Trend Reversal of Nitrate in Danish Groundwater - a Reflection of Agricultural Practices and Nitrogen Surpluses since 1950

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This paper assesses the long-term development in the oxic groundwater nitrate concentration and nitrogen (N) loss due to intensive farming in Denmark. First, up to 20-year time-series from the national groundwater monitoring network enable a statistically systematic analysis of distribution, trends, and trend reversals in the groundwater nitrate concentration. Second, knowledge about the N surplus in Danish agriculture since 1950 is used as an indicator of the potential loss of N. Third, groundwater recharge CFC (chlorofluorocarbon) age determination allows linking of the first two data sets. The development in the nitrate concentration of oxic groundwater clearly mirrors the development in the national agricultural N surplus, and a corresponding trend reversal is found in groundwater. Regulation and technical improvements in the intensive farming in Denmark have succeeded in decreasing the N surplus by 40% since the mid 1980s, while at the same time maintaining crop yields and increasing the animal production of especially pigs. Trend analyses prove that the youngest (0−15 years old) oxic groundwater shows more pronounced significant downward nitrate trends (44%) than the oldest (25−50 years old) oxic groundwater (9%). This amounts to clear evidence of the effect of reduced nitrate leaching on groundwater nitrate concentrations in Denmark.

Introduction

Danish drinking water supply relies on simple treated groundwater, and protection of groundwater is therefore a high priority. At the same time, Danish farming is among the most intensive in the world (*1*). Intensive livestock farming and extensive use of nitrogen (N) fertilization causes severe N losses to soil, water, and air. Numerous waterworks and wells have been closed due to nitrate pollution, and approximately 15% of Denmark has been classified as nitrate vulnerable groundwater abstraction areas (*2*). Commonly observed N-related environmental effects include a decline in biodiversity, eutrophication of ecosystems and surface waters (*3*), acidification (*4*), global warming via emission of N_2O (*5*), and diffuse nitrate pollution of groundwater. Both European policies (The Nitrates Directive, 1991/696/EC; The Water Framework Directive, 2000/60/EC; and The Groundwater Directive, 2006/118/EF) and national Danish legislation aim to protect groundwater resources and surface waters from the effect of N loss to the environment. Denmark has therefore introduced several political action plans since 1985 (*6*).

During the past 100 years, the agricultural development in Denmark has contributed significantly to the increase in societal prosperity owing to the growth in farming output and improved farming efficiency, especially after the Second World War. Like most countries in the industrialized world, Danish farming has experienced a significant structural development toward larger and more intensive farms, and Danish livestock farming in particular has grown significantly (*7*). Today, the Danish food production accounts for about 23% of the private sector's total turnover and investments, 21% of exports, and 16% of all employment (*8*).

The increase in the Danish agricultural production has been strongly spurred by the growing use of synthetic fertilizers and imported feed, which has resulted in more use of fertilizers and a higher nutrient turnover (*9*). The past 100 years have also seen the introduction of new crops in plant production and the emergence of new production branches in animal production. Crop yield per hectare has risen, and the yearly milk yield per cow has grown from approximately 2800 to 10,000 kg per cow from 1950 to 2007. Additionally, the production time of pigs and chickens is shorter today than ever before. The production of pigs has seen a dramatic rise from 3.2 million animals per year in 1950 to 11.2 million in 1967 and 20.9 million in 2007. Thus, pig production has been the largest Danish animal production branch since the mid 1970s (*8*).

Intensive farming causes leaching of N because of mineralization of the soil's N pools and because the amount of N used exceeds the nutrient demand of the crops (*10, 11*). This results in pollution of shallow groundwater that threatens drinking water resources and groundwater associated and dependent ecosystems (*12*). Nitrate leached to groundwater is expected to act as an inert tracer under the presence of oxygen and the generally low reactivity of organic matter below the root zone. Therefore, this study focuses on oxic groundwater, where the nitrate concentration represents the original nitrate leaching from the root zone.

Groundwater recharge age determination facilitates comparison of developments in the potential loss of N in agriculture and the measured groundwater nitrate concentrations (e.g. refs *13*−*18*).

This study aims to link nitrate trends in oxic Danish groundwater since 1950 to structural changes in agriculture related to the national, annual farming N surplus. The objectives is thus to present two separately statistical approaches: a) assessment of the general national trend of nitrate in oxic Danish groundwater and b) aggregation of the individual nitrate trends at the oxic groundwater monitoring points according to the age of the groundwater recharge.

