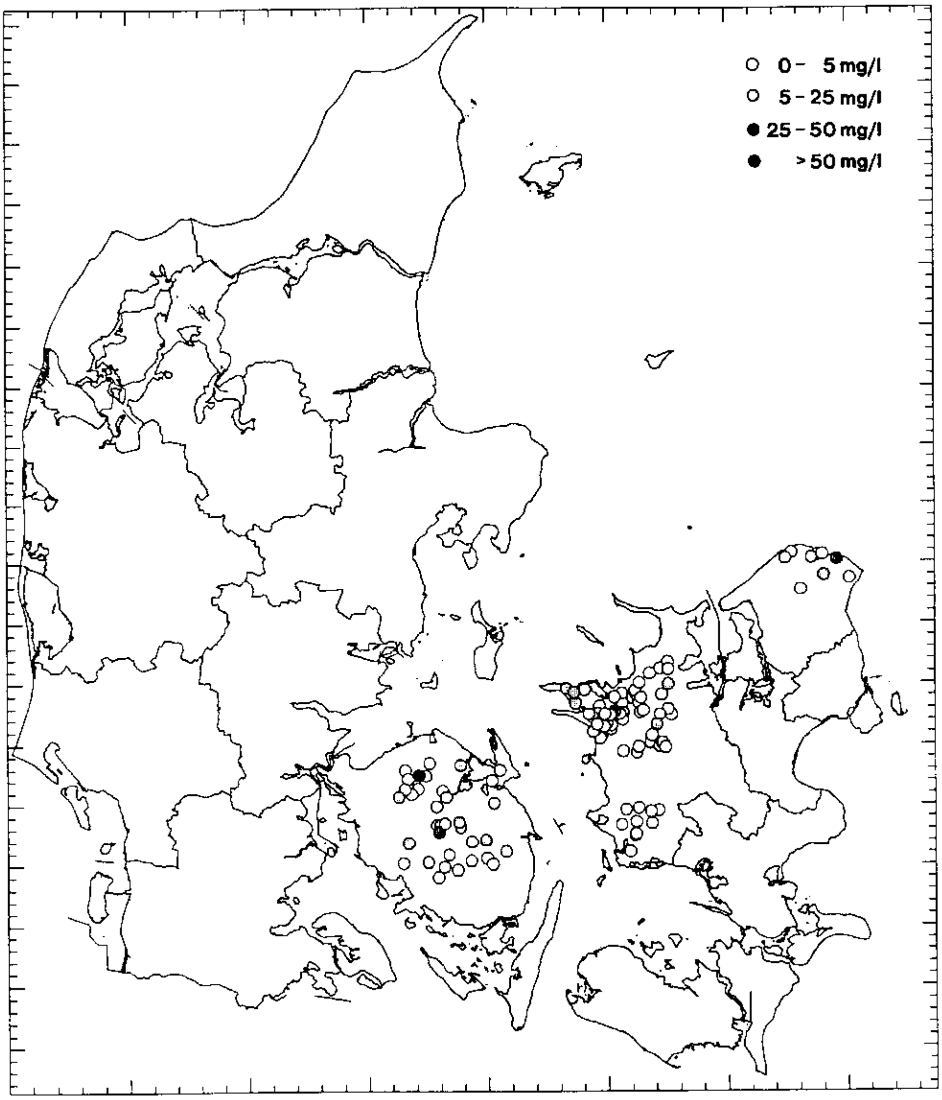

Fig. 6 Nitrate in drinking water from glaciofluviatile sand aquifers, Funen and Zealand.

concentrations in the range 0,05-0,15 mg/l. The highest concentrations are found in glaciofluviatile sand aquifers, and the lowest concentrations are found in limestone aquifers in Djursland (area No. 3) and Stevns (area No. 6).

4. Discussion and conclusion

4.1 Nitrate in ground water

The lithological character of the aquifer material are not found to influence the nitrate content. The thickness of covering clay layers and depth to aquifer have a deciding influence on the nitrate content. Technical conditions, especially insufficient well head protection, are often the cause to high nitrate content. The 90% quantile for the nitrate analyses are only in one case above the maximum permissible value for drinking water and in nine cases above the recommended value. The 75% quantile are in 2 cases above for the recommended value. The investigated aquifers are not critically contaminated with nitrate.

4.2 Nitrate in drinking water

It has not been possible to show a correlation between aquifer type and level of nitrate in drinking water.

In the same aquifer type a considerable variation in nitrate level is found from area to area. This variation is assumed to be caused by variations in the thickness and composition of the glacial sediments covering the aquifers.

The preliminary conclusion, therefore, is that the nitrate level in drinking water primarily is governed by the thickness and composition of sediments covering the aquifers and only to a lesser extent by the aquifer type itself.

4.3 Phosphate in ground water

Only 10-15% of the analyses from danish aquifers show values above the maximum permissible value 0,5 mg/l phosphate for drinking water. 37% of the analyses from dugged wells exceed the maximum permissible value. The higher percentages for the dugged wells are due to local pollution. No correlation between nitrate and phosphate concentrations are found.

4.4 Phosphate in drinking water

Only 1,8% of the waterworks in the investigated area exceed the drinking water guide level of 0,15 mg/l (total P).

72% of the waterworks show phosphate concentrations in the range 0,01-0,15 mg/l (total-P). There is no correlation between the nitrate concentration and the phosphate concentration.

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

Number B5

Transport and Transformation of Nitrogen and Phosphorus in the Rabis Creek Catchment Area

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Abstract

The Rabis Creek catchment area is a part of the Karup sandur in the western part of Jutland outside the border of Weichselian glaciation.

The deposits in the unsaturated zone and in the aquifer consist of sand and gravel.

In the deeper strata in the aquifer the Pleistocene sand and gravel have a small content of lignite fragments and pyrite originating from reworked material from the underlaying Miocene deposits.

The aquifer is unconfined, and the unsaturated zone has a thickness about 15 metre in the investigated area except in areas nearby the creek.

Groundwater samples and sediment samples for chemical analysis were taken from 8 borings carried out in a transect at a distance of about 2.5 kilometres along a groundwater flow line, passing areas with arable land as well as forrested areas.

Sediment samples were taken for every half metre interval under performance of the drill work, and the borings were equipped with a multisampler system allowing sampling of groundwater for every metre interval.

The chemical analysis of the groundwater samples showed groundwater with dissolved oxygen and nitrate in the upper strata of the aquifer down to a depth of 10 to 15 meter below the groundwater table. Groundwater from the

upper strata deriving from heather and plantation areas had small concentrations of nitrate (0 - 4 milligramme NO_3^- per litre), whereas water deriving from arable land has large concentrations (30 - 150 milligramme NO_3^- per litre).

Groundwater from the deeper strata in the aquifer was reduced and free of dissolved oxygen and nitrate.This groundwater contained dissolved ferrous iron (Fe^{2+}), however the concentrations of ferrous iron in groundwater deriving from arable land were up to ten time higher than the concentrations of ferrous iron in reduced groundwater deriving from heather and forrested areas.

It was concluded, that denitrification has taken place in the deeper strata of the aquifer caused by pyrite and probably also by lignite in the sediments.

Tritium analysis of groundwater samples showed, that groundwater deriving from precipitation fallen in 1963 has penetrated to a deeper strata, than the nitrate bearing water, and groundwater from 1963 as well as the nitrate front have pentrated to the deepest level in the upstream end of the transect nearest to the water divide.

It was concluded, that the progress of the redox cline (oxygen- and nitrate front) was a relatively slow process governed partly by the groundwater flow pattern and partly by the content of lignite and pyrite in the deposits.

Analysis of sediment samples showed, that leaching of phosphorous from the root zone and transport to the aquifer must be hampered by among other the content of reactive ferric hydroxide in the sediments in the unsaturated zone and in the oxidized strata of the aquifer.

1. Introduction

A sub project carried out as part of a larger investigation of the leaching, transport and transformation of nutrients in the Rabis creek catchment area in the western part of Jutland (figure 1) is described. In connection with this project processes of the nitrate reduction in a sandy aquifer were studied in detail by the Institute for Applied Geology, Technical University of Denmark (Postma and Boesen, 1990) and mathematic modelling of the movement of nitrate in a groundwater flow system was carried out by the Institute of Hydrodynamics and Hydraulic Engineering, Technical University of Denmark (Engesgaard and Jensen, 1990).

All the examinations within the Rabis Creek area were coordinated, and the results were utilized in coherence of the collaborating institutes.
Rabis Creek is a tributary to the river Karup Å. Nitrate pollution of groundwater in the catchment area to the main river system is well-known from earlier examinations, for instance from examinations under the International Hydrological Decade in 1965 - 1975.

Investigations carried out by the Geological Survey of Denmark in the years 1976 - 1982 showed that nitrate polluted groundwater was extended in the upper strata of the aquifers, and high levels of nitrate were found in groundwater originate from leaching from arable lands (Andersen et al., 1980) and (Andersen and Kristiansen, 1984).

Examinations of groundwater samples and sediment samples collected from different depths in two investigation wells showed that denitrification was going on in the deeper layers in the aquifer, where lignite and pyrite was present in the aquifer materials (Kristiansen and Zimmer Hansen, 1986).

The aim of the project described in this article was to get further informations about the occurence of reducing materials in the aquifer, the amounts and distribution of such materials, and their importance for the transport and transformation of especially nitrate in the aquifer.

2. Material and methods

The objectives of the project comprise the geological and the hydrogeological conditions as well as geochemical and hydrochemical processes important for the transformation of nitrate and the transport of phosphorous.

2.1 Geological model

A geological model covering the catchment area of the main river system was performed with emphasis on the Rabis creek field site, where detailed examination of the hydrological and geochemical condition was carried out. A cyclogram map in the scale 1:10.000 covering the Rabis creek area was produced, and 16 geological profiles were designed in the direction east - west with intervals of 200 metre.

Existent data from the well file data base at the Geological Survey and new data from 13 investigation borings were applied in the production of the geological map and the profiles.

2.2 Hydrogeological examinations

The hydrogeological examinations comprise sounding the groundwater level in existent wells, and in new borings carried out in the project.

The results of the sounding were used for determination of the groundwater flow direction and especially for selection of the location for 8 transect borings carried out along a flow line, in the drilling programme for the investigation area.

2.3 Drilling programme

The drilling programme for the area was carried out at two stages. At the first stage percussion drills were carried out on locations spread over the Rabis creek catchment area. From the percussion drillings groundwater samples were taken at half metre intervals from the groundwater table to a depth of 8 - 33 m. The groundwater samples were analysed for nitrate, sulphate, chloride, calcium, magnesiumm, sodium, potassium, among others. Furthermore, dissolved iron and manganese were determined on separate samples filtered on the site through a membrane filter with a pore size of 0.45 micron.

The aim at this stage was to elucidate the extension and the depth of the nitrate polluted groundwater.

After evaluation of the results obtained in the first stage, locations were selected for 8 transect borings along a groundwater flow line.

The locations were selected, to make it possible to collect samples of groundwater deriving from arable land as well as from plantation land and heather.

The land use in the Rabis creek field site and the locations for the 8 transect borings are show in figure 1.

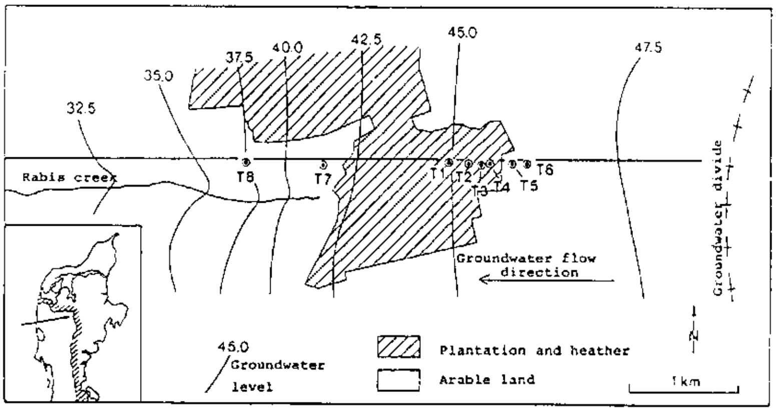


Figure 1. Rabis creek. Hydrological conditions, land use and location for the transect borings (T 1 - T 8). (After Postma et al., 1989).

The 8 transect borings were carried out to a depth of 30 - 35 m below the surface. Sediment cores were taken from every half metre interval during the execution. The sediment samples were taken by using a "Stade" sampler, which allows cores to be taken in PVC sleeves. The cores were frozen at the site and stored frozen until the chemical analysis.

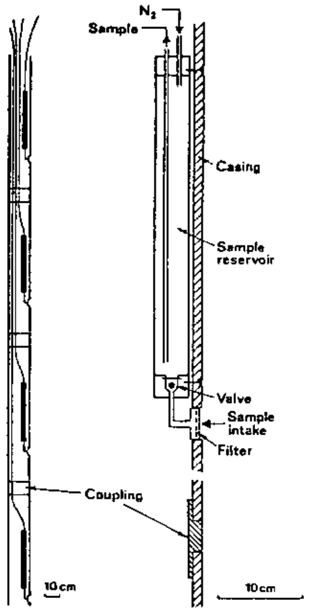


Figure 2. Drawing showing the framework of the multisampler system.

Finally the borings were equipped with multisamplers for every one metre interval from the groundwater table to the bottom of the boring.
The multisamplers were developed by the Geological Survey in close cooperation with the Institute for Applied Geology. The system of the multisamplers is shown in figure 2.

The multisamplers are equipped with a ball valve in the bottom which allow groundwater to penetrate into the sample reservoir, but will be closed under pressure. Furthermore, the samplers are supplied with a two line connexion of PVC tubes to the surface which allow groundwater samples to be taken by nitrogen pressure without air contact.
The 8 transect borings were carried out in 1987 - 1988.

In the autumn of 1989 additionally 3 deeper borings were carried out. The aim of these borings was to get more information about the strata in the levels below the bottom of the transect borings. Especially information about the redox cline and the maximum content of tritium upstreams in the transect, where these two frontiers were not reached in the deepest level of the boring T 6 (see figure 1). One of the supplying borings was carried out in a locality close to boring T 6 to a depth of 70 metre below the surface.

The total number of sample point in the transect is around 140 as the groundwater level in the main distance of the transect is about 15 meter below surface, and the depth of the 8 borings is between 30 and 35 meters. Only in the westernmost downstream boring no. T 8, the groundwater level was higher (7.9 metre below surface).

2.4 Groundwater sampling and field analysis

After installation, the samplers were left alone for a period of at least 3 months to make sure that the groundwater chemistry was stable after the drilling work.

Groundwater samples were taken in 2 to 3 series in the period from ultimo 1988 to primo 1990.

Groundwater samples were taken by application of nitrogen pressure. Before sampling every sampler was emptied 2 to 3 times.

Determination of the pH-value, ferrous iron and alkalinity was done in the field immediately after the sampling. Dissolved oxygen was measured potentiometrically using an oxygen electrode and a flow cell coupled directly to the outlet tube of the samplers.

Samples for measuring the stable main components were taken without any treatment. Separate samples for measuring dissolved iron, manganese, nitrate and ammonium were filtered on the site immediately after collection through a membrane filter with a pore size of 0.1 micron (Postma and Boesen, 1990).

Groundwater samples for determination of the concentration of tritium were taken from selected levels once.

These samples were taken in glass bottles closed with screew caps.

2.5 Chemical analysis

Sediment samples taken from the unsaturated zone were analyzed for aluminiumhydroxide (Al_2O_3), ferrichydroxide (Fe_2O_3) and phosphorous (P) on a solution prepared by extraction with an ammoniumoxalate solution (Schwertmann, 1964). Sediment samples taken from levels below the groundwater table were analyzed for total carbon, carbonate carbon and reduced sulphur components (pyrite (FeS_2), monosulfides and elemental sulphur) among others (Postma and Boesen, 1990).

Groundwater samples were analyzed for nitrate, sulphate, chloride, orthophosphate, calcium, magnesium, sodium, potassium, ammonium, total dissolved iron (Fe <0.1 micron), manganese and siliciumoxide.

The sampling programme as well as the chemical analytical programme were carried out in close cooperation with the Institute for Applied Geology, Technical University of Denmark.

Tritium analyses were performed by the Force Institutes.

3. Results

3.1 Geology

The catchment area the main river system Karup å and its tributary Rabis creek is a part of the Karup sandur. The whole area is located outside the boundary of the landscape of Weichselian age. The sand and gravel sediments of Weichselian age are deposited by braided rivers and are underlain by miocene quartz sand and micaceous sand and clay. To a lower or higher degree the miocene sediments contain lignite and pyrite. The lignite may be present in thin layers or scattered in the sandy sediments.

The prequaternary surface level is modulated with at least to deep valleys.

The layers of the Pleistocene deposits are of varying thickness with a maximum at 110 metre.

The investigated aquifer is located in the Pleistocene sand and gravel deposits, and the drillings carried out in this project have not penetrated these sediments. However, the Pleistocene deposits have inclosures of micaceous clay and, in varying degree, a content of reworked lignite fragments.

Lignite and pyrite are present in the deeper strata, below 30 metre under the surface. This could be explained as a result of the pattern of the sedimentation in the Weichselian but it is more probable that it was caused by chemical processes (oxidation) after the deposition in the last glaciation (Kristiansen et al., 1990).

3.2 Hydrogeology

The aquifer is mostly unconfined in the Rabis creek catchment area, except under the wetlands along the creek where strata of peat and gytja are present, somewhere up to a thicknes about 2.5 metre. The groundwater level is therefore up to 2 metre higher than the water level in the creek close to the line between the hillside and the meadows along the creek.

The watershed to the Rabis creek catchment area is following a direction North - South and is located about 1.5 kilometre east of the upstreams transect boring no. T 6 (figure 1). The groundwater level drop from an elevation of 48 metre at the watershed to 45 metre over 2.5 kilometre in western direction. The downward gradient is therefore approximately 1.4 per thousand. From this area to the stream the downward gradient is much higher, approximately 7 per thousand.

The groundwater flow direction is East - West, almost parallel to the streams. Only in the westernmost part of the catchment area, the flow direction deviate against the streams.

The catchment area to the creek from the outlet to the regional watershed is approximately 16 square kilometre. The minor catchment area to the downstreams and of the transect is only about 3 square kilometre.

The net precipitation in the investigated area is about 350 mm per yr. The infiltration time to the groundwater level is about 7 years near the watershed. Along most of the transect, the infiltration time is about 5 years, except near the downstream transect boring no. T 8 where the unsaturated zone is thinner (about 8 metre).

The flow of the groundwater is 30 - 60 metre per yr in the upper part of the aquifer, and the flow direction along the main part of the transect is nearly horizontal, except at the upstream end where the flow direction is more downward.

3.3 Tritium concentrations

The tritium content in groundwater samples from different levels in the eight transect borings and in a supplementary deeper boring (T 10) close to the upstreams boring no. T 6, is shown in table no. 1.

The tritium concentrations are given in Tritium Units (TU) corresponding to 1 tritium atom per 10^{18} hydrogen atoms.

Well no	T 8	T 7	T 1	T 2	T 3	T 4	T 5	T 6	T 10
Elevat.	+45.8	+57.2	+60.2	+60.6	+60.3	+60.9	+61.8	+62.2	+62.2
Depth m									
17				19.4					
18	38.2								
19				26.1					
20	52.9		31.3						
21				26.2					
22	55.6		36.1						
23				29.0					
24	18.9		36.4						
25	3.6		36.0	27.5					
26			59.8						
27	1.6	36.0	75.4	31.4	51.0		29.5		
28		47.1	83.5	36.5	45.2			27.4	
29	<1.0	61.7		63.4	56.0	32.3	27.9		
30		64.7	49.9	60.4	43.9	30.8		27.9	31.0
31			20.0	79.0	55.4	41.1			
32			33.4	105.0	71.8				36.6
33			28.6	99.9					42.9
34			12.1	75.2					42.9
35			2						42.6
36									68.4
37									75.0
38									89.3
39									100.7
40									112.8
42									96.8
43									96.7
44									104.1
45									97.0
46									98.1
47									100.6
51									86.8
54									38.8
57									48.0
60									15.1

Table 1. Tritium content in groundwater from different depths.

The results of the tritium determination show, that one tritium maxima in relation to the depths are found in the boring no. T 1 - T 2, and T 8. In boring no. T 10 tritium maximum is found in more than one level at depths from approximately from 39 to 47 meters below surface. The more diffuse distribution can be caused by differences in the groundwater flow velocity.
The tritium maxima can, with some uncertainty, be applied in an assessment of the age of the groundwater, and the groundwater layers with maximum concentrations of tritium are interpreted as deriving from precipitation fallen in 1963.
In the two borings no. T 1 and T 8 groundwater from 1954 or elder is found in the deepest levels.

3.4 Groundwater chemistry

The groundwater types can be devided into 4 main groups. The groundwater samples collected from the upper part of the aquifer above the redox cline contain dissolved oxygen (O_2) and nitrate and have small concentrations of dissolved iron (typically less than 0.1 milligramme Fe per litre).

Groundwater from this part of the aquifer deriving from plantation areas and heather areas has small concentrations of nitrate (typically 0 - 4 milligramme NO_3^- pr. litre), and groundwater deriving from arable lands has nitrate concentrations in the size of 30 - 150 milligramme NO_3^- per litre.

The figures 3 - 4 are show examples of chemical profiles of groundwater in relation to depth, and a profile showing the character of sediments in the different levels.

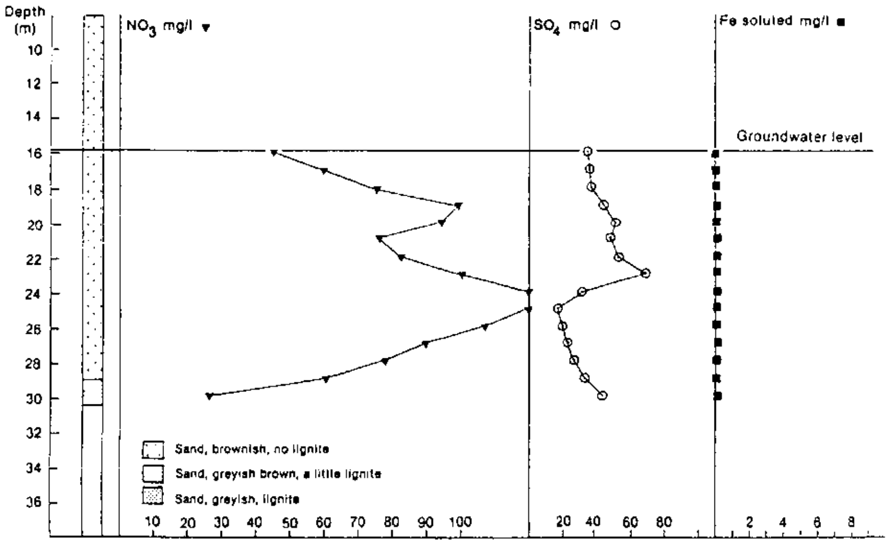
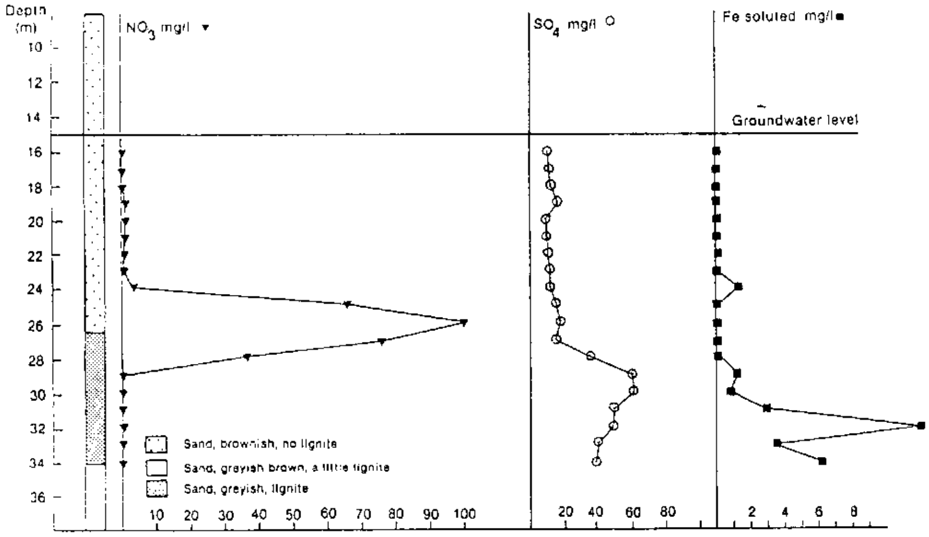


Figure 3. Boring no. T 6, arable land, chemical profiles, groundwater samples november 1988.

The boring no. T 6 is located in arable land upstream in the transect (see figure 1).

The profiles show oxidized groundwater deriving from arable land from the groundwater table to the bottom. The nitrate concentration decreases from a depth of 26 metre to the bottom, but groundwater free of nitrate is not reached in this boring. In a supplying boring T 10, carried out close to boring no. T 6, nitrate free groundwater was found in a depth of 35 metre below the surface.

The sediment profile shows brownish oxidized sand in most of the profiles except in the lowest 1 - 2 metre where a small amount of lignite is present.



<u>Figure 4.</u> Boring no. T 2, plantation, chemical profiles, groundwater samples, november 1988.

The boring T 2 is located in a plantation area approximately 300 metre west of arable land and downstream of this (see figure 1).
The profiles show oxidized groundwater from the water table to a depth of 24 metre below surface. This water has small concentrations of nitrate, small concentrations of dissolved iron and small concentrations of sulphate. In this upper strata the groundwater derives from the plantation area around the location.

From a depth of 25 metre to 28 metre, the groundwater has a high level of nitrate (40 - 100 milligramme NO_3^- per litre). This groundwater derives from the arable lands upstreams the boring locality.

The groundwater layer from 29 metre below surface to the bottom of the boring is free of nitrate, but the concentrations of sulphate and dissolved iron are at a high level. The composition of this groundwater is interpreted as a result of denitrification caused by pyrite after the equation:

$$5\ FeS_2 + 15\ NO_3^- + 5\ H_2O \text{ -----> }$$
$$7.5\ N_2 + 10\ SO_4^{2-} + 5\ FeOOH + 5\ H^+$$

(Postma and Boesen, 1990) and (Postma et al., 1990).

The sediments from the level of 27 metre to the bottom of the boring in 34 metre below surface consist of sand with lignite fragments.

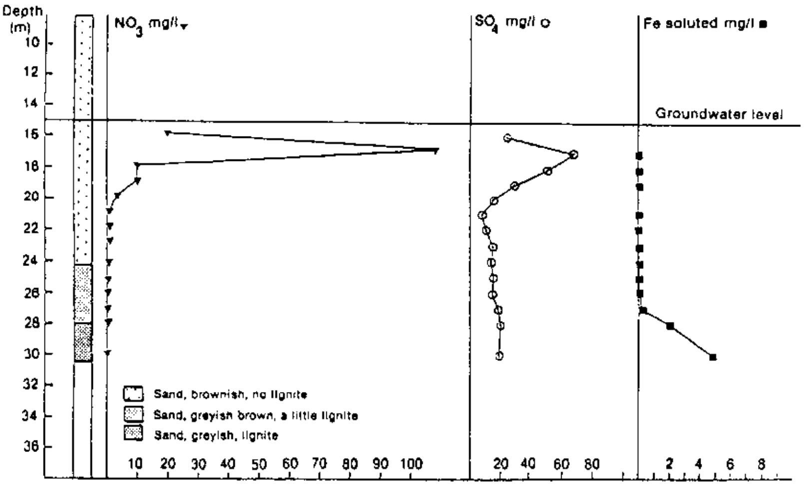


Figure 5. Boring no. T 7, arable lands, chemical profiles, groundwater samples july 1989.

The boring no. T 7 is located in arable land west of and downstreams the plantation area (see figure 1).

The profiles show oxidized groundwater with high levels of nitrate from the water table to a depth of approximately 18 metre below the surface. This groundwater derives from the arable lands around the boring location.

From a depth of approximately 21 metre to a depth of 27 metre the groundwater is free of nitrate but still oxidized with a very low level of dissolved iron. This groundwater derives from the plantation areas upstreams the boring locality.

The groundwater from the deepest level, below 27 metre is reduced with a concentration of dissolved ferrous iron of 2 to 5 milligramme Fe^{2+} per litre but there is no indication for impact of denitrification by pyrite, as this groundwater derives from plantation areas from which the seepage has only small concentrations of nitrate.

3.4.1 The content of orthophosphate in the groundwater

In general groundwater samples taken from the upper oxidized zone of the aquifer have concentrations of orthophosphate below the detection limit (0.02 milligramme PO_4^{3-} per litre). Higher levels (0.18 and 0.25 milligramme per litre) were found in two samples from the uppermost part of the aquifer in the boring no. T 6. The orthophosphate content in these two samples might originate from periodic seepage of phosphorous components from applied slurry, but it cannot be excluded that the higher level in these two samples could be caused by contamination of the samples.

In the deepest part of the aquifer higher concentrations of orthophosphate (up to 0.7 milligram PO_4^{3-} per litre) are common. It is concluded that this is caused by the geochemical conditions in the deeper strata.

3.5 Sediment chemistry

Chemical analysis of sediment samples for reducing matter (organic carbon and reduced sulphur components) showed a very low content (below 0.05 % C and below

0.001 % S) in samples taken from the upper strata in the aquifer above the redox cline. From the deeper strata below the redox cline organic carbon and reduced sulphur components were present in concentrations at the level of 0.1 - 0.3 % C and 0.05 - 0.02 % S.

It has been calculated that the reduction capacity of this content in a 10 centimeter soil layer correspond with approximately 2100 - 2300 kilogramme nitrogen (N) per hectare. Even if it cannot all be utilized in denitrification of nitrate leached from the arable land, the amounts are high in relation to the rate of nitrate leached annually (25 - 90 kilogramme nitrate (N) per hectare).

Determination of phosphorous extractable from sediment samples by ammoniumoxalate solution (Schwertmann, 1964) showed a level around 50 - 200 parts per million P in the uppermost soil layer from 0 - 1 metre below the surface, and, commonly below 50 parts per million in the deeper layer. The contents of aluminium hydroxide and especially ferric hydroxide extractable by the same solution were typically 4 to 10 times the equivalent amount of phosphorous in the soil layers from a depth of 1 metre below surface to the level of the redoxcline in the aquifer. Therefore, phosphorous leached from the root zone will be fixed in an unsoluble form in the strata above the redox cline, as well in the unsaturated zone as in the aquifer (Kristiansen et al., 1990).

4. Discussion and conclusion

Figure 6 shows a vertical section through the transect area.

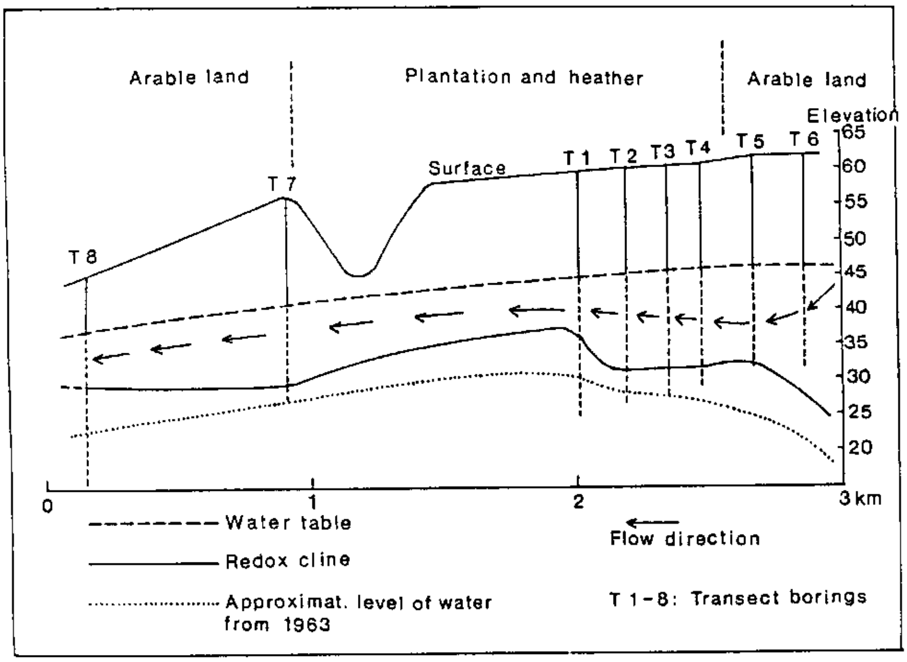


Figure 6. Vertical section of the investigation area.

The figure shows the summation of the results obtained in the combined examinations.

Nitrate leached from the root zone will reach the upper part of the aquifer without measurable denitrifikation, as the unsaturated zone and the upper part of the aquifer are fully oxidized. On the other hand a complete denitrifikation will take place in the groundwater which is transported to the strata below the redox cline.

The denitrification is caused mainly by the content of lignite and pyrite in the sediments in the strata below the redox cline.

Denitrification in water with high nitrate concentrations lead to an increase in the concentrations of sulphate and dissolved iron which must be considered a deterioration of the groundwater quality.

Groundwater from 1963 has penetrated to a deeper level than groundwater with nitrate, caused by the ongoing denitrification in the aquifer. Both groundwater with nitrate and groundwater from 1963 have penetrated to the deepest level in the upstream end of the transect.

This is a result of the flow pattern with a more vertical direction of the groundwater flow near the water divide.

If the redox cline progresses to a deeper level, the ratio of nitrate bearing groundwater reaching the water course will increase, but this seems to be a very slow process since the reduction capacity in the sediments is highly related to the annual leaching of nitrate, and especially because the depth of the redoxcline seems to be governed mainly by the flow pattern in the part of the aquifer covered by the transect. This can also be concluded from the fact that the level of the redoxcline is a result of both leaching of water with dissolved oxygen in 13.000 to 15.000 years since the last glaciation, as well as leaching of water from arable lands with high concentrations of nitrate in the last 40 - 50 years. Although water derived from arable land with the actual high levels of nitrate has a load of "electron quivalents" about five times larger, than water with dissolved oxygen derived from plantation areas (Postma and Boesen, 1990), the great difference in leaching time must be taken into consideration.

The progress of the redox cline and the nitrate front is probably more rapid under areas nearby the water divide, but the total volume of sediments through which the groundwater must pass under the transport to the water course from these areas are much larger, than the corresponding volume for water leached from areas closer to the creek.

Anywhere, there must be a requirement for further investigations of material and processes in the deeper strata in the aquifer near the water divide.

The leaching of phosphorous from arable land in the investigated area seems to be negligible as strata with a rather high content of especially ferric hydroxides in the unsaturated zone and in the upper part of the aquifer form a barrier against the transport of leached phosphorous to the deeper part of the aquifer and to the creek.

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Number B6

Transport and Transformation of N and P in the Catchment Area of Langvad River

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Abstract

In two geological type areas with clayey till dating from the Weichselian time, transport and transformation of nitrogen (N) and phosphorus (P) were investigated in the unsaturated zone and in the upper part of the saturated zone. Type 1, the Syv creek type, represents areas with confined aquifers overlain by a thick confining bed of clayey till (10-60 m), and type 2, the Glim type, represents areas with unconfined aquifers overlain by thin confining beds of clayey till (<10 m).

Below arable land, nitrate (NO_3^-) occurs normally in the oxidised zone of the soil only, and the content decreases markedly at the transition to the reduced zone (the redox line). The oxidised zone is 3 to 10 metre deep. Exchangeable ammonium (NH_4^+) occurs mainly in the reduced zone. Nitrogen in fixed ammonium, which is assumed to form a primary content in the clay minerals, exceeds the amount of nitrogen found in nitrate and ammonium.

The distribution of tritium in the soil water demonstrates that young water originally containing nitrate is now nitrate-free, so the original nitrate content must have been removed from the percolating water. The

results indicate that structural ferrous iron (Fe(II)) in the clay minerals is oxidised when the nitrate is reduced as the structural ferrous iron (Fe(II)) and ferric iron (Fe(III)) ratio changes markedly at the redox line. The nitrate reduction process has not yet been described in detail.

The primary content of phosphorus forms between 110 and 460 ppm P, and low concentrations of orthophosphate (PO_4^{3-}) in soil water show that phosphorus is adsorbed very effectively in the clayey sediments.

1. Introduction

Normally, drainage water from arable land contain high concentrations of nitrate. The increasing application of nitrogenous fertiliser since 1920 has increased the risk that nitrate may influence the aquatic environment.

However, in 1970 an investigation of the nitrate content in groundwater and surface water showed that water from confined aquifers did not contain nitrate whereas, water from near-surface, unconfined aquifers usually contained between 100-150 mg/l NO_3 (Christensen, 1970). The extension of nitrate-containing water in areas with clayey till seemed to be attached to the upper oxidised zone with low contents of easily accessible ferrous iron (Lind & Pedersen, 1976), and the structural ferrous iron in the clay minerals was assumed to form part of the nitrate reduction process (Ernstsen & Lindgreen, 1985).

The aim of this investigation was to describe the impact of nitrogen (N) and phosphorus (P) on surface water (streams), drain water and groundwater. The main stress was laid on a description of different nitrogen compounds as previous investigations had indicated that normally, P is adsorbed effectively in the unsaturated zone (Hansen & Pedersen, 1975 and Hansen, 1981).

The investigations of geology, groundwater hydrology, geochemistry and hydrochemistry were restricted to two geological type areas in the catchment area of Langvad river.

2. Materials and methods

Geology

The geology in the catchment area of Langvad river is described by well records which are shown in a cyclogram map on scale 1:25000, and in 9 profile lines, figure 1.

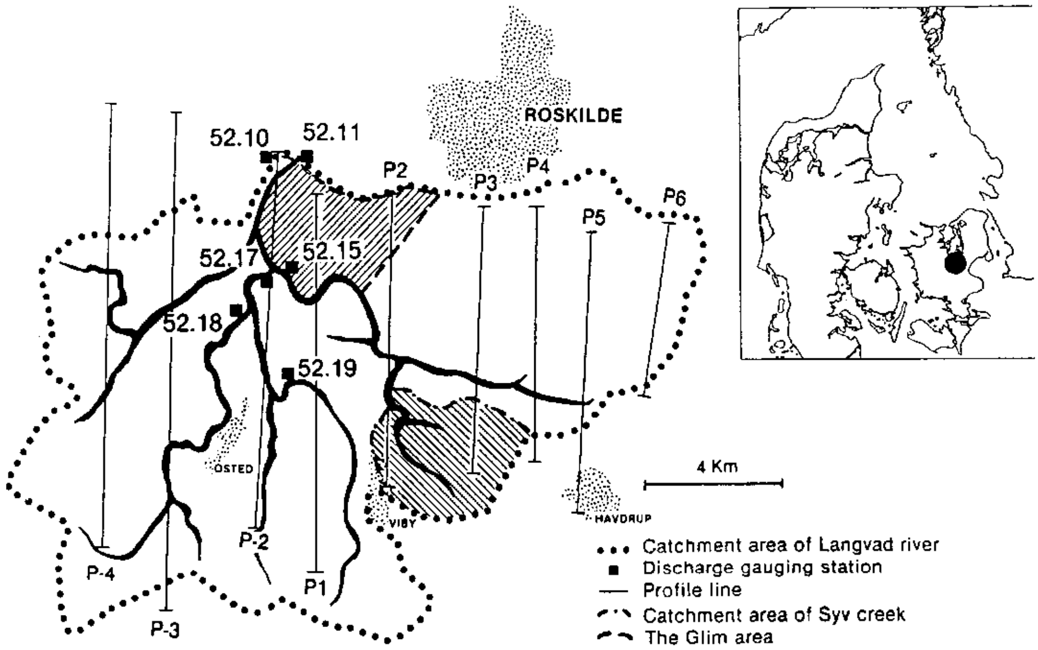
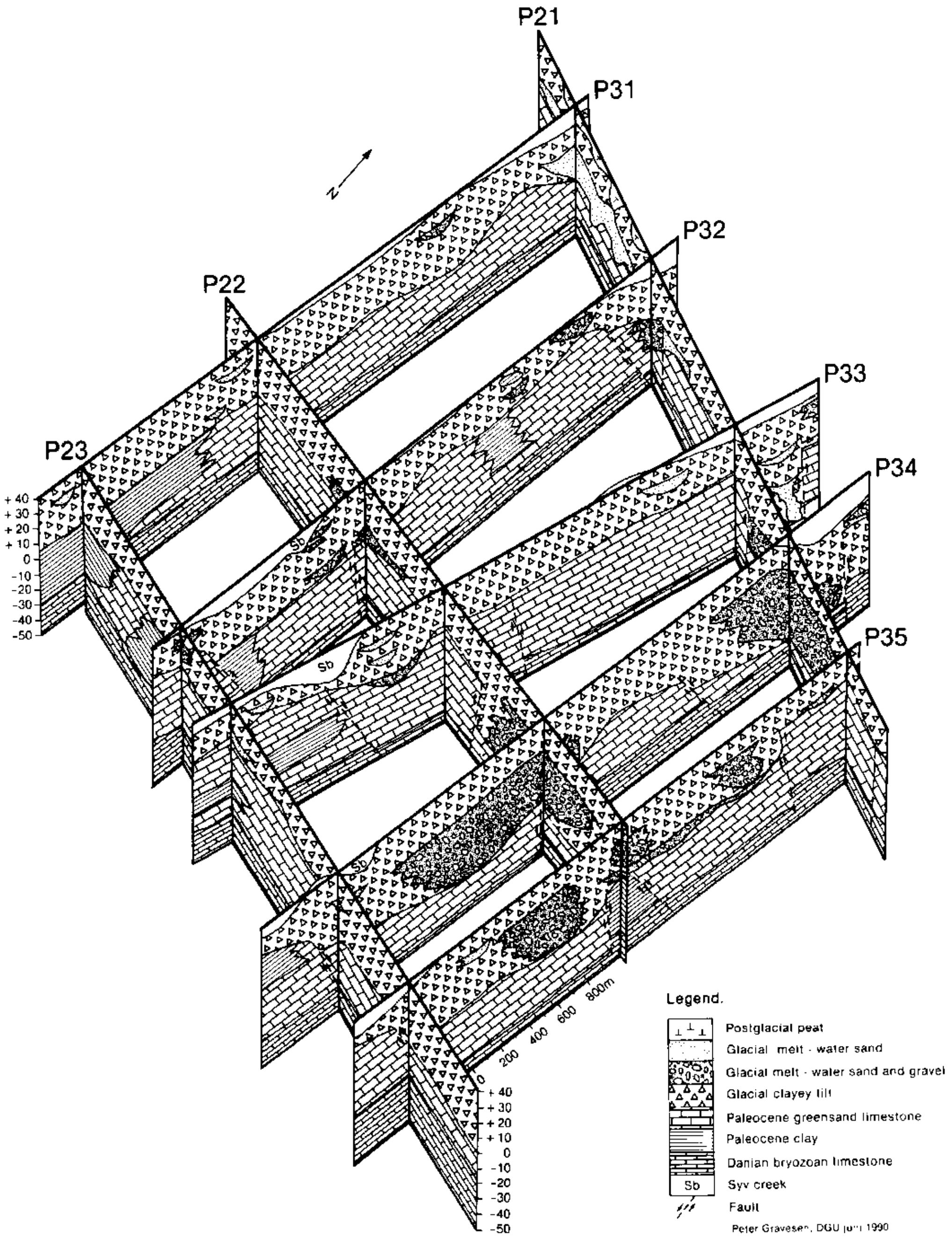


Figure 1. The catchment area of Langvad river, the Glim area and the catchment area of Syv creek. The profile lines are included in the description of the geology.

The geology in the Syv creek catchment area is illustrated by a fence diagram based on the well records, figure 2, together with 3 E-W profiles (P21-P23) and 5 N-S profiles (P31-P35), figure 3.
The geology in the Glim area is described by well records and geophysical logs at the wells 1A-7 which were used for estimation of the character and extension of clayey till.



Peter Gravesen, DGU juni 1990

Figure 2. Geology in the catchment area of Syv creek.

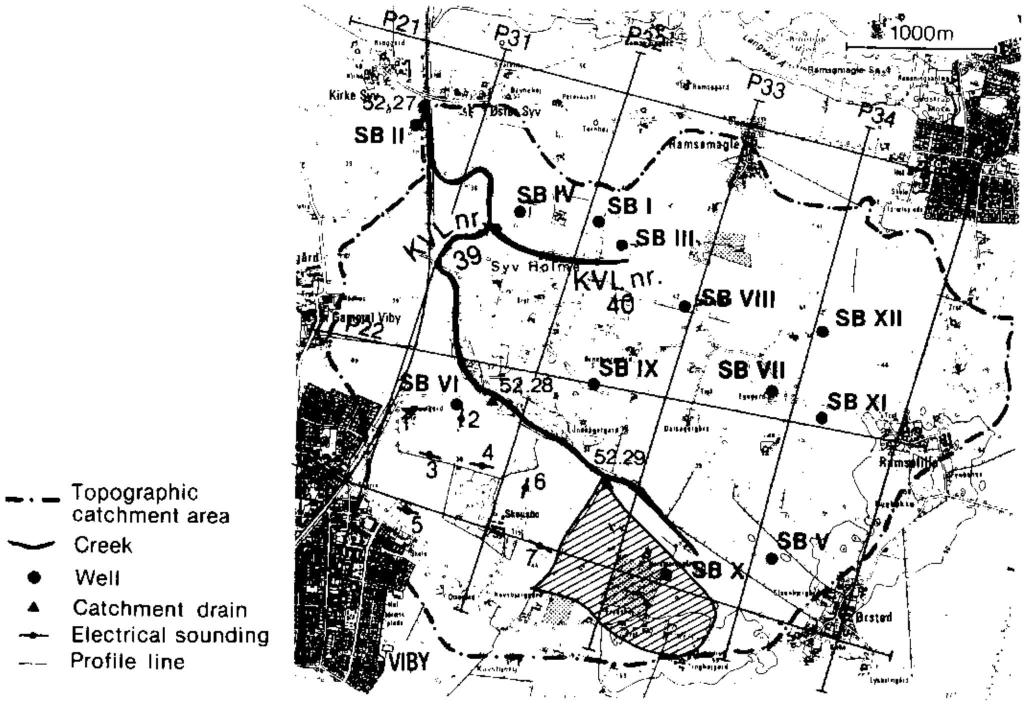


Figure 3. Investigation field, the catchment area of Syv creek. The profile lines are shown in figure 2.

