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# Nitrate reduction in the subsoil

*I. Introductory studies of the nitrate reduction in the subsoil, and its influence on ground water quality*

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**Summary**
This paper is the first in a series of four presenting the project: Nitrate reduction in the subsoil. The background for, and our intention with the project are given. Some general considerations about the water consumption and the ground water formation are mentioned. The Danish ground water quality with respect to nitrate content is elucidated, and a selection of foreign investigations is taken into account. The use of nitrogen fertilizer and its relation to ground water quality is commented. An introduction to the investigation in the field of inorganic chemical nitrate reduction in soil is given.

## Introduction

Through the last few decennia it has become clear, that protective measures have to be taken in order to prevent the drinking water resources of the world from being polluted in several ways. The problems have arisen in the rich countries, and they are also arising in the developing countries due to urbanization, industrialization and the growing use of agricultural chemicals.

The drinking water resources include surface water and ground water. With regard to surface water only a few remarks. The main pollution sources are urban or industrial waste water, and to some degree nitrogen leached from agricultural areas. These types of pollution may lead to eutrophications in streams and lakes with anaerobic putrefactions as a result. These problems may however only be of a technical and economical nature; a sufficiently large effort can make the protection nearly complete.

It is necessary to have knowledge about reactions and mechanisms of nature, protecting against man-induced pollution. Because of the very complex interactions between climatical, soil chemical and soil physical elements, the only way of protecting ground water is to trace and control the pollution sources.

In this paper an estimation of the problems will be given, and in three other papers a specific work on the nitrate reduction in the subsoil will be published.

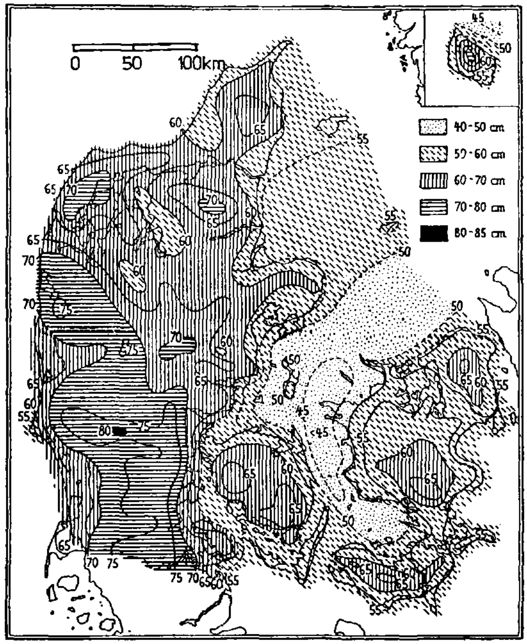
### *The ground water catchment and formation in Denmark*

In Denmark the primary source of drinking water is secured through ground water, and only 3–5 per cent of the drinking water is derived from surface water. *Berthelsen* (1970) estimates the annual consumption of water to be 750 mill. $m^3$, which corresponds to 3 per cent of the annual precipitation. Table 1 shows the quantitative distribution of the water consumption in Denmark. It is evident from Table 1 that the main consumers are the house-

*Table 1. The annual Danish water consumption, distributed on various consumption groups. Estimations made for the years 1970 and 2000* (Berthelsen, *1970*)

| | Consumption in mill. $m^3$ 1970 | Consumption in mill. $m^3$ 2000 |
|---|---|---|
| Households | 340 | 600 |
| Animal husbandry | 105 | 130 |
| Industry | 185 | 280 |
| Irrigation | 20 | 25 |
| Pisciculture | 78 | 40 |
| Summerhouses | 7 | 35 |
| Total | 735 | 1110 |

holds and the industry. Consequently the main catchment areas often are relatively small and placed near the consumers (towns, cities, etc.), and where, at the same time,, the ground water re-establishment is relatively quick.




the danish meteorological institute

Fig. 1. The annual mean precipitation in Denmark.

### *Climatical conditions for ground water formation*

The formation of ground water is primarily caused by an excess of precipitation. Figure 1 shows the mean annual precipitation, and in Table 2 the water balance is shown for the whole country. The evapotranspiration is relatively constant and depends chiefly on the surrounding physical factors, such as the net-radiation and the wind.