2. Methods

2.1. Agricultural, Geological, and Hydrological Conditions. Denmark is a small country with a total area of about 43,000 km^2 and a population approaching 5.5 million. About 2/3 of the total land area is under agricultural use. Compared with European and global averages, Denmark has a high N

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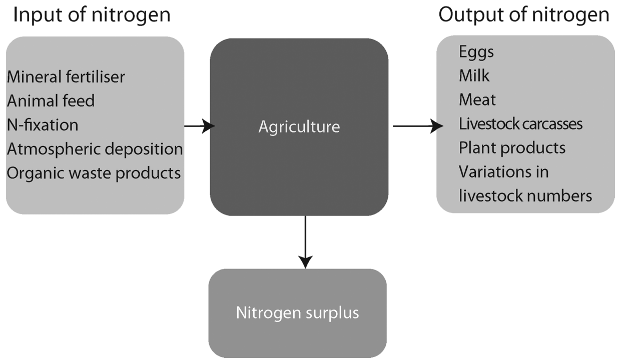

FIGURE 1. Input-output principle for nutrient balances in agriculture.

fertilization rate and a high livestock density (*1, 19*). The average livestock density in Denmark is about 0.8 animal units per hectare (*10*), and the average input of N to agricultural land is about 180 kg ha^{-1} yr^{-1} in 2008 (*8, 20*). The land surface has a modest topography with the highest point 170 m above sea level. Denmark has a coastal temperate climate where the precipitation varies from about 600 to 1000 mm/yr. The geological conditions in the upper layers are 50−200 m thick quaternary deposits which are underlain by tertiary deposits or Cretaceous limestone and chalk. Thus, the aquifers either consist of unconsolidated sands and gravels or fractured limestone and chalk.

2.2. N Surpluses in Agriculture. The surplus of nitrogen in agriculture is defined in terms of the balance between inputs (synthetic fertilizer, import of animal feed, organic waste products, net atmospheric deposition, and fixation) and outputs (export of plant and animal products) (Figure 1). The surplus of nitrogen, especially N, is regarded as the best overall environmental indicator of the changes in the agricultural impact on the environment over at certain time period (*19*). The surplus represents the amount of nitrogen pooled in the soil, or not being used up by the production system, and therefore at risk of being lost to the environment (*10, 11*).

2.3. The Danish Groundwater Monitoring Program. The principal aim of the approximately 20-year-old Danish Groundwater Monitoring Programme is to document the quantitative and qualitative status and trends of groundwater in order to evaluate the effect of the national action plans on the aquatic environment and thereby to meet the objectives of Danish legislation and the relevant EU directives.

The program covers 74 clustered catchments (Figure 2) covering areas of 5 to 50 km^2, each containing about 25 wells with short screens with a typical length of around 1 m capable of sampling a specific groundwater layer with minimal mixing of different water types. This gives a total of more than 1500 groundwater monitoring points with a median depth of 20 mbs (meter below surface) and a maximum depth of 164 mbs. The oxic subset of data used in this study has the monitoring points at a median depth of 17 mbs and a maximum depth of 68 mbs. The groundwater monitoring points are affected by different types of 1) agricultural land uses, 2) geological settings, 3) hydrological conditions, e.g. groundwater recharge rates, 4) depths, and 5) groundwater redox conditions.

The thickness of the unsaturated zone at the monitoring sites is up to 50 m with a median thickness of approximately 10 m. The oxic subset of data used in this study also has a median thickness of the unsaturated zone of 10 m but a maximum thickness of 36 m.

The wells are sampled annually for the main chemical components (nitrate, chloride, sulfate, ammonium, iron, etc.). Specific wells are analyzed for pesticides and their metabolites annually, while trace elements (arsenic, copper, nickel, etc.)

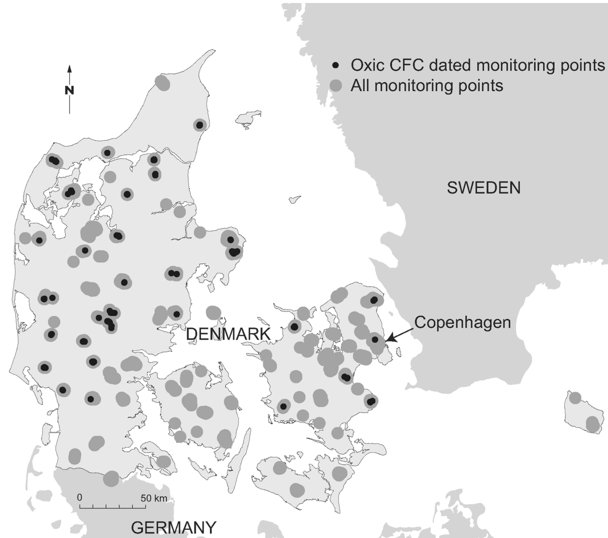

FIGURE 2. The groundwater monitoring points and the CFC dated oxic groundwater monitoring points in Denmark.

and organic pollutants are sampled with a lower frequency. More details on the Danish Groundwater Monitoring Programme can be found in ref *21*.