Groundwater hydrology

In the catchment area of drain well no. 52.29, figure 3, the water table was registered by the manometer principle in three fields. In each field 5 observation tubes with filtre (diameter: 7.5 cm, length: 90 cm) were installed in depths from 0.7 (assumed drain depth) to 2.4 metre (assumed lowest water table level).

Drilling programme

In the catchment area of Syv creek and in the Glim area 19 wells were drilled, and sediments were sampled for geological description and different chemical analyses. The sediment samples were stored frozen until chemical analyses, and sediment samples for tritium analyses were stored in plastic bags in airtight containers.

Chemical analyses of soil samples

The content of nitrate and exchangeable ammonium was extracted from the soil with 2M KCl, and fixed ammonium in the soil was determined after treatment with 5N HF: 1N HCl (Silva & Bremner, 1966). Easily accessible ferrous iron was determined after extraction with a 3% $AlCl_3$ solution (Lind & Pedersen, 1976). The total content of iron was determined by decomposing the soil with HF (Møberg et al., 1988). Different forms of iron were analysed by Mössbauer spectroscopy (Murad, 1988). Phosphorus was extracted with 0.02M sulphuric acid.

Tritium

The age of the soil water was determined by the content of tritium. 1 TU equals 1 tritium atom per 10^{18} hydrogen.

3. Results

Geology in the catchment area of Langvad river

Almost everywhere in the area Danien bryozoan limestone is found overlain by Palaeocene greensand limestone which is intersected by marked fault zones. Quaternary deposits dominated by clayey till overlay the pre-Quaternary layers. In the clayey till layers, which are up to 80 metre thick, numerous isolated lenses of glacial melt-water sand and gravel are found. Additionally, in the northern part of the catchment area two formations of glacial melt-water sand and gravel are found: the Thorkildstrup Formation and the Hedeland Formation, lying on either side of an erosion valley, (Jacobsen, 1984, Gravesen, 1990).

Geology in the catchment area of Syv creek

Danien bryozoan limestone and Paleocene greensand limestone and Paleocene clay are intersected by faults and joints. Because of movements along these faults the boundary between the Palaeocene and Quaternary deposits is found at different depths, figure 2. The Quaternary layers are thickest in the down faulted areas in the pre-Quaternary deposits. The Quaternary layers are between 10 and 60 metre thick and are dominated by clayey till which was probably formed as subglacial till. Glacial melt-water sand and gravel occur as lenses in the clayey till, and in the valleys as larger bodies. All the glacial deposits date from the Weichselian.

Geology in the Glim area

In the Glim area the clayey till overlies the Hedeland Formation which consists of melt-water sand, gravel and stone, which were deposited as an outwash plain related to the melting of a glacier in the Middle Weichselian time. The clayey till layer varies between 2 and 12 metre.

Groundwater hydrology in the catchment area of Syv creek

In the fields 1-3 the water table was registered once or twice a month in the period from September 1988 till May 1990. The results showed that in observation tubes with filtre in clayey till the water table responded faster to the changes in the soil water content than the water table in observation tubes in thin layers of sand or gravel, figure 4.

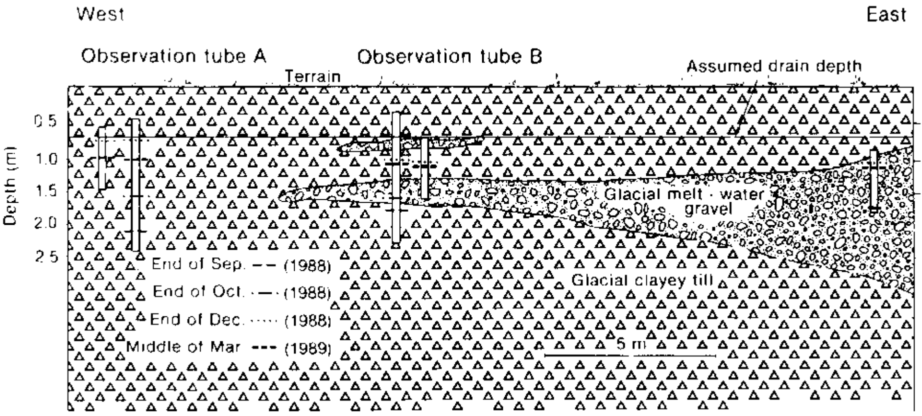


Figure 4. Field 1. Groundwater level in observation tubes A and B, and assumed drain depth.

In the drain season the water level was normally higher in observation tubes in clayey till than in those in sand/gravel, and the hydraulic gradient was orientated in direction of the layers of sand and gravel, figure 4. Furthermore, the results from field 3 showed that a very large part of the percolating water flows through near-surface layers of sand and gravel to the stream.

The water levels in observation tubes with filtre in clayey till (A) and in sand/gravel (B) are shown in figure 5. At A the water table rose to assumed drain depth only in short spans of time.

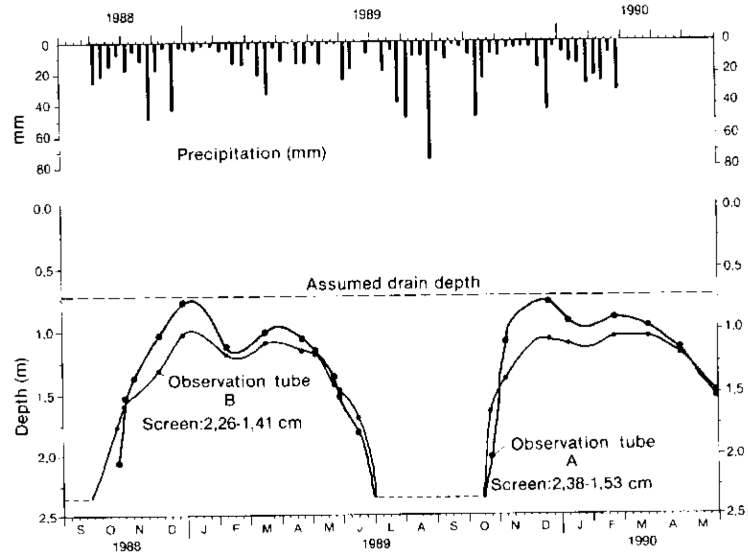


Figure 5. Water level in observation tubes A and B shown in figure 4.

Nitrate (NO_3-N) in the catchment area of Syv creek and the Glim area

In the catchment area of Syv creek the nitrate content was determined in 11 profiles below arable land, namely SBI and SBIII-SBXII, figure 6. Measurable amounts of nitrate occur in the oxidised zone. The largest amounts, up to a maximum of 17 ppm NO_3-N (mg NO_3-N/kg fine soil) were found in the root zone to a depth of 1 metre. Deeper down in the oxidised zone the nitrate content varies between 2-4 ppm NO_3-N.

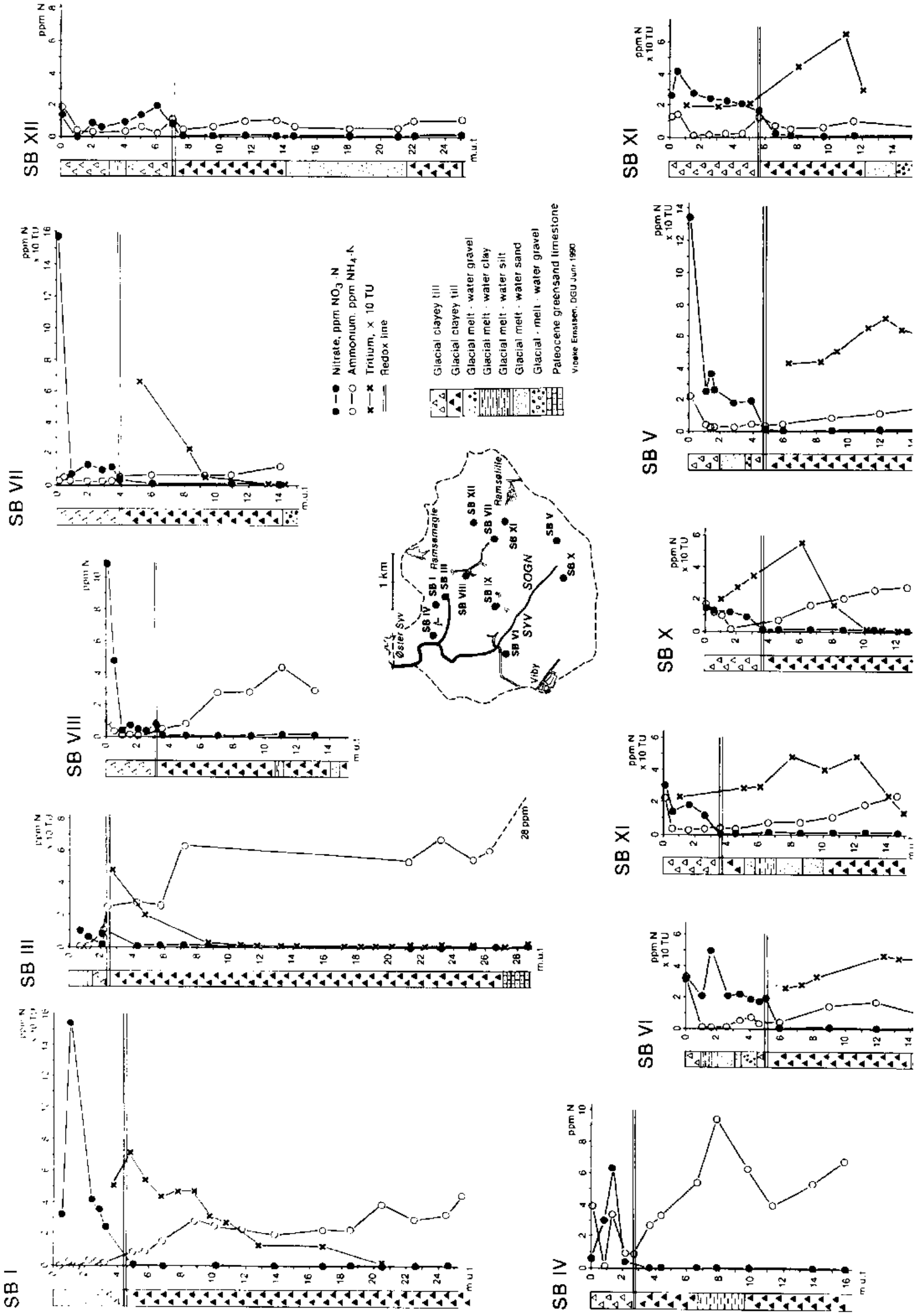


Figure 6. The catchment area of Syv creek. Nitrate (NO_3-N), ammonium (NH_4-N) and tritium below arable land.

At the transition to the reduced zone (the redox line) the content of nitrate decreases to under the detection limit.

In the Glim area the wells Glim 1A-5 and 7 were drilled in arable land, and Glim 6 was drilled in a former dung yard, figure 7.

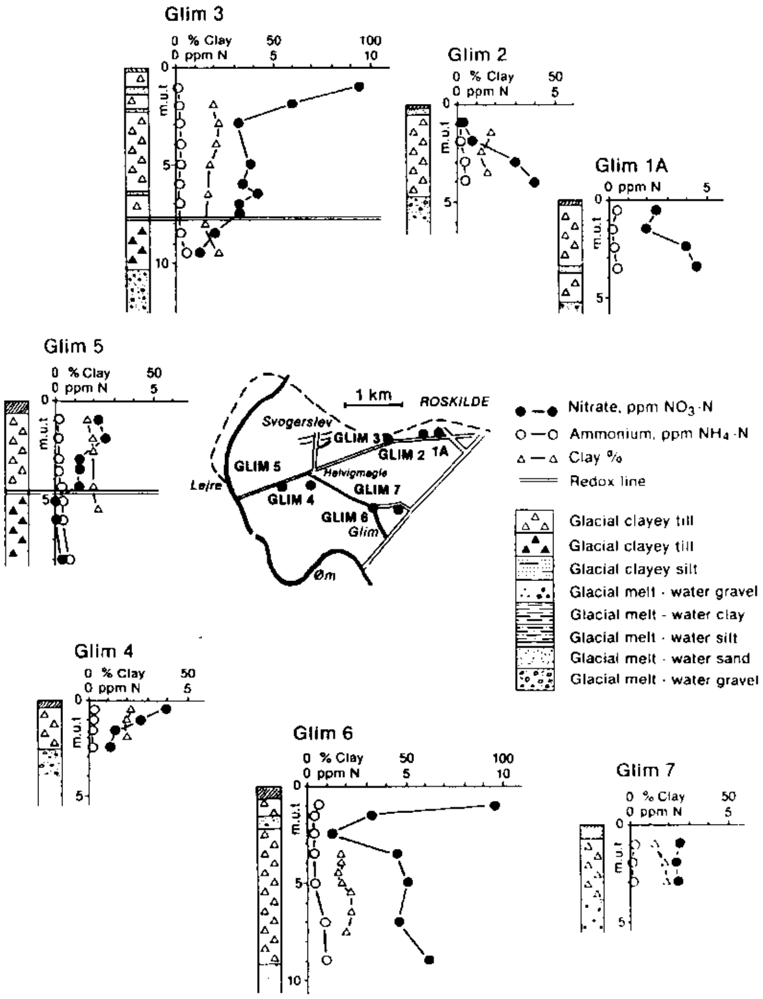


Figure 7. The Glim area. Nitrate (NO_3-N), ammonium (NH_4-N) and clay content below arable land (Glim 1A-5 and 7), and a disused dung yard (Glim 6).

In the profiles Glim 1A, 2, 4 and 7 with thin oxidised layers of clayey till, nitrate occurs at almost all depths. In Glim 5 the distribution of nitrate corresponds to that of the profiles in the catchment area of Syv creek. In Glim 3, below the redox line in the fractured clay layer overlying unsaturated sand, small amounts of nitrate are found. In the disused dung yard, Glim 6, the clay layer is oxidised and the amount of nitrate is rather large (1-10 ppm NO_3-N).

The distribution of nitrate in the oxidised zone below arable land will vary throughout the year in consequence of differences in climate (precipitation and temperature), crops, soil management etc. (Ernstsen et al., 1990).

Nitrate and the redox line

The redox line marks the shift between soil water with nitrate and soil water without nitrate. The transition from the oxidised zone to the reduced zone is established by the base colour and the colour pattern in the sediments determined after the Munsell Soil Color Charts. The results from the catchment area of Syv creek appear from figure 8.

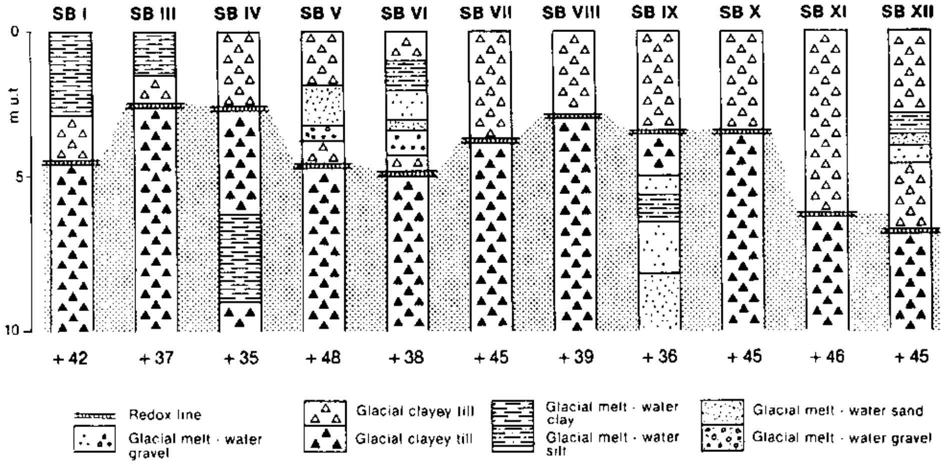


Figure 8. Geology and redox line at SBI and SBIII-SBXII.

At SBIII and SBIV the sediments are grey at all depths, and the redox line indicates the occurrence of red/yellowish brown mottles. In the other profiles the redox line marks the shift from reddish brown to grey base colour of the sediments.

In areas with thick layers of clay, e.g. SBVII-SBX, the redox line is found in a depth of 3-4 metre, and in areas with layers of sand/silt and glacial gravelly till the line lies deeper down (maximum 7 metre below surface). In the Glim area (Glim 1A, 2, 4 and 7) thin layers of clay (<5 metre) overlying unsaturated sand are oxidised, and in Glim 3 and 5 with thick layers of clay the redox line is between 5 and 8 metre below surface, figure 7. Below the dung yard, Glim 6, the oxidised layer of clay is 9 metre thick.

Nitrate and tritium

The age of soil water at different depths was suggested by the tritium content, and the results obtained for profiles from the catchment area of Syv creek appear from table 1 and figure 6.

	Soil water dating from:			
	After 1963	c. 1963	Before 1963	1950 or before
Well No.	Depth (m)			
SB I	5	5	5	>20.5
SB III	<3	<3	<3	9
SB V	12	12	12	>14.5
SB VI	13.5	13.5	13.5	>14.8
SB VII	c. 5	c. 5	5.5	>14
SB IX	8	8-12	12	>15
SB X	c. 6	c. 6	c. 6	11
SB XI	c. 11	c. 11	c. 11	>12

Table 1. Tritium in soil water in profiles from the catchment area of Syv creek.

Soil water with increased contents of tritium dating from 1963 is recovered at depths from <3 metre to 13.5 metre, and water dating from before 1950 is recovered below a depth of 9 metre. Soil water of similar age is recovered at different levels in the profiles which is caused by variations in the flow pattern of the percolating water.

Exchangeable ammonium (NH_4-N) in profiles in the catchment area of Syv creek and the Glim area

In SBI and SBIII-SBXII the content of exchangeable ammonium is high (1-4 ppm NH_4-N; ppm = mg NH_4-N/kg fine soil) in the root zone to a depth of c. ½ metre. With the exception of SBIV, the content of exchangeable ammonium decreases to <1 ppm NH_4-N in the deeper part of the oxidised zone. At the transition to the reduced zone the content increases to 1-3 ppm NH_4-N in clayey till, to 10 ppm NH_4-N in melt-water clay and to 28 ppm NH_4-N in Palaeocene greensand limestone and Palaeocene clay, figure 6.

In the Glim area the content of exchangeable ammonium is <0.5 ppm NH_4-N in oxidised clay layers below arable land, whereas the content below the former dung yard was <0.9 ppm NH_4-N, figure 7.

Fixed ammonium (NH_4-N) in profiles from the catchment area of Syv creek

Non-exchangeable ammonium, i.e. fixed ammonium, made up between 30-160 ppm NH_4-N in SBI, SBVII, SBX and SBXI. The results obtained in SBVII indicate that fixed ammonium occurs primarily in the clay particles (<2 μm), (Ernstsen et al., 1990).

Different forms of iron

The content of easily accessible ferrous iron in the subsoils of SBV and SBVI make up <25 ppm Fe (ppm = mg Fe/kg fine soil) in the oxidised zone, and 25-100 ppm Fe in the reduced zone.

The distribution of different forms of iron was determined by Mössbauer spectroscopy in SBI, SBIV, SBVIII and SBX, table 2.

SB I		Fine soil			
Depth (m)	Geology	FeII	FeIII	Fe^{3+} oxide	Total iron
		%			% Fe_2O_3
1.8	DS/DI	14	86	-	3.3
3.5	ML	20	80	-	3.8
5.3	ML	52	48	-	1.8
7.1	ML	49	51	-	1.9
19.5	ML	32	68	-	2.7

SB IV		Fine soil			
Depth (m)	Geology	FeII	FeIII	Fe^{3+} oxide	Total iron
		%			% Fe_2O_3
1.8	ML	31	69	-	2.0
2.6	ML	45	55	-	1.8
5.8	ML	48	52	-	2.4

SB VIII		Fine soil			
Depth (m)	Geology	FeII	FeIII	Fe^{3+} oxide	Total iron
		%			% Fe_2O_3
1.5	ML	10	64	26	2.0
3.5	ML	48	52	-	1.5
7.5	ML	52	48	-	2.7

SB X		Fine soil			
Depth (m)	Geology	FeII	FeIII	Fe^{3+} oxide	Total iron
		%			% Fe_2O_3
1.5	ML	11	48	41	2.5
4.5	ML	53	47	-	2.2
7.5	ML	50	50	-	2.7

Table 2. Structural ferrous iron (Fe(II)), ferric iron (Fe(III)) and free iron oxides plus total amount of iron. Redox line is shown as a double line. DS/DI: Glacial melt-water sand/silt, ML: Glacial clayey till.

The results indicate that structural ferrous iron (Fe(II)) and structural ferric iron (Fe(III)) in the clay minerals form the main part of the total content of iron. In the oxidised reddish brown zone of SBI, SBVIII and SBX Fe(II) makes up 10-20%, and in the oxidised zone with red mottles in SBIV Fe(II) makes up 31%, table 2. In the reduced nitrate-free zone the content varies be-

tween 45% and 50% Fe(II). In SBI, at a depth of 19.5 metre, the content of Fe(II) is only 32%, probably because the clayey till is thoroughly mixed with the underlying Palaeocene greensand and clay.
The change in the Fe(II)/Fe(III) is accompanied by changes in the composition of the clay minerals. For instance, chlorite is found only at or below the redox line (Ernstsen et al., 1990).

In clayey till the total amount of iron varies between 1.5% and 3.8% Fe_2O_3, table 2.

Phosphorus in the catchment area of Syv creek

The primary content of phosphorus varies between 110 and 440 ppm P (mg P/kg fine soil), and the content has increased only in the upper c. 10 cm of SBIV and SBXI after application of fertilisers containing phosphorus for several years, table 3.
In soil water from the upper part of the saturated zone, to a depth of 1.6 metre, the concentration of orthophosphate was below 0.01 mg/l PO_4-P, (Ernstsen et al, 1990).

Discussion and conclusion

In the catchment area of Langvad river two geological type areas have been investigated. The Syv creek type with thick layers of clay overlying confined aquifers, and the Glim type with thin layers of clay overlying layers of sand and gravel with unconfined aquifers. The two types are presumed to make up 80% and 20% of the catchment area of Langvad river.

In the catchment area of Syv creek calculations based on measurements of precipitation, evapotranspiration, groundwater level and tritium in soil water have demonstrated that 25-35% (approx. 60 mm/year) of the percolating water flow slowly (decades to centuries) to the confined aquifers, and the remaining 65-75% (approx. 120 mm/year) flow quickly (days to years) through near-surface saturated layers of sand and gravel plus through subsurface drain. In the drained clayey till the water table rose to 0.7 metre below surface in autumn and winter. In the Glim area the water flow downward through the unsaturated clayey till and sand to the unconfined aquifers.

SB I

Depth (m)	ppm P (mg/kg)
1.0	350
3.2	430
4.3	460
4.8	430
5.8	390
10.8	420
16.8	430

SB IV

Depth (m)	ppm P (mg/kg)
0.1	2100
0.8	440
1.8	370
3.6	370
6.7	370
9.5	390
16.8	390

SB VI

Depth (m)	ppm P (mg/kg)
1.9	490
2.3	410
3.4	360
4.6	450
5.1	270
8.9	370
11.9	350

SB XI

Depth (m)	ppm P (mg/kg)
0.1	570
0.5	280
3.5	330
6.5	340
7.5	430
16.5	240

SB XII

Depth (m)	ppm P (mg/kg)
0.1	440
1.0	330
2.0	315
2.5	450

SB X

Depth (m)	ppm P (mg/kg)
0.1	250
0.5	110
2.5	330
3.5	340
8.5	340
14.5	340

Table 3. Phosphorus in profiles from the catchment area of Syv creek.

Below arable land nitrate is normally present only in the oxidised zone above the redox line. In Glim 3, below the redox line in the fractured layer of clay overlying unsaturated sand, little amounts of nitrate may have formed by oxidation of ammonium. Deeper down than c. 3 metre the content of nitrate is higher below the disused dung yard than below arable land. The content and distribution of nitrate in the oxidised zone vary throughout the year in consequence of the variations in precipitation, mineralisation, denitrification, crops, soil management etc.

In areas with thick layers of clayey till, e.g. SBIV and SBVII-SBX, the oxidised zone containing nitrate is 3-4 metre thick, and in areas with clayey till overlying layers of sand or gravel the oxidised zone is maximum 9 metre thick. In the Glim type area the oxidised zone can be very thick as oxidation may happen from the surface as well as from below caused by air in the unsaturated layers of sand/gravel.

The age of the soil water was determined by the tritium content. By comparing the distribution of tritium and nitrate it was stated that nitrate is removed effectively from the percolating water. Soil water dating from before 1950, which must have contained considerable amounts of nitrate originally, now appears without nitrate. The nitrate and tritium profiles demonstrate that the extension of water containing nitrate depends on the redox line and not on the flow pattern of the water.

Exchangeable ammonium occurs especially in the reduced zone where the distribution seems to be determined by the clay content and the lithology. Fixed ammonium makes up a primary content in fine clay and coarse clay. The content of nitrogen in fixed ammonium exceeds that of nitrate and exchangeable ammonium.

The ability of the clay layers to remove nitrate, i.e. the nitrate reduction capacity, is probably due to structural ferrous iron, Fe(II), in the clay minerals. In clayey till the amount of Fe(II), which can be used in different oxidation processes, including the reduction of nitrate, was calculated to be c. 9,600 g ferrous iron/m^3 or c. 170 mol/m^3. The nitrate reduction process is assumed to take place according to the equation below:

$5Fe^{2+} + NO_3^- + 12H_2O \text{ ---> } 5Fe(OH)_3 + 0.5N_2 + 9H^+$

On an annual nitrate leaching of 50 kg N/hectare (0.355 mol NO_3^-/m^2) the capacity will be used up in a 1 cm thick layer, which corresponds to approx. 100 years per metre clayey till.

In an investigation of clayey till and glacial meltwater clay from the central part of Sjælland the consumption of reduction capacity has been calculated to be 0.6-1.6 cm/year on an annual nitrate leaching of 50 kg N/hectare (Ernstsen, 1990).

Furthermore, calculations have proved that the major part of the structural Fe(II) in the clay minerals may have been used up by oxygen dissolved in water which has flown through subsoil since the Weichsel (for c. 10,000 years). For this span of years the amount of dissolved oxygen has been calculated to be c. 4.8 kg O_2/m^2, and in comparison with this the loss of nitrogen from the root zone in the last 40 years is assumed to be c. 250 g/m^2 NO_3^-. Part of this has flown with the water through subsoil drains and near-surface layers of sand and gravel, and only a small part of the nitrate has reached the confined aquifers. Increased use of structural ferrous iron in the last 40 years as a consequence of the increased nitrate leaching from the root zone is registered only with difficulty in the Fe(II)/Fe(III) ratio at present. Thus dissolved oxygen in the percolating water has made it easier for nitrate penetrate into the subsoil.

In Syv creek type areas nitrate-containing water may occur in the upper part of the saturated zone, whereas water in confined aquifers is well protected against nitrate pollution. A reduced loss of nitrogen from the root zone will soon be measured in the nitrate concentration of the water flowing through subsoil drains and near-surface sand and gravel layers to the stream. Part of this nitrate may be removed in organic sediments, e.g. in meadows (Brüsch & Nilsson, 1990). This type is found in Sjælland, in the northern part of Fyn and in the isles Lolland, Falster and Møn which equal 45% of the areas with clayey till in Denmark.
In Glim type areas the groundwater is not, or only to a small degree, protected against nitrate from the root zone because the nitrate reduction is not effective in

thin oxidised clay layers. Groundwater below thin layers of clay will contain nitrate in various concentrations, and a reduced loss of nitrogen from the root zone will be registered in the groundwater on a long view. This type is found south of Roskilde and south of Ålborg plus locally in Sjælland which equal c. 5% of the areas with clayey till in Denmark.

The remaining part, approx. 50%, of the areas dominated by clayey till forms a mixture of areas with confined and nitrate-free water as described for the Syv creek type, and in other parts unconfined water containing nitrate as described for the Glim type. Therefore, the consequences of a reduced leaching of nitrate from the root zone will vary. Areas of this type are found in the southern part of Fyn and in Jylland north and east of the ice-border of the Weichsel.

The primary content of phosphorus makes up 110 and 460 ppm P, and only in two profiles, i.e. in SBIV and SBXI, did application of phosphorus fertiliser result in an increased content in the root zone. In the upper soil layers the original content of calcite ($CaCO_3$) is used up and here phosphate is adsorbed in iron oxides and aluminium oxides. Deeper down the phosphate is adsorbed in calcite which is found in large amounts (10-40%). In the upper part of the soil the phosphorus is adsorbed effectively, and below arable land the content of orthophosphate in the soil water is low.

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Number B7

Transport and Transformation of N and P in the Surrounding Area of Langvad River

Microbial Nitrate Reduction in the Unsaturated Zone

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Résumé.

In the surrounding area of Langvad Stream on Sealand 3 drillings were performed to the depth of 14 m. Soil samples from different depths were studied chemically and microbially in the laboratory to explain the possibilities of microbial nitrate reduction in unsaturated sandy loam profiles. By measuring the ATP contents of the soil the biomass of the deeper soil layers was found to be 0.1-1.5% of that in the surface soil. Denitrifying bacteria were found in all depths in numbers from 10^2 to 10^5 bacteria per gram of soil. The actual denitrification activity in the deeper soil layers was in most cases less than in the surface soil. Studies of the potential denitrification activity showed that in all depths there was a lack of an easily decomposable carbon source, and in some cases a lack of nitrate as well. The lack of easily decomposable carbon sources has thus a limiting effect on a major nitrate reduction down through the unsaturated zone. However taking into account the huge soil

volume below the root zone and the relative long infiltration time, it is possible that even the small denitrification activities measured can contribute to the removal of leaching nitrate.

1. Introduction.

Nitrate leaching in soil is mainly due to the fact that this nitrogen compound as opposed to many other plant nutrients does not bind to the soil particles. Once nitrate has left the root zone it is most likely to enter the ground water, unless it is reduced either chemically or microbially down through the unsaturated zone.

Nitrate in the ground water is undesirable, as it can be harmful to human health. Nitrate is only toxic at very high concentrations, but it can be reduced to nitrite, which is direct toxic at far lower concentrations. Moreover nitrate can combine with amides and amines into nitrosamines in the intestinal system, and this compound is considered to have carcinogenic effects.

The purpose of this study was to elucidate the possibilities of microbial nitrate reduction in unsaturated profiles in the surrounding area of Langvad Stream.

By microbial dissimilatory nitrate reduction nitrate is transformed into gaseous nitrogen compounds (denitrification) and into ammonium. The dissimilatory nitrate reduction into ammonium can be of importance in environments with low redox potential and relatively high contents of organic matter. However in most environments the denitrification will be the dominating process, for which reason we only have dealt with this process. In the following text the term denitrification is used synonymous with nitrate reduction.

The results from this study goes into the main project "Transport and transformation of N and P in the surrounding area of Langvad Stream", which aims at establishing typical patterns of watermovement, nitrate reduction and relevant chemical and biological conditions in the unsaturated zone and in the ground water zone.

2. Materials and methods.

Soil samples: The soil samples originated from 3 drillings performed in the surrounding area of Langvad Stream. The 3 drillings named Syv Bæk I, III and IV were made to the depths of 10, 5 and 14 meters respectively. Surface soil was only taken at one locality in the area. A more detailed description of locality, geology and hydrology is given in report B6: "Transport and transformation of N and P in the surrounding area of Langvad Stream. I. Geological, geochemical and hydrological investigations".

Chemistry: Some chemical parameters of the soil were determined according to Danish standard procedures (Ministry of Agriculture, 1988). This included determination of total-N, total-P, pH ($CaCl_2$) and the contents of CO_3-C. Furthermore, NO_3-N and NH_4-N were determined after extraction with 2 M KCl by measurement on a Flow Injection Analyser (Tecator 5020 Analysator). Total organic C was determined according to Ter Meulen, while water soluble organic C was determined on a TOC Analysator (Dohrmann DC-180); UV-promoted persulfate oxidation and measurement of the CO_2 product by infrared gas analysis.

Microbiology: The total microbial biomass was determined by measurement of adenosintriphosphate (ATP) in the soil as described by Eiland

(1985). The bacterial biomass (Colony forming units (CFU)) was enumerated by plate count on soil-extract agar and on 100 times diluted soil-extract agar. The number of nitrate reducing and denitrifying bacteria was estimated by the Most Probable Number (MPN) - method (Alexander, 1965) using a medium rich in nitrate (Vinther et al., 1982). Bacteria able to reduce nitrate to nitrite are named nitrate reducing bacteria, and bacteria able to reduce nitrate or nitrite to gaseous nitrogen compounds are named denitrifying bacteria.

Incubation experiments: In selected depths down through the 3 profiles soil samples were taken for incubation experiments. The incubations were performed in laboratory-bottles in which rubber membranes were placed in the lid to make removal of air samples possible. A quantity of soil corresponding to 40 g of dry soil was weighed out aseptically in each bottle and the water contents were adjusted to 13%. From each depth soil was weighed out in 10 bottles: After 2 days of incubation 4 bottles were added sterile filtered glucose-solution, and after 4 days further incubation, they were added sterile filtered nitrate-solution - of these 4 bottles 2 were incubated with 10% (of airvolume in the bottle) acetylene (C_2H_2) and 2 without. In addition 4 other bottles were added nitrate after 2 days of incubation and glucose after 4 days further incubation, and similary 2 of these bottles were incubated with acetylene and 2 without. The last 2 bottles were only added water, at the time the others were added glucose and nitrate - these 2 bottles were incubated with acetylene. Nitrate was added as KNO_3 to a concentration of 100 ppm N in the soil. Glucose was added to a concentration of 0.1%. All samples were incubated aerobic at

10°C, and at certain intervals air samples were taken for analysis of carbon dioxide (CO_2) and nitrous oxide (N_2O).

Gaschromatography: The CO_2-measurements were performed with a ML GC 82 gaschromatograph, which had a Poropak N column (1.1 m x 0.6 cm). The temperatures of the detector and the column were 150 and 60°C, respectively. The N_2O-measurements were carried out on a Varian 3300 GC, equipped with a Poropak T column (1 m x 0.3 cm) and a ^{63}Ni electron capture detector. The temperatures of the detector and the column were 350 and 45°C, respectively. A gas mixture of 95% Ar and 5% CH_4 was used as carrier gas at a flow rate of 25 ml/min.

3. Results.

Chemistry: The results of the chemical measurements are shown in Tab. 1, and there will in the following be referred to this.

Microbiology: The ATP contents (reflecting the total biomass) of the surface soil was about 650 ng ATP/g soil (not shown), and the contents of the subsurface soil varied from nearly 0 to about 10 ng ATP/g soil (Fig. 1). The ATP-contents of the soil after incubation with glucose and nitrate is shown along with the contents in the untreated soil (Fig. 1). The ATP-contents of the individual soil samples generally was from 2 - 10 times higher in samples after than before the addition of glucose and nitrate. This is probably because the addition of glucose has caused a microbial growth.

The results of the enumeration of bacteria (CFU) in the 3 profiles are shown in Fig. 2. The number of bacteria in the surface soil was about 10^7/g soil independent of the medium.

Tab.1. The contents of total N, NH_4-N, NO_3-N, total P, CO_3-C, total organic C, water soluble organic C and pH ($CaCl_2$).
• not measured.

	Depth (m)	tot-N (pct)	NH_4-N (ppm)	NO_3-N (ppm)	tot-P (ppm)	CO_3-C (pct)	total org.C (pct)	water sol.org C (ppm)	pH ($CaCl_2$)
Drilling I	0	0.13	2.9	16.1	537	<0.1	1.36	20.5	5.4
	1.2	0.01	0.3	13.6	337	2.7	0.53	18.0	8.7
	3.1	0.02	0.4	3.4	396	2.8	•	•	8.6
	5.1	0.01	1.2	<0.1	362	3.9	•	•	8.6
	7.1	0.01	2.1	<0.1	411	3.5	0.65	15.3	8.4
	10.3	0.01	2.8	<0.1	343	2.0	0.65	15.2	8.7
Drilling III	0	1.13	2.9	16.1	537	<0.1	1.36	20.5	5.4
	1.5	0.02	0.5	1.9	385	3.0	0.59	43.7	8.5
	3.0	0.02	1.8	<0.1	438	3.3	0.65	19.3	8.3
	5.0	0.02	2.6	0.4	391	2.9	0.65	15.7	8.1
Drilling IV	0	0.13	2.9	16.1	537	<0.1	1.36	20.5	5.4
	1.5	0.02	0.6	2.5	365	3.1	0.59	26.0	8.4
	3.0	0.02	1.3	<0.1	341	3.9	•	24.0	8.4
	5.0	0.02	4.1	0.1	403	3.2	•	20.3	8.3
	8.0	0.03	3.0	0.6	526	5.1	0.65	26.6	8.1
	11.6	0.01	3.1	0.2	316	3.2	•	25.5	8.4
	14.0	0.01	3.5	0.1	397	4.6	0.66	18.6	8.2

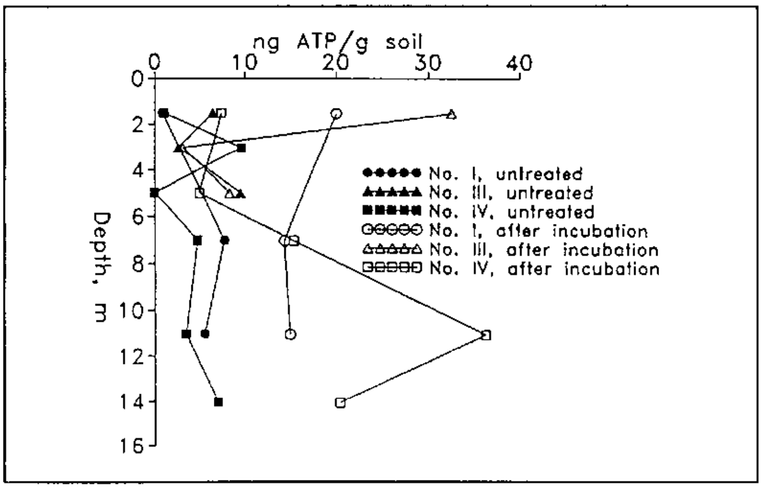

Fig. 1. The ATP-contents of untreated soil samples (dark symbols) and soil samples incubated with nitrate and glucose (open symbols).

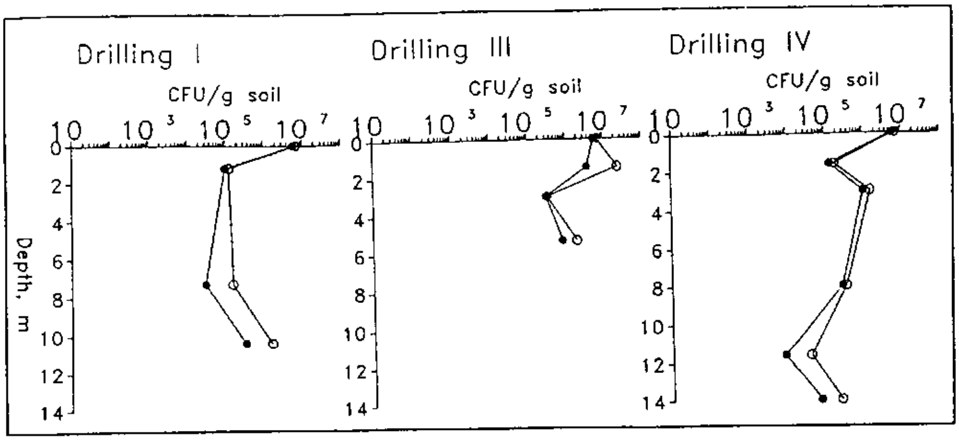

Fig. 2. The number of colony forming units (bacteria) estimated after plate count on a nutrient rich - (dark symbols) and a nutrient poor medium (open symbols).

The number of bacteria dropped to 10^5 - 10^6 bacteria/g soil in 2 - 3 m's depth and remained in this order of magnitute down through the profiles. In most cases the enumeration of bacteria in the subsurface soil was dependent on the medium as there was scored until 10 times more on the diluted medium (Fig. 2). It has been found (e.g. Ohta and Hattori, 1983) that bacteria from deeper soil layers, ground water and other oligotropic environments can be so adapted to these nutrient poor environments, that they are unable to make colonies on a medium rich in nutrients.

The number of bacteria able to reduce nitrate is shown in Fig. 3. The number of nitrate reducing bacteria (able to reduce nitrate to nitrite) in the surface soil was about 10^6/g soil and the number of denitrifying bacteria (able to reduce nitrate to gaseous nitrogen compounds) was about 10^5/g. This means, that in the surface soil the nitrate reducing bacteria made up 10% of the total amount of bacteria, and the denitrifying bacteria made up 1%.

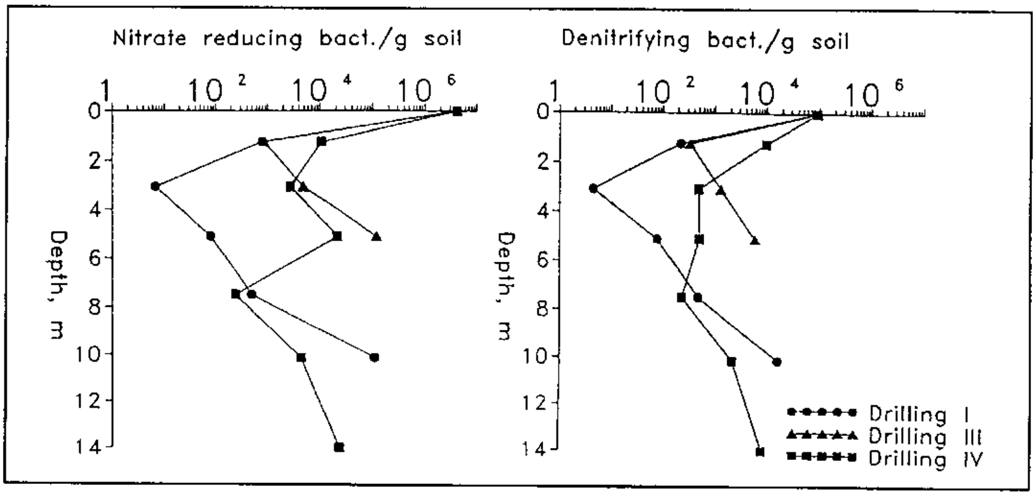

Fig. 3. The number of nitrate reducing- and denitrifying bacteria.

In all 3 profiles the number of both nitrate reducing and denitrifying bacteria dropped considerably from the surface soil to 1 - 2 m's depth. In higher depths the number either dropped further (drilling I), increased or remained more or less constant. The number of denitrifying bacteria below the root zone was as mentioned above less than in the surface soil, but apart from that, there was no correlation between depth and number of bacteria.

Incubation experiments: As an example from the incubation experiments only results from 2 depths in drilling IV are given (Fig. 4).

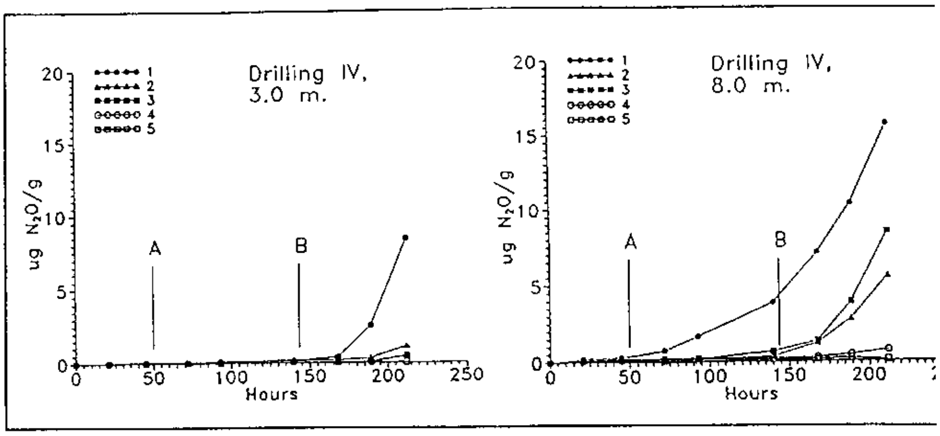

Fig. 4. Accumulated N_2O-production in soil samples from drill
IV in the depth of 3 and 8 m.

Treatment 1 = glucose added after 48 hours (A) and nitrate added after 140 hours (B). Incubated with acetylene.