The vertical drainage (drainage towards the ground water) depends on the geological and mineralogical conditions in the deeper soil layers, which the water passes through. It also depends on the amount of ground water pumped from a given area. The 100 mm vertical drainage, as indicated in Table 2, assumes adequate geological conditions, and near to maximum pumping activity on the ground water reservoir. Under these conditions, the most sensible parameter in the water balance, is the direct run-off: A change in one of the other parameters will greatly change this. (The direct run-off includes surface run-off and drainage to water course, etc.).

*Table 2. The annual water balance for Denmark (partly after* Aslyng, *1968 and* Berthelsen, *1970)*

| | |
|---|---|
| Precipitation | 500–800 mm |
| Evapotranspiration | 350–450 mm |
| Direct run-off (incl. art. drain) | 0–400 mm |
| Vertical drainage | 0–100 mm |

### *Geological conditions for ground water formation*

The Danish underground above the bed-rock is mainly from the Mesozoic and Cainozoic eras. The deposits forming good ground water reservoirs are the Cretaceous white chalk, bryozoan limestone, coral limestone, the Tertiary sandy marine sediments from different stages and the Quaternary, mainly glacial deposits. Figure 2 shows the pre-Quaternary and figure 3 the Quaternary formations.

The underground in the North of Jylland, Djursland, the North and South of Sjælland and Lolland-Falster is dominated by deposits from the Cretaceous period. Structurally the different chalck and limestone layers are very