2.4. Groundwater Chemistry Data. The groundwater samples were analyzed in the field as well as in the laboratory. Online measurements of pH, redox potential, oxygen concentration, temperature, and conductivity were performed during sampling in order to ensure a high analytical quality and representative groundwater samples. The sampling and field analyses were performed according to Danish technical standards. The remaining chemical constituents of the groundwater were analyzed by professional, certified laboratories (*22*).

2.5. Groundwater Recharge Age Determination. Groundwater recharge age determination with the CFC method (*23*) makes it feasible to compare long-term changes in N surplus in agriculture with changes in oxic groundwater quality (*16, 24*). Groundwater recharge age was determined at the groundwater monitoring points, typically only once in the period from 1997−2006, using the CFC method (*23*).

Determination of the groundwater recharge ages followed the procedure of refs *13 and 23*, and the CFC analyses were performed at the laboratory of Geological Survey of Denmark and Greenland (GEUS). The method allows determination of the age of groundwater younger than 1940 with an uncertainty of ±2 years under optimal conditions (*13, 23*). Determination of the groundwater age follows the procedure of Laier (*13*). Samples of groundwater are collected in flame-sealed 60 mL boron silicate ampules which have been flushed with pure nitrogen prior to sampling. Approximately 30 mL of the sample is transferred to a purge and trap system, and finally the gases are swept into a gas chromatograph equipped with an electron capture detector (EDC) to quantify the amount of CFC gases dissolved in the water. The CFC concentration in the atmosphere at the time of recharge and thus the age of the recharge of groundwater is calculated using the constants in ref *25*.

Dating using the CFC method assumes that infiltration water maintains equilibrium with the unsaturated zone air during recharge (*23*). Previous studies of sandy aquifers in Denmark have shown that the residence time of water in the unsaturated zone using tritium dating (Andersen and Sevel, 1974) is similar to that of air diffusion through the unsaturated zone determined by CFC-gases on pore-space gases (*13, 26*). However, at some monitoring sites, depending on the hydrological conditions, there might be a difference between the resistance time of water and air diffusion in the unsaturated zone especially in areas with a deep unsaturated zone of up to 36 m. If the diffusion of CFC through the unsaturated zone is faster than the advection of water particles, then the groundwater recharge age determined with the CFC method will be overestimated.

The groundwater chemistry data as well as the CFC-data were downloaded from the Danish national geo-database JUPITER in October 2009 and thus includes all data uploaded until September 2009 (*27*).

2.6. Statistical Methods. Significant upward or downward trends can be determined either with statistical, linear methods (e.g., linear regression), or with nonparametric methods (e.g., based on Mann-Kendall) (*14, 28, 29*).

Data analyses including determination of trends and trend reversal of nitrate time-series in groundwater were done using the SAS software system (*30*). Trend analysis of nitrate time-series in groundwater at each monitoring point was performed as simple linear regression with PROC REG. A single analysis of trend reversal was performed on data from all monitoring points as a two-section linear regression with one unknown change point and fitted with PROC MCMC. Distribution of trends between monitoring points grouped according to the age of oxic groundwater were compared in a regression model with separate regression lines for each age group and fitted as a random coefficient model with PROC MIXED to allow for repeated measurements at each monitoring point. For each model, probability plots of the residuals were checked for normality.

2.7. Preprocessing of Data. The entire data set was filtered via this ordered, stepwise procedure:

1. Monitoring points with oxic CFC dated groundwater are included.

2. Monitoring points with more than 8 years of data are included.

3. Monitoring points with unstable redox conditions are excluded.

4. Outliers, e.g. effects of establishment, are found and excluded.

Only monitoring points with oxic conditions are included because both nitrate and CFC gases used for dating are degraded in anoxic groundwater (*31, 32*). The concentration levels of the redox sensitive parameters (NO_3^-, Fe^{2+}, and O_2) are used to sort out 194 samplings points with oxic conditions. Oxidized groundwater is defined as $[NO_3^-] > 1$ mg/L, $[Fe^{2+}] < 0.2$ mg/L, and $[O_2] > 1$ mg/L. This definition minimized the uncertainty in the determination of the groundwater redox state by giving third priority to the most uncertain parameter (i.e., oxygen). Iron in groundwater is thus used as an indication of complete nitrate reduction. The concentration levels of the other redox parameters (nitrite and manganese) show that an oxygen concentration higher than 1 mg/L is sufficient to ensure oxic conditions. This is due to a high quality of the oxygen field measurements of the groundwater.