Treatment 2 = nitrate added after 48 hours (A) and glucose after 140 hours (B). Incubated with acetylene.

Treatment 3 = glucose added after 48 hours (A) and nitrate after 140 hours (B). Incubated without acetylene.

Treatment 4 = nitrate added after 48 hours (A) and glucose after 140 hours (B). Incubated without acetylene.

Treatment 5 = Control; water added after 48 hours (A) and after 140 hours (B). Incubated with acetylene.

There was no measurable denitrification activity in 3 m's depth until after 140 hours, where the samples had been added nitrate as well as glucose. This indicates, that there was a lack of both nitrate and an easily decomposable carbon source. In the samples from

8 m's depth the denitrification activity increased already after 48 hours in one of the treatments (treatment 1). In this case the activity increased after the addition of glucose, which indicates that nitrate was present and only an easily decomposable carbon source was in short. In Tab. 1 the contents of nitrate- and ammonium in the 3 profiles are shown, and actually some nitrate was measured in drilling IV, 8 m.

The pattern of the denitrification activity found in drilling IV, 3 and 8 m (Fig. 4) was observed in all the incubation experiments. In samples from depths with nitrate present (Tab. 1) the addition of glucose caused an increase in the denitrification activity, but in most samples the nitrate level was so low, that addition of both nitrate and glucose was required before the denitrification activity increased. In no subsurface samples addition of nitrate alone caused an increase in the denitrification activity.

The denitrification activity in the samples before the addition of glucose is assumed to be a measure of the actual event <u>in situ</u>.

The actual denitrification activity in the surface soil was 0.1 μg NO_2-N kg^{-1} $hour^{-1}$ without addition of nitrate and 0.2 μg NO_2-N kg^{-1} $hour^{-1}$ after addition of nitrate (Tab. 2). The activity after addition of nitrate would correspond to a disappearance of approximately 4 kg N ha^{-1} $year^{-1}$ in the ploughed layer, if the activity was constant throughout the year. The actual denitrification activity in the 3 profiles was in several depths too low to be measured, also after addition of nitrate, while it in other depths was equal to or even higher than the activity in the surface soil (Tab. 2). For instance the activity in drilling IV, 11.6 m after the nitrate addition was twice the activity in the surface soil. An activity of 0.4 μg N_2O-N kg soil^{-1} hour^{-1} would correspond to a disappearance of 40 kg N ha^{-1} year^{-1} in a soil layer of 1 m's thickness, if the activity was constant throughout the year.

Tab. 2. The denitrification activity without and with NO_3 (100 ppm NO_3-N addition).
• not measured.

		μg N_2O-N kg soil^{-1} hour^{-1}	
	Depth (m)	without NO_3-N	with NO_3-N
Drilling I	0	0.1	0.2
	1.2	0.0	0.0
	10.4	0.0	0.2
Drilling III	0	0.1	0.2
	1.5	•	0.0
	3.0	0.0	0.0
	5.3	0.0	0.0
Drilling IV	0	0.1	0.2
	1.5	0.0	0.0
	3.0	0.0	0.1
	8.0	0.0	0.1
	11.6	0.1	0.4
	14.0	0.1	0.1

4. Discussion and conclusion.

Although the total biomass in the deeper soil layers was only 0.1 - 1.5% of that in the surface soil, and the bacterial biomass was only 1 - 10%, it is not likely, that this was the reason for the often very low denitrification activity in samples from the deeper soil layers. The biomass (total as well as bacterial) in the subsurface was low in proportion to the biomass in the surface, but in itself it was fairly high. Denitrifying bacteria were found in all depths down to 14 m, and as a result of the incubation experiments with nitrate and glucose addition, it could be concluded, that there was a potential for denitrification all the way down through the unsaturated zone. And it could be concluded, that the denitrifying bacteria in the subsurface apparently were quite as effective in reducing nitrate as the surface organisms as long as they were supplied with an easily decomposable carbon source. The actual denitrification activity - i.e. the activity without addition of glucose - in the deeper soil layers was in most cases less than in the surface soil. This is probably because the subsurface is an oligotropic environment, where the microorganisms are living with a more or less constant lack of organic matter. Decomposable organic matter serves the purpose of being both carbon- and energy source for most microorganisms, and the lack of it results in a low microbial activity. In most of the samples from the subsurface the microbial activity was quite low before the addition of glucose - both the denitrification activity as already mentioned, and the total activity expressed by the CO_2-evolution (not shown).

The lack of easily decomposable carbon sources in the subsurface soil will thus be limiting to a major nitrate reduction down through the unsaturated zone. In some of the samples the actual denitrification activity was relatively high. Taking these locally higher activities and the huge soil volume into account it is still possible, that microbial nitrate reduction can contribute to the removal of nitrate in deeper soil layers. It has not been possible to explain the locally higher denitrification activities. The contents of organic matter was the same in all depths, but it is possible that the decomposability has differed.

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Ministry of the Environment
National Agency of Environmental Protection
Denmark

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

Number B8

Processes of Nitrate Reduction in a Sandy Aquifer

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SUMMARY

Nitrate distribution and reduction processes were investigated in an unconfined sandy aquifer of Quaternary age. The groundwater chemistry was studied in a series of 8 multisamplers along a flow line, deriving water from both arable and forested land. Results showed that plumes of nitrate containing groundwater emanate from the agricultural areas and spread through the aquifer. The aquifer can be subdivided into a upper oxic zone of 10-15 m with ground waters containing O_2 and NO_3 and a lower anoxic zone characterized by Fe^{2+}-rich waters. The redox boundary is very sharp and suggest that reduction processes of O_2 and NO_3 occur at a rate which is fast compared to the downward water transport.

The total content of dissolved ions is 2 to 4 times higher in nitrate containing groundwaters derived from arable land than in groundwaters derived from forest areas. The persistence of the high content of total dissolved ions in the NO_3-free anoxic zone indicates that active nitrate reduction is taking place. These deductions are only possible because the sediment contains no carbonate.

Possible electron donors in the reduced zone of the aquifer are organic matter, present as reworked brown coal fragments from the underlying Miocene and low amounts of pyrite at an average level of 3.6 mMole/kg. Electron balances across the redoxcline, based on concentrations of O_2 , NO_3, SO_4 and TIC indicate that pyrite is by far the dominating electron donor even though organic matter is much more abundant. Apparently the reactivity of the brown coal fragments is too low to affect the chemical composition of the groundwater significantly. Furthermore, nitrate pollution increases the total electron acceptor load on the aquifer by a factor of five.

Transport and chemical reactions of both natural waters and nitrate containing waters from agricultural areas, in an unconfined sandy aquifer were modelled using the 1-D code PHREEQM, which combines an equilibrium model with a mixing cell transport model. Only the vertical component of the water transport was modelled since, in contrast to rates along flowlines, the vertical rates are close to constant as required by the one-dimensional model. A further advantage of this procedure is that data from different borings can be collected in a single depth profile, normalized to elevation, yielding a more general picture of changes in water chemistry. Average

vertical transport rates of water in the saturated zone were obtained by tritium dating.

The modeling process is a two step procedure. First the sediment column is initialized with natural water containing only oxygen as electron acceptor. Subsequently agricultural waters containing both oxygen and nitrate are fed into the column and spatial and temporal variations in groundwater chemistry can be modelled.

The quasi-steady state profile predicted by the model for natural waters containing oxygen as electron acceptor and pyrite as the only electron donor is in good agreement with the field data. However, the model predicts that a non-carbonate buffer is in operation and this is presumably FeOOH.

The nitrate concentration of agricultural waters entering the saturated zone varies with time and an input function was therefore constructed by linear mixing, using PHREEQE, of natural waters and agricultural waters. This input function was fed into the column initialized with natural water, and the model run forward in time to the year 1988 were field data are available. Comparison with field data shows that major changes in groundwater chemistry are well described by the model comprising reduction of oxygen and nitrate and pyrite oxidation.

Downward progression of the redoxcline is accelerated with a factor of five by the nitrate pollution of the aquifer, but absolute rates remain small in the order of cm/yr. The controlling factor for nitrate migration through the aquifer, once it has reached the anoxic zone, is the concentration and distribution of pyrite in the sediments.

Ministry of the Environment
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Number B9

Runn-off and Plant Nutrient Transport in the Brooks, Rabis and Syv

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SUMMARY

Run-off and transport of plant nutrients have been measured in streams and drains in the selected NPo-workshop areas near the brooks, Rabis and Syv.

Rabis brook

The 660 ha catchment area of Rabis brook consists of diluvial coarse sand to a great depth, and the inflow to the stream takes place almost entirely by ground water. There is no subsurface drainage in the area. Compared to other streams the concentrations and quantities of plant nutrients are low. The average annual transport per ha of the most important plant nutrients has been: NH_4-N 0.3 kg, NO_3-N 9.2 kg, PO_4-P 0.32 kg, total P 0.5 kg, K 13 kg, Ca 125 kg, Cl 100 kg and SO_4 113 kg.

Syv brook

The 1170 ha catchment area of Syv brook mainly consists of till. The annual plant nutrients transport per ha at the stream station has been 19 kg NO_3-N, 21 kg total N, 0.3 kg PO_4-P, 0.4 kg total P and 8 kg K. Average quantities for the subsurface drainage water stations have been 35 kg NO_3-N, 40 kg total N, 0.4 kg PO_4-P, 0.7 kg total P and 7 kg K. Average P-quantities at the drainage water stations show traces of waste water discharges, however. In addition there seems to be a considerable decomposition of some parameters in the upper part of the stream.

1. INTRODUCTION

Objective

Run-off and plant nutrient transport have been measured in the two streams which drain the selected NPo-workshop catchments areas as well as in selected drainage systems. The measurements are an integrated part of several projects which include water and plant nutrient balances for the two catchments.

Rabis brook

The catchment area of Rabis brook consists of diluvial sand down to a great depth. The soil type is coarse sand, and there is no subsurface drainage within the area. The ground is generally flat; the upper part of the stream, however, runs in a quite deep melt water valley. The inflow to the stream takes place almost entirely from ground water.

Syv brook

The catchment area of Syv brook mainly consists of till. The ground is rather flat in the major part of the area, some parts are quite hilly, however. The soil type is mainly sandy clay. The mapping of subsurface drained areas is insufficient, but according to information from the owners approx. one half of the agricultural areas is pipe drained (Hansen, 1990). In the upper part of the stream there is a couple of smaller ponds which the stream runs through. Furthermore, the slope of the upper half of the stream is very small and so delays the run off.

2. MATERIALS AND METHODS

Rabis brook

At Rabis brook the water and plant nutrient transport is determined at 2 measuring stations in the stream. The placings are chosen so that the stations - as far as possible - represent areas of different uses. The catchment area of the down-stream station is mainly agricultural areas. The topographic catchment area is approx. 980 ha. The up-stream station is placed so that heather and plantations make up as great a part of the catchment area as possible. The topographic catchment area of this station is approx. 660 ha and is part of the catchment area of the down-stream station. For both stations the ground water catchment area is considerably smaller than the topographic catchment area.

Syv brook

At Syv brook a measuring station was established in the stream, and 2 measuring stations were established in selected subsurface drainage water systems near Damgaard and Nordmarksgaard.

The topographic catchment area of the stream station is approx. 1170 ha. For the drainage water station near Damgaard the drainage system covers approx. 55 ha. However, only a small part of the drainage system near Nordmarksgaard has been mapped. The topographic catchment area of this drain outflow is aprox. 60 ha. According to the collected information (Hansen, 1990) approx. 15 ha are systematically pipe drained. Of the remaining part aprox. 35 ha are partly drained, that is some of the fields are drained in depressions. There is not any information available about drainage of the remaining 15 ha of the area.

Measurements

The run-off at the measuring stations has been determined by continuous registration of the water level. Furthermore, water samples have been taken regularly for chemical analyses.

Manual measurements of all drainage outlets

For financial reasons it was not possible to carry out continuous measurements of run-off and regular sampling from all drainage outlets into Syv brook. Therefore, in addition to the continuous measurements on the two largest drainage systems, manual measurements were carried out on the other drainoutlets 9 times during the period.

3. RESULTS

3.1 Rabis

Precipitation and run-off

The monthly average run-offs are shown in Figure 1, which also show the monthly precipitation. From this it appears that at both stations there are relatively small variations in the run-off. This corresponds to the fact that there is almost entirely inflow of ground water to the stream.

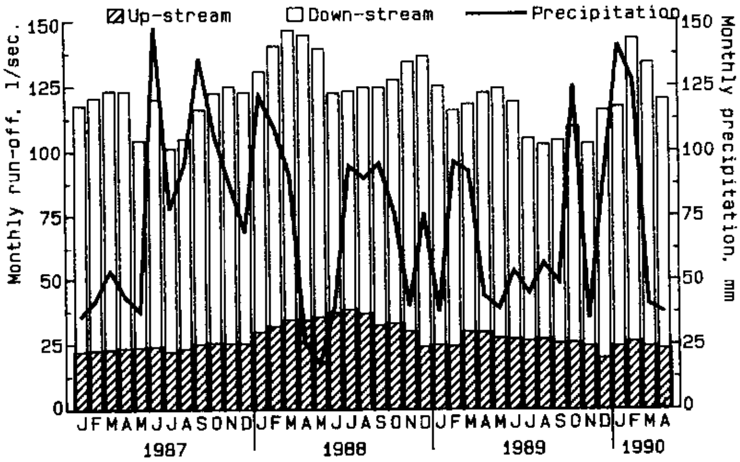

Figure 1. Monthly average run-off and precipitation at Rabis brook.

Increased runoff

Comparisons with earlier measurements near the down-stream station (Hansen, 1986) show that the run-off in 1988 has been 10-20% higher than normal. Near the up-stream station the run-off this year has been correspondingly higher than the previous and following year. This is due to exceptionally large rainfalls in the summer and autumn of 1987. At both stations the increased run-off is delayed several months compared with the increased precipitation. The delay is least at the down-stream station, where the run-off culminated in March 1988, while the run-off at the up-stream station first culminated in July 1988.

Chemical analyses

Average concentrations for each analysis parameter at the 2 stream stations are shown in table 1.

Table 1. Average element concentrations in Rabis brook.

	HCO_3	TOC	NH_4-N	NO_3-N	PO_4-P	tot-P	Ca	Cl	T-Fe	Fe^{++}	K	Mg	Mn	Na	SO_4
Station	mmol/l	<---------- mg/l ---------->													
up-stream	0.72	2.1	0.014	0.82	0.035	0.093	18	18	0.77	0.11	1.1	3.2	0.14	14	17
downstream	0.92	1.9	0.064	1.88	0.041	0.106	25	20	0.79	0.12	2.7	3.7	0.18	13	23

Compared with analyses from other Danish streams the concentrations of plant nutrients are generally low. Variation for the analysis parametres with the highest variations is shown in Figure 2. For NO_3-N, NH_4-N, Ca, Mn, SO_4 and especially K there is an increase in the concentrations from the up-stream to the down-stream station, Table 1 and Figure 2.

Plant nutrient transport

The plant nutrient transport has been calculated by multiplying daily run-off with daily concentrations. As the concentrations are only determined once every month, the concentrations for the intervening days are calculated by linear interpolation between the nearest previous and following analysis.

Quantities per ha

The size of the catchment area of the down-stream station has earlier been estimated by water balance calculations at approx. 770 ha (Hansen, 1986). Assuming the run-off in mm in the measuring period has been the same for the two measuring stations, the ground water catchment area of the up-stream station can be estimated at approx. 200 ha. Plant nutrient transport per ha calculated under these circumstances is shown in Table 2.

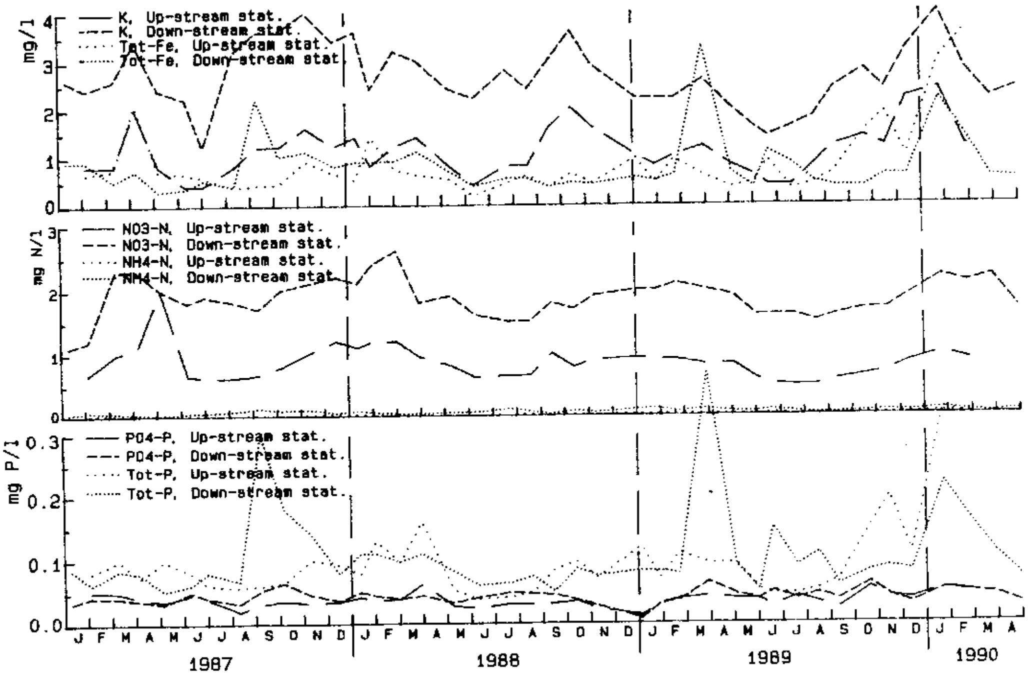

Figure 2. Variations in plant nutrient concentrations at Rabis brook.

Table 2. Plant nutrient transport, kg/ha, at the measuring stations in Rabis brook.

	month	HCO_3	TOC	NH_4-N	NO_3-N	PO_4-P	tot-P	Ca	Cl	tot-Fe	Fe^{++}	K	Mg	Mn	Na	SO_4
Upstream station																
1987	2-12	2.7	7.0	0.05	3.3	0.13	0.27	65	65	2.5	0.47	3.6	11	0.42	53	69
1988	1-12	3.7	11.9	0.06	4.5	0.17	0.42	90	103	3.0	0.65	5.9	17	0.80	76	87
1989	1-12	3.2	7.9	0.07	2.9	0.15	0.39	83	71	3.3	0.31	4.1	14	0.65	52	73
Down-stream station																
1987	1-12	4.1	9.2	0.32	8.9	0.20	0.50	120	90	3.4	0.45	13.7	17	0.75	69	102
1988	1-12	5.0	10.8	0.33	10.3	0.21	0.45	132	116	3.5	0.90	15.2	21	0.92	77	126
1989	1-12	4.5	7.6	0.31	8.3	0.20	0.56	123	94	4.1	0.48	10.4	18	0.89	56	112

3.2 Syv brook

Precipitation and run-off

Precipitation and average run-off at the 3 stations with continuous measurements at Syv brook are shown in Figure 3. From this it appears that there are high seasonal variations in the run-off at all 3 stations. The variations are rather uniform for each station; however, the run-off is reduced a little faster in the spring and after rainfall periods at the drainage water stations near Damgaard than at the other stations.

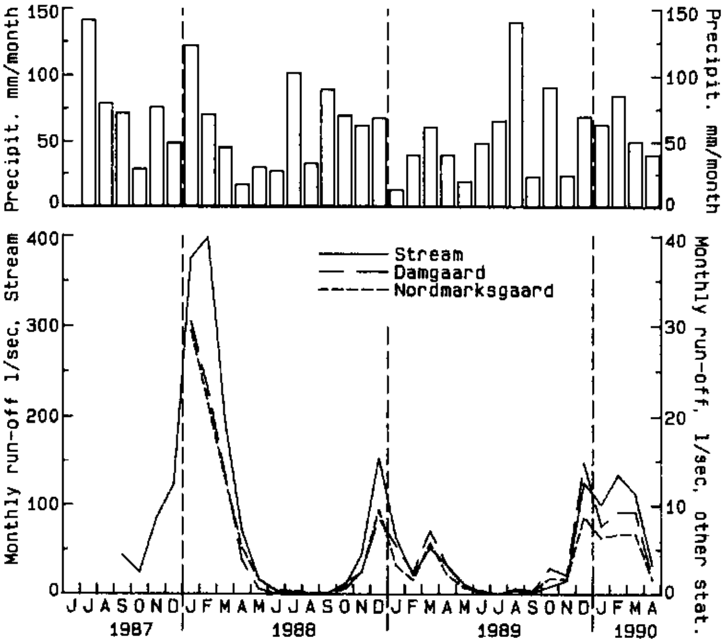

Figure 3. Monthly precipitation and average run-off at Syv brook. Notice that there are 2 different scales for run-off.

The run-off has been much higher in the 1. half-year of 1988 than in any other half-year period, Table 3. The difference in run-off cannot apparently be explained by the precipitation figures alone. The distribution of precipitation with large quantities in the 1. quarter of 1988 combined with large rainfalls in the summer and autumn of 1987 is probably a contributing cause.

Table 3. Half-yearly precipitataion, mm, and run-off at Syv brook.

Period year month	precipitation	Stream 1000 m^3	mm	Damgaard 1000 m^3	mm	Nordmarksgd. 1000 m^3	mm 1)
1987 7 -12	445	653 2)	56 2)				
1988 1 - 7	312	2763	236	171	311	171	428
1988 7 -12	420	562	48	31	56	36	89
1989 1 - 7	222	476	41	50	91	36	90
1989 7 -12	415	414	35	55	100	34	84
1990 1 - 4	238	983	84	72	131	55	138

1) Subsurface drained area estimated at 40 ha
2) Run-off in September - December

At all 3 stations there have been periods without run-off in the summer months.

Chemical analysis

The average concentrations for each analysis parameter at the 2 measuring stations at Syv brook are shown in Table 4.

Table 4. Average for plant nutrients koncentrations at Syv brook.

Station	COD mg/l	NH_4-N mg/l	NO_3-N mg/l	tot-N mg/l	PO_4-P mg/l	tot-P mg/l	Cl mg/l	K mg/l	SO_4 mg/l
Stream	22.5	0.15	11.2	12.8	0.143	0.225	37	5.0	46
Damgaard	18.7	0.07	11.3	13.2	0.071	0.103	38	1.8	57
Nordmarksgaard	16.0	0.29	13.0	13.8	0.204	0.358	30	2.9	58

The temporal variation for each analysis parameter is shown in Figures 4-6.

Average plant nutrient concentrations (Table 4) and the variations in the parameters (Figure 4-6) indicate that the stream and drainage water near Nordmarksgaard - as expected - are polluted with waste water or other pollulants. Especially in summer periods with low run-off there are high concentrations of NH_4-N, PO_4-P, total P and K at these stations.

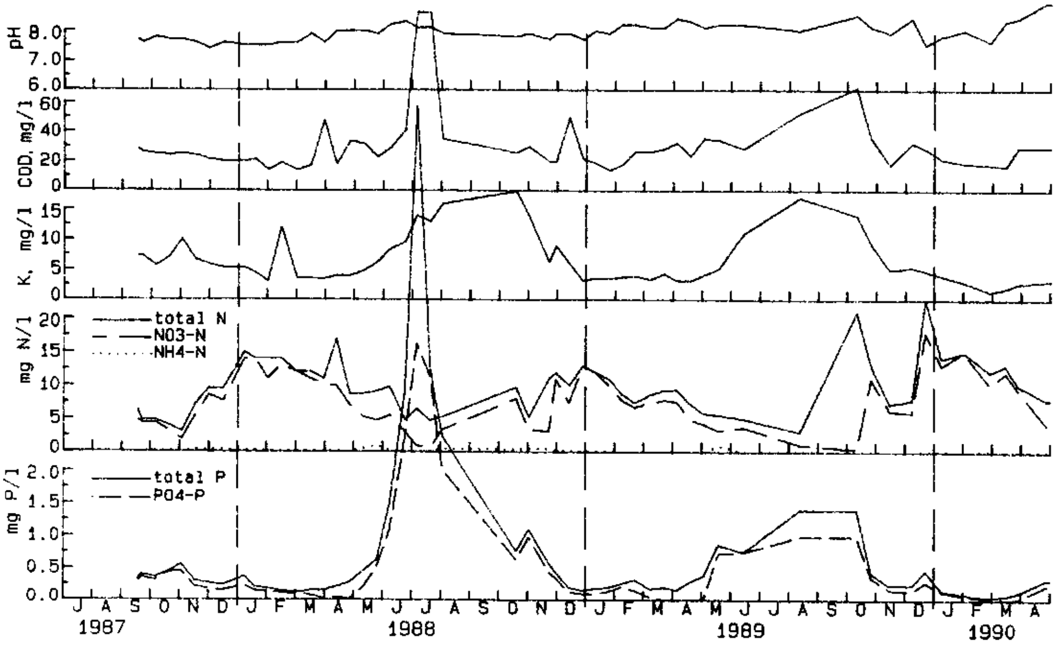

Figure 4. Plant nutrient concentrations at the stream station, Syv brook.

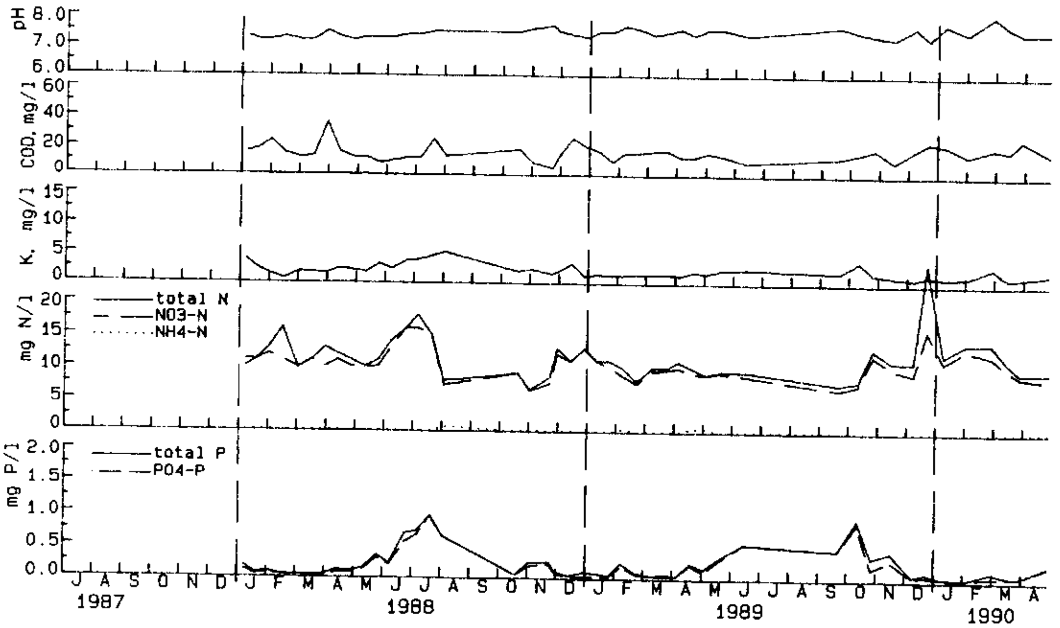

Figure 5. Plant nutrient concentrations at the drainage water station at Damgaard.

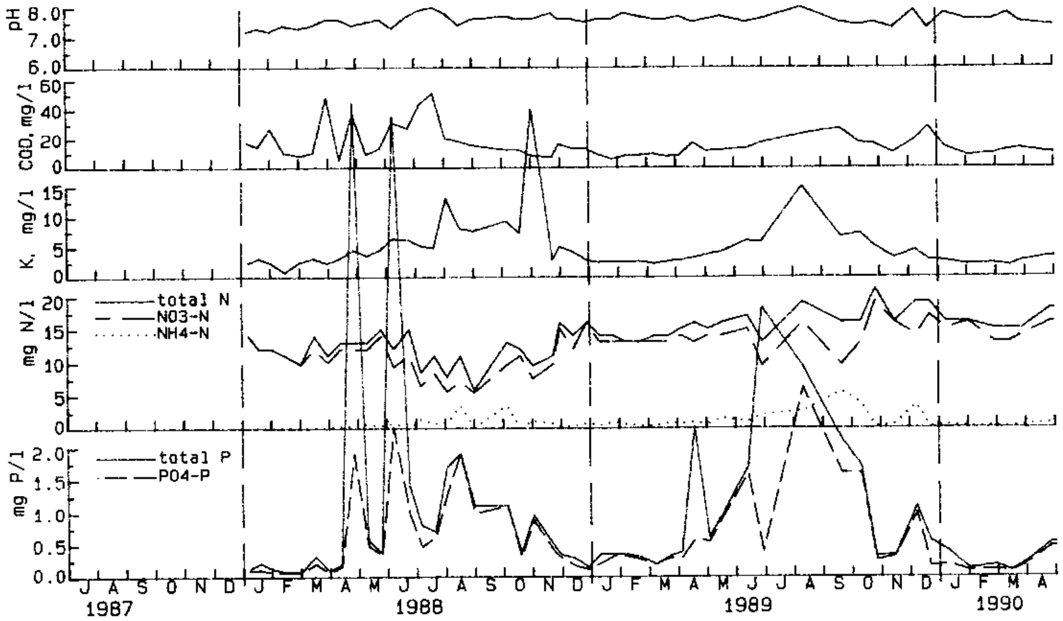

Figure 6. Plant nutrient concentrations at the drainage water station at Nordmarksgaard.

Annual quantities

Quantities of plant nutrients per area unit are shown in Table 5. In the calculations it is supposed that the ground water catchment area of the stream station is of same size as the topographic catchment area (1170 ha) and that the subsurface drained areas of the drainage water stations near Damgaard and Nordmarksgaard are 55 and 40 ha respectively.

Variation in quantities

Due to high run-off rates the amounts of plant nutrients has been highest in the first six months of 1988. The lower quantities in the last part of the measuring period are similarly due to lower run-off. At the stream station the quantities of NH_4-N, PO_4-P, total P and K are greatly reduced in the measuring period because of reduced discharges.

Tabel 5. Yearly plant nutrient transport, kg/ha, at Syv brook.

Station	Period	COD	NH_4-N	NO_3-N	tot-N	PO_4-P	tot-P	Cl	K	SO_4
Stream	1987/88$^{1)}$	58	0.44	32.9	36.8	0.40	0.61	94	15.7	109
	1988/89	26	0.16	7.9	9.3	0.19	0.30	39	4.9	49
	1989/90	29	0.13	15.6	18.1	0.14	0.22	51	4.3	73
Damgaard	1987/88$^{2)}$	58	0.19	33.6	37.9	0.17	0.24	89	5.8	136
	1988/89	24	0.16	15.1	15.8	0.10	0.15	66	2.6	90
	1989/90	46	0.14	29.2	37.3	0.23	0.32	104	4.1	165
Nordmarksgaard	1987/88$^{2)}$	77	0.32	48.4	49.8	0.53	1.12	113	10.0	291
	1988/89	21	1.12	24.8	26.7	0.58	0.93	56	7.7	88
	1989/90	35	0.97	34.9	38.4	0.59	0.92	77	6.8	103

1) September 1987 - April 1988
2) January 1988 - April 1988

Manual measuments of drain outlets

Manual measurements of all drain outlets were carried out 9 times during the measuring period. At the same time the run-off was measured, and water samples were taken at the measuring station in the stream.

The results showed that the major part of the inflow to the stream takes place by drainage flow, but that there is also a considerable inflow directly from ground water. There is a tendency that run-off and plant nutrient quantities in drainage outflows make out a greater part of the quantities at the stream station by high than by low run-off.

The results also show that N predominantly originates from subsurface drainage outflows. For the other analysis parametres the results are apparently more uncertain. This is probably due high decomposition rates in the stream and/or that a greater part of the quantities in drainage outflows come from waste discharges from farm buildings. Discharges from agricultural holdings increase the sampling error, especially when as in this case instantaneous samples are taken, as discharges form agricultural holdings are usually irregularly.

4. DISCUSSION AND CONCLUSION

Rabis brook

There are only small variations in run-off and plant nutrient transport at the 2 stream stations in Rabis brook. This agrees with the fact that the inflow to the stream almost entirely takes place by groundwater inflow.

Compared with other streams the nutrient concentrations and transports are low. For the downstream station the average annual quantities per ha of the most important ones have been: NH_4-N 0.3 kg, NO_3-N 9.2 kg, PO_4-P 0.32 kg, total P 0.5 kg, K 13 kg, Ca 125 kg, Cl 100 kg and SO_4 113 kg.

The nutrient concentrations and transport per area unit have generally been lowest at the upstream station where a great part of the surrounding area is plantation and heather.

Syv brook

There are high seasonal variations in the run-off at Syv brook. Most of the investigated stream stretch is usually without run-off a part of the summer period. This corresponds with the fact that the major part of the inflow to the stream takes place by subsurface drainage outflow, especially at high run-off intensity. Apparently there is also a substantial groundwater inflow to the stream.

The determination of the pipe drained area is uncertain because the mapping of the drains in the area is inadequate, but according to information from the owners approx. one half of the catchment area is drained.

The instantaneous manual measurements of the run-offs from drainage outlets show that N is predominantly conveyed from drainage outflows. For the other elements the sources are uncertain.

Apparently there is a considerable nutrient decomposition in the upper part of the stream. This is especially due to the low slope of the stream and to the bog holes through which the stream passes and therefor delays the run-off.

The annual plant nutrient transport per ha for the stream station at Syv brook has been 19 kg NO_3-N, 21 kg total N, 0.3 kg PO_4-P, 0.4 kg total P and 8 kg K. Average quantities for the drainage water stations have been 35 kg NO_3-N, 40 kg total N, 0.4 kg PO_4-P, 0.7 kg total P and 7 kg K. Average P-quantities for the drainage water stations show traces of waste water discharges, however. The plant nutrient quantities at the measuring station in the stream have been affected by discharges of small amounts of waste water and especially in the beginning of the measuring period. Furthermore there is a substantial plant nutrient decomposition in the upper part of the stream. The plant nutrient quantities in the stream are therefore not necessarely representative for the quantities which are conveyed from agricultural areas.

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Number B10

Nitrate Reduction by Pyrite and Lignite in a Sandy Aquifer

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Abstract.

Fladerne Brook watershed is an intensive agricultural area with more than 75% cropped fields. It is situated in an outwash plain and the geological material is mainly sand with minor contents of pyrite and lignite. The annual loss of nitrate to the groundwater is 120 kg N/ha, while the discharge from the watershed is 3.3 kg N/ha. The brook is acid with high iron content.

The aquifer is 20 meter thick and the nitrate reduction front is located in 6-9 meter. Below this depth nitrate is reduced in the aquifer by oxidation of pyrite and lignite.

Laboratory experiments has proved that the reaction is microbiological and a 1. order reaction with respect lignite and pyrite. By addition of bactericide the reduction process is stopped, while addition of glucose accelerated the reaction.

A calculation of the total reduction capacity of the upper aquifer results 80 000 kg N/ha, equivalent to 650 years loss from the cropped fields.

1. Introduction.

In large areas of western Jylland outside the deglaciation line the river water is acid and iron rich. Although some of the watersheds is intensively agricultured the discharge is low in nitrate. A former study from Fladerne Brook watershed showed an annual discharge of 3 kg N/ha in spite of a calculated leaching from the arable land of approximately 80 kg N/ha, Hansen & Sommer (1987). Consequently, it is believed that nitrate is reduced in the groundwater by oxidation of pyrite and lignite.

The aim of present study is to demonstrate the chemical and biological reactions in the aquifer and in the root zone under a intensively cropped farmland. Additionally, the acidification of the groundwater is determined and a kinetic approach towards the nitrate reaction with pyrite and lignite are setup. A programme of field measurements and laboratory experiments is combined.

2. Materials and Methods.

Location.

Fladerne Brook watershed is situated 25 km north of Herning i midwest Jylland, Fig. 1. It is a tributary of Karup river system and covers an area of 250 ha. The surface is rather flatten tilting towards west from 45 m.b.sl. to 39 m.b.sl. at the river station. The area is located in a outwash plain, mainly consisting of diluvial sand overlaying Tertiary quartz sand with a low pyrite and lignite content.

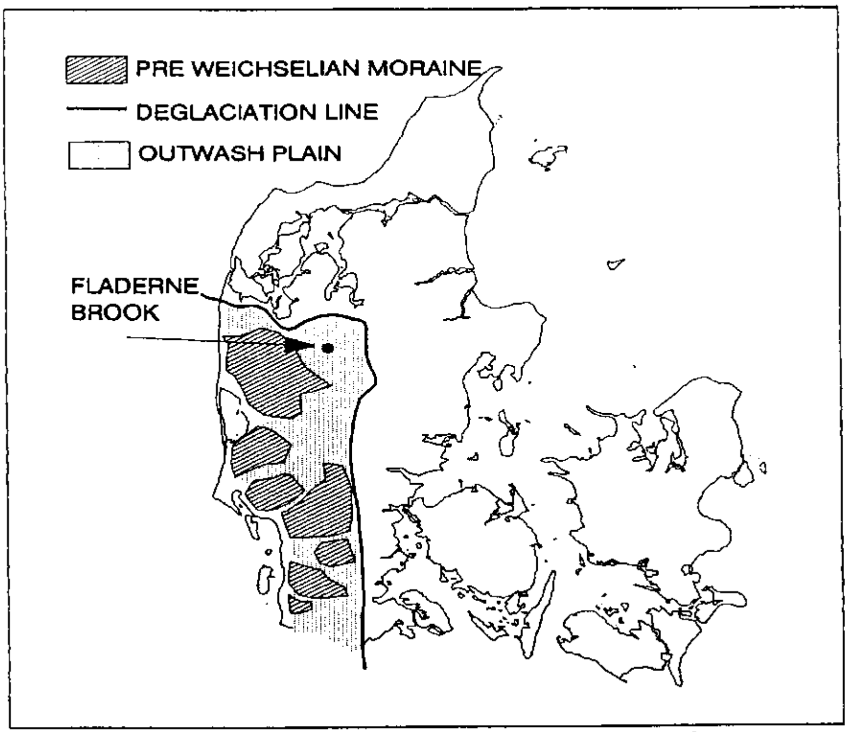

Fig. 1. The investigation area, Fladerne Brook.

Field station.

Based on hydrogeological information four groundwater stations (B1-B4) were placed along a groundwater flowline, Fig. 2. On each field station a well was drilled to a depth of 12.5 meter below water table. The boring was equipped with 7 groundwater 0.5 m filters with 1 meters interval and soil-air filters. Soil samples for geochemical analyses and experimental use were collected while drilling.
At each station (B1-B3) 3 lysimeter (42 * 32 * 22 cm) with an electronic percolation gauge was placed in 1.0 meter below surface.
At station B2 four teflon suction cups attached to an automatic vacuum pump were installed in 1.0 meter for soil water sampling. A climate station was placed at the fringe of the field recording soil and air temperature,

precipitation, percolation and groundwater level averaged hourly.

Adjacent to the station B4 a river station was setup, collecting water from the brook each hour. A plate weir in the brook enabled discharge measurements. For further information on technical equipment, see Jacobsen (1991).

Analyses and measurements.

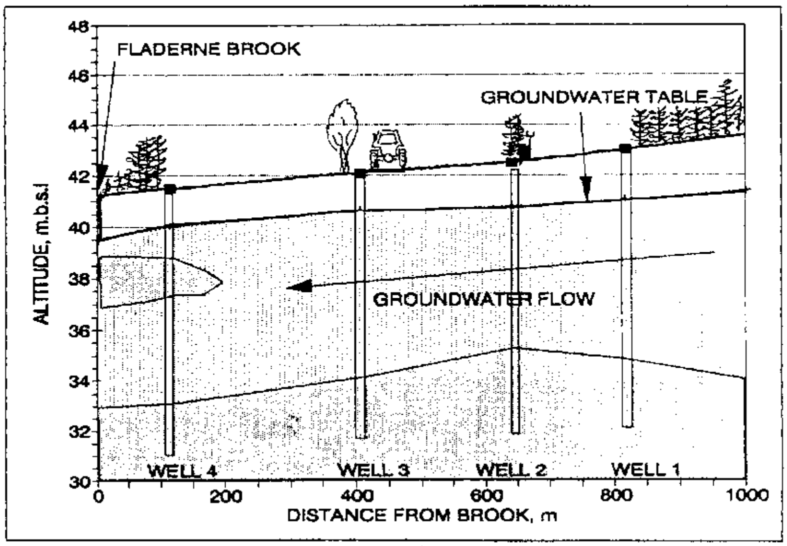

Fig. 2. Transect of the aquifer.

Soil samples from the borings were described geologically and chemical analyzed by the Geological Survey. Analyses of TOC, $CaCO_3$, pyrite, reduced sulphur and mobilizable organic matter (MOM) were performed. Analyses of N_2O were carried out on a Varian GC 3300 and CO2 was measured on a ML GC 82 at Danish Research Service for Plant and Soil. Water analyses were performed on unfiltered samples immediately after return to the laboratory. Analyses of pH, alkalinity, NO_3, NH_4, SO_4, Fe^{++}, K, Cl, PO_4, total-N and total-P were processed;

for further analytical information, see Jacobsen et al. (1990).

Periodically sampling.

With intervals of approximately one month groundwater, water from lysimeters and teflon cups, soil air samples and climatic records were collected. Groundwater is pumped up by a impeller pump trough a flowcell with a temperature and pH probe attached. Analyses of Fe^{++} and PO_4 was carried out instantaneously.

Experiments.

Experiments were setup to determine the nitrate reduction in the saturated zone. Kinetic experiments were carried out in batch runs. Soil samples, 200 g in 1000 ml groundwater, were added nitrate and incubated in a N_2 atmosphere in sealed blue cap bottles at 22 °C or 10 °C. Some soils were added 1% pyrite, 2% lignite or 0.1 mg glucose/l. In some parallel runs the microbial activity was stopped by addition of a bactericide (NaN3). Water samples were extracted during a period of 112 days and analyzed for pH, alkalinity, SO_4, NO_3 and NH_4. In some runs PO_4 was determined in order to detect a release of phosphate from the lignite decomposition.

Water balance.

Based on climatic records from the field stations it was possible to calculate a water balance for each field. The model in use, Evacrop, take into account precipitation, temperature, global radiations and type of crop, Olesen & Heidmann 1990. The model is based on WATCROS / NITCROS concept, Aslyng & Hansen, 1982 and Hansen & Aslyng, 1984.

3. Results.

Geology and chemistry.

Fladerne Brook watershed upstream the weir station covers an area of 250 ha. The groundwater level is 1 - 2.8 m.b.s. The longitudinal span is 2700 meter and the width 900 meter. The brook covers approximately 1200 meter open water coarse downstream with no drain systems and nearly 500 meter upstream in pipes with minor drain systems. The top soil is mostly sand with exception of areas near the brook where peaty soils are abundant. The soils below 1 meter consists of more than 98% sand fraction :

Well no B1:
0-0.5 m sandy soil, Post Glacial
0.5-4.5 m diluvial sand, Glacial
4.5-12.5 m quartz sand, Miocene

Well no B2:
0-0.5 m sandy soil, Post Glacial
0.5-3.0 m diluvial sand, Miocene
3.0-13 m quartz sand, Miocene

Both profiles contains no carbonate and the organic carbon content (TOC) is in the subsoil part between 0.04-0.09 %, Fig. 3. The reduction capacity of MOM is less than 200 mg O_2/g soil. A well for household water supply 200 meter from well B2 showed a clay layer in 20 meter. Using this information a pumping test showed a hydraulic conductivity $6.5 \cdot 10^{-4}$ m/sec, corresponding to a transmissivity $1.2 \cdot 10^{-2}$ m^2/sec. Using corresponding data of precipitation and groundwater level, the unsaturated conductivity is estimated to $1.2\text{-}1.5 \cdot 10^{-5}$ m/sec equal to a pistonic translocation time of 28-36 hours from soil surface to groundwater.

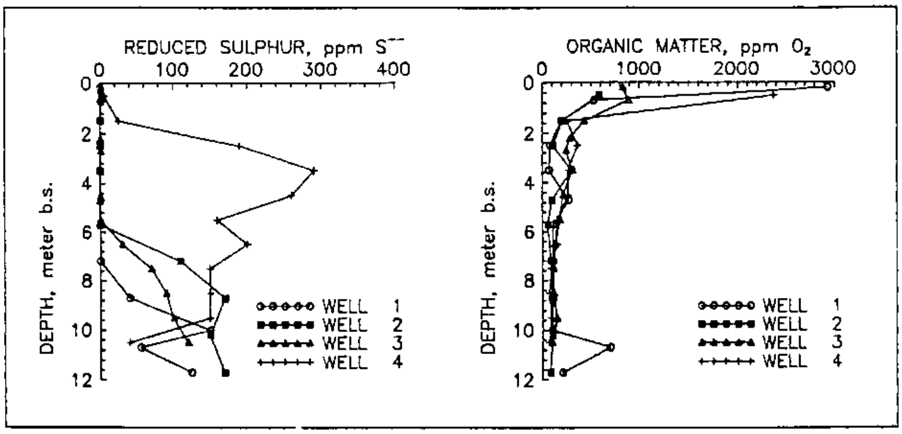

Fig. 3. Reduced sulphur and organic matter in the four soil profiles.

Nitrogen, agriculture and leaching from top soil.