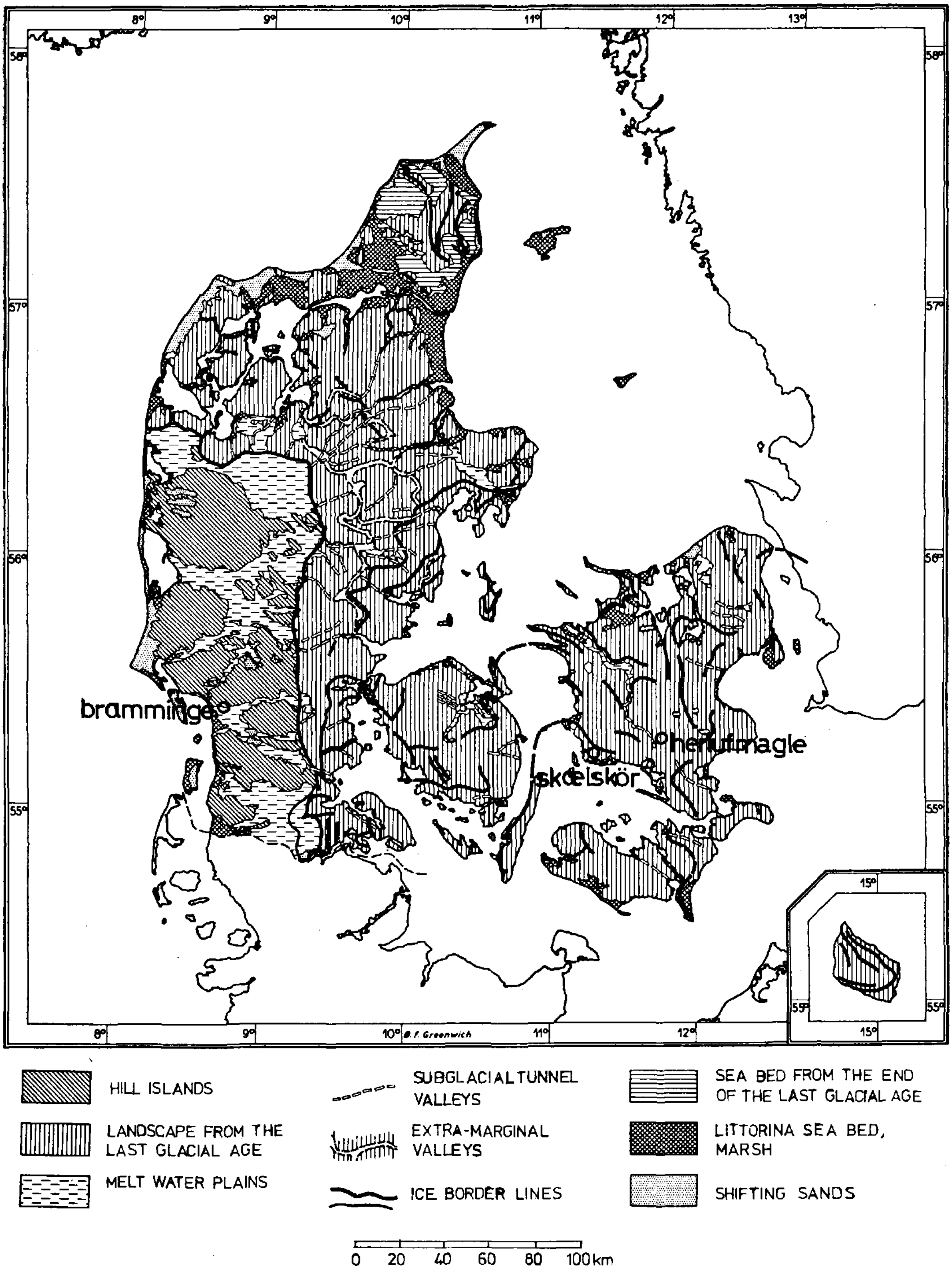



Fig. 2. Geological map of Denmark. The formations at the basis of the Quaternary.

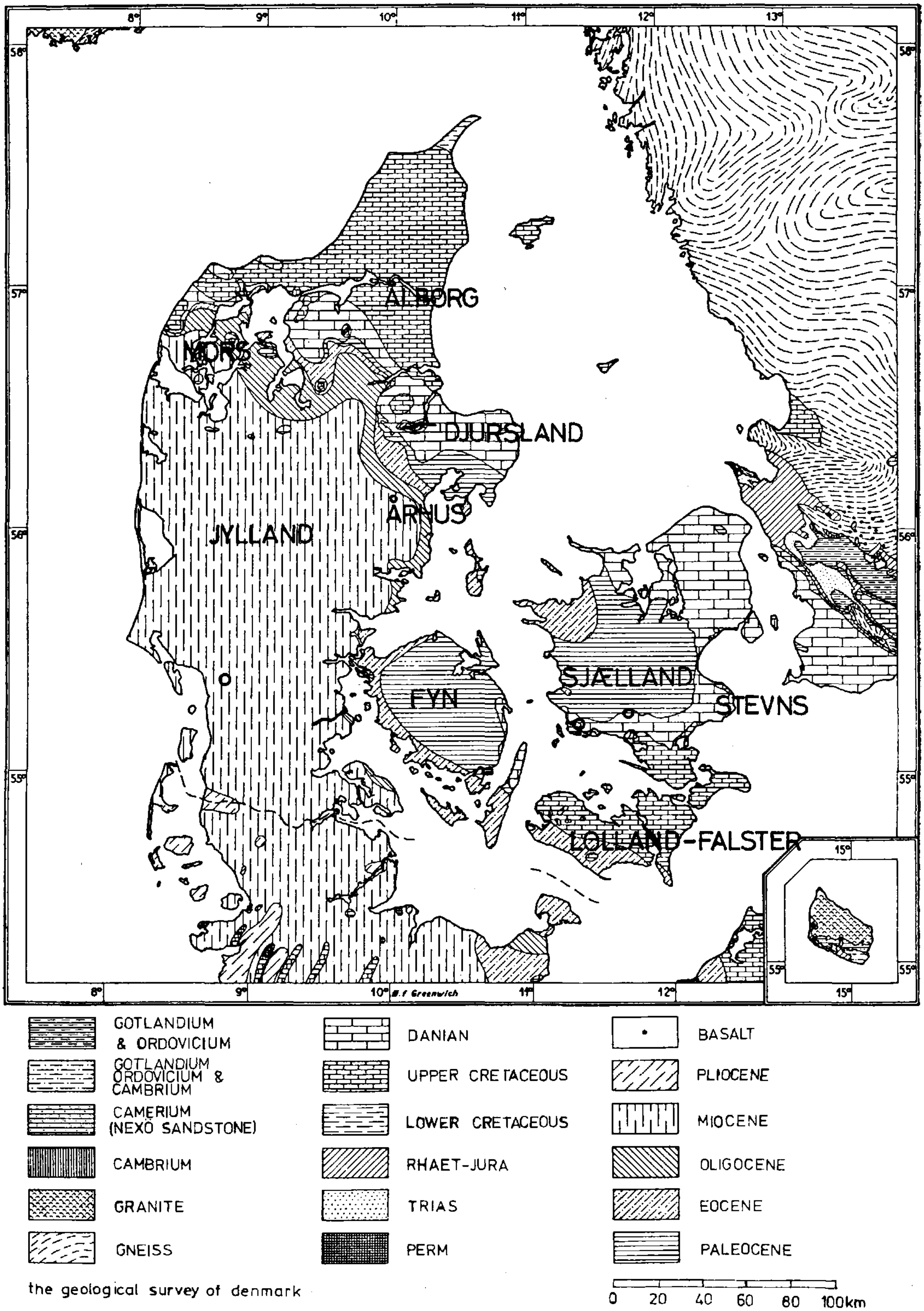



Fig. 3. Geological map of Denmark. Main features of the Quaternary landscape.