During the past 20 years, the Danish groundwater monitoring program has been continuously adapted to scientific, environmental, and economic demands. The data from this program are therefore not entirely uniform, for example as regards the length of the time-series of chemical analyses. When performing trend analyses, the length of the time-series of nitrate analyses at each sampling point should be consistent (*33*). In this study, monitoring points with 8−20 years of data were accepted for trend analyses. Approximately 85% (165 monitoring points) of the oxic monitoring points have consistent time-series.

Some groundwater samplings points showed changing, unstable redox conditions due, among others, to i) mixing of groundwater with different redox conditions, ii) variable hydrological (precipitation, water table) conditions, and iii) influences by nearby groundwater abstraction. In this study, 92% (152 monitoring points) of the oxic monitoring points with more than 8-year time-series had stable redox conditions.

Both sampling and analytical errors may arise in groundwater sampling and chemical groundwater analyses. Drilling of groundwater wells can affect the chemical composition of the groundwater up to two years after the drilling, depending on the chemical substances used during drilling, the natural flow of groundwater, and the degree of flushing and pumping. Times-series from the 152 monitoring points were therefore examined for clear outliers and the effects on the water chemistry of the establishment of the wells; approximately 99% of the data was accepted.

The entire Danish monitoring data set with more than 8-year time-series counts 37,372 nitrate analyses from 1189 monitoring points sampled from 1973−2009. The subset of oxic CFC dated data used in this study for trend analyses comprises 5321 nitrate analyses from 152 sampling points sampled from 1988−2009.

3. Results

3.1. Trend Reversals of N at the National Level. Figure 3 illustrates the groundwater recharge age and the matching nitrate concentration at the year of the CFC measurement of the 194 oxic groundwater monitoring points found in step 1 described in the preceding section 2.7. In those monitoring points where the nitrate concentration is measured more than once a year the average nitrate concentration at the CFC sampling year is used.

The level of nitrate concentration at the year of groundwater recharge can be described by a piece-wise linear regression line with one unknown change point, as required by the EU Water Framework Directive, and shows a trend reversal at the year 1980 (±3.4 years) with a significant upward trend before and a significant downward trend after 1980 (see Figure 3). The slopes of the upward (c. 1.83 mg/L/yr) and downward (c. −1.61 mg/L/yr) curves are significantly different from zero at the 0.05 probability level.

The trend reversal in 1980 can also be illustrated by means of a simple 5-year moving averages curve relating nitrate concentration and recharge age. The time period under consideration saw a dramatic increase in N surplus in agriculture from approximately 60 to 180 kg N/ha/yr from 1950 to about 1981. After a 15-year stagnation period, the N surplus in agriculture started to decrease approximately in 1995, and in 2007 the average N surplus was 117 kg N/ha/yr. Thus, Figure 3 shows that around 1980 there is a trend reversal in the groundwater nitrate concentration and the increase of N surplus in agriculture in 1960s and 1970s levels out.

3.2. Distribution of Nitrate Concentrations at Each Monitoring Point. The choice of method used for trend analyses of the chemical composition at each monitoring point is determined by the distribution of the measurements (*29*). In this study, the distribution of nitrate was assessed for each of the 152 oxic monitoring points by inspection of standard normality plots. An example is given in Figure 4.

The residuals of the nitrate concentration at each of the 152 monitoring points are considered typical for normally distributed data. We therefore chose a simple linear regression for evaluation of trends (see Figure 4). Overall, the trend analyses at each point were found to meet the assumptions for linear regression based on scatter plots and normal probability plots of the residuals.