The landuse in Fladerne Brook watershed is 79% agriculture and 12% forrest. In 1984 Hansen and Sommer (1987) made a calculation on the frequency of crops. Compared to the present study a remarkable change has occurred as pulses crops increased from 2% to 27%, whereas cereals decreased from 34% to 10%. The area covered with root crops is rather constant 31-34%.

Most of the fields are irrigated during the sommer desiccation.

Information on the amount of fertilizer and manure applied to the fields was obtained from the farmer and the farmer consultants. Using data on crops and recorded climatic parameters a water balance of the root zone was simulated by use of the EVACROP model. Leaching of nitrate and sulphate from the root zone could then be estimated from the infiltration volumes and soil water concentrations obtained in teflon cups and lysimeters, Fig. 4. The annual loss of nitrate from 1 meter was in 1989-90 about 120 kg N/ha equivalent to a mean con-

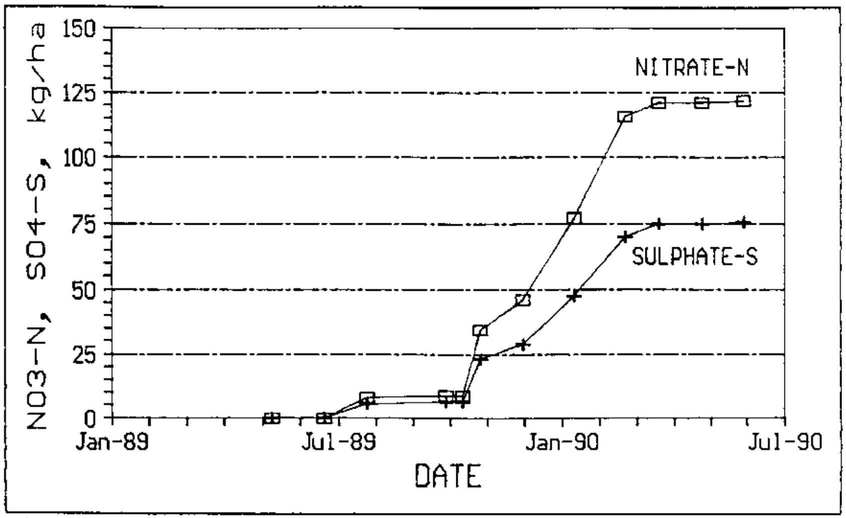

Fig. 4. Leaching of nitrate and sulphate from the root zone at station B2.

centration of 25 mg NO_3-N/l. The corresponding values for sulphate was 75 kg S/ha and 15 mg SO_4-S/l.

Soil air.

The composition of soil air showed rather low values of N_2O and CO_2, whereas O_2 is about constantly 19 %, similar to an earlier study, Lind (1986) and Jacobsen (1986). The N_2O content varied between 0.63-1.43 ppm compared to the atmospheres 0.27 ppm, and thus indicate a low denitrification activity in the unsaturated zone and the upper groundwater. The CO_2 contents was about ten times the atmospheric value and confirmed the low microbiological activity in the unsaturated zone.

Watershed discharge.

The outflow from the watershed has been measured in the period 1989.10.01 to 1990.06.01 which mean that not an annual value could be calculated. The discharge was estimated to 375 mm compared to 488 mm of infiltration. The outflow of nitrate and sulphate made up 3.3 kg N/ha and 84 kg S/ha.

The transect.

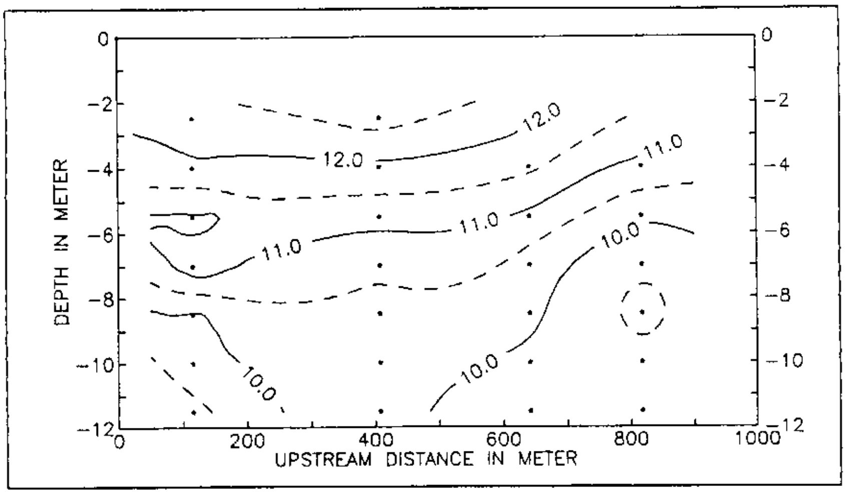

Fig. 5. Groundwater temperature in September 1989.

The physical and chemical parameters of the groundwater along the transect may give indications of the dynamics in the reservoir. It is general accepted that the groundwater temperature is 8°C in average. Present study has, however, shown a temperature in 11 meters depth of 10.2°C in September, Fig. 5., while in March only 8.4°C. This indicates a rapid flux of groundwater through the aquifer.

A further indication of the flow pattern can be obtained from the potassium content in the transect. As the clay content in the soil is less than 1% the potassium concentration reflects influence from agricultural leachate, Fig. 6. The limit in concentration between water from cropped and uncropped areas is usual set to 10 mg K/l, and leachate measured in teflon cells varies between 15-40 mg K/l. Hence, agricultural water is present down to approximately 10 meter b.s.

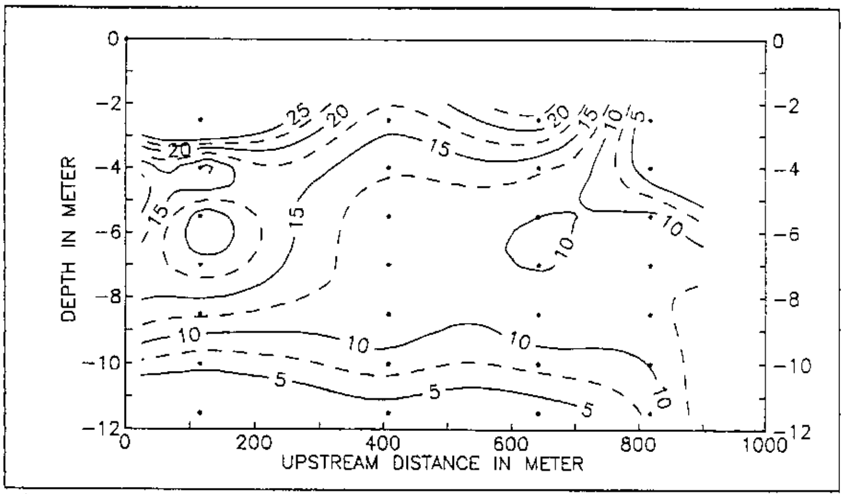

Fig. 6. Potassium concentration in groundwater in March 1990, mg K/l.

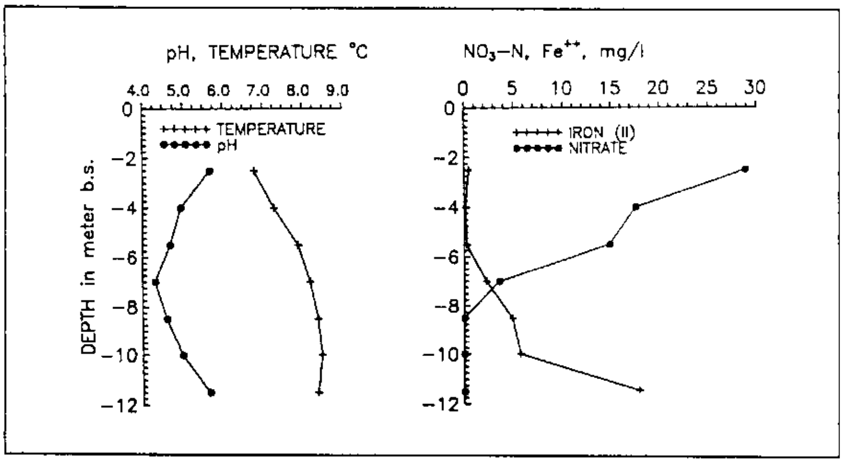

Fig. 7. Temperature, pH, nitrate and iron(II) profiles at station B2, March 1990.

The nitrate concentration in the profiles decrease with depth caused by a reduction by pyrite and lignite, Fig. 7. As pyrite is oxidized by nitrate, Fe++ and H+ is released, which consequently decreases pH. It has been observed that the nitrate reduction front is not stable through the year. The zero isoline fluctuates vertically about 2 meter, (7-9.5 meter b.s.). In March after the winter infiltration the nitrate front is at the lowest, Fig. 8.

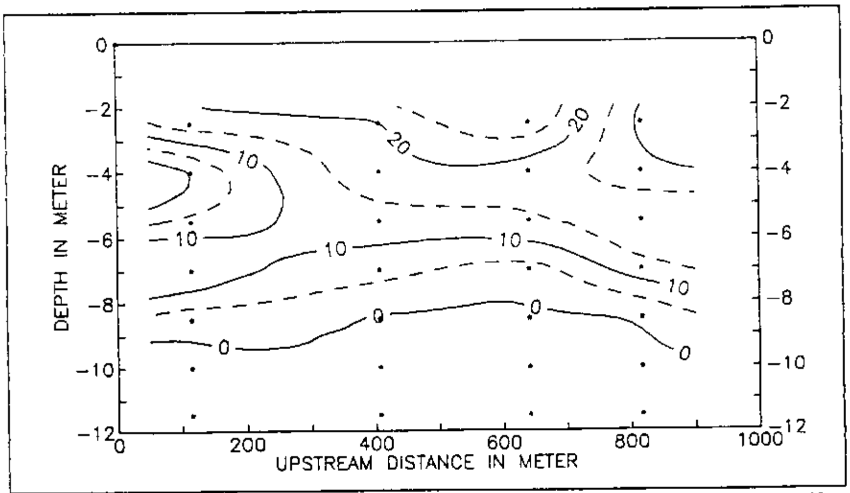

Fig. 8. Nitrate in groundwater in March 1990, mg NO_3-N/l.

Laboratory experiments.

In order to describe the kinetics of the nitrate reduction by oxidation of lignite and pyrite laboratory experiment with reservoir soil were processed.

In runs without addition very low activity was recorded, Fig. 9. Addition of 2% lignite increased the reduction rate about ten times. The presence of pyrite accelerates the reduction significant and deplete the nitrate in 130 days. This corresponds to a reductions rate of 0.4 mg N/kg soil day. If both pyrite and lignite is in the batch the reaction rates are summed.

The nitrate reduction using glucose as carbon source very rapid and diminished the oxidation of pyrite, Fig. 9.

Addition of bactericide to the batch causes no activity could be detected, not even in batch runned for a period of 280 days. The nitrate reduction is consequently believed to completely controlled by microbial metabolism in the aquifer.

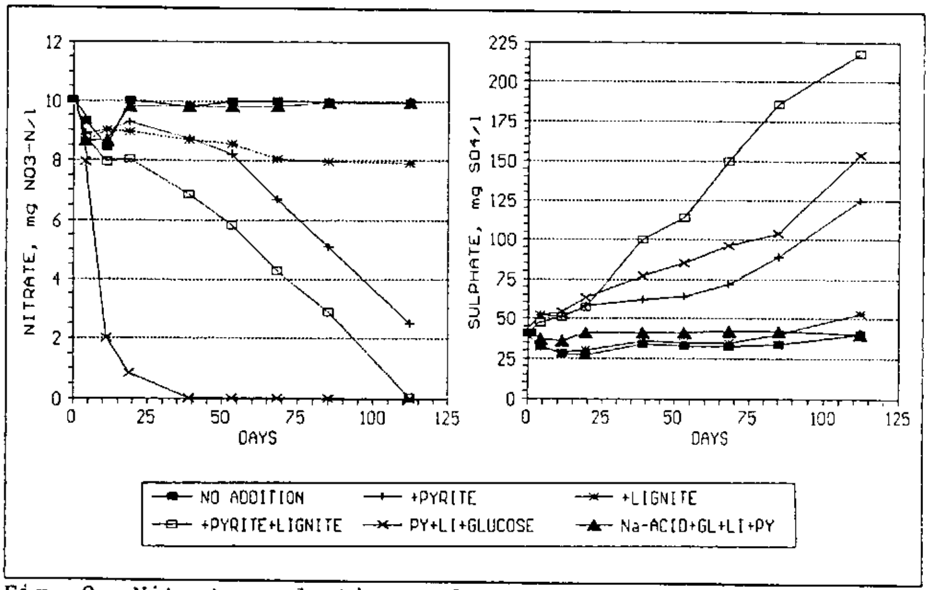

Fig. 9. Nitrate reduction and sulphate production in batch experiments.

In batch experiments with inoculated material from a lignite mine the reaction rate increased considerably, apparently caused by the increase in the bacteria population, Andreasen & Larsen (1989a, 1989b, 1989c).

4. DISCUSSION AND CONCLUSION.

The aim of this study was primarily to evaluate the impact of nitrate from intensive farmimg on the groundwater and the processes in the aquifer which enables a reduction of nitrate.

Fladerne Brook watershed has an annual precipitation of 800 mm and the infiltration is near 400 mm. The annual loss of nitrate to the groundwater is about 120 kg NO3-N/l, which gives an average concentration of 25 mg NO3-N/l. This value is higher than an earlier study based on calculated values, Hansen &

Sommer (1987), but lower than obtained by Kölle et al. (1985) on a similar soil. Only a minor denitrification occurs near or above the groundwater and is estimated 5-10 kg N/ha year, similar to values recorded by Jacobsen & Vinther (1990).

The calculated discharge of nitrate amounts to 3.3 kg N/ha year which imply a mean reduction of 115 kg N/ha year.

Investigations of the groundwater transect indicate that the nitrate reduction mainly occurs in 6-9 meter b.s. Coincidentally, a decrease in pH and a increase sulphate is determined, which demonstrates that pyrite oxidation is a part of the reaction. Studies in sandy aquifers near Hannover, Germany, has indicated this reaction, Kölle et al. (1985) and Kölle & Schreeck (1982). The predominant processes in nitrate reduction have been examined in laboratory experiments. The three main reactions in the aquifer are:

$$5\ FeS_2 + 14\ NO_3^- + 4\ H^+ \rightarrow 7\ N_2 + 10\ SO_4^{--} + 5\ Fe^{++} + 2\ H_2O \quad (1)$$

$$5\ Fe^{++} + NO_3^- + 7\ H_2O \rightarrow FeOOH + 0{,}5\ N_2 + 9\ H^+ \quad (2)$$

$$5\ C_7H_8O_4 + 28\ NO_3^- \rightarrow 14\ N_2 + 28\ HCO_3^- + 7\ CO_2 + 6\ H_2O \quad (3)$$

Reaction 1 and 2 are related to pyrite and iron, while reaction 3 is a general oxidation of organic matter (lignite/humus). Oxidation iron generates a decrease i pH, while oxidation of organic matter tends to increase the alkalinity. As the two processes usually run synchronously the change in pH will be less. The laboratory experiments showed that sediments below the oxidation front were able to reduce quantitative amounts of nitrate. The reaction rate was estimated to 0.022 mg N/ kg soil day, equivalent to 135 kg N/ha year per meter of sediment, the same magnitude as the leached from the root zone. Increasing concentration of pyrite and lignite in the sediment raise the reduction rate, correspondingly, probably following a 1. order reaction. By adding bactericide to the batch experiments no reactions could be detected. This confirm that the nitrate reduction in the aquifer is totally biological governed.

Earlier studies in clay soils indicated a geochemical nitrate reduction, Lind (1980), while Hendry et al. (1984) and Lind (1986) showed that nitrate reducing bacteria was present in clayey soils. The temperature dependency has been described by Vinther (1990). An estimation of the nitrate reduction capacity in the upper aquifer (0 - 12 meter) gives following values:

pyrite	18 000 kg NO3-N/ha
lignite (organic)	61 000 kg NO3-N/ha

totally 80 000 kg N/ha equivalent to 650 years loss from the root zone at the present level. To this capacity a considerable quantity must be added as no recognition of leached organic matter is considered in the calculation, Jacobsen & Vither (1990). Further, the aquifer is known to be at least 20 meter deep.

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Impact in Groundwater Quality from two Manured Farmlands on Sandy Soil

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IMPACT ON GROUNDWATER QUALITY FROM TWO MANURED FARMLANDS ON SANDY SOILS.

Abstract.

In two sandy soils in mid Jylland, the N-transport and N-transformation processes in the unsaturated zone were investigated during a two year period. The nitrogen leaching was estimated to 45 to 205 kg N/ha year, and was largest when liquid manure was spread on bare soil followed by a rainy period. Leaching of organic N was found to be app. 25 % of the total N-leaching. Acidification of soil due to nitrification was registered after spreading of manure. A high potential for nitrate reduction was measured in soil layers around the ground water table. It was estimated that app. 120 kg N/ha year was denitrified from a 1 meter thick soil layer.

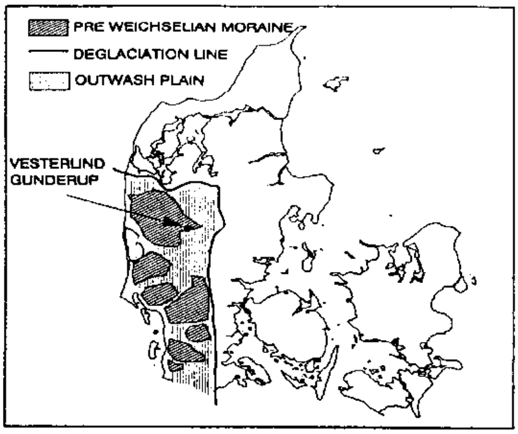
No phosphor leaching of any importance was measured in the two soils.

1. Introduction.

Leaching of nitrogen from agricultural areas in Denmark has been investigated in different types of farming practices. However, some farming practices involving heavy manure loads on sandy soils may cause changes in the groundwater quality of the upper aquifer. Opposite will the use of catch crops reduce the leaching of nutrients from manured soils. A large livestock cause an extended load of ammonia and organic nitrogen, which after leaching to the subsoil may produce an secondary acidification.

The aim of the present study was to demonstrate the chemical and biological reactions in the root zone and in the unsaturated zone under two manured farmlands. The one has had regularly catch crop during several years, the other has not. Both farmlands are situated on sandy soils and has used manure.

2. Materials and Methods.



Figur 1. Location of field stations.

Two farms.

Two farmlands sandy soils in mid Jylland were selected as field stations. Vesterlind situated 5 km south of Herning has an annual pig production of 2000 pieces. The manure/liquid manure was applied to the fields once a year. Before 1988 no catch crop has been grown (black soil practice). The other farm, Gunderup, is situated 1.5 km east of Vesterlind and had until 1988 pig production of the same size. Opposite to Vesterlind, Gunderup has a 25 year catch crop practice and a monoculture of spring barley.

Field station.

On each field station a boring was drilled to a depth of 1-2 meter below water table. The boring was equipped for ground water and soil air sampling. Soil samples for experimental use were collected while drilling. Teflon suction cups for soil water sampling were installed at different depths in the unsaturated zone. A lysimeter (40 x 60 x 15 cm) with percolation meter was placed 1 meter below surface. At the fence a climate station was placed for recording average temperatures, precipitation, percolation and light.

Analyses and measurements.

Soil samples from the borings were chemical analyzed according to the Danish agriculture standard and geological description were performed by the Geological Survey. In addition, bacterial counts and identification were made on uncontaminated soil samples. The total microbial active biomass was determined by the ATP content, Eiland 1985. The bacterial biomass (Colony Forming Units (CFU)) was encounted by plate spreading procedure and nitrate reducing bacteria and denitrifiers was estimated by the Most Probable Number method, Alexander, 1965, modified by Vinther et al. 1982.

Analyses of N_2O were carried out on a Varian GC 3300 and CO_2 was measured on a ML GC 82.

Water analyses were performed on unfiltered samples immediately after return to the laboratory. Analyses of pH, alkalinity, NO_3, NH_4, SO_4, Cl, PO_4, SiO_2, total-N and total-P were processed; for further information see Jacobsen & Vinther 1990.

Periodically sampling.

With intervals of approximately one month water and air samples and climatic records were collected.

Nitrogen mineralisation, nitrification plant uptake and leaching from the upper soil layer was determined by incubation of intact 35 cm long soil columns in the field, using the 'in-situ method', Debosz & Vinther 1989.

Denitrification was measured a few times during the investigation. Soil columns (30 x 3 cm) in a number of 15 were taken, brought to the laboratory, acetylene added, then sealed and incubated at actual temperature for 24 hours. Head space gas was analyzed for N_2O production. Kinetics were carried out with respect to water content and temperature, Vinther 1990.

Laboratory experiments.

Experiments were setup to determine nitrogen metabolism in the unsaturated zone. Kinetics were carried out on intact soil columns as well as in batch runs. Soil samples added nitrate, or slurry were incubated in sealed bottles at 20 °C and the N_2O production was determined during 14 days. Acetylene was added to 6 out of the 12 runs from each depth.

Soil samples from the same depths were incubated at 22 °C in open plastic jars in a vapored box allowing soil-air exchange. Nitrate, ammonia or liquid manure was added and changes in pH, ammonia and nitrate was analyzed during 79 days incubation.

Water balance.

Based on climatic records from the field stations it was possible to calculate a water balance for each field. The model in use, Evacrop, take into account precipitation, temperature, global radiations and type of crop, Olesen & Heidmann 1990. The model is based on WATCROS / NITCROS concept, Aslyng & Hansen, 1982 and Hansen & Aslyng, 1984.

3. Results.

Geology and chemistry.

The geological profiles on Vesterlind and Gunderup are interpreted as follows:

Table 1. Soil description.

Vesterlind:
0-0.5 m sandy soil, Post Glacial
0.5-1-0 m diluvial sand, Glacial
1.0-4.0 m quartz sand, Miocene

Gunderup:
0-0.5 m sandy loam, Post Glacial
0.5-4.5 m sandy till, Glacial
4.5-5.0 m sandy clay
5.0-9.5 m quartz sand, Miocene

The top soil at Vesterlind is classified as JB1 and at Gunderup as JB3 according to the Danish Soil Classification System, Fig. 2. Although, the total profiles are sandy, a minor clay layer at Gunderup may have some hydraulic effect on the infiltration rate and on the water retention capacity.

Both profiles contains no carbonate and the

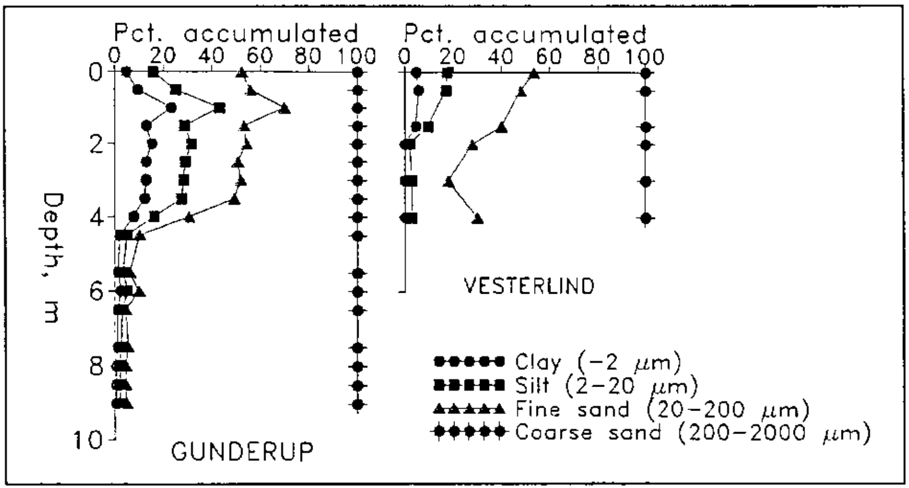


Figure 2. Soil texture of the two profiles.

organic carbon content (TOC) is in the subsoil around 0.02 %. In the topsoil of Vesterlind and Gunderup the values are 1.45 % and 1.9 % respectively. The corresponding values for total-N are 0.09 % and 0.15 %.

The phosphorus level is in general very high in the topsoil, 1000 ppm, and low in the quartz sand 20 ppm. At Gunderup the clay layer in 1-4 meter total-P raise to about 160 ppm. These values coincide with other observations for topsoils and for some profiles, Jacobsen 1986.

Microbiology.

The microbial active biomass was estimated as the soil content of ATP (adenosintriphosphate). The topsoil showed values 380-480 ng ATP/g soil, which is a normal level in Danish agricultural soils, Andersen et al. 1983. The subsoil content was quite low, less than 20 ng ATP/g soil.

Plate countings on soil extracts with high and low nutrient levels showed that no significant distinction, indicating that the bacteria may be adapted to low nutrient level. Opposite to

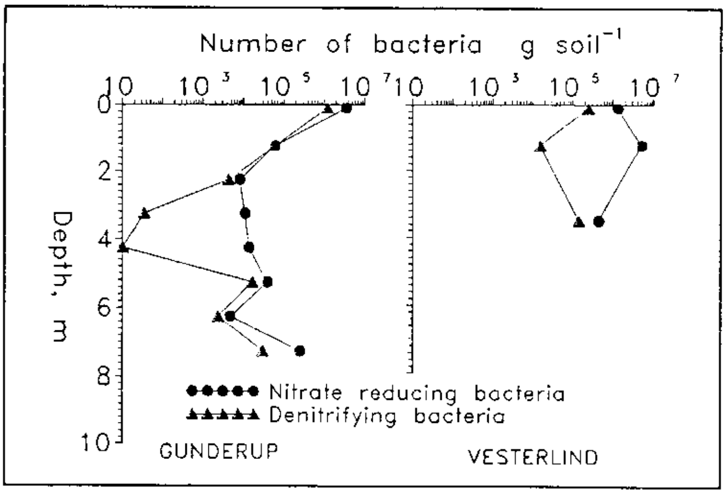


Figure 3. Number of denitrifying and nitrate reducing bacteria.

the ATP measurements the CFU levels in the profile were not decreasing notable with depth. The quantity varied between 10^4 and 10^6 CFU/g soil.

Only a part of the total bacterial biomass is able to reduce nitrate. In the topsoil the counts were in the same range of 10^6 /g soil, whereas in some depth the counts decreased to 10^4 /g soil (Fig. 3). These figures are in accordance with findings from several Danish soils, Lind 1980 & 1986, Vinther et al. 1982, Zeuthen et al. 1990.

The denitrifiers accounted nearly 90 % of the total nitrate reductive bacteria, except for the clay layer from 1 -4 meter at Gunderup, where they made up less than 15 %.

Nitrogen metabolism in top soil.

Results of N-mineralization in the root zone are included i Table 4. The denitrification rates are based on five measurements during the investigation, and therefore the annual rate is only to be considered as estimates. However, the values have been evaluated by a denitrification model, Vinther 1990, which documents a rather good consensus. The measured annual denitrification estimates resulted in 8 kg N/ha and 2 kg N/ha, whereas the model resulted in 3 kg N/ha and 2 kg N/ha for Gunderup and Vesterlind, respectively.

Soil air.

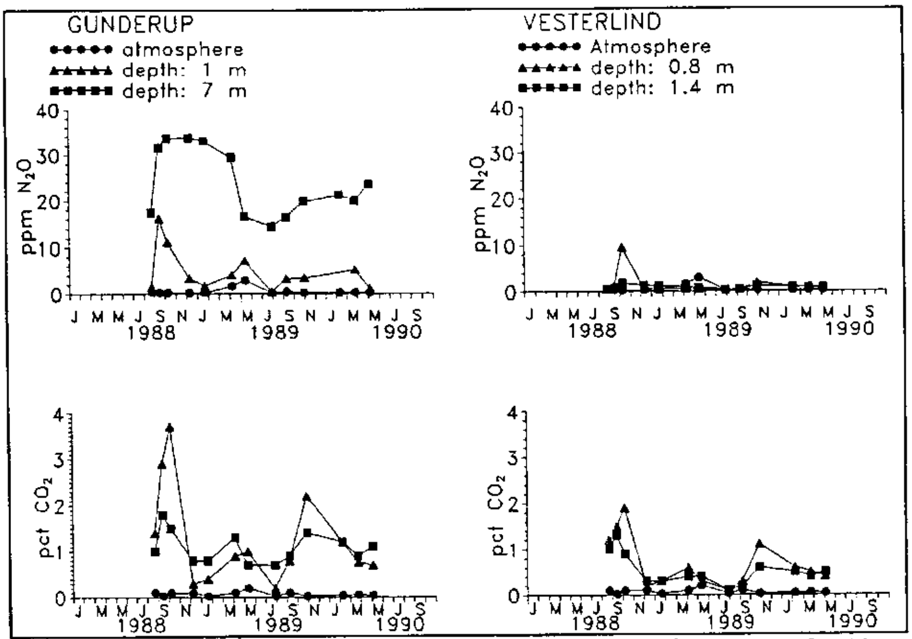


Figure 4. Composition of soil atmosphere at different depths.

The composition of soil air during the period showed considerable variation concerning N_2O and CO_2, whereas O_2 constantly was about 19 %. Very high concentrations of N_2O were found at Gunderup near the groundwater table at 7 meter b.s., Fig. 4.

At Vesterlind station only one measurement was high corresponding to a slurry spreading event in late 1988.

Incubation experiments.

In order to verify the high nitrous oxide contents above the water table at Gunderup, experiments were setup to determine the nitrogen metabolism. In some experiments the

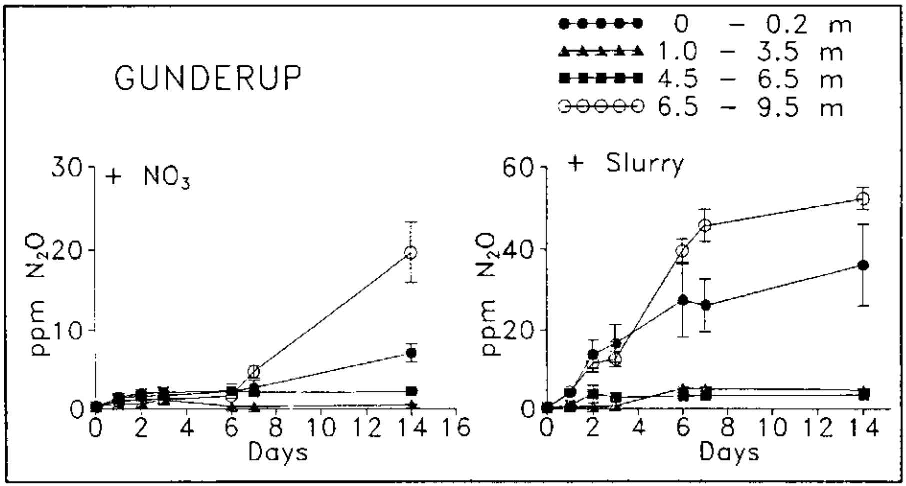


Figure 5. Denitrification capacity in different soil depths at Gunderup.

nitrification and the N_2O reduction was blocked by addition of acetylene, Fig. 5.

The very high activity in 6.5-9.0 meter, which is even higher than the activity in the top soil confirms the soil air measurements.

Denitrification above the water table was calculated based on this results to the annual range of 35 -120 kg N/ha y. Nitrate reduction requires an organic source, either mo-bile or fossil or-ganic matter. Measure-ment of TOC in soil water support this as the con-tent of soluble organic matter de-creased 150 mg C/l from 5 to 9 meter b.s., Fig. 6. If the nitrate reduc-tion is based on organic decomposition the gross reaction may

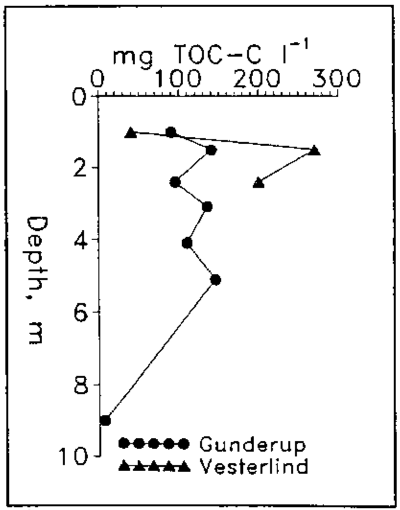


Figure 6. Content of total organic carbon.

follow

$$5\ C_7H_8O_4 + 28\ NO_3^- \rightarrow 14\ N_2 + 28\ HCO_3^- + 7\ CO_2 + 6\ H_2O$$

which give a C/N ratio of 1.1 equivalent to a reduction of 135 mg NO_3-N/l at Gunderup Station.

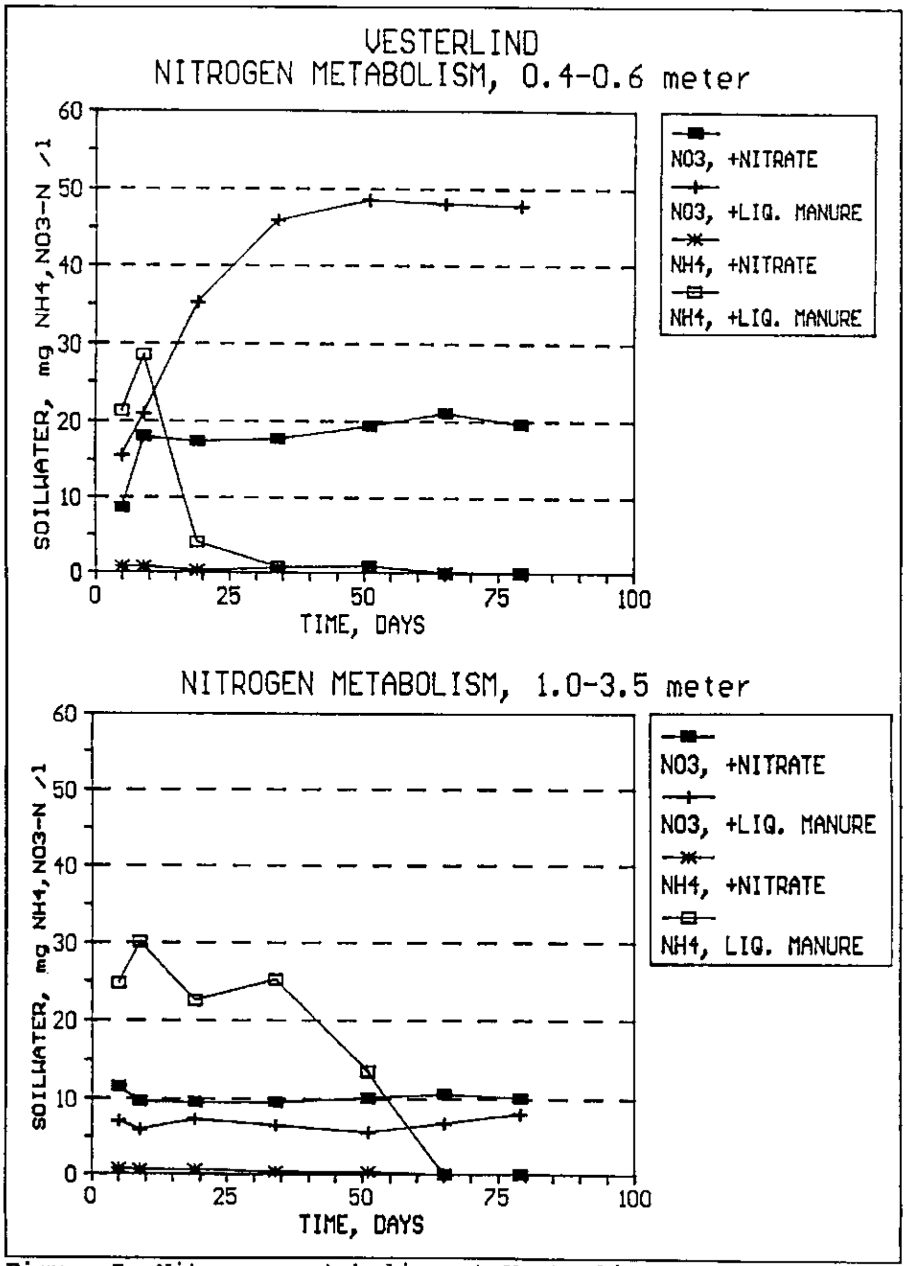


Figure 7. Nitrogen metabolism at Vesterlind and Gunderup.

Laboratory experiments.

Soil sample experiments with addition of nitrate and liquid manure showed that nitrification of ammonia was completed within two months in the clay from Gunderup, Fig. 7. In the sandy soil from Vesterlind a total nitrification was complete in less than one month, whereas no nitrate reduction was observed. In Gunderup clay nitrate seems to be reduced as fast as it generates.

N transport through the soil profile.

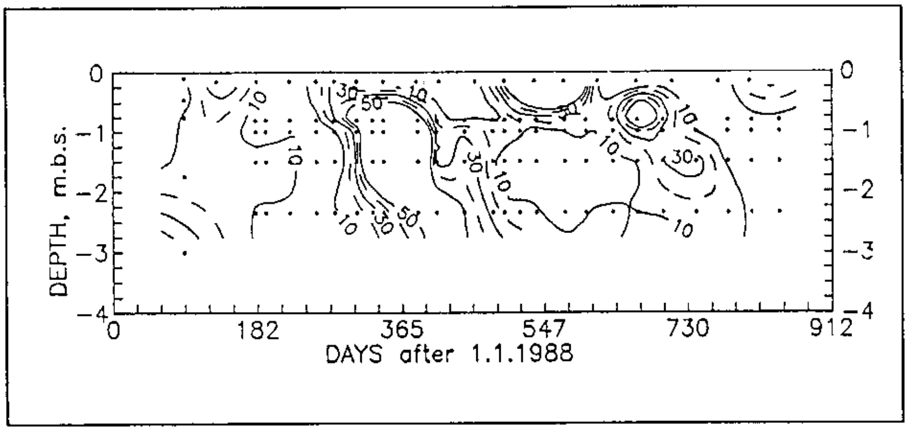


Figure 8. Concentration of nitrate-N (mg/l) in soil water at Vesterlind.

In a period of more than two years the nitrate and ammonia concentrations were measured in the unsaturated zones of Vesterlind and Gunderup, Fig. 8 & 9.

In the sandy soil at Vesterlind movements of nitrate is very easily recalled. The liquid manure spreading on uncropped soil in autumn 1988 of 120 kg N/ha was recognized as a plume moving through the subsoil. During mid winter it reached the ground water table with a concentration exceeding 50 mg NO_3-N/l. As considerable amounts of organic nitrogen and some ammonia was leached, the oxidation to nitrate ($NH_4^+ + 2\ O_2 \rightarrow NO_3^- + H_2O + 2\ H^+$), could cause a decrease in pH.

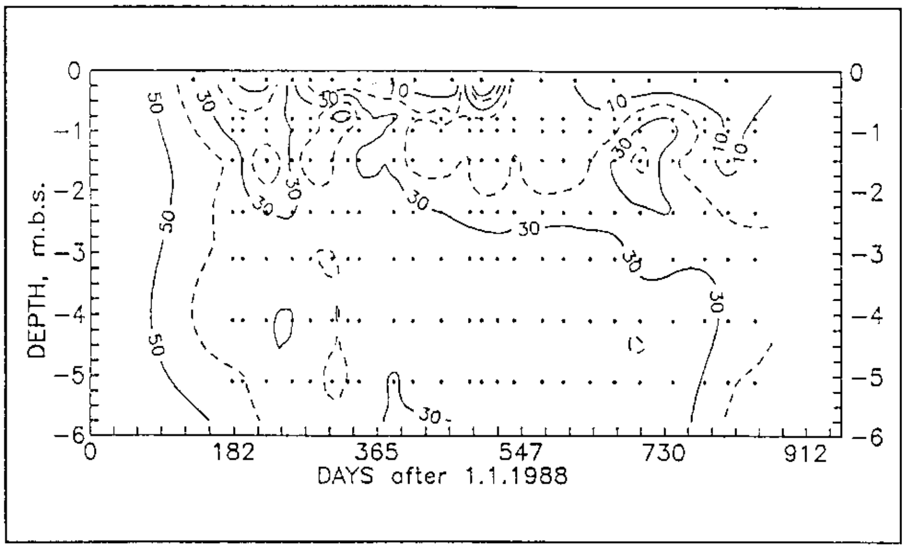


Figure 9. Concentration of nitrate-N (mg/l) in soil water at Gunderup.

This took place within 1.5 meter and caused a decrease in pH to around 5.

Next summer very high concentrations was found in the topsoil as fertilizer excess and low precipitation occurred. Late autumn only a minor leaching of nitrate take place.

The situation at Gunderup was more complicated as manure spreading stopped spring 1988. Furthermore the clay layer in 1 - 4 meter attend to delay the water movement in the upper unsaturated soil. In 1988 the profile had concentrations on 20 - 50 mg NO_3-N/l, Fig. 9. As only moderate fertilizer was applied during 1989 and 1990 on the perennial grass, low concentrations moved slowly from top soil towards the ground water.

The upper ground water had nitrate concentrations of 7 - 22 mg NO_3-N/l at Vesterlind, whereas the concentrations were as high as 34 - 48 mg NO_3-N/l at Gunderup. This may reflect a more extended load prior to this investigation at Gunderup.

Water from two supply wells adjacent to the field showed contents between 12 and 20 mg NO_3-N/l i 15 meters depth.

Water balance.

Based on climatic records from the two stations and records of crops, a water balance was calculated with the EVACROP model, Olesen & Heidmann (1990).

Table 2. Crop rotation at the two stations.

Crops	From	To
Gunderup.		
Bare soil	01.01.1988-	15.04.1988
Spring barley w. Catch crop	16.04.1988-	01.03.1989
Spring barley	02.03.1989-	01.09.1989
Grass	02.09.1989-	__.05.1990
Vesterlind.		
Bare soil	01.01.1988-	15.04.1988
Peas	16.04.1988-	31.08.1988
Winter wheat	01.09.1988-	15.09.1989
Winter barley	16.09.1989-	__.05.1990

Due to the simulations precipitation and infiltration is given below in hydrological periods terminating 1. May :

Table 3. Precipitation and infiltration at the two stations.

Period	Vesterlind	Gunderup
Precipitation:		
1988-89	961 mm	1047 mm
1989-90	768 mm	918 mm
sum	1729 mm	1965 mm
Infiltration:		
1988-89	537 mm	579 mm
1989-90	368 mm	470 mm
sum	905 mm	1049 mm

It is assumed that the lysimeter used, estimates the macropore transport through the top soil. This transport was measured also in periods with water contents below field capacity and hence tends to bypass top soil water volumes. During the investigation period, macropore transport accounted for 223 mm and 57 mm, corresponding to 12.9 % and 2.9 % of the precipitation at Vesterlind and Gunderup, respectively.

Leaching of nitrogen.

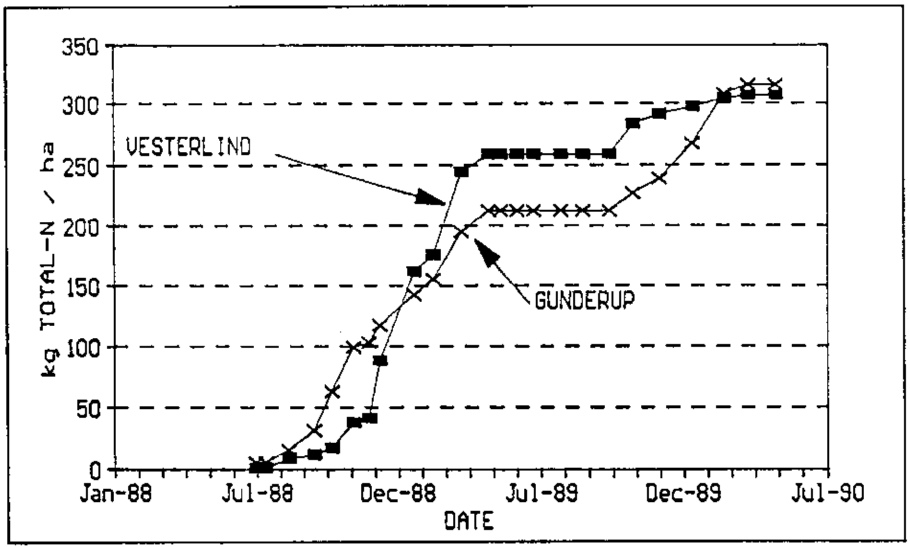


Figure 10. Leaching of total nitrogen at Vesterlind and Gunderup.

Based on the simulated infiltration and the measured concentrations of nitrate, ammonia and organic nitrogen in the teflon cups, the leaching of total nitrogen from the root zone was calculated, Fig 10. Analogous to this the macropore transport of was calculated using lysimeter measurements of infiltration.

Throughout the period the loss of nitrogen was nearly the same for the two sites. However, the autumn loss at Vesterlind after manure spreading accounted for approximately half the total loss at Vesterlind. Correspondingly, 60 % of the total macropore transport took place following the same event, Fig. 11.