heterogenous, changing in all intermedia between coarseporous to fissured and compact bed-rock. These layers are very often excellent as reservoirs of water, and at Sjælland the utilization of this water is great.

Deposits from the Tertiary period constitutes the substratum in the rest of the country. Within a zone from Mors in north-west across Jylland over Århus to Fyn and Sjælland in south-east, it is glauconitic sandy chalk and Kerteminde clay from the Paleocene. Both of these act as poor water reservoirs. Below the rest of Jylland, Miocene deposits consisting of micacoeous clay and sand with layers of gravel may be very excellent as water reservoirs, but in some places the water is discoloured by lignite.

The superjacent Quaternary sediment consist mainly of glacial deposits as tills and outwashed materials, which make up nearly 100 per cent of the surface. At the islands Sjælland and Fyn it has been evidenced that areas with local gravel and sand deposits, e. g. in subglacial tunnel valleys, create the necessary conditions for the formation of ground water, but these areas are small. The conditions are the same in the North and the East of Jylland, but in the Southwest outwashed sand from the last glaciation (*Würm*) cover the land, only with a few hill islands from the *Riss* glaciation, reaching the day. In the coarse outwashed (alluvial) deposits, the ground water formation is very fast, but because of the relatively high ground water level some complications arise, as pointed out in the next section.

The practicabilities of getting ground water in Denmark in general are shown in Figure 4. While preparing the map attention only has been given to the physical conditions of the soil and to the intrusion of sea water (*Berthelsen,* 1970).

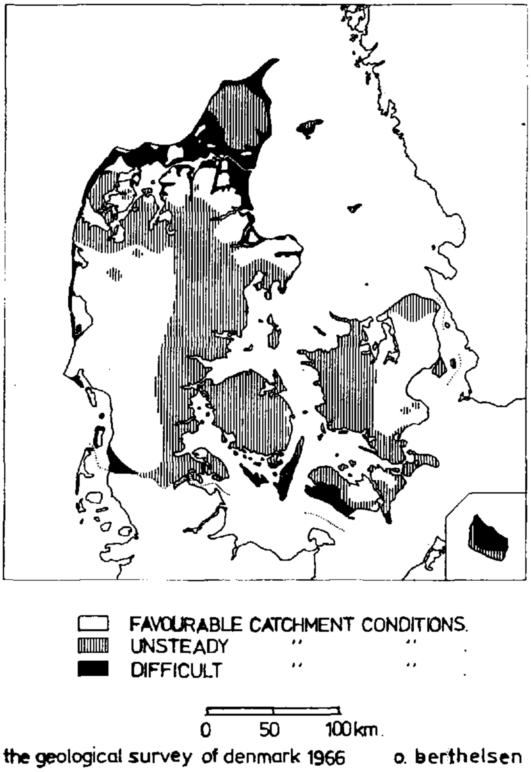



Fig. 4. The possibilities of ground water catchment in Denmark.

*Chemical properties of the soil and of the ground water*

The quality of the ground water depends on the chemical composition of the deposits, which the water has passed through. The hydraulic conductivity of the sediments determines the time in which water and a given strata have contact for chemical interchange. Therefore, in areas with coarse-textured deposits, like the previous mentioned outwashed sand, chemical reactions between the mineral particle surfaces and the seepage water will be very incomplete. The same may happen in clayey soils where cracks and fissures conduct an extremely large part of the water. In this case the water only contacts a very small part of the soil matrix. Tills often have this structure, e. g. in the thin layer of till which lies above the limestone near Ålborg and the peninsula of Stevns in Sjælland. On the other hand, a homogenous clayey deposit with good conditions for chemical interchanging, often have a hydraulic conductivity which does not allow the ground water table to be reestablished after pumping.