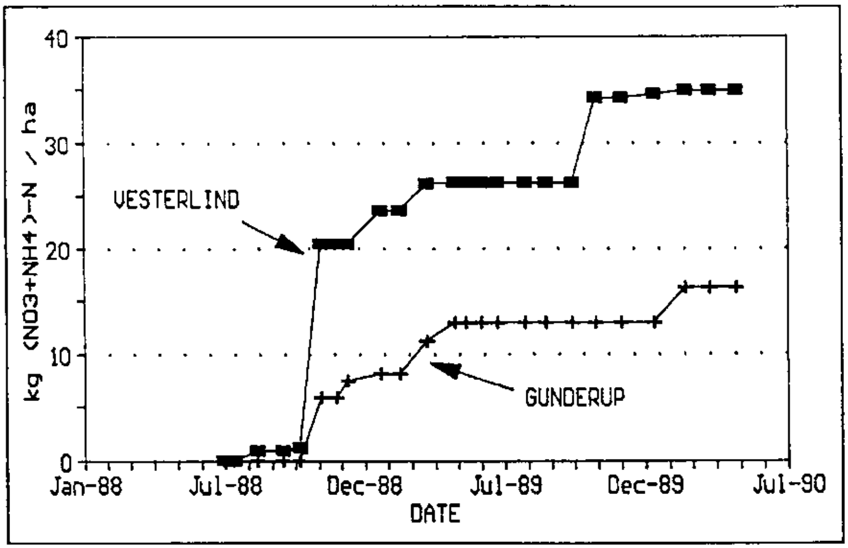


Figure 11. Macropore transport of nitrate and ammonia.

Nitrogen balance.

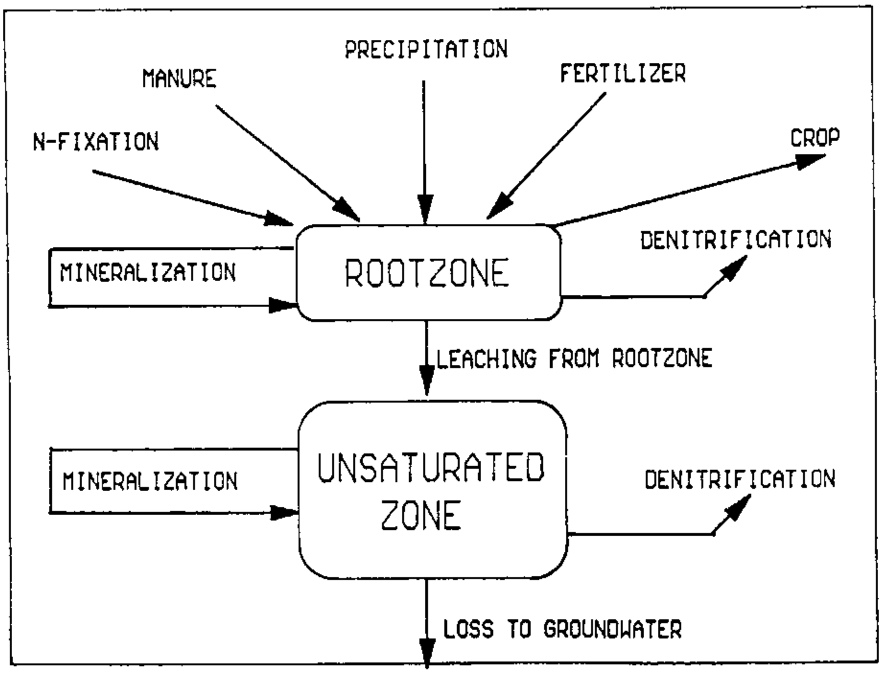


Figure 12. Diagram showing the principles of the N-balance calculated in Table 4.

Combining the measured field data with the experimental results of mineralization and denitrification, an estimate of nitrogen balance at the two sites is enabled, Fig. 12.

	VESTERLIND		GUNDERUP	
	1988-89	1989-90	1988-89	1989-90
ROOT ZONE				
PRECIPITATION	33	10	28	24
MANURE	118	151	0	0
FERTILIZER	121	108	72	72
N-FIXATION	100	0	0	0
MINERALIZATION	118	171	241	76
INPUT TOTAL	490	440	341	172
CROP YIELD	134	141	75	75
DENITRIFICATION	10	10	40	40
LEACHING	258	48	212	103
LOSS TOTAL	402	199	327	218
BALANCE	88	241	14	-46
UNSATURATED ZONE				
INFILTRATION	258	48	212	103
DENITRIFICATION	-50	-30	-80	-50
LOSS TO GROUNDWATER	-223	-58	-315	-162
BALANCE	-15	-40	-183	-109

Records on crop yields, applied fertilizer and manure was given by the farmer consultants bureau. N-fixation i the pea-crop was estimated to 100 kg N/ha, Hansen & Kyllingsbæk (1983).

The N-balance is of course restricted due to the inaccuracy of the data and of areal variability. The post 'Balance' covers some of this inaccuracy together with changes in the storage capacity in the soil and ammonia evaporation from the manure spreading, Christensen & Sommer (1989). Further, the mineralization and denitrification in the unsaturated zone seems underestimated as assumed from the soil water concentrations during the pass of liquid manure autumn 1988, Fig. 8.

Comparable situation was detected during the same period at Gunderup, Fig. 9.

Phosphate.

Precipitation, soil water and groundwater was analyzed for PO_4-P and total-P. The general trend shows that concentration seldom exceed 0.005 mg P/l. The calculated leaching of total-P during the two year period and using identical methods as for nitrogen showed that 0.3 kg P/ha and 1.5 kg P/ha leaving the top soil at Vesterlind and Gunderup, respectively.

DISCUSSION AND CONCLUSION.

The original purpose of this project was to elucidate the impact on the ground quality from the use of permanent catch crop practice. The legislation on obligatory use of green fields, however, has done that the field areas has been cropped all year during the period of investigation. Besides this change in practice, the field stations showed up to be more unlike regarding texture. At Gunderup a clay layer is present in 1-4 meter depth, and the top soils are JB1 and JB3 at the stations. On the other hand, the project has given an extraordinary opportunity to study the leaching of nutrients from a field with heavy manure load and a field with perennial grass. The other field may be regarded as a conventional farm practice with annual manure spreading.

The leaching of nitrogen on the two station has varied during the period depending on manure load, crops and precipitation. At Vesterlind 245 kg N/ha was leached in 1988-89 compared to 45 kg N/ha in 1989-90. In 1988-89 more than 100 kg N/ha was lost within one month due to manure spreading in the rainy autumn on bare soil. Similar records has been obtained by Lind et al. (1990). Macropores transport during this period accounted for nearly 60 % of the total loss. In the period 1989-90 macropores were responsible for 10 % only of the total nitrogen transport.

At Gunderup the leaching of nitrogen made up 166 kg N/ha in 1988-89 and 95 kg N/ha in 1989-90. Concurrently the soil solutions of nitrate were decreasing steadily through the whole period as a consequence of the stop in manuring and the perennial grass from late summer 1989.

The analyses of soil water have shown that a significant leaching of organic nitrogen may take place. The amounts may be as high as 20-30 % of nitrate leached. Mineralization and nitrification of organic nitrogen in the unsaturated zone may subsequently cause a decrease in pH, which has been recorded in the profiles.

The transport of nitrate through a sandy unsaturated zone is not a passive translocation, as previously accepted. As the leaching of nitrate is accompanied of minor amounts of organic matter a base for microbial activity is present as shown. At Vesterlind a decrease in nitrate concentration from 140 to 60 mg N/l in 2.35 meter b.s. after 2 months residence is partly due to a nitrate reduction.

The active microbial biomass was measured by ATP, the total bacterial count (CFU) and the number of nitrate reducing bacteria do not disagree with findings from investigation at similar soil types, Andersen et al., 1983; Lind, 1980 & 1986; Vinther et al., 1982; Zeuthen et al., 1990. At Gunderup very low counts were made in 1-4 meter b.s. in the clay. The activity in deeper soils may normally be low, Zeuten et al. 1990, due to lack of organic carbon. In spite of this, nitrate reducing bacterial in deeper soils, up to 40-50 meter, has found to be quite numerous, Hendry et al., 1984; Lind, 1986.

Several studies on sandy soils have shown that the potential denitrification is low, Andersen et al., 1983, Christensen et al., 1990, Lind et al., 1990, Vinther 1990., identical to the results in this investigation. In contrary, results from the experiments and soil air has indicated a significant nitrate reduction near the water table. In the interval 6 to 9 meter b.s. high N_2O contents in the soil atmosphere corresponded to a decrease in both nitrate and TOC. On yearly base the capacity may account for a nitrate reduction of 120 kg N/ha. The incubation experiments indicate correspondingly a potential reduction of 35 - 120 kg N/ha per meter soil ≈ 675 kg N/ha y. As no increase in sulphate is detected, a nitrate reduction by pyrite, FeS_2, is negligible.

The leaching of phosphorous was measured to be less than 1 kg P/ha y and as the concentrations was lower than 0.005 mg P/l no implication of thread to groundwater is introduced.

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Fluctuations of Nitrate in Groundwater

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INTRODUCTION

Nitrate fluctuations

"Chimney Effect"

"Irrigation Effect"

Seasonal fluctuations of the nitrate content in pumped water from a number of private water-supply wells in Western Jutland, Ringkøbing County, during the last decade have not been evidently explained. Changes in input of nitrate or leakage around the well casing ("Skorstenseffekten" ("Chimney Effect")) have been given as explanation of the fluctuations (Petersen, 1986 & 1987). And as an experience, during the investigation of this project, the authors put forward that seasonal pumping from a nearby well, named "Irrigation Effect" was the causal explanation of this type of fluctuations (Andersen & Kelstrup, 1989).

Goal and purpose

The goal of this investigation was to explain or throw light on the causes of the observed fluctuations.

Selection of observation wells

Two wells with fluctuations of nitrate content were selected, Figures 1, 2 and 3. The geology and hydrogeology were described, together with their technical completion, i.e. screened interval, degree of penetration and vertical distribution of the nitrate zone. The investigations were made on the basis of existing data or data from new drilled or driven wells, constructed for level-accurate water sampling at the sites where the fluctuations were observed.

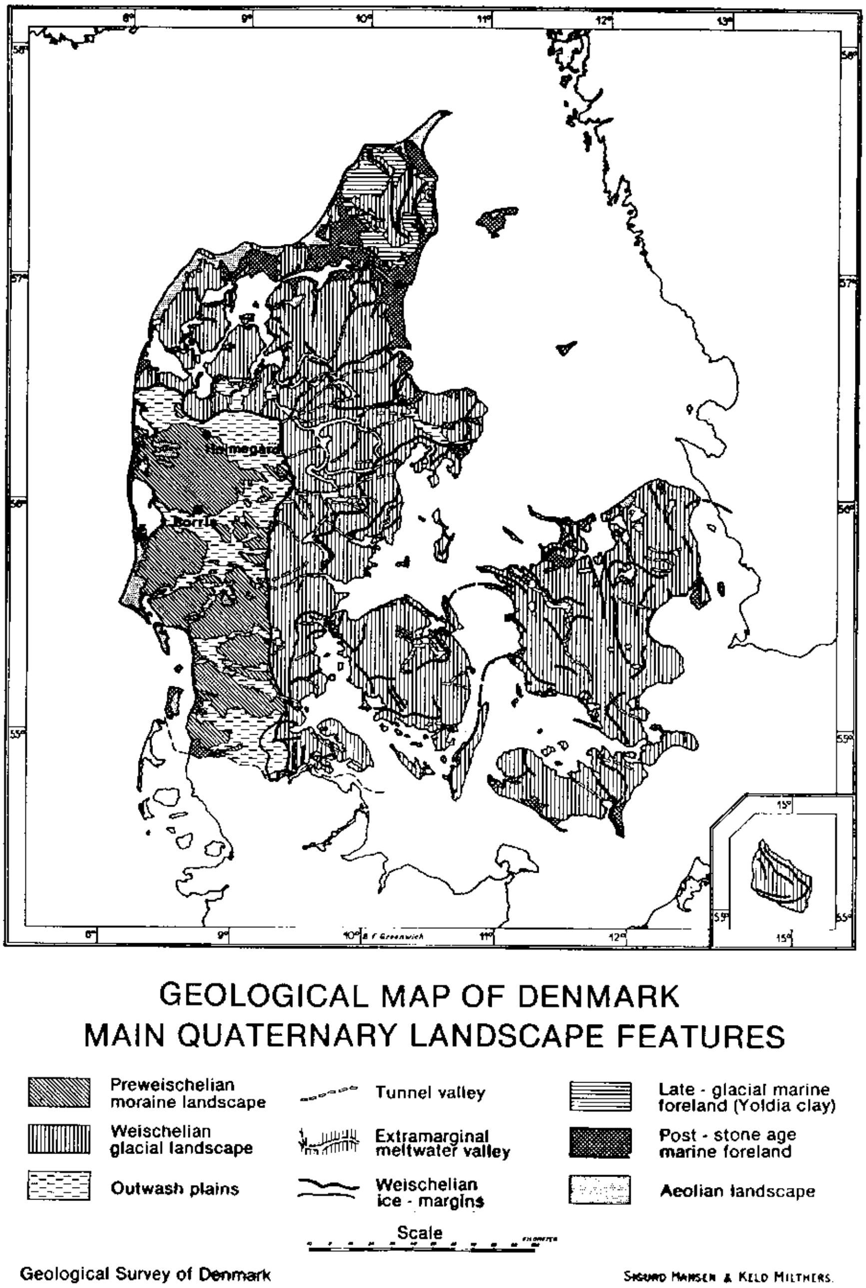

Figure 1.: Location of the test sites of Holmegård and Borris.

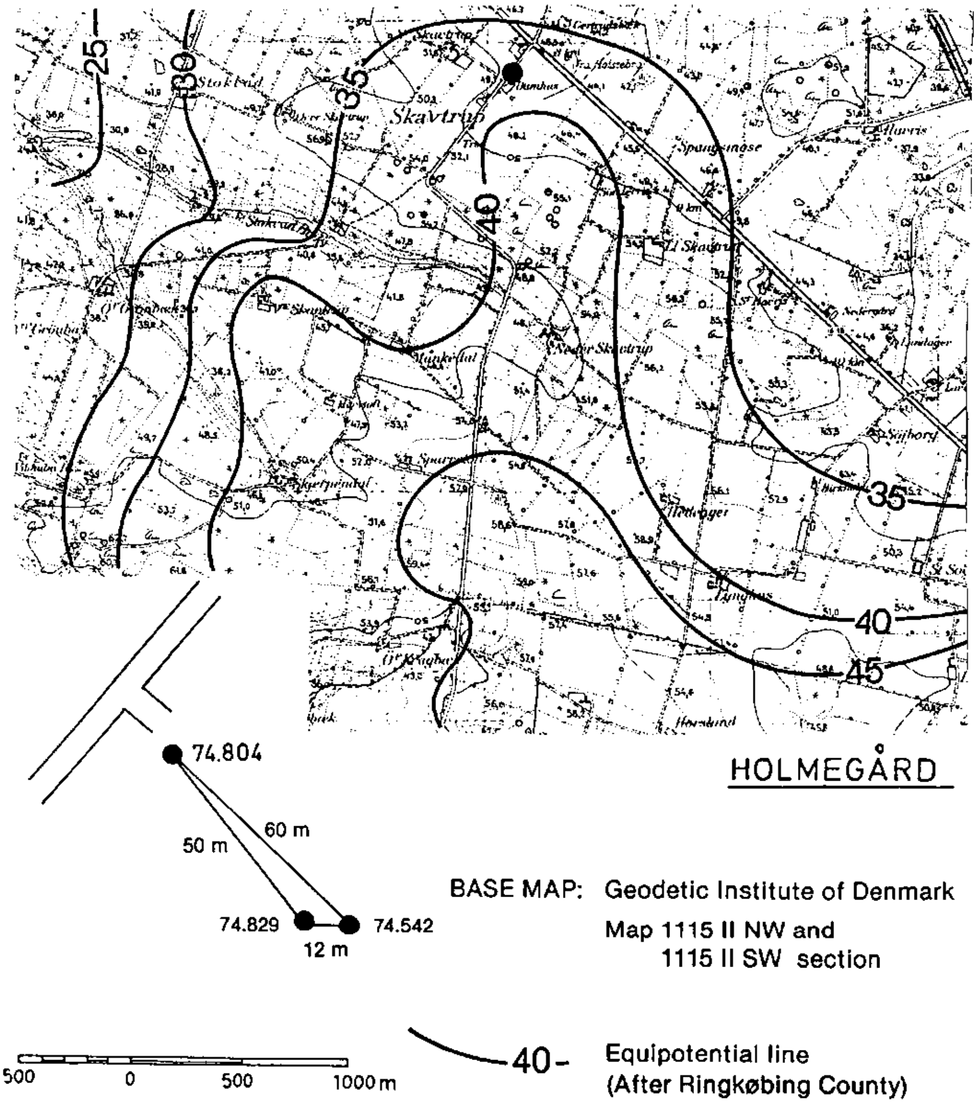

Figure 2.: Map with location of the test site Holmegård and sketch with the possitions of the wells.

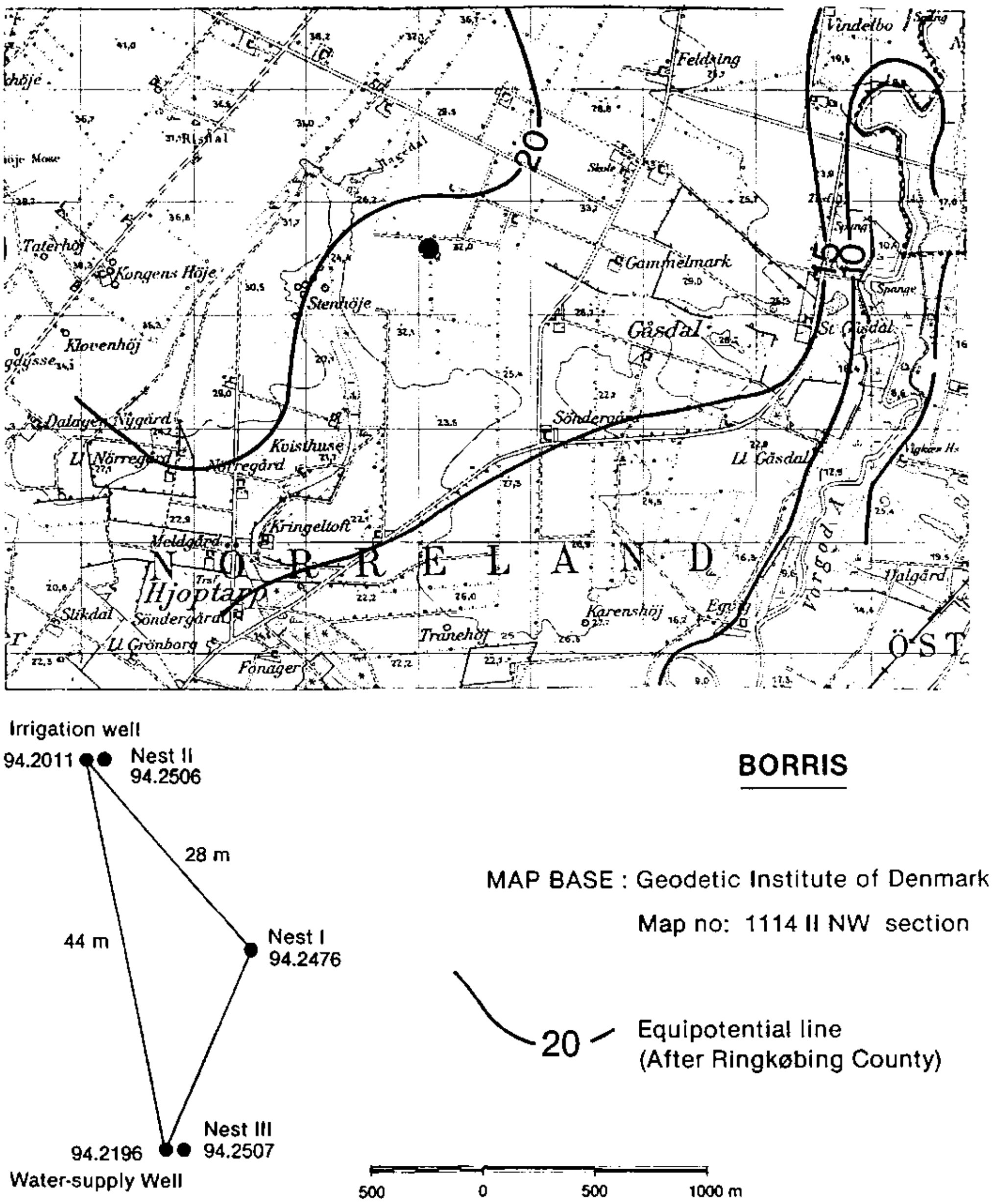

Figure 3.: Map with the location of the test site Borris and schetch with location of the wells and nests.

INVESTIGATION METHODS

Test pumping

The selected wells were test-pumped with constant pump rate and sampling of pumped water, regularly over a period about 1 or 2 weeks (Fig. 4 and 5). The water samples were analysed for nitrate and some other major components. Furthermore test pumpings were run simultaneously at two neighbouring wells in the same aquifer at different depths. The

Separation pumping

last mentioned pumping method is named separation pumping test (Andersen et al., 1989). Finally, during the period of investigations, 1987-90, regularly sampling of water was made, about quarterly, for analysis of nitrate content.

RESULTS

Holmegaard and Borris

The two sites: Holmegaard (Figure 2) and Borris (Figure 3) were investigated in details. Technical and geological data of the well completion are given in Table 1, and results of nitrate as function of time or depth are given in Figures 6, 7 and 8.

Nitrate graphs

These analyses give the time series of nitrate during the whole period, while the analyses from the test pumpings give the changes during pumping from the well itself or nearby situated wells.

Pumping-affected nitrate content

The results of the performed test pumpings and analyses show that the nitrate content of the pumped water and the aquifer water were significantly influenced by pumping and governed by the duration of the pumping, see Figures 2 &

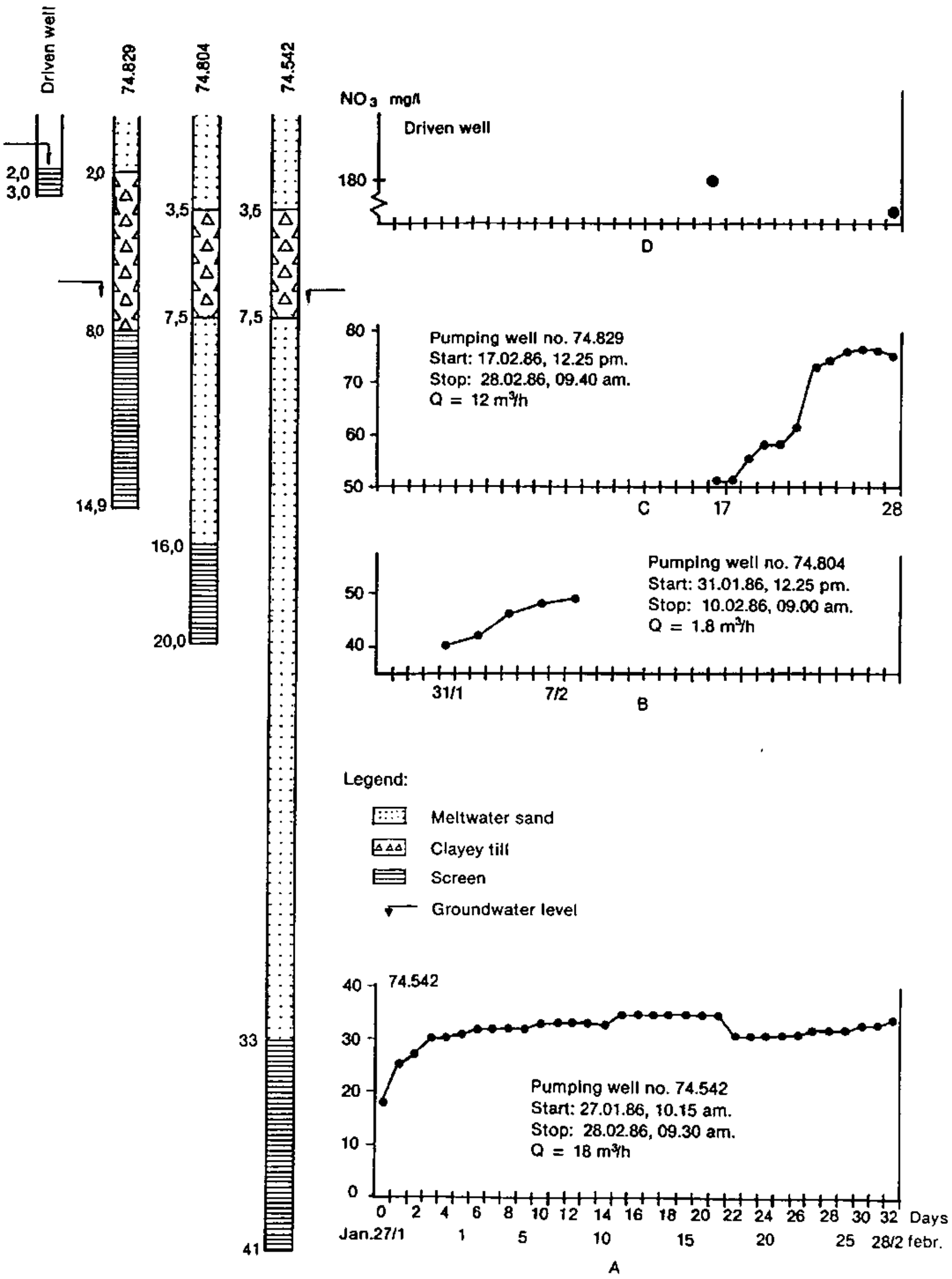

Figure 4.: Test site Holmegård. Well logs and nitrate graphs of pumped water as a function of test pumping time. Location of wells, se Figure 2.

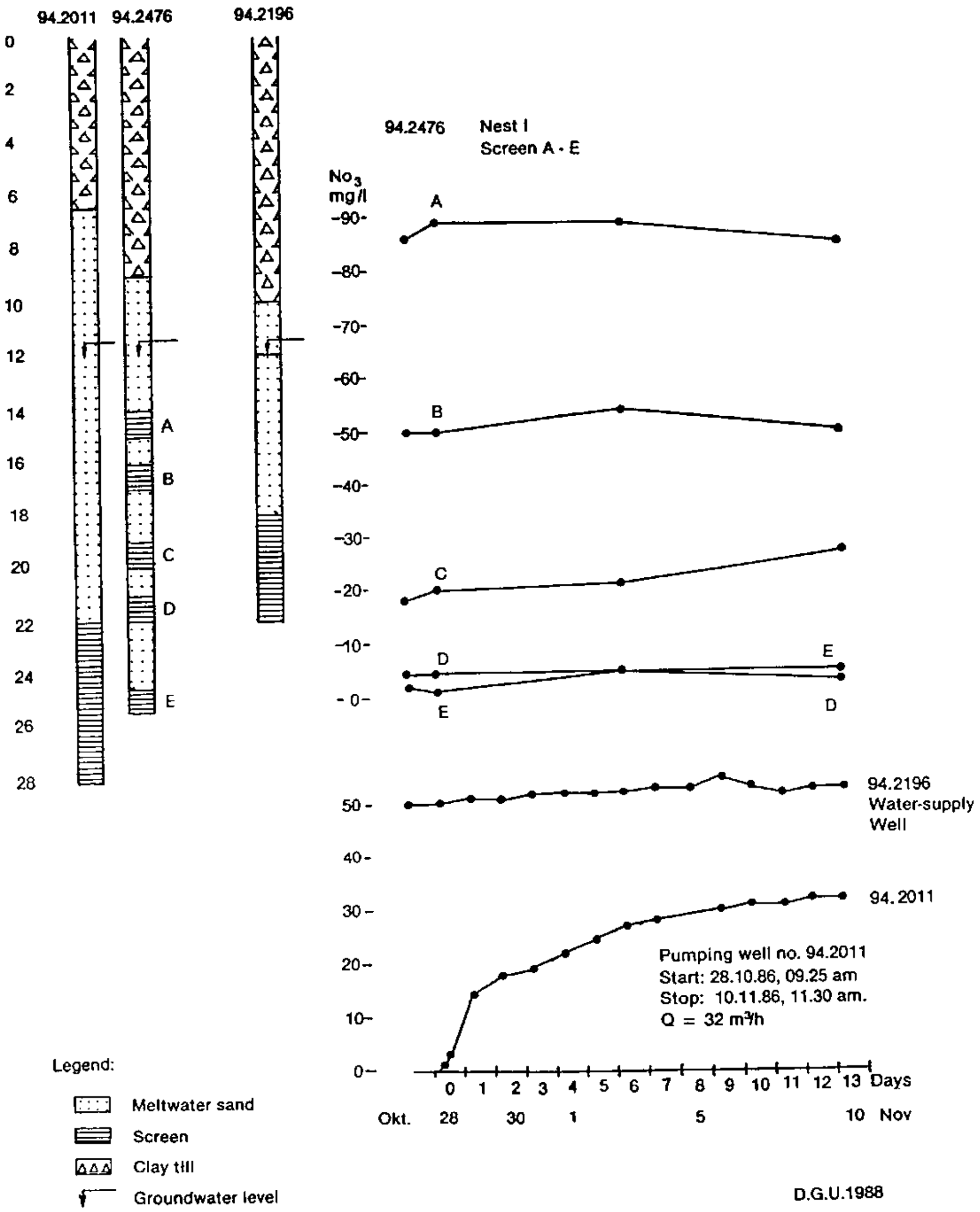

Figure 5.: Test site Borris. Well logs and nitrate graphs of pumped water, sampled water from water supply well and screens of nest I. Location of wells, se Figure 3.

NEST I - DGU File No. 94.2476

TECHNICAL DATA - NEST I: 8 inch percussion drilled well to 25.5 m.b.s., 27 mm X screen with restricted valve, screen length 1 m with 0.3 mm slots.

GEOLOGICAL LOG: 0.0 - 0.5 m.b.s Sand
(DGU File no. 94.2476) 0.5 - 9.0 m.b.s Clayey till
9.0 - 25.5 m.b.s. Meltwater sand

DGU File no.	Screen no.	Screen top and bottom m.b.s
94.2476	A	14.00-15.00
94.2476	B	16.00-17.00
94.2476	C	19.00-20.00
94.2476	D	21.20-22.20
94.2476	E	24.25-25.25

NEST II - DGU File no. 94.2506 and IRRIGATION WELL - DGU File no. 94.2011

TECHNICAL DATA - Nest II: 3/4 inch driven well with removable drive point, 16 mm X PVC screen with restricted valve, length: 0.27 m and slots: 0.03 mm

TECHNICAL DATA - IRRIGATION WELL: 270 mm percussion drilled well, 200 mm PVC casing, 160 mm X PVC screen - 6 m long and with 0.6 mm slots.

GEOLOGICAL LOG : 0.0 - 0.5 m.b.s No information
(DGU File no. 94.2011) 0.5 - 6.5 m.b.s. Clayey till
6.5 - 28.0 m.b.s. Meltwater sand

DGU File no.	Screen no.	Total drill length m.b.s	Casing bottom m.b.s	Screen top and bottom m.b.s.
94.2506	A	13	11	12.23-12.50
94.2506	B	16	14	14.73-15.00
94.2506	C	18	16	17.23-17.50
94.2506	D	21	19	19.73-20.00
94.2506	E	23	21	22.23-22.50
94.2506	F	26	24	24.53-24.78
94.2011	-	28	-	22.00-28.00

NEST III - DGU File no. 94.2507 and WATER SUPPLY WELL - DGU File no. 94.2196

TECHNICAL DATA - NEST III: 3/4 inch driven well with removable drive point, 16 mm X PVC screen with restricted valve, length: 0.27 m and slots: 0.03 mm

TECHNICAL DATA - WATER SUPPLY WELL : 270 mm percussion drilled well, 125 mm X PVC casing, 120 mm PVC screen - length: 4 m and slots: 0.6 mm.

GEOLOGICAL LOG : 0.0 - 10.0 m.b.s. Sandy till
(DGU File no. 94.2196) 10.0 - 22.0 m.b.s. Meltwater sand

DGU File no.	Screen no.	Total drill length m.b.s	Casing bottom m.b.s	Screen top and bottom m.b.s.
94.2507	A	18	14.5	14.55-14.82
94.2507	B	18	16	17.23-17.50
94.2507	C	21	19	19.73-20.00
94.2507	D	23	21	22.23-22.50
94.2507	E	26	24	24.73-25.00
94.2196	-	22	-	18.00-22.00

Table 1.: Technical and geological data of the wells and monitoring nests attest site Borris, Jutland, Denmark.

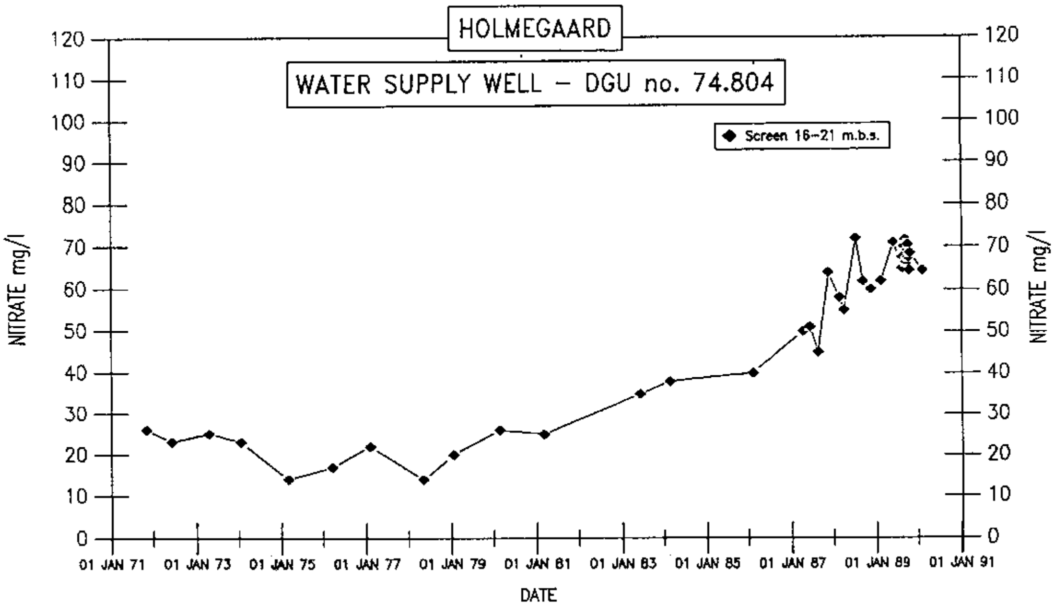

Figure 6.: Nitrate content versus time, water-supply well, Holmegård, 1971-1990.

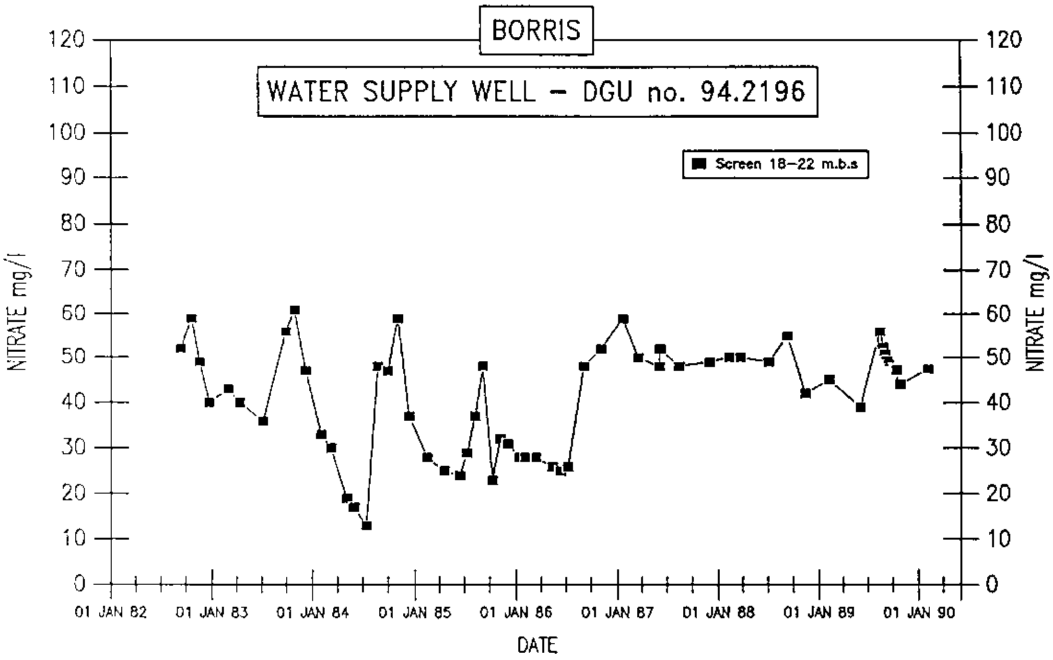

Figure 7.: Nitrate content versus time, water-supply well, Borris, 1982-1990.

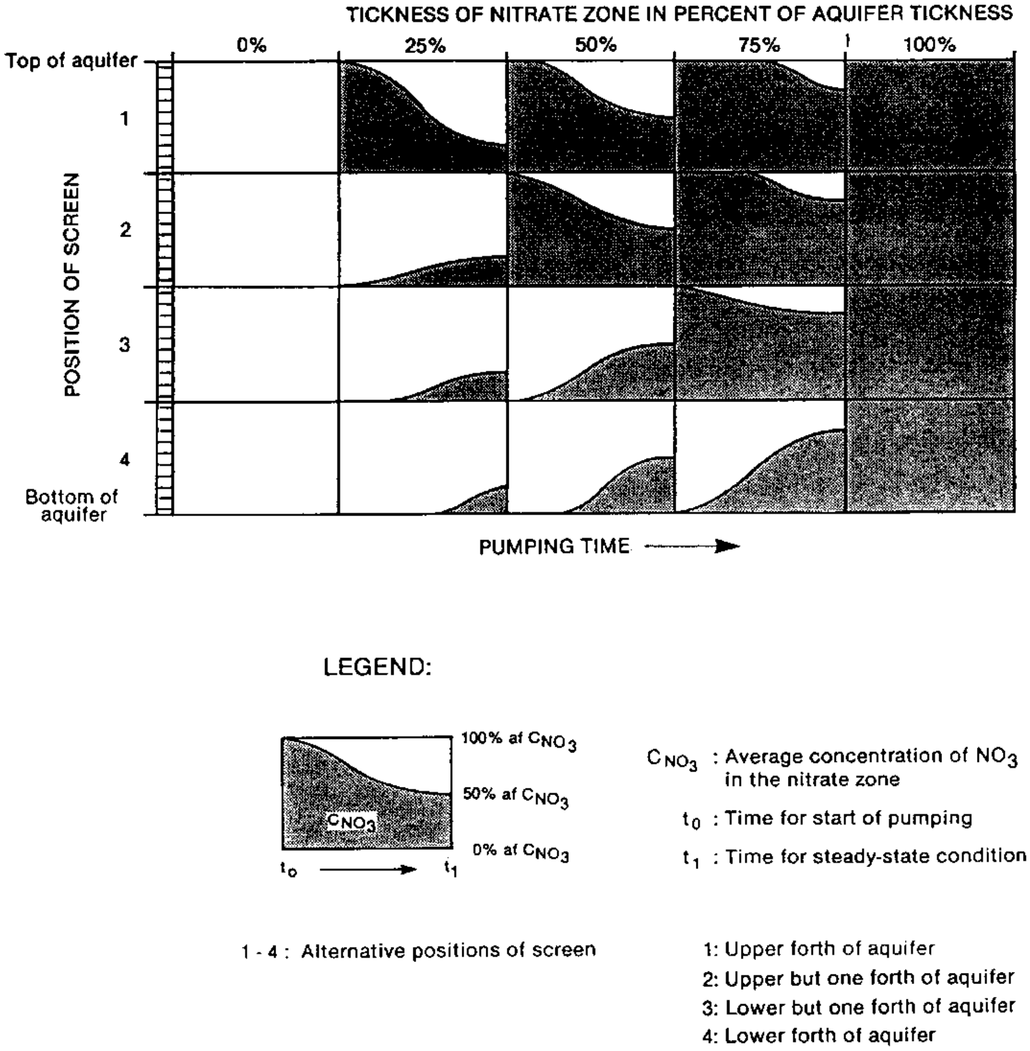

Figure 8.: Principle sketch illustrating the conceptual model of nitrate consentration of the pumped water as a function of pumping time, nitrate zone percentage of aquifer thickness and position of screened interval.

3. In some wells the nitrate content was increasing with the pumping time (Figures 4 & 5), and in other wells it was decreasing. At a single site the nitrate content was nearly constant during the pumping period.

CONCEPTUAL MODEL

Model of pumping affected water quality

These results were the background for establishment of a conceptual model which was used for the interpretation of the observed nitrate-graphs obtained during test pumpings at the various wells, Figure 8.

In the model 15 different types of change of nitrate content in the pumped water versus time are described, of which 14 is schematically shown on Figure 8. The established model is applied for the interpretation of the observed nitrate-graphs from the performed test pumping and the interpretations are correlated with the well logs and aquifer information.

Conditions for the fluctuations

The conditions under which "seasonal" nitrate fluctuations as described above can appear are: that the well is pumped seasonally, that the well is partially screened, and that the water quality of the aquifer, from which the well take the water, is stratified, in this case by nitrate.

VERIFICATION OF THE MODEL

Change of the flow regime by pumping

It is the opinion of the authors that the model has been able to explain the observed nitrate-graphs in a satisfactory way, and the main conclusion of the investigation is: that the seasonal fluctuations of nitrate concentration in pumped water and groundwater are pumping affected. The fluctuations are caused by a changed flow regime and by a different mixing ratio between groundwater, above and below the nitrate front, in an aquifer pumped by a partially penetrating well.

THE IRRIGATION EFFECT

Seasonal Irrigation pumping

Intermittent pumping from a well can result in change of quality of the pumped water from or in the water quality in a nearby well. In case of seasonal pumping from such a well, seasonal fluctuations will appear in the observed well. As irrigation wells mostly are seasonally pumped, irrigation wells are often the origin to such fluctuations in chemistry of the pumped water. Therefore the phenomenon is termed "Irrigation Effect" as described by Andersen & Kelstrup (1988). The explanation of the Irrigation Effect appears form Figure 9.

Irrigation Effect

Passage of nitrate cone of depression

In the two described cases from Borris and Holmegaard a nearby irrigation well exists. In these cases the fluctuations of the nitrate content in the nearby water-supply well could be interpreted as changes of the position of the nitrate front within the area of influ-

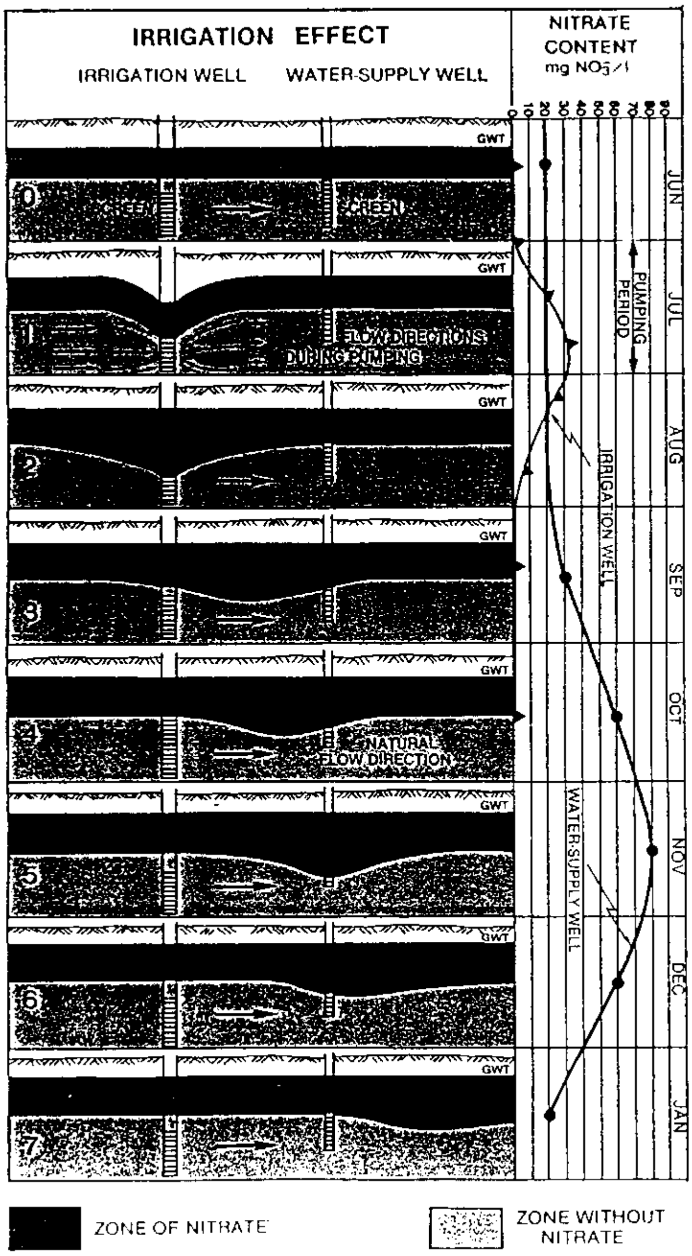

Figure 9.: Principle sketch illustrating the nitrate content in a water-table aquifer with a nitrate zone and an intermittent pumping from a partially penetrating irrigation well in pumped water from the inigation well and a nearby water-supply well. (After Andersen & Kelstrup, 1988).

ence in a nitrate stratified aquifer pumped by a partially penetrating well. In cases when the fluctuations appear in a water well placed in a greater distance from the irrigation well the fluctuation can be explained from Figure 9.

Modification of the fluctuations

At Holmegaard the increase of the nitrate content during 1987-1990, Figure 6, has been up to 5 times as big than that during the period before 1987. However, this increase has modified the seasonal fluctuations, but not destroyed them.

On the other hand during the period before 1987 seasonal fluctuations were not detected most likely due to low frequency of observation, Figure 6.

INADVERTENT INFLUENCE

Monitoring wells

As intermittent pumping may influence the water quality in a well, attention should be paid to the Irrigation Effect in connection with monitoring of groundwater quality.

Determining the reduction capacity

In cases when the cone with water containing nitrate moves through aquifer material below the nitrate zone, the decrease of nitrate in the cone along its flow path might be a result of the reduction capacity of the aquifer material. If this assumption is correct the Irrigation Effect can be used for determining the nitrate reduction capacity of aquifer materials.

CONCLUSIONS

Pumping from partially penetrating wells can change the vertical distribution of the nitrate zone and consequently the nitrate content of pumped water from a nearby well, situated either within the area of influence or downstream. This phenomenon is named the Irrigation Effect.

The changes of the water quality in monitoring wells with their screen placed within the transition zone of nitrate may be due only to seasonal pumping and therefore without any relation to climatic events or land-use activities.

The Irrigation Effect may be utilised to get information about the nitrate reduction capacity of aquifer materials.

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Ministry of the Environment
National Agency of Environmental Protection
Denmark

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

Number B13

Flow and Transport Modelling - Rabis Field Site

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1. Introduction

The unconfined aquifers in the western part of Denmark have increasing problems with nitrate contamination. The vulnerability of the unprotected aquifers is dependent on a balance between the mass flux of nitrate to the aquifers and the amount of nitrate removal by denitrification processes ocurring in the aquifers. These processes take place when nitrate oxidizes pyrite and lignite, which are both present in the glacial outwash sands.

The field site

The Rabis Creek field site, Figure 1, is located in the western part of the country. The aquifer at the site can be divided into an upper, fully oxidized zone, 10-15 m thick, and a lower, reduced zone.

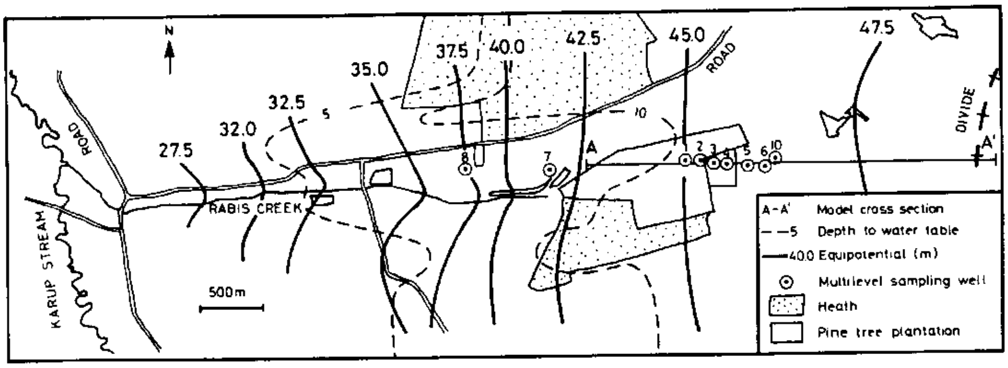

Figure 1
The Rabis Creek field site.

The oxidation-reduction or redox front separating the two zones is characterized by chemical/biological processes, where first oxygen then nitrate oxidize pyrite and organic material like lignite. The significance of the denitrification process is dependent on the fraction of the nitrate leached to the aquifer, which is subsequently transported vertically to the reaction zone.

Scope of the study

The primary objective of the project has been to determine, through application of numerical groundwater flow and geochemical transport models, which processes control the extent of nitrate contamination at the site. If a large fraction of the total flux of nitrate to the aquifer is transported to the reaction zone, the nitrate problem is in essence controlled by chemical/biological processes, if not, the nitrate problem is controlled by the groundwater flow system.

2. Results

Groundwater flow

Figure 2 shows the observed and simulated water table in March 1989. Figure 3a and 3b show calculated velocity vectors in a cross-section coinciding with the model cross-section shown in Figure 1 and in another cross-section one km south of here, respectively. The simulation results are based on the application of a three-dimensional groundwater flow and transport model. The figures show that groundwater flow is primarily horizontal with most of the flow ocurring in the upper one-third of the aquifer with only a small vertical flow component. However, close to Rabis Creek, Figure 3a, significant upward flow from the deeper parts of the aquifer takes place.

Hydrodynamic dispersion

Simulations of tritium transport and comparisons with measurements in three of the wells shown in Figure 1, indicate that the amount of dispersive mixing in the aquifer is low, especially in the transverse direction. The combination of almost horizontal flow right at the redox front, Figure 3, and low transverse dispersion thus indicate that the nitrate problem at the site might be groundwater flow controlled.

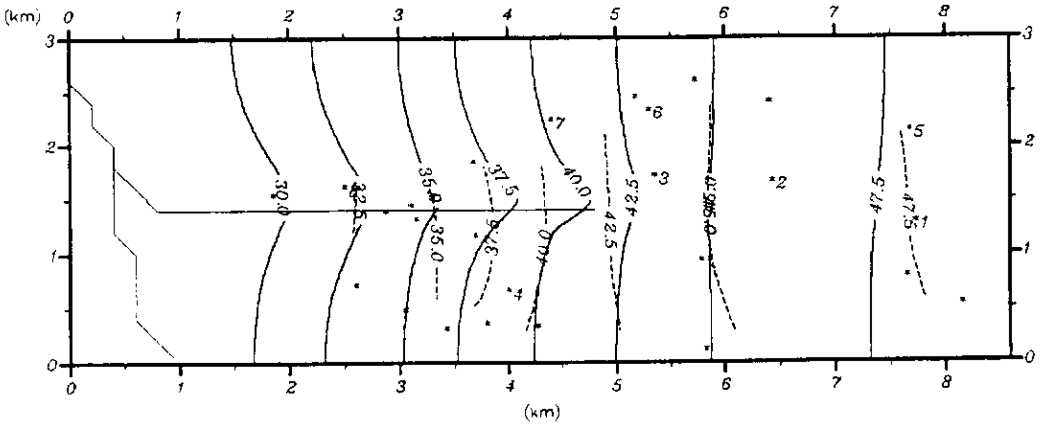

Figure 2
Observed and simulated water table contours (m), March 1989.

Nitrate contamination

A comprehensive geochemical model accounting for mineral and aqueous reactions has been applied to a one-dimensional streamtube crossing the redox front. Assuming a representative interstitial groundwater flow velocity of 25 m/yr normal to the redox front and choosing average conditions for the chemical inlet and background conditions, gave model predictions of the vertical rate of redox front movement of the order of 40 cm/yr.
A vertical flow velocity of 25 m/yr is close to a factor of 50 higher than those simulated with the three-dimensional model. Since the rate of redox front movement is proportional to the interstitial flow rate, the actual redox front movement rate can be calculated to be less than 1 cm/yr.

This rate of movement agrees with the prediction based on simulations with the three-dimensional model coupled with a simple nitrate reaction model.

Figure 4 shows simulated nitrate concentrations in a cross section coinciding with the model cross section shown in Figure 1. The characteristic plume of nitrate below the plantation area has been observed based on measurements in the transect of wells. Figure 4 shows that the plume will reach the redox front in the mid 70's, and that the plume will persist for an extended period. The latter is due to the mixing of deep nitrate-free groundwater, see Figure 3a, and upper contaminated water close to Rabis Creek. The low concentrations of nitrate found in Rabis Creek is a consequence of this mixing, but, also because the actual flow to the creek, where water trickles across the adjacent meadows is responsible for a further reduction in concentration by denitrification processes. Based on the model results the reduction is estimated to be at least 50%.

From a 95 year simulation it is calculated that a little more than one-third of the total flux of nitrate to the aquifer is removed at the reaction zone while close to one-half is discharged to the creeks. The remainder of the total flux of nitrate to the aquifer is change in storage in the aquifer.

3. Conclusions

The problem of nitrate contamination of the groundwater and surface water at the Rabis Creek field site is groundwater flow controlled, be-

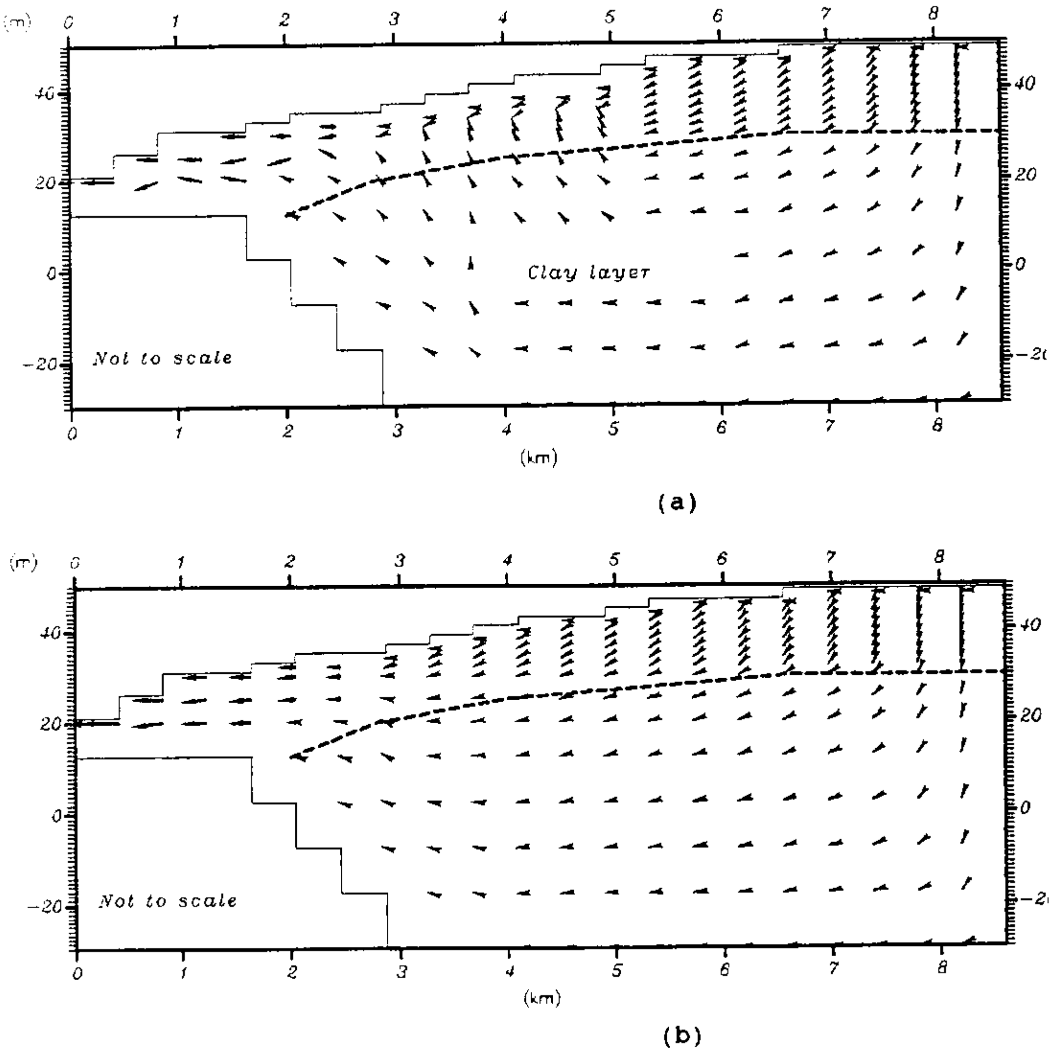

Figure 3
Calculated velocity vectors at the transect of wells (a) and 1.0 km south of here (b). Each velocity vector represents a computational node point. No attempt has been made to properly scale the velocity vectors. The redox front is shown as a dashed line.

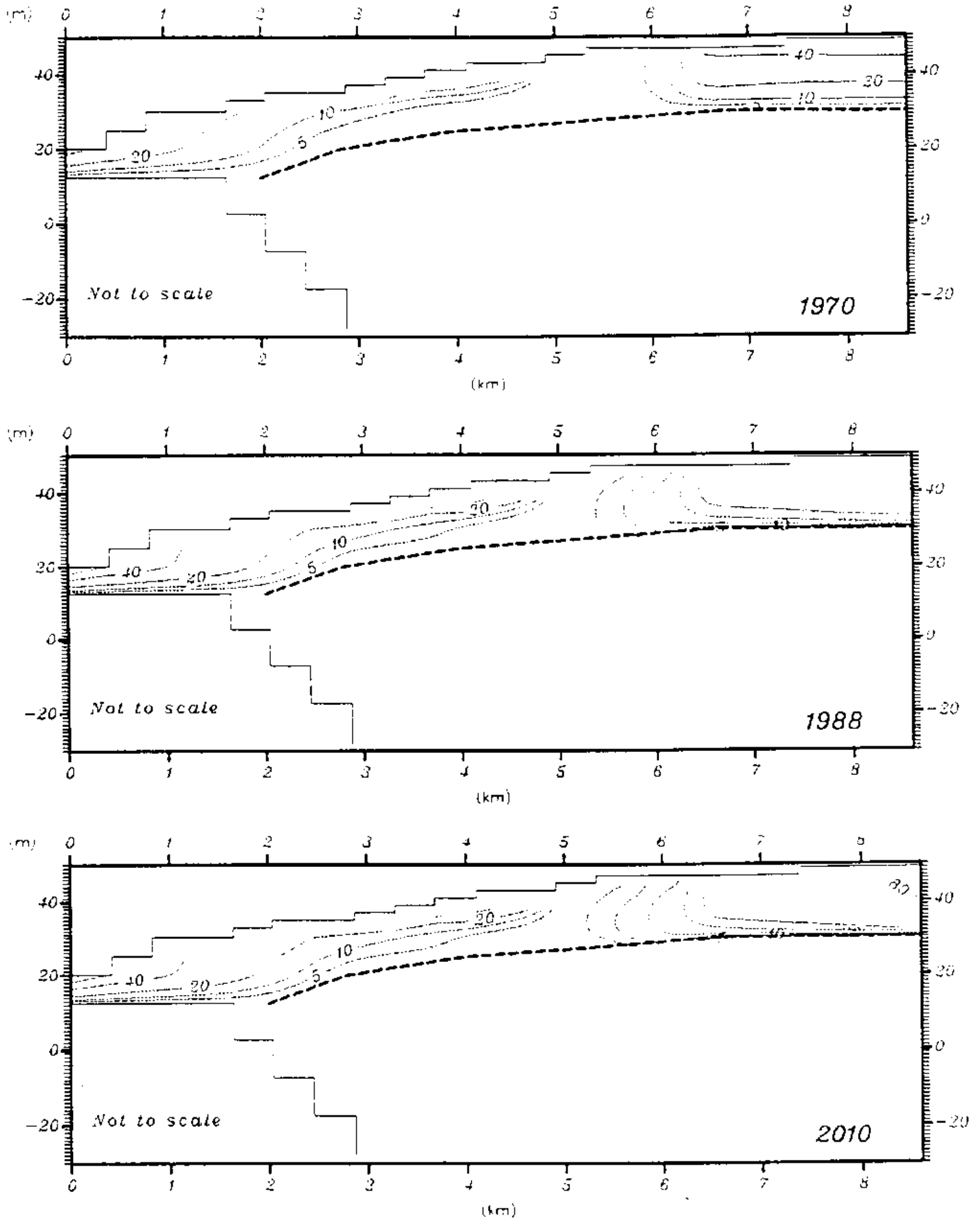

Figure 4
Nitrate concentration contours (mg/l) at the transect of wells in 1970 (top), 1988 (middle) and 2010 (bottom). The redox front is shown as a dashed line.

cause, the simulations show that the combination of dominating lateral flow and low transverse dispersion right at the reaction zone, located 10-15 m below the water table, results in a low vertical flux of nitrate to the pyrite depositions.

The groundwater flow system then results in an upper contaminated zone and a lower uncontaminated zone.

The groundwater flow to Rabis Creek is a mix between deep nitrate-free groundwater and upper contaminated groundwater, which, in combination with the estimated 50% reduction in nitrate concentration ocurring when water trickles across the creek meadows, results in relatively low nitrate concentrations in Rabis Creek.

The model simulations indicate that on a long-term basis a little more than one-third of the total input of nitrate to the aquifer will be removed by nitrate reduction processes while close to one-half will be discharged to the creeks.

Ministry of the Environment
National Agency of Environmental Protection
Denmark

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

Number B14

Drainage Flow Modelling - Syv Field Site

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1. Introduction

Scope of study

The study reported has the objective to investigate the influence of soil heterogeneity and preferential flow on the rainfall-discharge relationship using a very simplistic modeling approach, but, on the other hand compare and analyze the predictions against reliable real-life data. The study does not attempt to develop or improve the mechanistic process descriptions of these two flow problems, but it is rather an attempt to address these problems through a parameter sensitivity analysis using a simple model analysis.

Soil variability

Transport of water and nitrate in the upper soil horizons is significantly influenced by the complicated and apparent random composition of the soil. Furthermore, many soils have structures arising from drying cracks, earthworm channels, decayed roots, interpedal voids and fractures, which provide preferential pathways (macropores) for water and nitrate. Soil variability and preferential flow must therefore be considered in a modeling effort.

Syv field site

The Syv field site, Figure 1, was established in order to investigate the impact of nitrate leaching to surface water and groundwater systems. Specifically, the outflow through two drainage systems to the Syv creek was of interest. The two drainage catchments shown in Figure 1, were monitored all year long from the beginning of 1988 to the summer of 1990. Such tile drain systems are sampling devices which can provide information on the cumulative or integrated recharge and nitrate contamination load from large-scale soil systems.

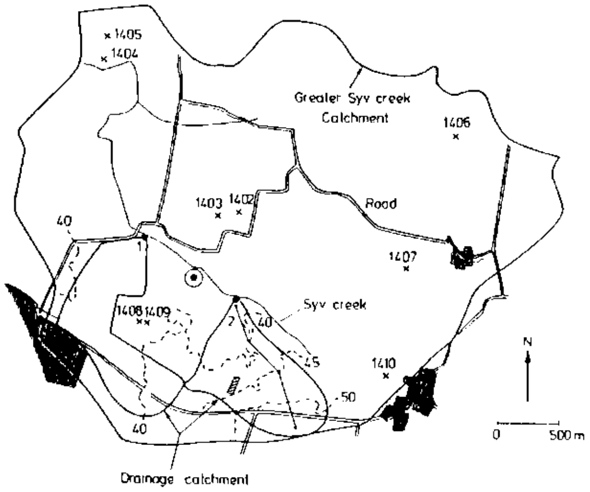

Figure 1
Syv field site

Soil profiles

Small variations in recharge characteristics arising from soil heterogeneity or preferential flow paths are to a certain degree filtered out and the outlet response in itself does not provide detailed information on the processes taking place in the system. However, by interpreting the response in combination with model simulations, it is possible to assess the significance of spatial variability and preferential pathways on the flow behaviour. Spatial variability in soil properties are available from measurements of retention characteristics in nine soil profiles, see Figure 1. In all of these profiles worm and root channels were present at a density of 1-10 per square decimeter. Data for hourly rainfall and daily potential evapotranspiration have been collected at the climate station, see Figure 1.

Flow model

The SHE-model has been used for analyzing the rainfall-discharge relationships of the two catchments. The unsaturated zone component of the SHE-modelling system, extended with an empirical description for bypass flow, together with a simple groundwater and river flow description, is used to simulate movement of water through the unsaturated zone and the subsequent discharge to the creek either through the drains or from the groundwater, Figure 2.

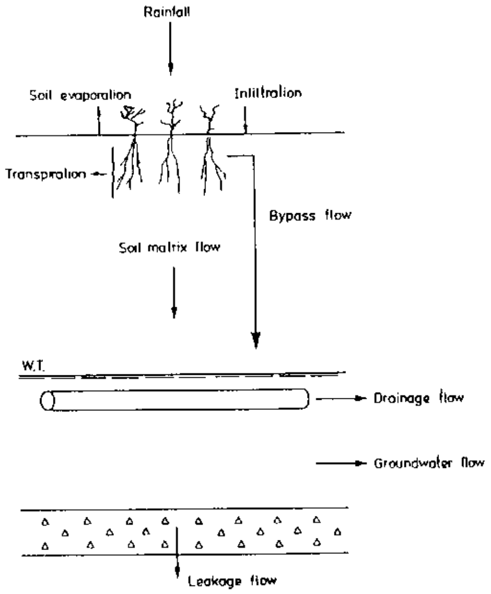

Figure 2
The flow model

Bypass flow

The unsaturated zone component is thus a two--domain model, idealizing the soil as consisting of two domains; the porous matrix domain, where a darcy-type flow occur and a macropore domain with more rapid bypass flow. The amount of bypass flow is determinded by the moisture content of the soil. When the soil is at a moisture content above field capacity, bypass flow is determined by a bypass ratio expressing how much of the rainfall will bypass the soil matrix. When the moisture content is below residual no bypass flow occurs. Between field capacity and residual there is a linearly dependency on the actual moisture content. All bypass flow is routed directly to the groundwater, because the absorption of water from the macropore domain to the porous matrix domain is assumed to be negligble. This simple empiricial bypass flow description includes a bypass ratio, which can only be assessed through calibration.

2. Results

A parameter sensitivity analysis was carried out in order to explore the significance of the spatial variability and bypass flow and included three simulation case studies. In case 1, retention data from only one location are applied

Case simulations

assuming the data are representative for the whole cathcment area. Two sets of retention curves measured at the two locations closest to the drainage catchments are tested. In case 2, the two sets of retention data from case 1 are now assumed to represent half of the drainage area and the total drainage outflow is thus obtained as the equal weighted sum of the two individual responses. In case 3, all nine sets of retention curves are included, each representing 1/9 of the outflow response.

Case 3

Figure 3 shows the simulated integrated outflow response for catchment 2 when all retention data are considered and either 0% or 50% bypass flow is allowed for. A comparison with the results from the other two cases clearly indicated, that it is necessary to introduce all the field-documented soil variability, in order to obtain the best match of the recorded outflow. However, Figure 3 also indicate that bypass flow is a likely mechanism in the drainage catchment.

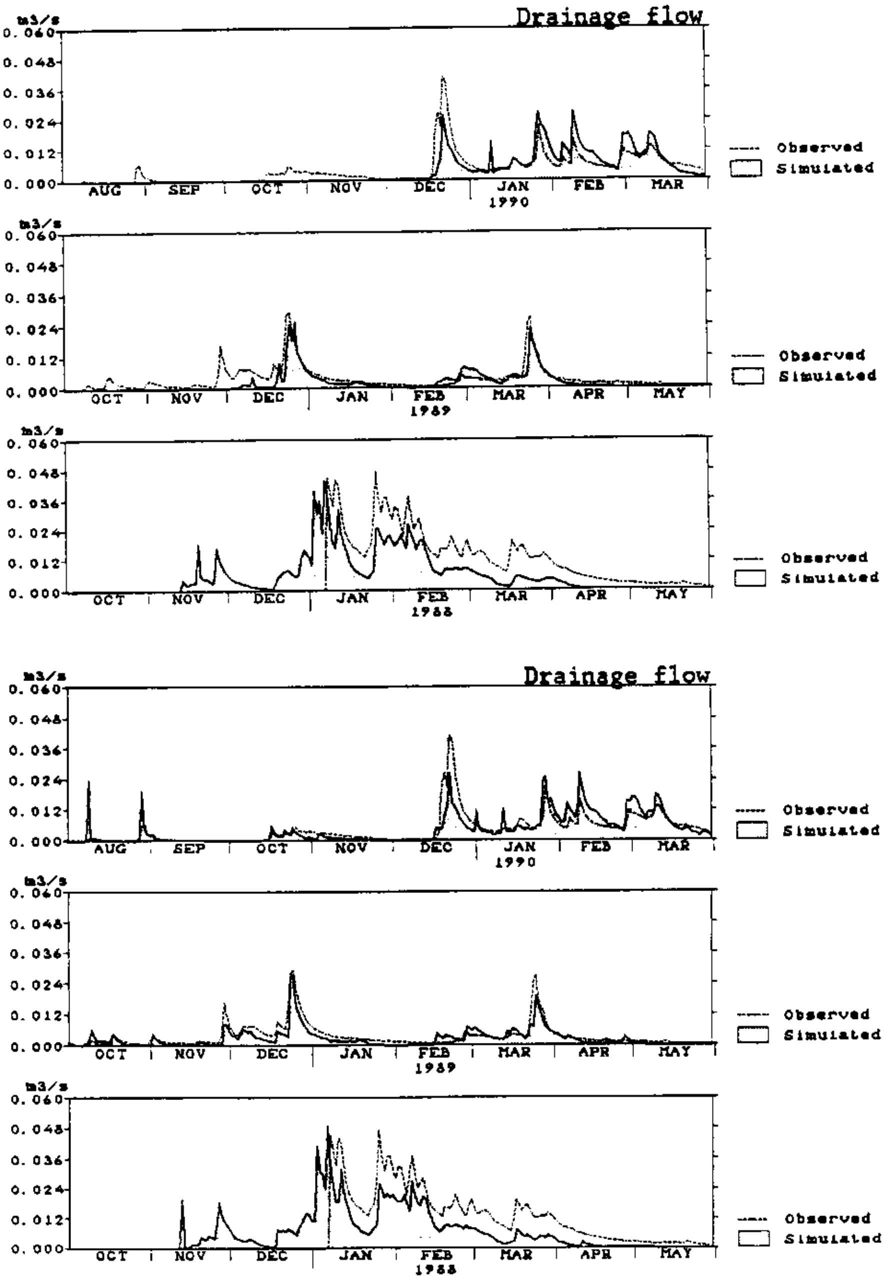

Figure 3

Simulated and observed outflow from catchment 2 for case 3. Zero bypass flow (top) and 50% bypass flow (bottom)

Without bypass flow, the early discharge events are not described satisfactorily, and a bypass ratio of the order of 50% must be introduced in order to generate outflow at the same time as that observed. The same kind of results are also obtained for catchment 1. The discrepancy between the simulated and observed outflow during the first part of 1988 is probably due to measurement problems of either the outflow or rainfall, because, with the available data it is not possible to obtain a water balance.

The sequence of simulation case studies demonstrate that bypass flow is a likely mechanism in both catchments. However, using a modelling approach based on a simple and empirical description of bypass flow and given the available field data it is not possible to provide an in-depth quantification of the bypass flow mechanism. Other phenomena may also interfere, such as variations in drain depth and water table position over the cachtment area. These other phenomena are probably the reason why a high bypass ratio of 50% is needed in the case 3 simulation.

3. Conclusions

The outflows from two drainage catchments have been analyzed using a two-domain model for unsaturated flow coupled with a simple description of drainage and groundwater flow.

Soil variability

It has been demonstrated that the best simulation of the outflow from both catchments are obtained by including all the field-documented variability in retention properties.

Bypass flow

Despite the inclusion of the full field-documented retention variability, it was not possible to simulate the early drainage flow events occuring in the months before the drains start flowing continously. This behaviour can be explained by the existence of preferential flow paths in the soil. Allowing 50% of the rainfall to bypass the soil matrix and flow directly to the groundwater gave better simulations.

A bypass ratio of 50% is probably in the high range, and could indicate the contribution from other phenomena, such as variations of drain and water table depths over the catchment areas.

Leaching risk

Although the problem of bypass flow can not be quantified more directly, it does show, that there is a risk, that a good part of fertilizers or manure applied prior to a rainfall event, may be leached directly to the surface waters.

Ministry of the Environment
National Agency of Environmental Protection
Denmark

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

Number B15

Three-Dimensional Modelling of Nitrate Transport in a Catchment

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Resumé

The main objective of this study is to develop a hydrological model for simulation of water and nitrate transport on catchment scale. The developed modelling system, SHE(DK), includes a three-dimensional groundwater component and an integrated solute transport model for the unsaturated and saturated zones. The SHE(DK) has been applied in combination with the DAISY model (Hansen et al., 1990) to simulate the transport and transformation of nitrogen from application on the fields to the streams in two catchments in Denmark, the 445 sq.km Karup Å catchment, and the 178 sq.km Langvad Å catchment.

The results of the simulations show a considerable variability in NO_3^--concentration in time and space in the groundwater aquifer. The various time lags in the catchments with respect to nitrogen transport from the field to the streams have been estimated.

1. Introduction

The problem: Increasing amounts of nitrate in groundwater

In recent years, nitrate concentrations in the groundwater have been reported to increase in many areas of Denmark. The transport of nitrate via streams may contribute to the nutrient load in the inner Danish seas, which have frequently caused periods with serious depletion of oxygen.

The aim of the study is to develop a modelling tool which includes water and solute transport

In order to solve these problems it is necessary to fully understand the complex mechanisms of water and nitrate transport in the catchments. The aim of this study has been to develop a modelling tool, which includes the basic hydrological processes and can be applied to catchments with different hydrological regimes and of various sizes. The modelling system developed, SHE(DK), is also intended as an operational tool which can support action agencies in regulatory and planning functions.

The study areas represent important hydrological regimes in Denmark

The SHE(DK) has been applied to the 445 sq.km Karup Å catchment and the 187 sq.km Langvad Å catchment. These represent the two most important and at the same time most common hydrological regimes in Denmark. Based on historical information on farming practices in the areas and the available basic information on geology, climate and other characteristics of the catchments, the water and nitrogen regimes have been modelled. The output from the modelling exercises includes spatial and temporal variations in the nitrate concentrations in the groundwater and nitrate contribution to the streams.

Regional simulations may form the basis for extrapolations and national assessments

A rigorous modelling approach offers several advantages compared to simpler methods. However, as the size of the areas to be modelled increase, larger uncertainties on the simulation results are expected, because of uncertainties in the input data. On the other hand, regional analyses, compared to small studies on research fields, provide estimates which may form basis for extrapolations and data for national assessments.

2. Material and Methods

2.1 Model Description

Simulation of the water and nitrogen transport on catchment scale requires a comprehensive modelling effort. During the project, an extended code SHE(DK) of the European Hydrological System, SHE (Abbott et al., 1986) has been developed.

SHE(DK)

The SHE(DK) is fully distributed and the flow of water and solutes in the catchment are calculated by solving the governing equations of the major processes in the hydrological cycle of the land phase. The flow in the soil water zone is calculated by the one-dimensional Richard's equation. In the groundwater zone the three-dimensional Boussinesq equation is applied. Utilizing the computed velocities from the above equations, the transport of the solutes is calculated from the corresponding advection-dispersion equations in the two subsurface zones.

Simplified chemical reaction model included

Denitrification plays only a minor role in the unsaturated zone below the rootzone, wherefore, nitrate is treated as a conservative solute here. A simple chemical reaction model has been introduced in the groundwater zone, assuming that all the nitrate reaching the redoxcline is removed instantaneously. The redoxcline is considered stationary and form part of the initial conditions. In the Karup Å catchment this approach is based on the results from field experiments and modelling in the Rabis Creek subcatchment carried out by Postma and Boesen (1990), and Engesgaard and Jensen (1990).

Spatial discretization in the SHE(DK)

The catchment characteristics are represented in the horizontal directions by a network of squares. Within each square the soil columns are divided in a series of horizontal layers of variable thickness. In the unsaturated zone it varies from 5-40 cm. The vertical discretization in the groundwater zone may be carried out in two ways. In the Karup Å catchment, which is mainly a single unconfined aquifer of glacial deposits, the saturated zone is divided into layers of e.g. 5 metres (Fig. 1), except for

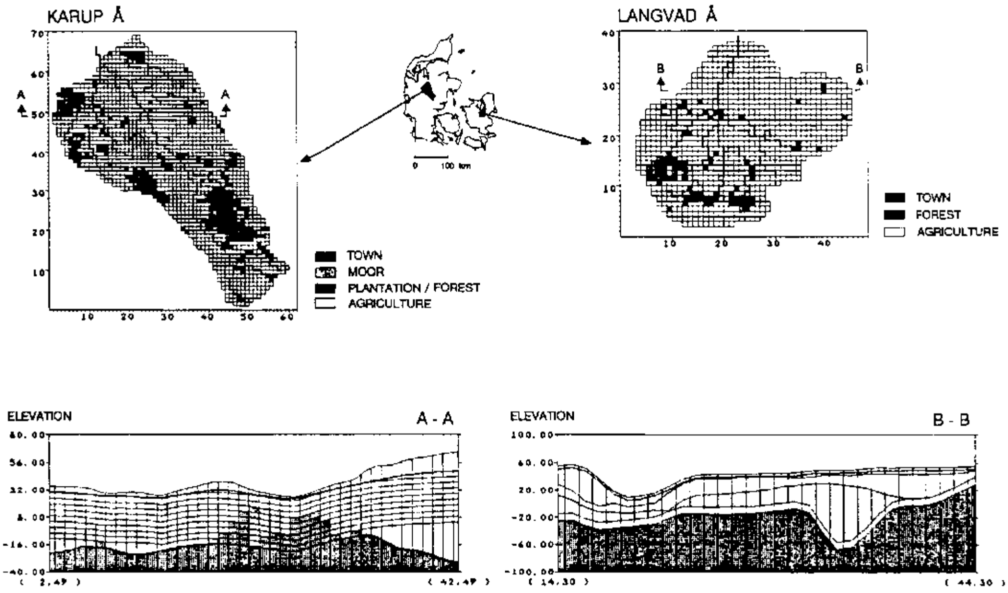

Figure 1 SHE(DK) model set up for (a) the Karup Å catchment, and (b) the Langvad Å Catchment.

the upper layer, which has a variable thickness depending on the actual watertable position, and the lowest layer, which extend to the impermeable bedrock. In the Langvad Å catchment, which is situated in a moraine clay landscape with several isolated aquifers the boundaries between the layers in the model follow the boundaries between the individual aquifers (Fig. 1).

The SHE(DK) does not include a detailed soil-plant-atmosphere description which can account for plant growth and nitrogen transformation in the rootzone. To complete the description of the nitrogen transport from the field to the streams the rootzone processes are modelled separately by the DAISY model developed by Hansen et al., (1990). The DAISY model is a one-dimensional mechanistic model, in which the flow description is compatible with the one in the SHE(DK). The two models are run stepwise by first simulating the nitrate leaching for all combinations of crop rotations identified in the catchments, with corresponding estimates of fertilizer and manure applications and farm management schemes. Time series of daily crop status and nitrate leaching (in kg/ha) are distributed spatially in the SHE(DK) grid network.

DAISY simulates the growth of agricultural crops and root zone processes

Output data from DAISY are transferred to SHE(DK)

2.2 Data Provision

Data requirements:

Geology

Vast amounts of data and information are required in applications of the models. The three-dimensional flow description in the groundwater requires a detailed geological description of the catchment which has been carried out by the Danish Geological Survey (Hansen and Gravesen, 1990, and Gravesen, 1990). A pre-processing package attached to the SHE(DK) have been used to digitize geological layers, contour lines and other features.

Climate

The climatological data, rainfall and potential evapotranspiration, are the driving variables, and discharge data and groundwater levels form the basis for model evaluation of the simulated hydrological regime.

Landuse and farming practices

To assess the farming practices and the development in fertilizer and manure applications in the areas, statistical information and information from local agricultural advisers has been assembled.

3. Results

Results from the Karup Å catchment presented below

The modelling procedure followed in the two catchments has been very similar. Since the major emphasis has been put on the analysis of the results from the Karup Å catchment, the results presented here are confined to this catchment. The results are based on twenty years of simulation.

3.1 Nitrate Leaching from the Root Zone

Nitrate leaching from the rootzone varies from 2-190 kg NO_3^--N/ha/y, depending on the crop rotation

The amount of nitrate leaching has been calculated for 15 crop rotations in the catchment. Fig. 2 shows the results for three typical rotations in Karup. The amount leached varies substantially between fields. Under permanent grass, the leaching is limited to approx. 2 kg NO_3^--N/ha/y, while under rotations with beets, barley and grass receiving cattle manure, the average from 1969-88 is between 97 and 117 kg/ha/y, due to the large amounts of manure distributed to the beets. Without beets, this type of rotations leach 26-71 kg/ha/y, depending on the amount of grass included. Rotations receiving pig manure (mainly barley and potatoes) show the most severe leaching, 180-190 kg NO_3^--N/ha/y. The average leaching over 20 years for all rotations in Karup are approx. 75 kg NO_3^--N/ha/y.

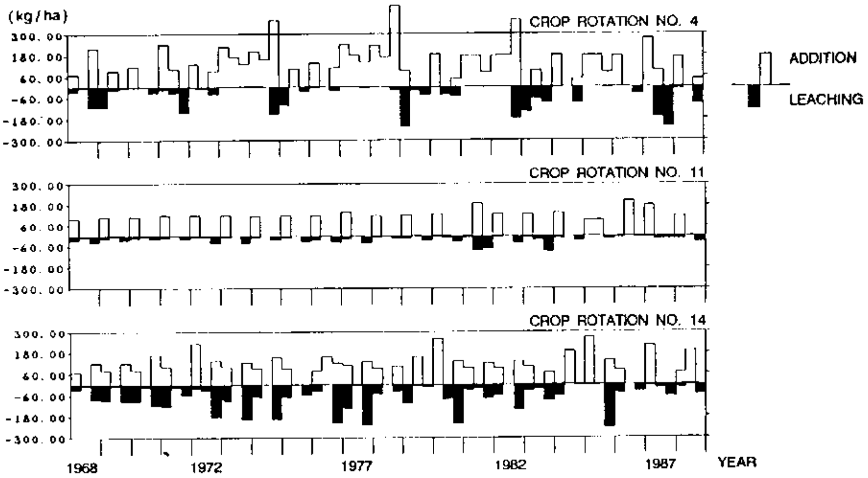

Figure 2 Nitrate leaching from various rotations calculated with the DAISY model. NB: The results in 1968 are influenced by initial conditions.

Leaching losses have been reduced with 20% since 1984

The average leaching has been calculated for the periods 1970-74, 1975-79, 1980-84, and 1985-88. The relative values are 77, 83, 100 and 81%, respectively. The decrease in leaching during the last years is due to a decrease of the amount of manure available (approx. 11% less), a small decrease in the amount of fertilizer used, less manure being spread during autumn and winter, and more green fields during autumn.

Climate influences leaching

Climate has been found to influence the nitrate losses and final nitrate concentrations, partly by determining the plant growth, partly by determining the amount of percolation in which the nitrate will be dissolved. Bypass, which may occur in Langvad is not adequately described by the model.

3.2 Water Balance and Water Flow

A good description of the hydrological regime is a prerequisite for a reliable simulation of the nitrate transport. The SHE(DK) has been calibrated using records of streamflow and well observations.

Simulated and observed streamflow show good agreement

The simulated and the observed streamflow at the outlet of the catchment is shown for the years 1981-88 in Fig. 3a. For the entire period the water balance show an excellent agreement, however, with a tendency of overestimation (max. 12%) in dry years, and a slight underestimation (max. 6%) in wet years. Daily flows are simulated reasonably accurate, with a tendency to underestimate the peaks. Surface runoff during the winter is limited to wetland areas adjacent to the streams.

Groundwater levels and variations are simulated successfully

Simulated groundwater levels have been compared with observations from a large number of bore wells. As shown in Fig. 3b both levels and yearly variations are simulated successfully.

Average percolation: 482 mm/y in agricultural areas

The average percolation from agricultural areas is calculated to 482 mm/y. This is in good agreement with the average measured runoff of 456 mm/s, considering that plantations and areas with shallow ground water usually show higher actual evapotranspiration and that a net storage in the groundwater zone has been observed during the simulation period.

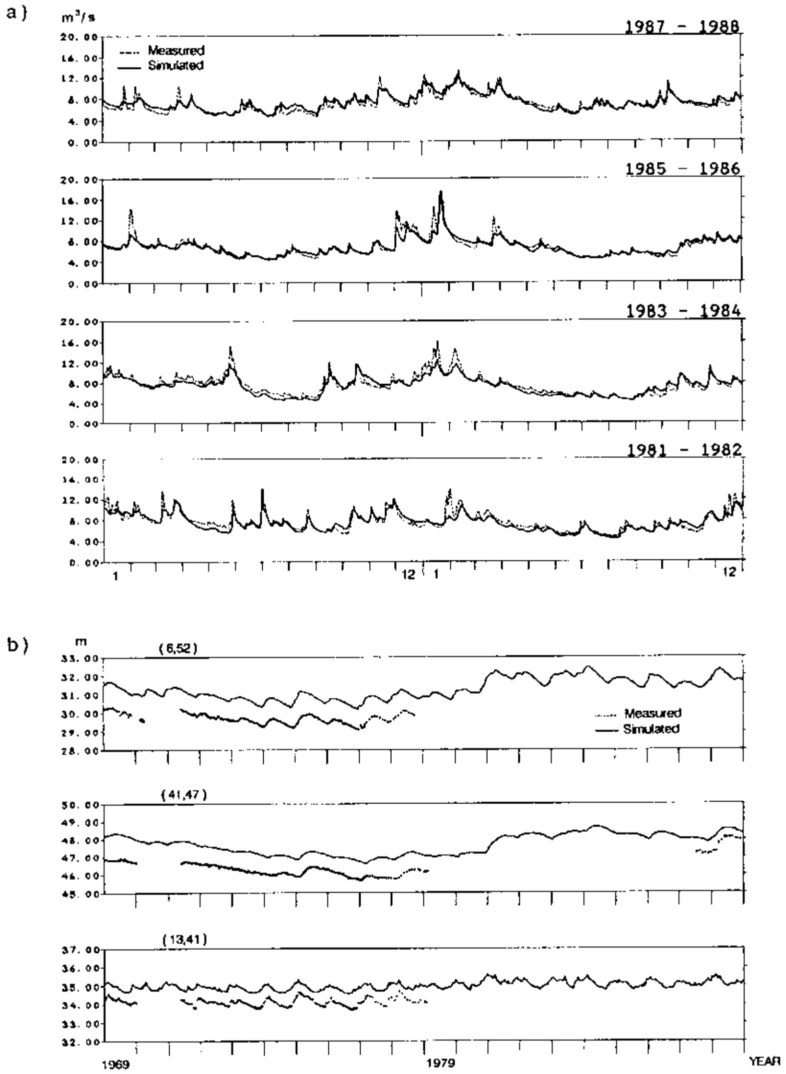

Figure 3 (a) Simulated and observed runoff for the period 1981-88 at Hagebro, Karup Å catchment, and (b) Simulated and observed groundwater table (1969-88) in selected wells.

Simulated front propagation and particle velocities

An average front propagation and a particle velocity of 3,5 m/month and 4-6 m/y respectively have been simulated for areas with a deep soil water zone. The simulations show that the solute moves down the profile in a step-wise manner, the movements taking place primarily during the autumn.

3.3 Nitrate in Groundwater and Streams

Nitrate concentrations in groundwater depends on leaching, rainfall, distance to the groundwater table, geochemistry,

The variations in the nitrate concentration in the groundwater is a function of the amount of nitrate leached, the rainfall, the distance to ground water, and geohydrological and geochemical conditions in the ground water. The nitrate leaving the rootzone will, after some time be found in the upper layer of the ground water, and the concentration is directly related to the leached amount. However, the solute becomes dispersed in the unsaturated zone. This averaging process is most pronounced where the unsaturated zone is deep.

and flow pattern

The flow conditions in the groundwater depends on the hydrogeological conditions. In the Karup Å catchment, the flow has a significant vertical component near the groundwater divide (downwards) and near the streams (upward). Water which has passed the redoxcline will mix with water containing nitrate in the areas close to the streams. A certain degree of dilution therefore takes place in these areas.

The nitrate concentrations vary widely in time and space

Fig. 4 shows the wide variation in the simulated nitrate concentration in the upper groundwater layer in the autumn 1984 and 1988 in the grid squares with agricultural land use. Nitrate free water occurs in the grid squares where SHE assumes 100% reduction in the first node below the water table. The large nitrate concentrations are typical for areas receiving large amounts of farmyard manure.

The decrease in leaching in the late 80'ies results in a decrease in the number of grids with high concentrations of nitrate.

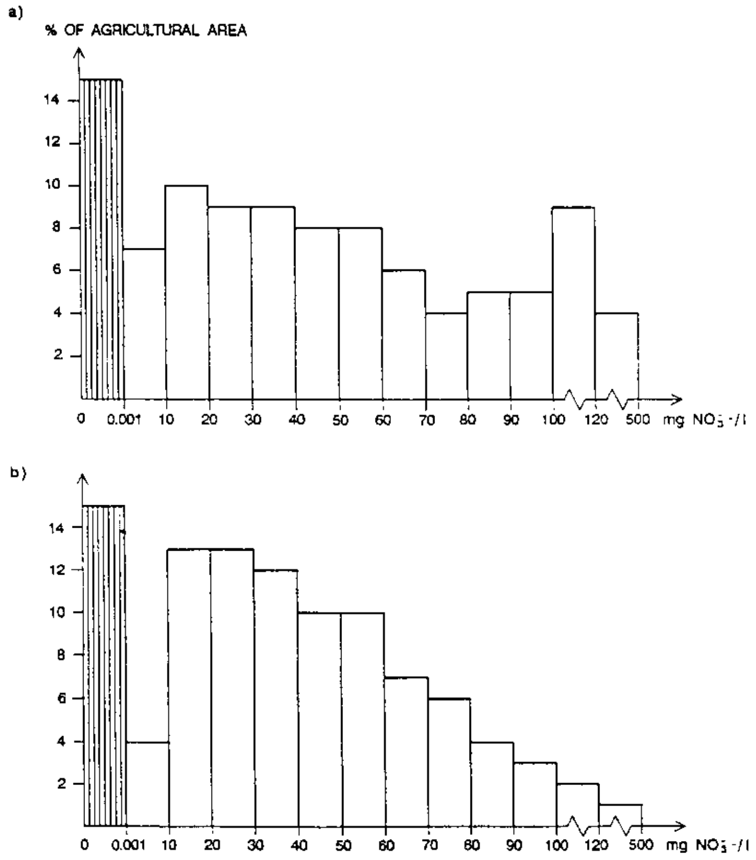

Figure 4 Distribution of NO_3^--concentrations in the upper groundwater layer below agricultural areas in the Karup Å catchment - (a) autumn 1984, and (b) autumn 1988.