The chemical processes under consideration may be interchanging cations and anions, adsorption of dissolved organic matter, and/or chemical reactions between dissolved and adsorbed substances. The following is concentrated on parts of the nitrogen metabolism in the soil and the substrata, and its relation to the ground water quality. The content of nitrogenous substances as nitrate and nitrite in the cround water depends om the biological activity in the root zone, the amount of seepage, and the chemical conditions in the subsoil.

*The use of nitrogen fertilizer in agriculture*
A pollution source that in some respect may be called natural, is the leaching of nitrate from the root zone. It is natural in the sense that leaching occurs in all plant communities. Agricultural methods, including the use of large amounts of fertilizers to monocultures, have however increased the potentiality of nitrate leaching.

It is not the aim of this paper to discuss the hazards of diseases which may be caused by nitrate-holding drinking water. Examples of relevant literature are *Cornblath & Hartmann* (1948), *Rosenfield & Huston* (1950), *Phillips* (1971), *Aune* (1972), *Klarns & Tamplin* (1972).

The mean supply of nitrogen in Danish agriculture and an assessment of the removed nitrogen are shown in Table 3. The use of artificial nitrogen fertilizers have increased nearly three times during the last 10 years (47 kg/ha, 1962–63). The item 0–25 kg N/ha/year (leaching to underground) is that of special interest in this connection. The only N-containing compound in the soil with high mobility is the nitrate ion, and a leaching of e. g. 25 kg nitrate-N/ha/year will cause a N-concentration equal to 6.25 ppm per metre of ground water in the soil (assuming no nitrate reduction in the soil and a soil density (dry): 1.6 g/cm$^3$).

*Table 3. The supply of nitrogen in Danish agriculture, and the removal of nitrogen from the field, 1972/73 and 1973 (partly after* Aslyng, *1971)*

| Source (to the field) | kg N/ha |
|---|---|
| Art. fertilizers | 113 |
| Manure | 50 |
| Precipitation | 15– 20 |
| N-fixation in soil | 30– 40 |
| Total | 208–223 |
| Removed from the field by | kg N/ha |
| Crop | 120 |
| Evaporation to air | 40– 50 |
| Leaching to drain (surface) | 10– 40 |
| Leaching to underground | 0– 25 |
| Immobilization | 38–(–12) |
| Total | 208–223 |

*Danish research concerning the nitrate content in ground water*
Some investigations have been made to determine and describe the ground water quality concerning the nitrate content.

Based on about 10,000 older analyses on water from borings and wells, *Christensen* (1970) has concluded that the Danish ground water contains very little or no nitrate. Several wells are polluted, but from local sources. *Hansen & Grunnet* (1973) have collected a number of analyses from public water works (unsystematic) and their conclusion is in accordance with that in the above mentioned paper.

**Some foreign investigations**
Several investigations from different foreign localities show that ground water may be polluted by farming activities. They show that leaching of nitrate depends strongly on the amount of excess water (*Hedlin* 1971, *Nightingale* 1972) and some crops remove the nitrate more effectively than others (*Adriano et al.* 1972).

A special kind of pollution sources are feedlots and other types of intensive livestock farms. In this field *Stewart et al.* (1967), *Elliott et al.* (1972), *Borneff & Adade* (1973), and *Mielke et al.* (1974), and others have done very valuable studies.

Transport phenomena of anions and especially of the nitrate ion are discussed in papers by *Lindhard* (1967), *Preul & Schroep-*

*fer* (1968), *Scalf et al.* (1969), *Pratt et al.* (1972), *Felizardo et al.* (1972), *Jung* (1972), *MacGregor et al.* (1974), and *Smith & Davis* (1974).

The conclusions from these and other studies show that leaching of nitrate often occurs from the upper soil layers. Great quantities fade away into the deeper layers, however, and this is usually explained by denitrification. Whether there is nitrate in the real ground water (not temporary) depends on the geological and meteorological conditions and to some degree on the type of farming.

It has not been demonstrated as to what extent the penetrating nitrate is derived from the agricultural supply of nitrogen fertilizers. Preliminary Danish investigations show the annual leaching of nitrate-N to artificial drain to be about 22 kg/ha/year (SFP, 1972). This value lies behind the figure in Table 3, and the order of magnitude of the leaching to the underground is chosen a little smaller. Leaching from natural plant communities seldom exceeds 2–4 kg nitrate-N/ha/year, but due to human intervention in the nature, such as clear-cutting of forest and new cultivation of soil, the leaching to drain depth is greatly increased (*Bormann et al.* 1968, *Reinhorn & Avnimelech* 1974). This demonstrates the influence of cropping monocultures, which cover the soil surface only a part of the year, but it does not tell whether the leaching increases with increasing use of nitrogen fertilizer.