Fig. 5 shows the temporal variation in nitrate concentration simulated for three crop rotations. The cropping history influences the pattern substantially and may superimpose other trends. The values shown are average values for 25 ha and approx. 3 m depth. Point observations may show even larger variations in time and space.

Point measurements are expected to vary more than simulated estimates

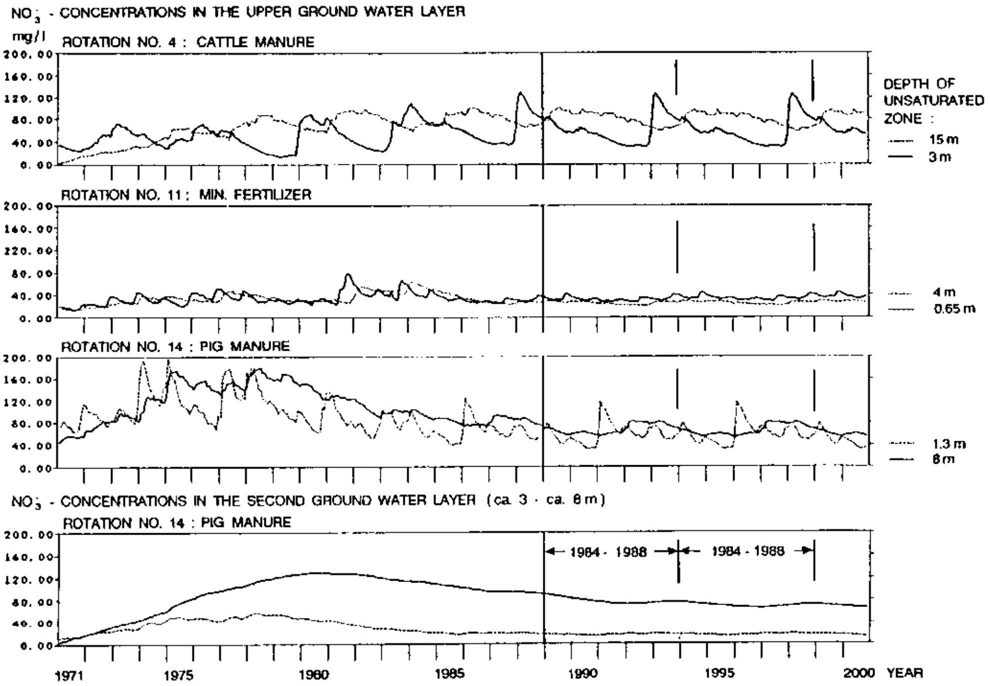

Figure 5 Temporal variation in NO_3^--concentrations in the upper groundwater layer below three selected rotation schemes, with two different distances to the groundwater table.

The increase in the concentration in the first few years of the simulation for areas with a deep unsaturated zone is influenced by the initial conditions, and does not reflect reality. The effect of climate may be deduced from rotation 14 (shallow groundwater table). In 1976 and 1980, the leaching was 256 and 312 kg respectively. Due to a larger percolation rate in 1980 compared to 1976, the concentration in the ground water was larger during the winter 1976/77 than in 1980/81.

The amount of nitrate reaching the stream depends mainly on leaching totals and position of the redoxcline

The total amount of nitrate reaching the stream depends on the land-use and the depth of the redoxcline. The lowest concentrations of nitrate reaching the stream are found in areas with superficial redoxcline and with a large percentage of moose or plantation. The highest concentration are found in areas with large distance to the redoxcline, and with a high population of pigs, see Fig. 6. The simulations show that in average, half of the leached nitrate is reduced in the aquifer.

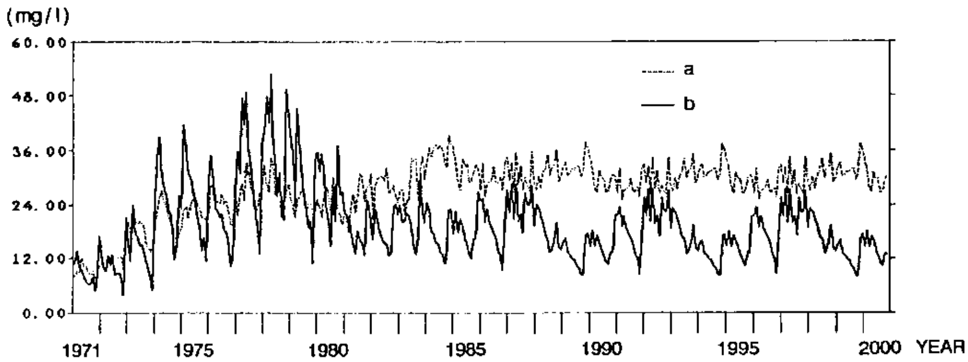

Figure 6 Temporal variation in NO_3^--concentrations in the contribution to the streams from two areas in the Karup Å catchment. NB: The trend in the first half of the 70'ies is influenced of initial conditions.

Denitrification in wetlands is

The yearly variations are larger in areas with a high groundwater table. In the calculations, the denitrification taking place in wetlands near the stream has not been included. All the not included in the SHE(DK)

experimental field site in the Karup Å catchment, Ambus et al. (1989) found a reduction of approx. 50%, however, it may vary through the catchment. In total approx. 25% of the leached nitrate may reach the streams.

3.4 Effects of Changes in Agricultural Practices in the Karup Area

With simple measures, leaching losses may be reduced with at least 35% in Karup

Results from the analysis of various changes in agricultural practices indicate that part of the benefits of moving the time of ploughing and the spreading of manure from autumn to spring have already been gained. The leaching by the end of the 80'ies is only 80% of the leaching in the beginning of the decade. When expanding these practices and combining them with a more uniform distribution of the manure, the level of leaching decreases to 65% in the model simulations.

The maximum possible effect of recommended measures is approx. 50%

The analysis may have two errors which leads to an overestimation of the leaching. Firstly, the amount of mineral fertilizer may not be reduced sufficiently in the rotations receiving manure. Secondly, the amount of manure produced in the catchment has decreased approx. 70.000 T over the 5 year period being cycled. This decrease may not be taken into account correctly in the analysis. Taking into account both of these errors, a total reduction in nitrate leaching of 47 % (compared to the 1980-1984-level) can be reached. This is close to the goals set by the National Agency of Environmental Protection.

Reduced leaching leads to reduced concentrations in

The scenarios lead to less variation in the concentrations in the groundwater, as well as a reduced average concentration. The time to streams within 5 years

equilibrium in the groundwater is, however, large, while for the stream, the average concentration will be reduced corresponding to the decrease in leaching already after 3-5 years.

4. Discussion and Conclusion

The model development includes:

The SHE(DK) is a generalized and improved version of the SHE, which is able to describe the movement of water and nitrogen in most Danish hydrological catchments. The project has comprised several new developments:

A three-dimensional groundwater model

a. Development of a three-dimensional groundwater component which can be used for artesian and free ground water aquifers, or combinations of the two.

An integrated solute transport model

b. Development of an integrated solute transport model for the unsaturated and saturated zones.

and operationalization

c. Operationalization of the model system with programmes for data processing and graphical presentation.

The animal population in the catchment plays an important role in leaching

The results of the rootzone model, DAISY, shows farmyard manure to be a very important factor for nitrate leaching. A reduction in nitrate leaching of 50 % in Karup is only possible because of the decrease in the animal population which have taken place during the last half of the 80'ies. From the beginning to the end of the 80'ies, the leaching has been reduced with 20 % in Karup.

The location of the redoxcline influences the NO_3^--contribution to streams

An important factor in Karup is the location of the redoxcline since it determines the percentage of the nitrate which will reach the river. In average, half of the leached nitrate is reduced in the aquifer. In addition, a significant denitrification may also take place in the areas around the streams, as has been shown in other NPo-studies, and it is estimated that only approximately 25% of the nitrate leached from the root zone in the Karup Å catchment will enter the streams.

Modelling provides information on variability, sensitivity and time lags

The main advantages of simulations carried out with the combined modelling system compared with e.g. monitoring alone, are related to estimation of the variability of investigated variables in time and space, evaluation of the importance of different components and processes, and estimation of the time lag between changes on the surface and measurable changes in groundwater and rivers. For Karup it is obvious that point measurements of nitrate concentrations are representative for small areas and timespans only. The nitrate concentration in the upper groundwater layers varies with the cropping history of the soil, the thickness of the unsaturated zone and the amount and distribution of the rainfall. In deeper layers, the variations are less.

The model system SHE(DK) now present is unique, also in an international context. It has several possible uses. Among these are future studies of the dynamics of nitrogen movements, modelling of catchments subject to monitoring programmes, support to planning of future studies, testing of alternative or proposed solutions, as well as support to management and decision making.

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Ministry of the Environment
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Mapping of the Nitrate Reduction Potential in a Regional Area.

An example from a Sandur-Hilly Island Test Area, Western Jutland, Denmark

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Summary

A map of the nitrate reduction potential is prepared from a sandur-hilly island area in western Jylland. The map is based on existing geological, hydrogeological and geochemical data in manual archives and databases, results and data from other NPO-projects and data from eight wells carried out during the project. The map shows the nitrate reduction capacity of the geological layers below the redoxcline and areas of equal capacity are separated from other areas. The map can be used in the planning of ground water abstraction and protection.

1. Introduction

The ground water projects of the NPO research pr gramme have investigated nitrate transport and d nitrification processes in the saturated and uns turated zone in small catchment areas. The colle ted data are used in mathematical models, which have synthesized hydrogeological, hydrological a geochemical processes in these areas. The transport and proces results are also used in mapping projects together with older record data.

This project is an attempt to develop a method to map on a regional scale the nitrate reduction potential of Danish sediments. The processes and materials in the subsurface beds, which cause reduction of nitrate, vary according to the geological setting. Therefore, the concentration of nitrate in the ground water is dependent also on the geological conditions as well as the climatological and agricultural factors.

2. Material and methods

2.1 Geological conditions

The test area in this pilot study is situated in the western part of Jylland, Denmark (Fig. 1.). The deposits which are relevant as aquifers or protection layers are of Miocene and Quaternary ages (Gravesen et al., 1990).

The Miocene aquifers are build of alternating, interfingering marine and limnic deposits such as quartz sand and -gravel and mica sand, often with a content of fine-grained organic matter, pyrite and also lignite. The Miocene aquitards consists of mica silt and mica clay, often with fine-grained organic matter and pyrite. Also layers of lignite may act as aquitards. Quaternary deposits from the Saalian and Weichselian glaciations are found above the Miocene deposits. The aquifer sediments are glacio-fluviatile sand and gravel, which often contains reworked Miocene material with lignite fragments and pyrite. The aquitards of glacial age are clayey tills and glacio-lacustrine fat clays.

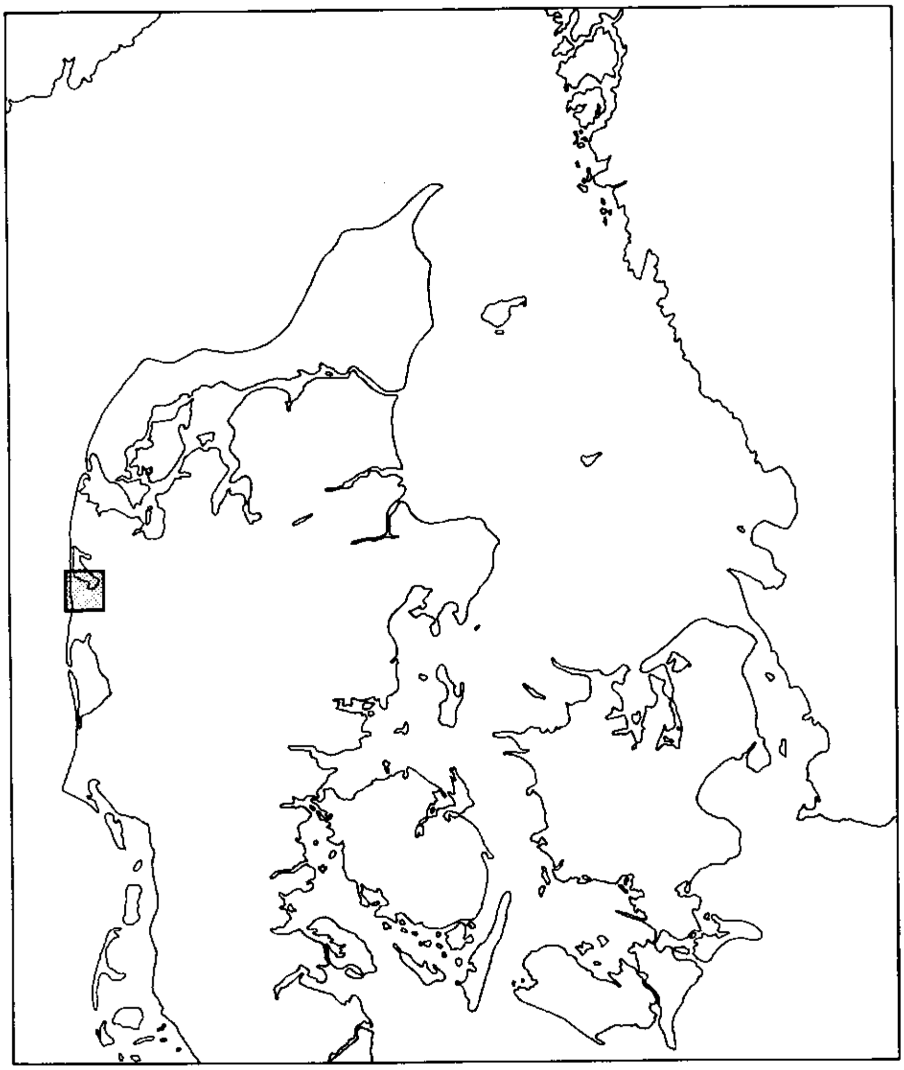


Fig. 1. Locality map

Post-glacial sediments, of no importance as aquifers but with some protecting effect, consist of marine and freshwater muddy sand with some organ matter.

The boundary surface between the Miocene and Quaternary deposits is formed due to the fluviatile erosion at the end of the Miocene Epoch and glacial and fluviatile erosion during the Quaternary glaciations. The topography of this surface is very irregular with deep erosion valleys in the Miocene layers, which act as important aquifers when filled with glacio-fluviatile sand and gravel.

2.2 Nitrate reduction capacity

The nitrate reduction capacity of the sediments at a specific locality can be measured by analyzing sediment samples from drill cores. This is done by determining chemical parameters suitable to express reduction conditions such as COD or TOC. In this study, which is an attempt to map the nitrate reduction capacity of sediments on a regional scale, it is obvious that the above mentioned procedure is much too costly if the whole area should be covered by reduction capacity values.

The chosen procedure, therefore, is to convert the results from a few intensive studies to the regional scale. This includes evaluation of drilling results, TOC and COD determinations, geological prospecting, chemical properties and lithological properties. Data including parts of these properties, are available in a great quantity from numerous wells with information of lithological logs stored at the Well Record Department at the Geological Survey of Denmark (Gravesen, 1986).

Reduction of nitrate from NO_3 to N_2 in a natural environment involves oxidation of natural occurring components such as organic matter, methan, reduced sulphur compounds and ferro iron compounds. Studies in connection with other projects (Pedersen, 1990) have shown that COD (Chemical Oxygen Demand) can be used as an indicator for th nitrate reducing capacity for sandy sediments. Th COD expresses the total amount of the above mentioned reducing components. The available nitrate reducing capacity is somewhat lesser, as a small amount corresponds to the COD of sediments, which has no reducing capacity. This basic value can be calculated from COD determinations of sand sample from the unsaturated zone and from yellow oxidize sand samples from the saturated zone. It has been calculated to 50 meqv. oxygen or nitrate per kilo sediment. For grey sand samples from the reduced zone with a content of lignite and pyrite the reduction capacity has been calculated from TOC (Total Organic Carbon) determinations (Kristianse et al., 1990).

The COD determinations on clayey sediments have proven to give unrealistically high values of 10-20 g nitrate per kilo sediments. These large values are probably due to an almost complete degradation of the clay minerals, which are not believed to occur under natural conditions. Instead of COD values, the variation of the total ferro-iron content has been used to measure the nitrate reducing capacity, and half the amount of the ferro-iron content is estimated to be available for nitrate reduction (Ernstsen, 1990; Ernstsen et al., 1990).

3. Results

3.1 Auxiliary maps

In order to be able to construct the conclusive nitrate reduction capacity map it is necessary to make use of a series of auxiliary maps and sections, and as a final step to be able to translate lithological terms into nitrate reduction categories.

The auxiliary maps and sections are:

- map of the Quaternary deposits
- geological basic data map (a well log map showing lithology and ground water level)
- map of the pre-Quaternary surface
- aquifer map (showing thickness of aquifers and aquitards)
- map of the level of the oxidation zone/nitrate reduction zone (redoxcline).
  The calculation of the nitrate reduction capacity must start at the level of the nitrate reduction zone or front in the saturated zone, which separates layers with nitrate (above) from layers without nitrate (below). Several studies have shown that this reduction border zone coincide with a change in colour in the sediment from yellow or yellow brown to brown grey or grey. Therefore, the level of the nitrate reduction zone is the same as the level of the oxidized zone. A regional map of the border zone can be done from the colour description in the lithological logs.
- geological sections used to analyse the geological build up of the area, and to make correlations between the geological units.

The last step is to catagorize the different sediments according to their ability to reduce nitrate, see table 1.

Table 1.

THE NITRATE REDUCTION CAPACITY

Category	Available nitrate reduction capacity mg nitrate per kg sediment	Sedimenttype
0 No reduction capacity	0	Sand, oxidized yellow to yellow brown Clay, yellow brown
1 Low reduction capacity	0 - 620	Sand, oxidized with silt and clay
2 Medium reduction capacity	620 - 2500	Sand, grey black with lignite, pyrite Clay, grey
3 High reduction capacity	>2500	Clay, fat, grey Mica clay and silt Lignite All seminents with high organic content

3.2 Construction of the nitrate reduction capacit map

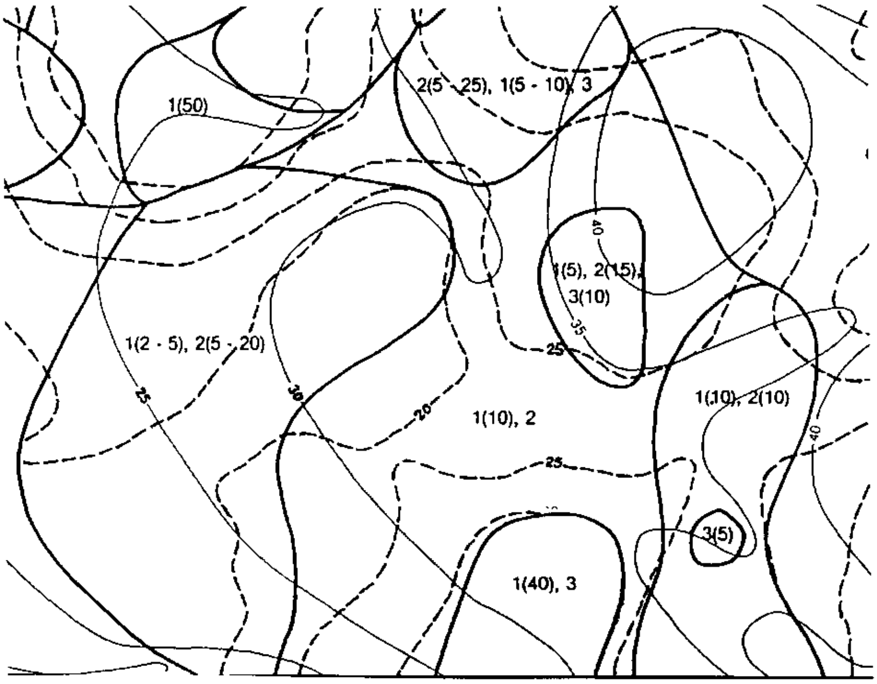
The nitrate reduction map is now constructed by assigning the different sediment types in a 50 m thick zone below the border between the oxidized pand the reduced zone to one of the three categories low, medium and high, see table 1. Areas with the same or similar aquifer build up are then grouped together in larger units. By this procedure some details were lost, but it was found necessary to make the map in the scale 1:50.000 readable. In each of the above mentioned units are given a reduction capacity profile, for instance: 1 (10), 3 (5), 2 (15) (fig. 2). This should be read 10 m of low reduction capacity above 5 m sediment with high reduction capacity, above 15 m of a sediment with a medium reduction capacity.

The final nitrate reduction capacity map includes 3 themes (fig. 2):

- nitrate reducing capacity covering areas with the same value as described above
- boundary between the nitrate zone and the nitrate free zone equal to the boundary between the oxidized and reduced zones in m a.s.l.
- piezometric surface m a.s.l.

4. Discussion and conclusion

The map is constructed from existing geological, hydrogeological and geochemical data. From most parts of Denmark large amounts of relevant data exist in manuel records or in databases and therefore, it is possible to produce this kind of map from other areas. The map is prepared by generalizing and compiling of these data and a geological model of an area is supposed, which describe the distribution, composition, depositional environment and age of the beds. This model is the basis for the aquifer map and the evaluation of the distribution of the reduction capacity of the sediments.



- - - Piezometric surface
______ Boundary between oxidized and reduced zone
1 (2) the nitrate reduction capacity areas. Explanation in the text.
Fig. 2. Map of nitrate reduction potential

The nitrate reduction capacity map may be used together with information about the nitrogen loac on certain areas in the planning proces for grour water withdrawal and ground water protection.

The map may also be used to explain causes for high nitrate concentrations in certain areas.

4.1 Conclusion

- It is possible to prepare an operational map of the nitrate reduction potential from archive data.
- The large amount of data have to be computer stored, when they are processed in the mapping procedure.
- The scale of the map is most appropriate 1:50.000.
- The map is a thematic map of the nitrate reduction conditions in the saturated ground water zone, and it is not a vulnerability map of the traditional kind.

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Climate Measurements at the Research Locations

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CLIMATE MEASUREMENTS AT NPO RESEARCH LOCATIONS

Summary

Climate stations

Climatic measurements were carried out during the period November 1987 through June 1990 at two locations, Rabis Bæk and Langvad Å. Measurements were performed with automatic climate stations and the following parameters were measured: air temperature at 2 m, soil temperature at depths of 10 and 30 cm, relative humidity at 2 m, wind velocity at 2 m, precipitation at 1.5 m, global radiation and surface wetness.

Database

Data from the two stations are stored in a database as hourly and daily values. Measurements of precipitation intensity and wind velocity are used to correct precipitation amount for aerodynamic error.

Deviations from normal

The climatic conditions during the measurement period deviated considerably from the normal pattern. All three winters were very mild, especially during January and February, and the precipitation amounts for the three winter half years were larger than the normal, especially at Rabis Bæk.

1. Introduction

Climatic data requirement

The research activities at the NPO research locations have demanded climatic measurements at the locations. The climatic data are used as a basis for evaluating other measurements and as input to models.

The climatic measurements must be compatible to the nation-wide measurements carried out in a network of automatic climate stations managed by the Danish Meteorological Institute and the Danish Research Service for Plant and Soil Science (Olesen, 1988).

2. Material and methods

Locations

Climatic measurements were carried out with an automatic climate station at each of the two research locations at Rabis Bæk and Langvad Å.

Rabis Bæk

The station at Rabis Bæk was placed on a field with grass. The size of the field was about 1 ha, and it was located just north of Rabis Bæk (56°21'N, 9°10'E). The height above mean sea level was 56 m.

Langvad Å

The station at Langvad Å was placed on a plateau above the area where the stream flows. The area was not cultivated. The station was located at (55°33'N, 12°03'E), and the height above mean sea level was 35 m.

Measurements

The following meteorological parameters were measured by the automatic climate stations:

- Air temperature at a height of 2 m.
- Soil temperature at depths of 10 and 30 cm.

- Air relative humidity at a height of 2 m.
- Wind velocity at a height of 2 m.
- Precipitation at a height of 1.5 m.
- Global radiation.
- Surface wetness.

These parameters were measured with sensors connected to a datalogger, which scanned wind velocity each 10 seconds, precipitation each 2 minutes and the other sensors each minute. Based on these measurements, various hourly statistics were calculated and stored.

Sensor types

Temperature was measured with Pt-100 sensors, relative humidity with a hair hygrometer, wind velocity with a cupanemometer, global radiation with a class 1 pyranometer, precipitation with a Geonor total precipitation recorder, and surface wetness with an electric grid.

Database

The recorded data were afterwards treated with a number of computer programs, which adjusted the measurements for individual sensor calibrations and calculated the amount of precipitation, duration of precipitation, etc. Daily values were calculated, and both hourly and daily values were stored in a database at Department of Agrometeorology.

Precipitation

The precipitation was measured at a height of 1.5 m and had to be corrected for aerodynamic error. Wetting loss can be ignored due to the low surface area of the sampler. As practically no snowfall occurred in the period of measurements, a procedure for correcting liquid precipitation proposed by Allerup and Madsen (1979) is employed. This method uses information on precipitation intensity and wind velocity.

Evapotranspiration

Daily values of potential evapotranspiration is calculated with the Makkink equation (Makkink, 1957) with modifications by Aslyng and Hansen (1982). This equation uses daily values of mean air temperature and global radiation.

Measurement period

The climate station at Rabis Bæk was set up on 27 October 1987, and the station at Langvad Å was set up on 28 October 1987. Both stations were closed in autumn 1990. This paper only treats the period from November 1987 through June 1990.

In cases where either the datalogger or the sensors failed, measurements were taken from stations close by. At Rabis Bæk data from Foulum (56°30'N, 9°35'E) were used, and at Langvad Å data from Ledreborg Alle (55°37'N, 12°03'E) were used. In most cases it was possible to reconstruct the precipitation series at the two stations, as the accumulated precipitation was measured.

3. Results

Actual and normal climate

Fig. 1 shows monthly values of mean air temperature and water balance at the two stations. Tables 1 and 2 show mean temperature, precipitation and potential evapotranspiration during the summer and winter half year, respectively. The summer half year is here defined as April through September, and the winter half year as October through March. The measurements are in the tables compared with normal values for the periods 1931-60 and 1961-88. Normal values are taken from stations near by, for 1931-60 from Danish Meteorological

Institute (1975) and for 1961-88 from Mikkelsen (1990).

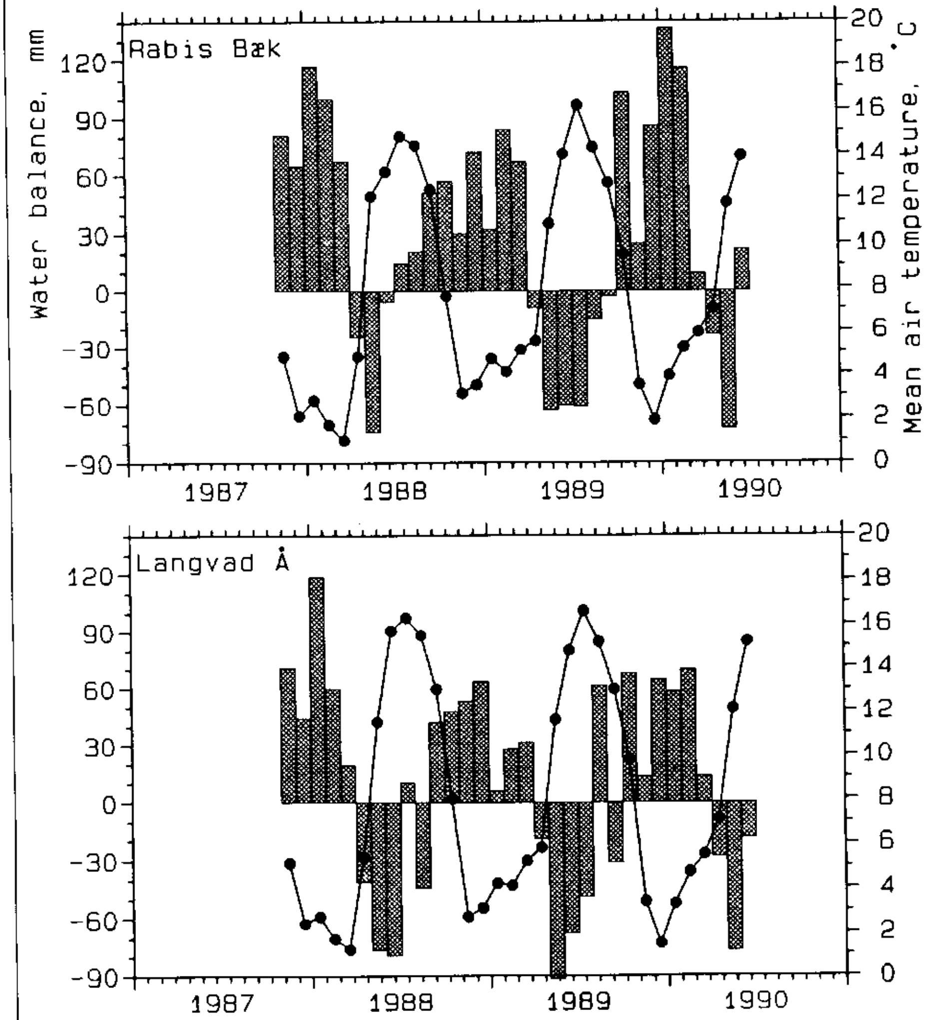

Figure 1. Monthly values of air temperature and water balance (corrected precipitation minus potential evapotransporation) at Rabis Bæk and Langvad Å. Air temperature is shown with dots connected with lines, and water balance is shown with bars.

Table 1. Mean temperature, precipitation and potential evapotranspiration at Rabis Bæk and Langvad Å during April through September. Temperature is in °C and precipitation and potentiel evapotranspiration is in mm.

	Mean air temperature			Corrected Precipitation			Potential evapotranspiration	
Period	Period	Mean 31-60	61-88	Period	Mean 31-60	61-88	Period	Mean 61-88
Rabis Bæk								
1988	12.6	12.7	11.8	361	436	422	458	458
1989	12.3	12.7	11.8	286	436	422	498	458
Langvad Å								
1988	12.9	13.2	12.7	298	345	367	487	484
1989	12.8	13.2	12.7	338	345	367	535	484

Table 2. Mean temperature, precipitation and potential evapotranpiration at Rabis Bæk and Langvad Å during October through March. Temperature is in °C and precipitation and potential evapotranspiration is in mm.

	Mean air temperature			Corrected Precipitation			Potential evapotranspiration	
Period	Period	Mean 31-60	61-88	Period	Mean 31-60	61-88	Period	Mean 61-88
Rabis Bæk								
1987-88*	3.5	2.6	2.1	592	393	462	70	78
1988-89	4.7	2.6	2.1	418	393	462	75	78
1989-90	5.0	2.6	2.1	557	393	462	83	78
Langvad Å								
1987-88*	3.8	2.7	2.3	390	290	364	79	82
1988-89	4.5	2.7	2.3	315	290	364	85	82
1989-90	4.7	2.7	2.3	384	290	364	96	82

*) Values for October 1987 were taken from a station near by.

The normal values for precipitation are corrected using the monthly correction factors for standard normals for moderately sheltered stations proposed by Allerup and Madsen (1979).

The annual mean temperatures for 1988 and 1989 were higher than normal. This was predominantly due to very mild winters. The annual precipitation in these years were about normal for 1931-60, reflecting a higher winter precipitation and lower summer precipitation.

4. Discussion and conclusion

Climatic change

During the period November 1987 through June 1990 climatic measurements were performed at Rabis Bæk and Langvad Å. The climatic conditions during the period of measurements deviated considerably from normal, especially during winter. Snowfall was virtually absent. Therefore the measured precipitation was corrected for aerodynamic error solely based on measurements of precipitation intensity and wind velocity.

Winter conditions

All three years in the measurement period had very mild winters, especially in January and February. If only temperatures in January and February are used, all three winters belong among the four warmest in Denmark since 1874, whereas the preceding three winter were among the 16 coldest.

The precipitation amounts for the winter half year were all larger than the normal for 1931-60. The precipitation was largest at Rabis Bæk during the winters 1987-88 and 1989-90, when the mean value for 1961-88 was exceeded as well. The precipitation at Langvad Å corresponded roughly to the mean value for 1961-88.

Summer conditions

Mean temperatures during summer season in 1988 and 1989 were about normal for 1931-60, and thus above the 1961-88 average. The amount of precipitation during this season was considerably lower than normal in both years, especially at Rabis Bæk. The summer of 1989 was also very sunny, which gave rise to a large soil moisture deficit.

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Implementation of Groundwater Monitoring in Denmark

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Résumé.

68 monitoring catchments

A groundwater monitoring network has been implemented in Denmark. The network is made of 68 monitoring areas, each representing the catchment area to a regional public water-supply well, and up to 15 local monitoring wells. The 15 local monitoring wells are either, small existing water-supply wells, or special designed and implemented, monitoring wells. The monitoring cathment areas, are distributed in a geographic balance. The following items has been considered in the design of the monitoring network:

- Point-, line- and volume monitoring.
- Level-accurate sampling.
- Uniform sampling technique.
- A broad list of analysis parameters.
- High analyses accuracy.

Forecasting

The implementation of the monitoring network, makes it possible, in the future, to forecast the groundwater quality and quantity. Hence, it will be possible to make avoiding reactions if any pollution are forecasted.

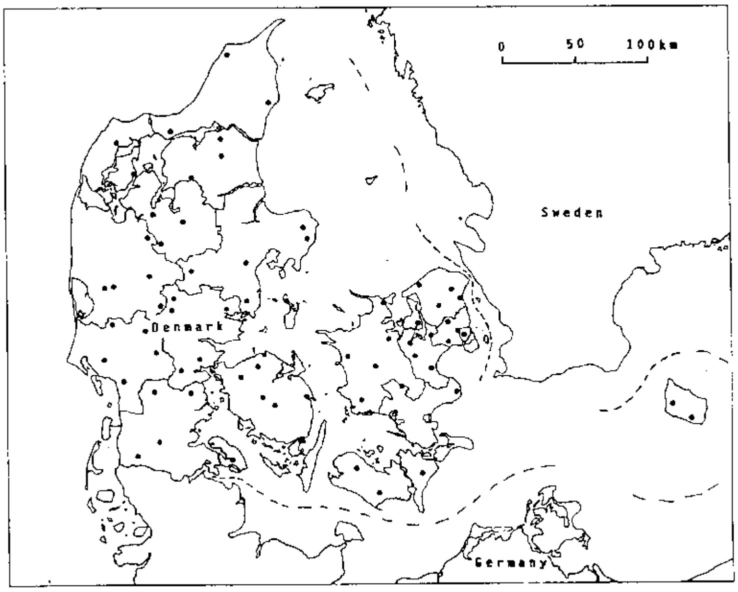
A possiblity, for demonstration of an effect of the industrialization, has been made by the introduction of a broad list of analysis parameters.

Short cuts between aquifers.

Due to the level-accurate sampling, has some demonstration been carried out, on the effect from wells with long screens, on the hydrology and groundwater chemistry. This can be important, in addition to the natural flow through the geological stratum.

14 Danish countyes and Geological Survey of Denmark

The 14 Danish counties have implemented 49 catchment areas, and the Geological Survey of Denmark has implemented 19 catchment areas, see figure 1. The counties, are responsible for the sampling and analysis work, and the Geological Survey of Denmark, are responsible for the accumulation of data, and for the data processing.



<u>Figure 1</u>: Location of 68 monitoring catchment areas with 1200 monitoring well screen in total.

<u>Introduction.</u>

Monitoring and warning service

The Danish groundwater, is so pure, that it with treatment for iron and manganese only, normally are used as drinking water. It is a must, to protect the groundwater in this way, for which reason the groundwater monitoring network has been implemented. The monitoring network itself does not have any protection effect. However, by monitoring it is possible, to follow the change in quality and quantity of the groundwater.

Two reasons for monitoring

There are two important reasons, to the establishment of monitoring wells in different parts of the subsurficial section of the hydrologic cycle. The first one, is the fact, that the recharging water, spends a lot of time, to percolate, from the ground surface, and down to the water-supply wells in the deep aquifer. Hence, if a pollution are discovered in the water-supply well, a big part of the aquifer has allready been polluted, and it is too late to do any avoiding action. The second one, is that it will take long time, to heal the damage, even if the pollution source is eliminated.

Material and methods.

Monitoring in several part of the hydrologic cycle

The groundwater are monitored in seveal points of the subsurface part of the hydrological cycle as a method to obtain a fast and efficient monitoring, see figure 2. It is assumed, that any pollution are emitted to the surface, from either a point pollution, or a diffuse pollution, and it is assumed, that the major part, of the pollution, percolates to the groundwater through the geological formations, and that it is diluted by dispertion. Hence, these effects are taken in consideration, by the level-accurate sampling, and in that way, the front genesis from nature (landuse and waste disposal from above, and salinity from belowe), and the pollution, are considered by this design of the monitoring network. Any other unexpected effects, might be identified, and the monitoring can be supplied with more detailed investigations, if necessary.

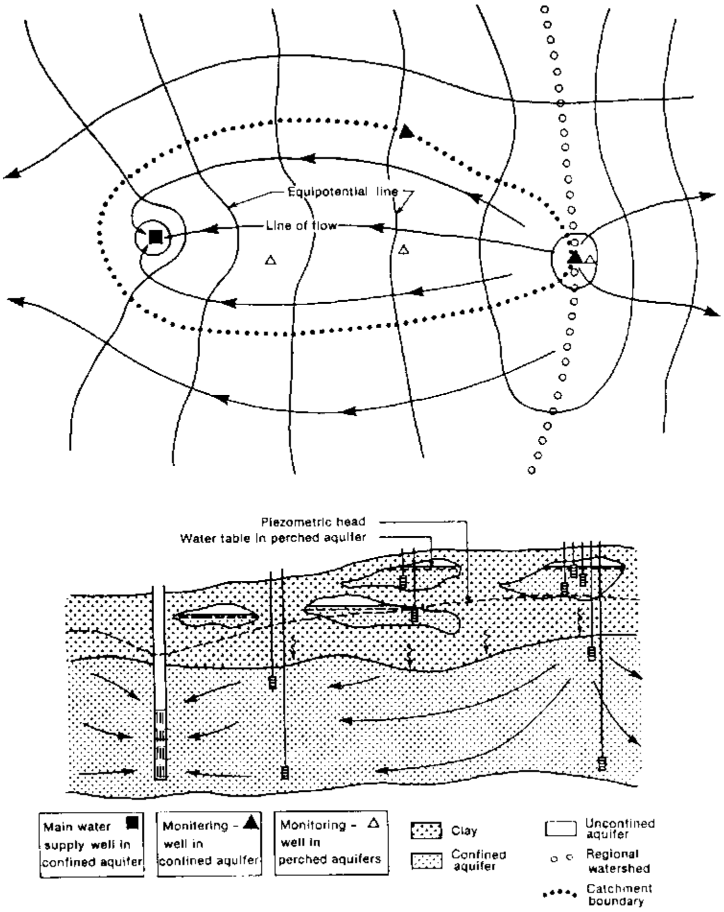


Figure 2: Principle design of the monitoring stratum of a catchment area. (After Andersen, 1987).

Three types of

Three types of monitoring wells, defined as point-, line- and volume monitoring wells, are defined in the monitoring network. Together they gives a wiev over the generel state, and a wiev over the more detailed variations, in the groundwater chemistry and hydrology (Andersen, 1987).

Point monitoring wells	A point monitoring well, is defined as, a well with a short screen, located in the groundwater divide. There is no pumping from the well. A point monitoring well, are monitoring the particular area above the well, since the location is in the groundwater divide. Several point monitoring wells, with screens at different levels, are normally placed at the same location, to make some time depending monitoring, along a vertical flow line.
Line monitoring wells	Line monitoring wells, are defined as, wells with short screens, without water withdrawal, and located somewhere between the regional waterdivide, and the regional watersupply well. Because of the location, and because of the nonpumping conditions, the linemonitoring wells give a monitoring, of the influence, along the flowpath upstream the well. Several linemonitoring wells, with screens in different levels, are normally established, at the same location, to make some monitoring, of the vertical distribution of quality.
Volume monitoring wells	The volume monitoring wells, are defined as, a production well. They are monitoring the integrated volume, of the cachment area to the well. Hence, there is a monitoring of the integrated effect of all point pollutions in the cachment area, and the interactions from the geology on all the flow pathes in the aquifer. On the other hand, the samples are mixed, and a pollution is diluted, and then difficult to identify and locate.
Background information from the water with highest residence time	The volume monitoring wells are even distributed in the monitoring area, giving an effective monitoring to demonstrate any pollution in the total monitoring cachment.

Sampling, from the bottom of the volume monitoring wells, gives water, from the bottom of the aquifer, which might be the groundwater with the highest residence time. Hence, these samples, gives some background information, about the groundwater, recharged, before the industrialization.

Small, existing water supply wells, in the catchment area, are used as volume monitoring wells.

Permanent sampling device in existing water supply wells

For the reason, to avoid the stagnant water, above the intake of the water-supply pump, special sampling device, has been permanent installed in the water-supply wells. In some cases, two sets of such sample devices, have been mounted, - one pipe, with intake in the bottom of the exsisting screen, and one pipe, with intake, above the top of the screen. This combination of samling device, in one well, gives information about differences, between the water from the bottom of the well, and the mixed water, from the top of the well, and there is no interaction, from the stagnant water above the pump, when sampling is done during pumping.

Drilling methods

New completed monitoring wells, are either made as hammered wells, or as percussion drilled wells, with short PVC screens with separate tubing to the surface. They are all point- or line monitoring wells.

Monitoring paraparameters

The groundwater are monitored by routine soundings and sampling, and five packages of analysis parameters are defined. The use of the packages, depends on the property of the monitoring well:

5 groups of analyses

- Normal, elementary parameters
- Microbiologic parameters
- Non-organic tracers
- Organic micro-pollutants
- Special pesticides

Results.

The antropogene impact on the hydrological regime, has allready been noticed, during the implementation of the monitoring network:

Measurements

A conductivity log, has been made, in an undisturbed well. Subsequently, a flow log, has been made. A number of short screens, with separate tubing to the surface, were mounted in the well, and the bottom part, of the original open hole, were filled up with gravel pack and sealing, as shown in figure 3. (The original inflow section, of the well, was an open hole, in the bryozoan limestone.) The water level, in the well, were measured, the day before the filling-up work, and the hydraulic head, were measured in the separated screens, the day after the filling up work. These heads are shown on figure 3. Measurements one year later, in the tubes from the screens, showed the same distribution of the hydraulic heads. The electric conductivity, has been measured, in water samples from the new screens, both three, and six months, after the filling-up work. The results of these measurements, are shown in figure 3 (together with the EC-log from the open well).

Antropogene impact on hydrology

The results of the distributed head measurements demonstrates an increased head (app. 1 meter extra), in the screens, at the bottom of the filled up well, hence the open well, has caused an internal flow in the upward direction, before the sealing of the well. - I.e. the hydraulic effect of the drilling operation, or antropogene impact on hydrology.

Antropogene impact on hydro chemistry

The electric conductivity log, in the multiscreened well are quite different from the electric conducticity log in the open well, and shows the chemical effect of the antropogene impact on the hydrochemistry. I.e. short cut between separated parts of the aquifer.

Saline water in top of limestone

The high value of electric conductivity measured in the screen 33 m.b.MP., might be caused of some other matter, for eksample internal upward flow of saline water in another nearby well.

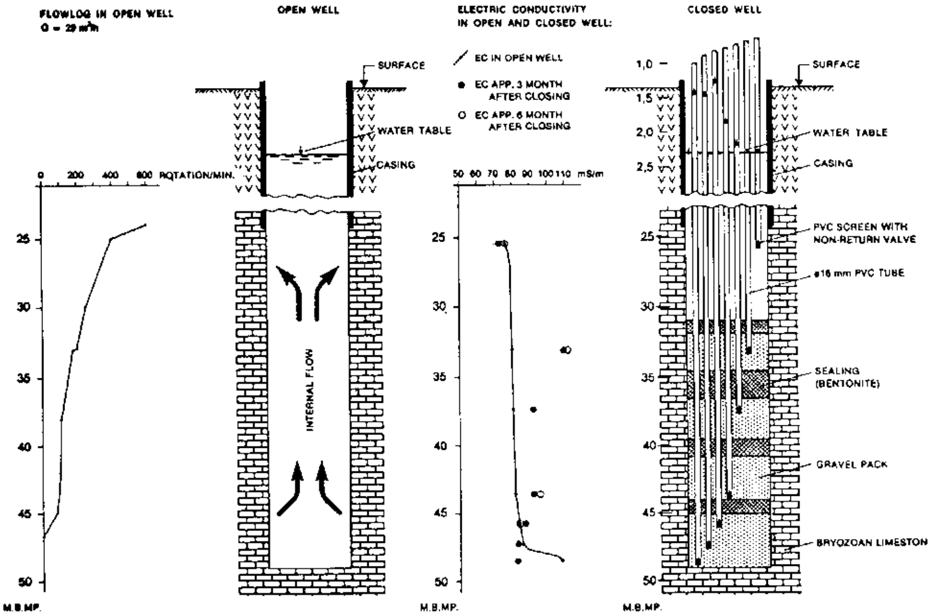


Figure 3: Demonstration of the effect of the antropogene hydrogeology. (The restricted valves on the top of the monitoring filters, are a part of the sampling device. The water above the restricted valves were removed, and the water table recovered, before the water table were measured. - Only for the reason of a possible failure, due to the restricted valve.)

Old water table and new water table

The results demonstrates that the hydraulic head measured in the open well, are equal to the head of the highly permeable parts in the top af the inflow part of the well (or the bryozoan limestone), and in any case a weighted average of the heads over the penetrated section. This is important for determination of flow diretion, and hence, for the determination of the distribution of a potential pollution.

Discussions and conclusion.

Applicability of the monitoring

The implementation of a groundwater monitoring network with systematic and level-accurate sampling, uniform sampling technique, a broad list of analysis parameters, great analysis accuracy, point-, line- and volume monitoring, and a geographically balanced distribution of monitoring catchments, makes it possible to generate reliable series of chronometrie data, for a broad list of common or rare parameters. And for the importance, for both the protection of the groundwater, and for the science, is it possible, to forecast the groundwater quality and quantity.

Short cut of aquifers

Due to the implementation of the level accurate sampling, at least one possible troublesome effect, has been identified (short cut of aquifers), and further investigations on the matter can be carried out.

Recommendations

Based on these results, is it recommended to take the following preventive arrangements in consideration:

- Making more stringent control about drilling operations. A special attention, ought to be offered, to the risk of increasing the dispersion of a pollution, when plumes of pollution from waste disposals sites, are investigated and penetrated by drilling operations or of wells with long screened sections.

It is recommended to initiate the following invstigations:

- Investigations on existing water wells, for the reason, to determinate the effect, on the general water quality.
- Development of restoration techniques for leaching wells, for the purpose to protect the groundwater ressources from leaching through bad constructed wells.

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Field investigations of Preferential Flow Behaviour

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Summary

Chloride was used in a tracer study to document and qualitatively evaluate the effects of preferential flow at field scale. Very fast response of a subsurface drain at 1.3 m depth upon surface application of water and solute that can not be explained by a displacement flow mechanism was taken as an indication of preferential flow. Further documentation was obtained from distinct bypass flow manifesting itself in two ways, one being surface applied water free of chloride bypassing a soil matrix with high chloride content, the second being surface applied chloride bypassing a soil matrix with little chloride content. The implication of preferential flow for leaching of surface applied fertilizers and pesticides is discussed.

Introduction

Preferential flow

Preferential flow is an established term and a recognized phenomenon in water and solute transport in soil systems.

Preferential flow refers to a flow mechanism where transport of water and dissolved or suspended substances is primarily associated with a smaller fraction of the total soil pore volume. There is a whole spectrum of possible flow situations. One extreme is that the majority of the soil is totally bypassed by the fluid, and active transport only occurs in unhindered flowpaths, the intermediate being a random distribution of flowrates throughout the porous medium, to the other extreme being a uniform flow field. This range of flow situations is determined by the soil physical properties as well as the scale of observation. At the smallest scale, the pore scale, water will always move preferentially in the center of the soil voids. If the soil is texturally homogeneous and uniform, these microscopic effects will average out when the observation scale increases and macroscopic approaches using Darcy and Fick's law will be applicable in the flow description (Nielsen et al. 1986).

If, however, the soil exhibits heterogeneity or discontinuity in the soil physical properties at the larger scale the simple macroscopic approach is no longer sufficient. It has been proposed to include stochastic and geostatistic methods in the traditional approach to account for the randomness of soil and hydraulic properties (see e.g. reviews by Warrick and Nielsen, 1980, and Dagan et al., 1988). However, preferential flow represents a further degree of complexity. Discontinuities in the soil characteristics give distinct different flow behaviour, and the traditional one-domain macroscopic approach (applied either in a deterministic or stochastic sense) seems inadequate.

Cause of preferential flow

Preferential flow can be related to discontinuities in poresize, meaning that water and solutes will be transported primarily in relatively large and continuous pores or openings (macropores) in the soil whenever the conditions are favourable.

Macropores can be indigenous to the soil like cracks in desiccating clay soils, or interpedal voids between surface aggregates or subsurface structural blocks or peds, or they can be created biologically by borrowing soil animals (e.g. earthworms and ants) or roots.

A distinct definition of a macropore has been proposed based on an equivalent diameter (see e.g. Luxmoore et al., 1990), but it is arbitrary since many other factors influence the potential of a pore to promote preferential flow, i.e. its continuity and orientation, its tortuousity, its surface characteristics, its connection to the surface and its stability.

The effect of preferential flow

The effects of preferential flow have been observed in numerous field and laboratory studies (for references see Thomas & Phillips, 1979, Beven & Germann, 1982, White, 1985). In laboratory experiments involving soil cores accelerated initial breakthrough of surface applied substances with asymmetrical long tailed breakthrough curves have been attributed to preferential flow phenomena. Also the non-homogeneous wetting of soil cores is associated with a bypass flow mechanism.

In field situations it has been possible to detect surface applied substances at depth far in advance of the time corresponding to a leached amount of one pore volume, indicating preferential flow. Sampling has been done through subsurface drains (Everts et al., 1989), lysimeters (Andreini & Steenhuis, 1990) or porous suction cups (Jardine et al., 1990).

The two first-mentioned works also describe the noted effect on chemicals with adsorbing properties, namely a decreased retardation in the soil matrix with increasing dominance of preferential flow. The implications of these findings is that fertilizers and pesticides applied to the soil surface might be carried below the root zone and into drains or shallow aquifers with a contamination of surface and groundwater systems and little intended crop related benefit as a result (Barraclough et al., 1983). The direct conduits to drains and groundwater might also be relevant in the consideration of atmospheric acidic deposition. With little residence time and hence contact possibilities with neutralizing agents in the soil the rainwater will be transported fairly unaffected to receiving water bodies (Potter et al., 1988 and Shanley & Peters, 1988). Increased infiltration associated with macropores in the soil surface reduces the risk of soil erosion in erosion prone areas due to less surface runoff, whereas slope stability might be affected positively or adversely depending on the drainage possibilities (Cheng, 1988).

Rain or irrigation water will be more or less available for plants compared to a less-macroporous soil depending on whether or not the macropores extend beyond the rootzone (van Stiphout et al., 1987).

Untackled problems

In field and laboratory experiments the extent and effect of macropore flow have been observed to depend on factors such as rainfall intensity or solute application rate and soil moisture conditions. An increase in application rate (Trudgill & Coles, 1988, Kanchanasut & Scotter, 1982 and Kluitenberg & Horton, 1990) as well as moisture content (Trudgill & Coles, 1988 among others) generally favours preferential flow which is in accordance with the conceptual picture of the flow mechanisms. Flow into larger voids in the soil surface is initiated when the infiltration capacity of the surrounding soil matrix is exceeded or ponding occurs. For an initially dry soil the macropores will be less effective because of lateral loss to the soil matrix. However, the effect of soil moisture is ambiguous. It has been reported that fast response in initially dry soil could be associated with hydrophobic conditions of the soil surface and worm hole channels (Edwards et al., 1989), and with clay cracks that swell upon wetting (Reid & Parkinson, 1984). To account for these factors modeling approaches that can accept highly variable and multi-pulse inputs are necessary. Furthermore, the physical relations responsible for preferential flow need further systematic investigation in order to find more quantitative descriptions.

Large-scale effects

The effect of preferential flow is typically related to the hydrological response of larger areas and diffuse contamination sources. Hence in gaining further insight into the problem a relevant observation scale is equivalent to the extent of such contamination. In agricultural aspects it could be a field or an ensemble of fields. A practical and convenient way of observing flow responses is by means of subsurface drainage systems which was pointed out by Richard & Steenhuis (1988). In Denmark this is feasible since extensive areas already have artificial drainage facilities. The spatial variability of preferential flow which might be pronounced on a smaller scale (Andreini & Steenhuis, 1990) will be integrated to give a spatially averaged response. Also for distributed catchment models such as the SHE-model (Abbott et al., 1986) the unit grid size is principally equivalent to the field size making parameter determination at this scale important.

In this paper the preliminary results of a tracer study on the intake area of a single drain are presented. The purpose is to examine the effect of preferential flow at field scale and especially the influence of water application rate and soil moisture condition. Furthermore, the application timing for a conservative tracer is studied in relation to the retaining capacity of the soil. The hydrological response of a larger area, encompassing this field site, is investigated in terms of preferential flow effects by Engesgaard & Jensen (1990).

Field site

The field site is located within the farmland of Syv Creek catchment in the central part of Zealand, Denmark (Fig. 1). The soil is developed mainly on clayey glacial till but with a rather mixed texture ranging in places from clayey to pure sandy. Soil type is a pseudo gley brown earth with the gley development evident below approximately 80 cm indicating partly imperfect drainage. The drainage system consists of 40-50 year old tile drains (diameter 5.5 cm) installed at 120-140 cm depth and at individual spacings of about 20 m. The topography is rather flat with a slope less than 1 percent. The field site had been cropped with wheat during the season prior to the experiment which took place in the spring of 1990.

From excavation of a soil profile visual macrostructure in the form of worm holes and root channels in the upper soil layers and peds of different order and size in the lower layers was noted. Worm holes and root channels were predominantly cylindrical and vertical with diameters of 1-3 mm and with an intensity in a horizontal plane of approximately 5 per 10 cm^2. Between 40 and 120 cm depth distinct peds of 1-5 cm were seen.

The total intake area of the drain involved in the tracer study was approximately 0.2 ha. For reasons explained later the site was divided into two experimental plots which were investigated separately (Fig. 2).

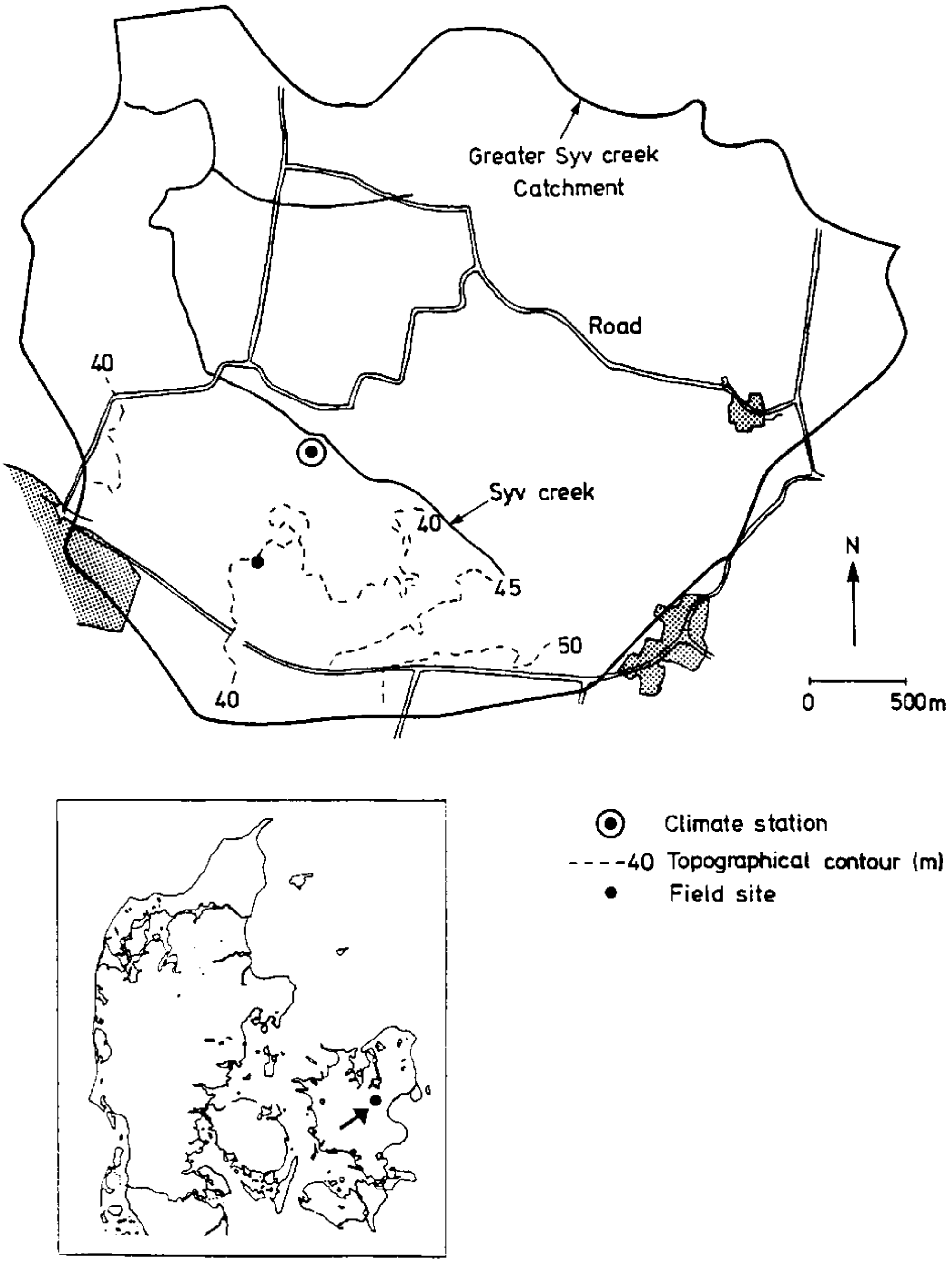

Fig. 1 Location of field site.

Chloride application

The chloride-ion was chosen as an appropriate tracer. It has transport properties equivalent to the nitrate-ion which is of major concern in relation to contamination from fertilizers, yet it is practically chemically stable and biologically inactive. Furthermore, detection via a chloride specific electrode made continuous monitoring of the tracer in the drainage outflow possible.

The chloride tracer was applied as flakes of 77/80% $CaCl_2 \cdot 2H_2O$ by manually spreading on the soil surface, attempting a high degree of uniformity. An amount of 0.75 kg Cl/m^2 was applied in 2 m wide and approximately 50 m long strips around the drain line leaving a 1 m chloride-free zone to each side of the drain.

This was done to minimize chloride movement through soil that might have been disturbed by the tile installation (Fig. 2). For plot 2 chloride was only applied to one side of the drain since results from Plot 1 showed that a lateral flow away from the drain could be responsible for chloride loss.

The two experimental periods were as folows with the first date indicating the day of chloride application:

Plot 1:	8/3 - 12/4
Plot 2:	26/4 - 28/4

It is seen that the first plot was monitored almost twelve times longer than the second.

Monitoring program

Instrumentation for monitoring flow rate and chloride concentration of the drainage water was installed in a collector well at the lower end of the field site (Fig. 2.). Water level in a 60 l container were measured with 5 minute intervals and converted to flow rate. An automatic pump released the water to the downstream end of the drainage system whenever the container was filled. The ion selective electrode was placed in a separate much smaller container that continuously received drainage water from the bottom and was equipped with continuous stirring. The data were collected by a datalogger.

Piezometres were placed inside as well as outside the plots (Fig. 2) to follow the groundwater level fluctuations.

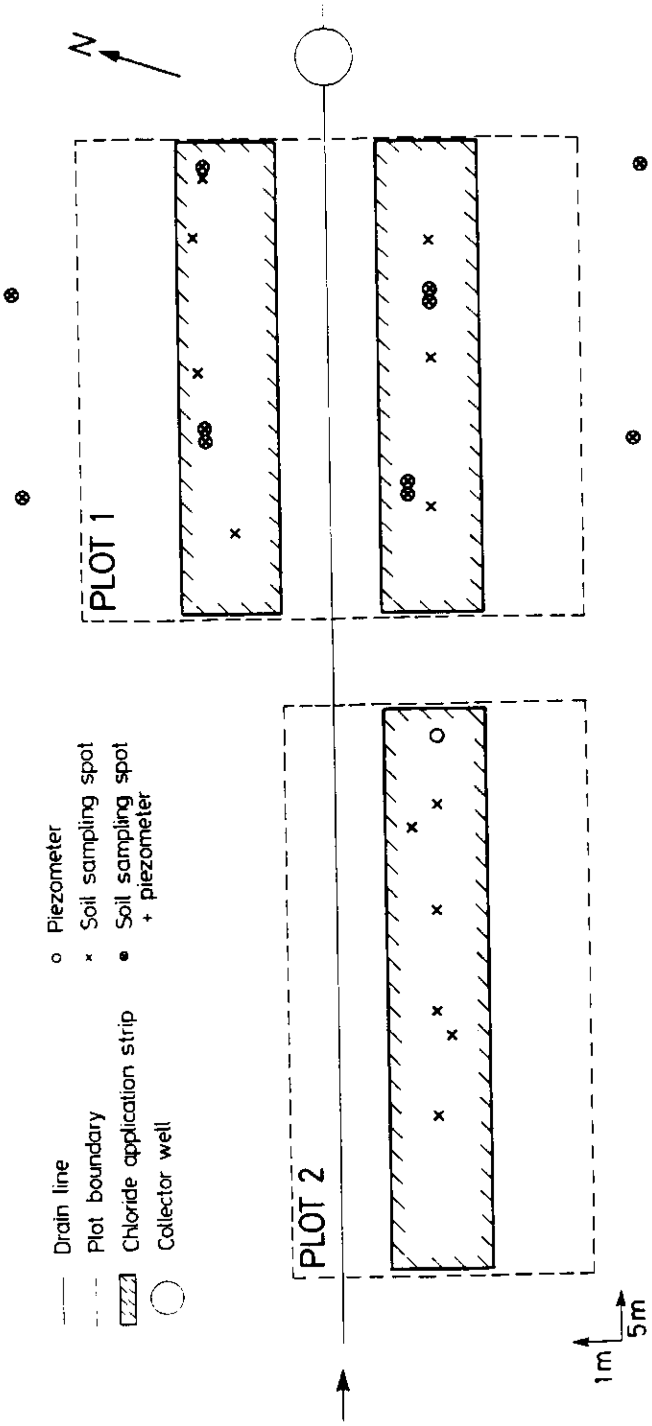

Fig. 2 Schematic plane view of the experimental field.

Soil profile samples were taken (Fig. 2) prior to and after the experimentation periods for a mass balance analysis of water and chloride. Sampling was done at depth increments of 20 cm with a 6 cm diameter hand auger to a depth ranging from 80-150 cm, depending on accessibility and groundwater level. Water extracts from these samples were analysed photometrically using flow injection analysis, except for final soil samples from Plot 2, which were analysed by the argentometric method.
Precipitation data on an hourly basis were obtained from a climatological station located less than 1 km from the field site.

Results

The field installation of the ion selective electrode together with unreliable performance of the datalogger posed problems in the beginning of the experiment. Satisfactory implementation of the chloride measurement was not obtained till the end of the first experimental period which means that the chloride data from Plot 1 reported here originate from grap samples taken at irregular times, but with higher frequency during high flow periods (Fig. 3). Ground water levels were monitored in conjunction with the water sampling.

Plot 1

As seen from Fig. 3 chloride was applied to Plot 1 prior to an increase in drainage flow. No breakthrough of chloride was detected over the 28 day period that followed. At that time drainage flow had ceased due to an insufficient supply from rain and an increase in evapotranspiration. Water was then applied artificially from two hoses which could be moved manually over the plot including a zone of 1 m around the edges. The irrigation intensity was approximately 6 mm/hr, and irrigation was carried out over a two day period, about 3 hrs each day. Surface ponding during irrigation was observed while surface runoff was restricted to distribution of water within the microrelief of the nearby soil surface. A sudden rise in drainage flow was observed 2.5 hours after the irrigation was started on the second day. This flow peak was, however, still not associated with an increase in the chloride concentration.

An interpretation based on these findings is that the chloride initially applied at the soil surface had infiltrated into the soil matrix together with the rainwater and a percolation and diffusion process had distributed the solute in the upper soil layers. The gradual rise in drainage flow in the beginning of the experiment is likely to be caused mainly by a displacement type of flow. For the irrigated period the rise in flow was abrupt indicating that preferential flow paths through the soil profile were activated. This is supported by the fact that the drainage water was practically chloride-free and hence must have originated from water bypassing the chloride in the soil matrix.

Plot 2

The tracer experiment was repeated on Plot 2 with the aim of detecting the preferential flow directly, that is by a rapid breakthrough of the chloride. Water was mainly supplied by intermittent irrigation and again at fairly high intensities (approx. 11 mm/hr). Plot 1 was covered with a plastic sheet to avoid interference from this plot in case of natural rain. A moveable perforated hose that could be controlled from outside the irrigated area was used to minimize soil surface disturbance which may have been significant during the first experimental period. Again surface ponding, but minimal surface runoff was observed. Chloride was applied when the drain had started running again and just prior to an irrigation event (Fig. 4). The peaky appearance of the drainflow as before suggests preferential flow. In this case it is supported by the fact that chloride is also transported to the drain practically instantaneously, again an indication of a bypass mechanism. Hence a fraction of the surface applied chloride was not retained in the soil matrix and leaching occurred.

Condition for preferential flow

From this study it can be inferred that relatively high water application rates are necessary to initiate preferential flow. Rates of 4 mm/hr which corresponds to the heaviest rain during the start of the first experiment did not produce distinct signs of preferential flow whereas an intensity of 6 mm/hr did. However, the existence of a distinct threshold value of application rate is not stated, since other factors are influencial.

If the drain was not running prior to high intensity application no immediate response in drainage flow was observed. Parts of the applied water could be conducted in preferential flow paths through the mainly unsaturated soil profile with lateral loss to the soil matrix and recharge to the ground water below the drains leading to drainage flow once the ground water level reached the drains. The exact mechanism for flow under ponded yet unsaturated conditions can not be evaluated from this experiment.

Condition for leaching

Preferential flow and fast breakthrough of water is associated with leaching of surface applied substances if the application is carried out just prior to the occurrence of preferential flow. A second peak in the chloride concentration was observed in the second experiment when one day had elapsed since the tracer application indicating that some chloride was still free to move in preferential flowpaths. White et al. (1985) and Trudgill & Coles

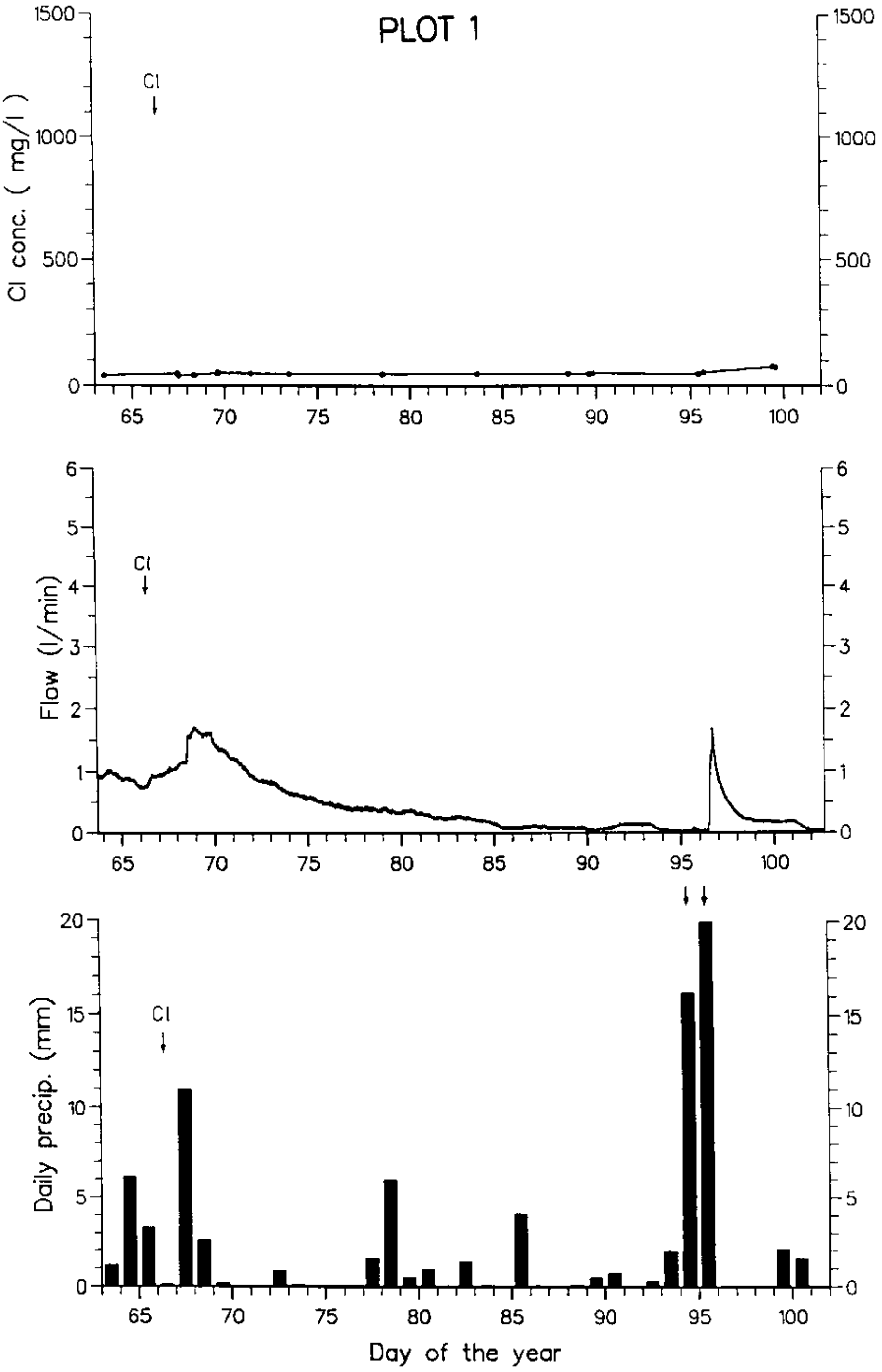

Fig. 3 Chloride concentration and flow rate in drain water outflow and dailyprecipitation for Plot 1. Arrows indicate application of chloride and water.

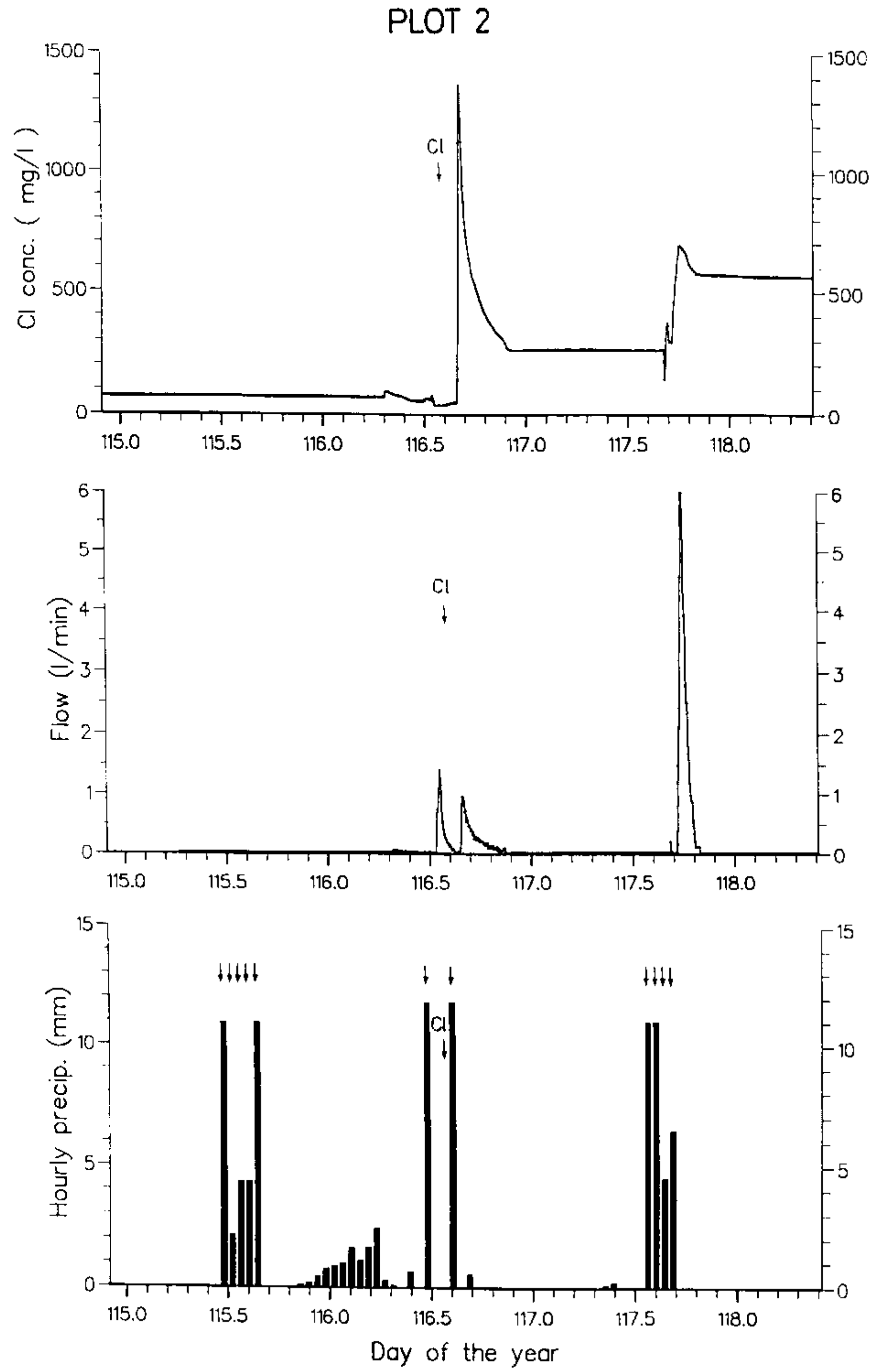

Fig. 4 Chloride concentration and flow rate in drain water outflow and hourly precipitation for Plot 2. Arrows indicate application of chloride and water.

(1988) have likewise called attention to the timing of surface application in relation to subsequent flow conditions. Besides the application time in relation to flow conditions factors such as the application method could be important for the leaching potential of surface applied substances. Application of chloride in dissolved rather than solid form might have generated a different leaching pattern. This issue is addressed by Kanchanasut & Scotter (1982), but no experimental work has to the authors' knowledge been published on the matter.

Mass balance analysis

A chloride mass balance was attempted to get indications of the relative fate of the applied tracer. Also, a water mass balance was carried out to evaluate the recovery of water and hence indirectly of chloride. The results for the two plots are presented in Figure 5 and Table 1 for chloride and water, respectively. The amount of chloride accumulated in the soil profile is calculated as the difference in chloride content prior to and after the experiments. Areally averaged values for each depth increment of 20 cm are used.

In Plot 1 and Plot 2 50% and 82%, respectively, of the total amounts of chloride applied at the soil surface were detected as drainage outflow and an increase in the soil storage. The amount of chloride not accounted for can likely be attributed to variability and uncertainty in the quantifications. The figure associated with greatest uncertainty is the amount of accumulated chloride in the soil, partly because of the large spatial variability over the plot and partly because of lack of soil sampling of the very top soil layer mainly consisting of organic matter. The average chloride concentration in this layer could be substantially larger than just a short distance below. This is emphasized by the obtained chloride profiles at both plots after the experiments (Fig. 6).

Chloride and water profiles

The chloride concentration after the experiments decreases with depth with a maximum concentration at the first soil sample depth. Of the total chloride content in the soil profile to a depth of 140 cm an estimated amount corresponding to 77% and 64% were found in the upper 40 cm of the soil in the two plots, respectively. The lack of an apparent maximum in the chloride concentration at depth could be explained by a more continuous supply of chloride at the soil surface, rather than a pulse-type application. This is possible if the $CaCl_2$-flakes were not dissolved during the first irrigation event after application. It could also explain that a secondary peak in the chloride

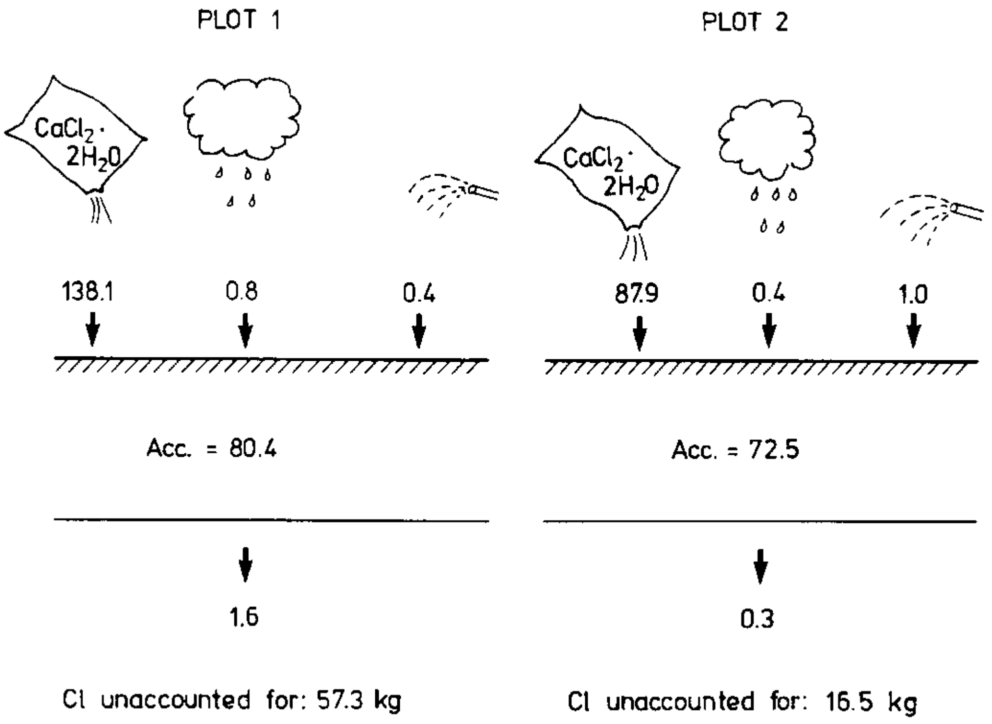

Fig. 5 Chloride mass balance. Figures in kg.

concentration was observed when preferential flow started drainage flow a day later during the second experiment. A similar pattern in tracer concentration with several individual peaks coinciding with high input rates were found in a comparable study (Richard & Steenhuis, 1988). This further underlines the importance of additional investigation into the effect of surface application method.

Other fates of chloride not accounted for in the mass balance could be uptake by vegetation, loss to deep percolation and to lateral flow out of the field site. Piezometer measurements outside Plot 1 indicated that water flow could be transverse to the drain direction. Plant uptake was probably minor, even though it was not confirmed by measurements. Van Ommen et

Table 1: Water balance. Figures in m^3.

	Plot 1	Plot 2
Rain	112	25.3
Irrigation	14	19.7
Drainage	25	0.5
Balance	101	44.5
	~ 1 mm/day	~ 7 mm/day

al. (1989a) report a 3% loss of bromide tracer in a drainage study. Loss to deep percolation could be significant especially since the drain is barely actively flowing during the experiments, and hence the hydraulic gradient towards the drain is small. During no-drainage flowsituations water is directly routed to below drain depth. To support the chloride loss due to these sources the water balance also indicate loss of water (Table 1). A larger loss per day for the second experiment could be explained by an increase in evapotranspiration with denser plant cover and more loss to deep percolation since drainage flow was more discontinuous than in the first experiment. In agreement with this the water content in Plot 1 was fairly uniform throughout the soil profile and practically equal before and after the experiment. In Plot 2 more variation is seen, and the water content after the experiment is smaller (Fig. 7).

The chloride detected in the drainage water amounted to 1.2% and 0.3% of the total amount of chloride applied to the soil surface in the two experiments, respectively, while the amount of drainage water from the plots corresponded to 20% and 1%. This means that the drainage water from the second plot was five times as chloride enriched as the water from the first plot, another way of detecting that leaching from surface applied chloride occurred preferentially in the second plot.

Discussion

The importance of preferential flow

The extent and the importance of the leaching of surface applied substances primarily caused by preferential flow is difficult to judge from this preliminary study. Based on figures of retrieved tracer amounts in the drainage water of less than 1% of the

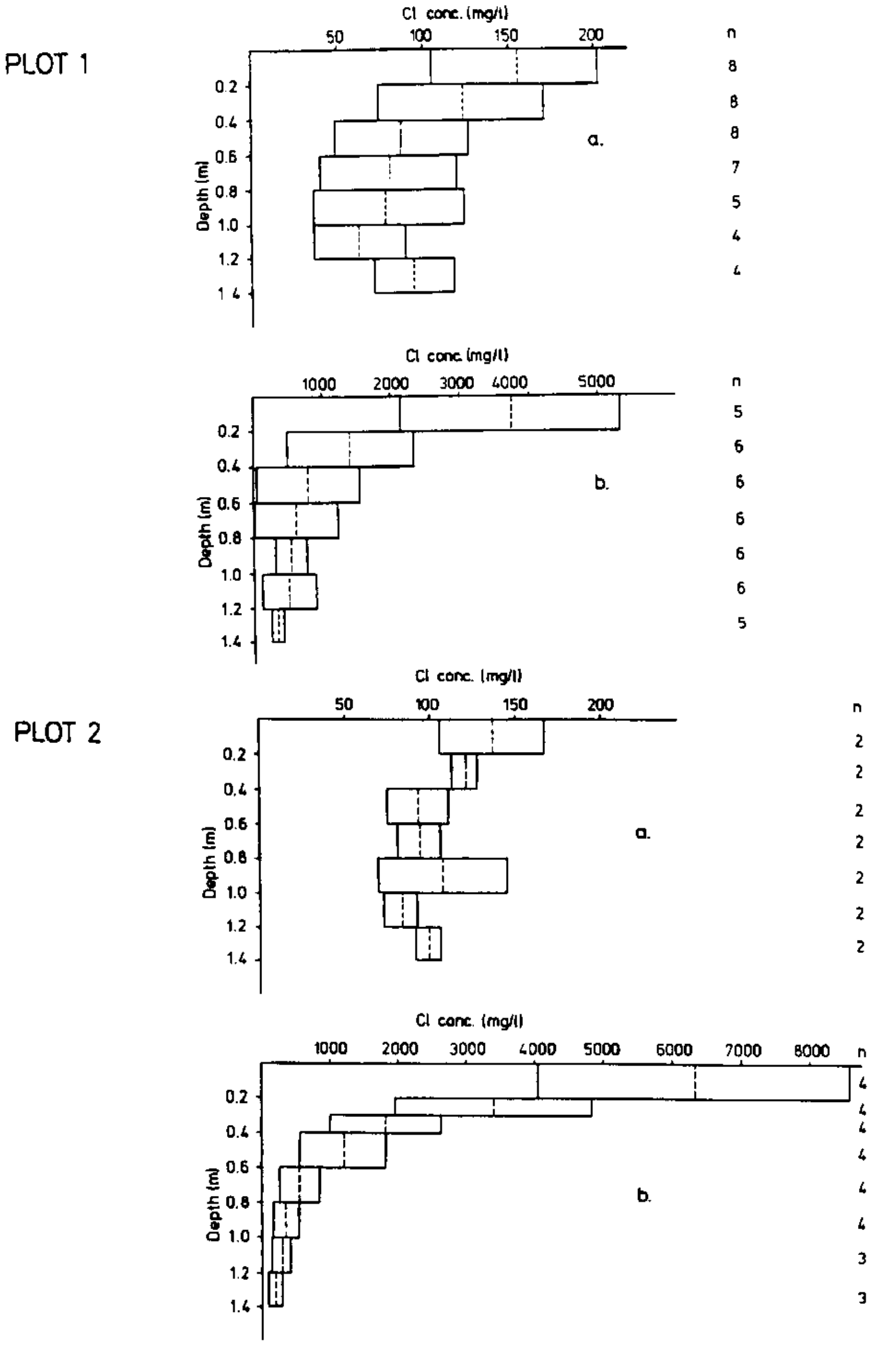

Fig. 6 Chloride concentration profiles, (a.) prior to, (b.) after the experiments. n indicates number of samples.

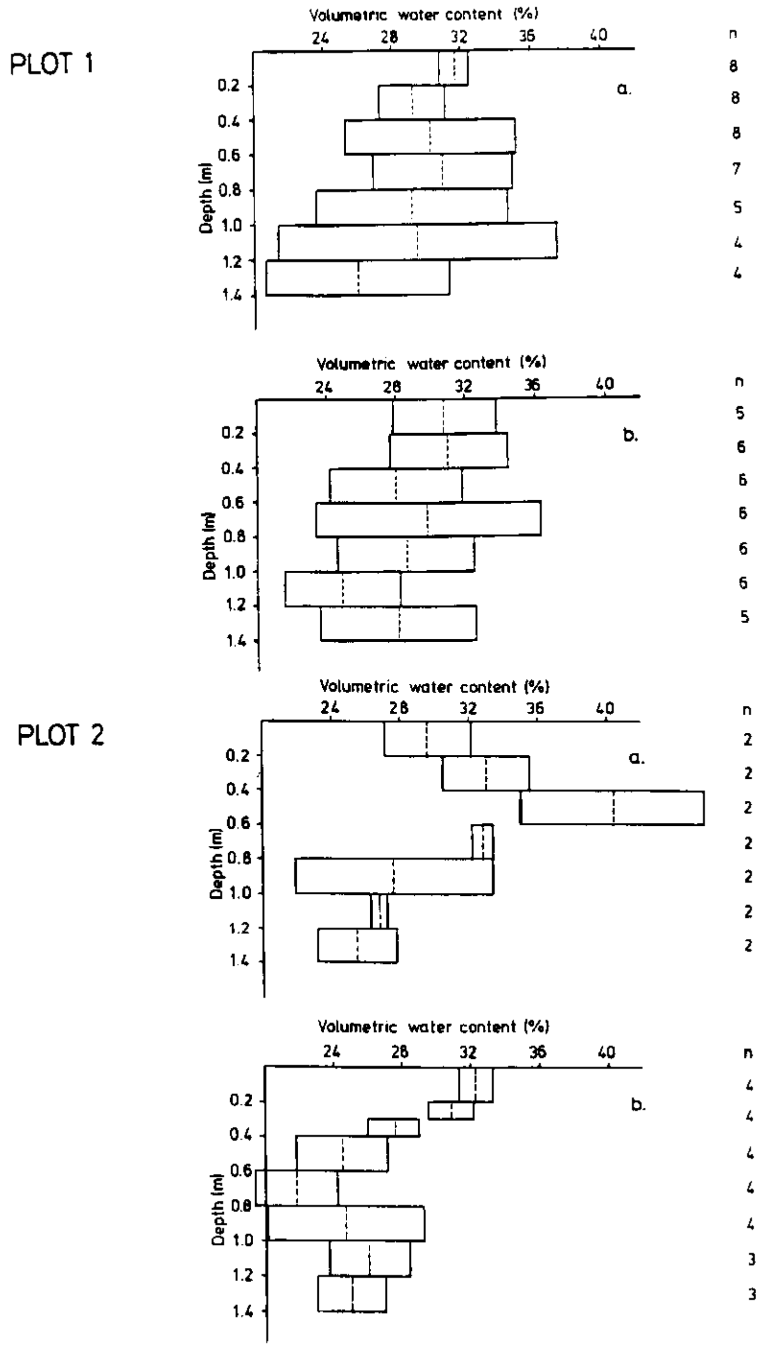

Fig. 7 Volumetric water content profiles, (a.) prior to, (b.) after the experiments. *n* indicates number of samples.

applied amount the significance appears to be minor. However, some aspects related to the experimental conditions might be crucial to this statement and need further investigations.

Need for further studies

Firstly, this experiment was carried out at the end of the natural yearly drainage season and the drain system was barely active during the experiment where preferential flow was observed. It was stated that a loss of chloride from preferential flow to deeper soil layers is possible, but quantification has not been attempted. Performing the tracer study during a period of larger and more reliable flow in the drain could give a better measure of the extent of leaching due to preferential flow.

Secondly, a more intensive and preferably continuous monitoring of the groundwater level to a depth below the drain along with soil water content measurements would yield further inside into the hydrological response of the system.

Thirdly, the application method of the tracer might show to be important as pointed out in this study. Controlled experiments that can be reproduced under different application conditions need to be carried out to shed light on this aspect.

Conclusion

Preferential flow effects at the field scale have been observed in a combined tracer/drainage study. High water application rates leading to surface ponding conditions excites the preferential flow mechanisms. Unfavourable drainage conditions made the evaluation of the extent and importance of leaching of surface applied substances by preferential flow inconclusive. However, it appears that the greatest risk of loss of surface applied substances, such as fertilizers and pesticides caused by bypassing is prevalent when a heavy rain succeeds the application within a relatively short time, in this study found to be of the order of one day. Further research is needed to evaluate the effect of soil moisture conditions and surface application method.

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