*Vahtras & Wiklander* (1974) have in a Swedish investigation shown a strongly increased nitrate content in the ground water, when an area had been fertilized with large amounts of sewage sludge. However, when artificial nitrogen fertilizers have been used, the increase was weak. The ground water level was only 1.5 m below the surface, which is fairly unusual for Danish field conditions.

There is a lot of literature concerning nitrate metabolism and leaching from the uppermost soil layers, but what happens to the nitrate in the subsoil is not very well known. A dilution in the soil water takes place, and there may occur a nitrate adsorption on the anion exchange site of the soil minerals (*Jurinak & Griffin* 1972). A denitrification occurs, if an appropriate population of microorganisms exists (*Woldendorp* 1968, *Nash & Bollag* 1974). All this together does not add up enough to explain the fact that we have none or only very little nitrate in the ground water, though a weak leaching of nitrate has perpetuated since the last glaciation 10,000 years ago. In the deeper soil layers the number of relevant microorganisms is too small to carry out the requisite denitrification.

*Christensen* (1970) has suggested that the chemically reduced substances in the soil, in this case especially the ferrous compounds adsorbed to the soil mineral surfaces, may react as electron donors in a pure chemical reaction, reducing nitrate to nitrogen oxides or elementary nitrogen.

The thermodynamic conditions for the reactions of nitrate-N leading to elementary nitrogen are fulfilled, both in basic and acid media (*Chao & Kroontje* 1966). *Meek et al.* (1970) note a relation between soluble iron in the soil and the nitrate reduction, but the issue has been subjected to very few investigations. Several works have suggested that a possible relationship exists between soil redox potential and the nitrate reduction, but the technical difficulties are large and the results are not unambiguous (*Bailey & Beauchamp* 1973, *Patrick* 1960).

During the preliminary work to this study, we made a number of contacts with waterworks. In all the analytic results we have had at our disposal, the relation between dissolved ferrous compounds and the nitrate content, mentioned above, has been the same: When the water contained ferrous ions, there were never nitrate ions.

**Conclusion**

The three subsequent papers (*Lind & Pedersen* 1976a, 1976b, *Pedersen & Lind* 1976) will deal with an investigation on Danish subsoil profiles, based on the matter discussed in this and in earlier papers by *Lind* (1971) and *Lind & Pedersen* (1973). These profiles are selected prototypes of very common soils in Denmark. They will be described from physical and chemical points of view. Their suitability as intermediate layers between an intensive cropped field and a ground water reservoir will be discussed. The investigations on the ability of the soil to reduce nitrate will mainly deal with the pure chemical reactions, especially the ferrous iron-nitrate redox system.

**Sammendrag**

Beretningen er den første af fire med fællestitlen: Nitratreduktion i undergrunden. Den er væsentligst baseret på studier af dansk og udenlandsk litteratur med relation til emnet og beskriver desuden projektets baggrund.

Ud fra nævnte litteratur gives en oversigt over vandforbrug, samt geologiske og klimatiske betingelser for grundvandsdannelse i de forskellige egne af Danmark. Mere end 95 pct. af drikkevandsforsyningen hentes fra grundvandet som for langt størstedelens vedkommende er nitratfrit til trods for, at der siden istiden er sket en svag nedsivning af nitrat til de dybereliggende jordlag.

Disse kendsgerninger har givet anledning til en teori om, at der må foregå en – formentlig rent kemisk – reduktion af nitrat i jordlagene mellem rodzonen og grundvandet. Teorien bestyrkes af, at der aldrig findes nitrat i vand, som indeholder ferrojern.

Ved studier af såvel inden- som udenlandsk litteratur er der imidlertid ikke fundet resultater af undersøgelser, som har kunnet bekræfte eller afkræfte teorien. Denne kendsgerning i forbindelse med den stigende kvælstofanvendelse i jordbruget gør det påkrævet at få teorien underkastet en nærmere undersøgelse.

De følgende tre beretninger beskriver de anvendte metoder hertil, de opnåede resultater, samt de konklusioner der kan drages heraf.

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