3.3. Trends in N Concentration in Oxic Groundwater of Different age. The results from linear regression analysis of the nitrate concentration versus time for each of the 152 oxic monitoring points are illustrated in Figure 5 as a quantile plot of the slope of each of the linear regression lines. The slopes represent the changes in the nitrate concentration per year, and the quantile plot of the slopes illustrates the overall variability between the monitoring points. Negative

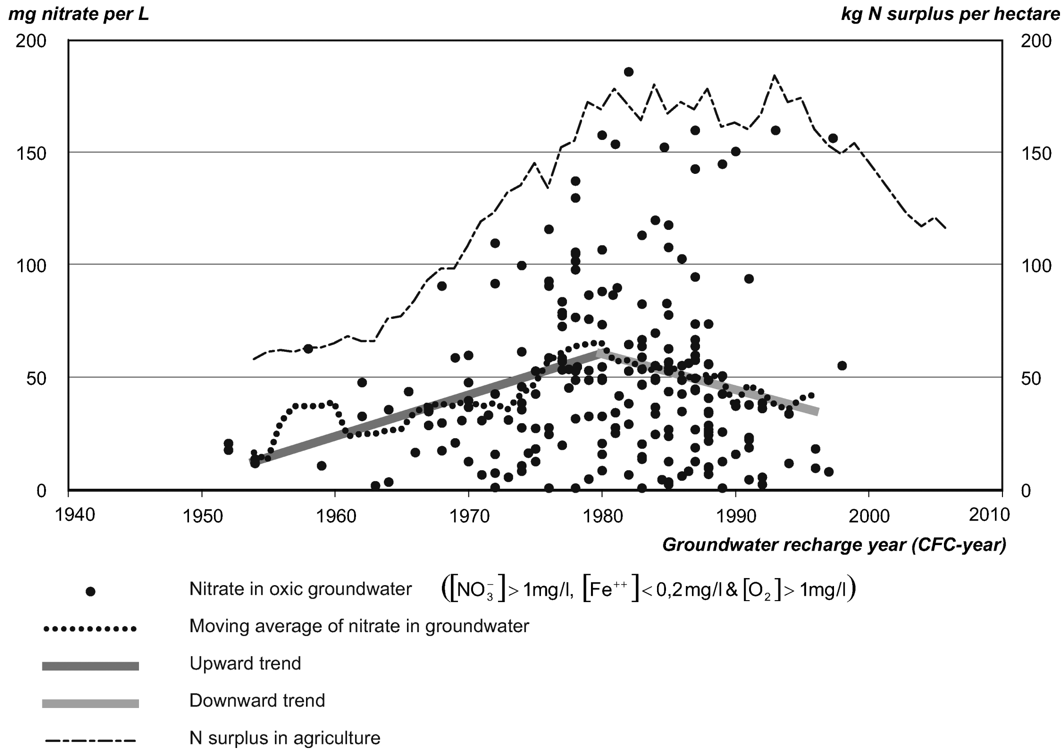

FIGURE 3. Time series of N surplus in agriculture and nitrate in oxic groundwater versus recharge age (CFC age) on an annual mean level.

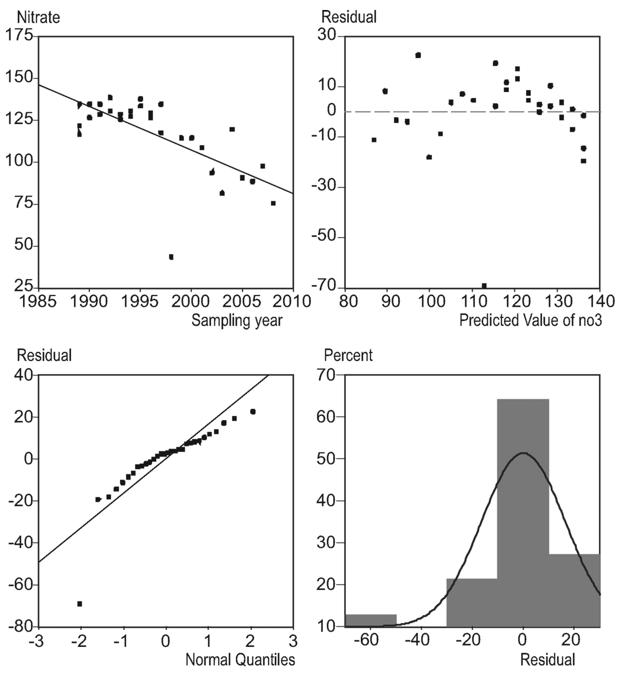

FIGURE 4. Linear regression and check for normality of an example with a downward statistically significant trend on a probability level of 0.05. Units are mg nitrate per L.

x-values represent downward trends, while positive x-values represent upward trends. At a probability level of 0.05, 71% of the monitoring points show significant trends, with 38% downward and 33% upward trends. The remaining 29% show no significant trends at a probability level of 0.05 (Table 1).

The data shown in Figure 5 are divided into three groups according to the age of the groundwater, which was determined as the difference between the sampling year and the groundwater recharge year. Consistently with the data analysis in Figure 1, the youngest oxic groundwater has more

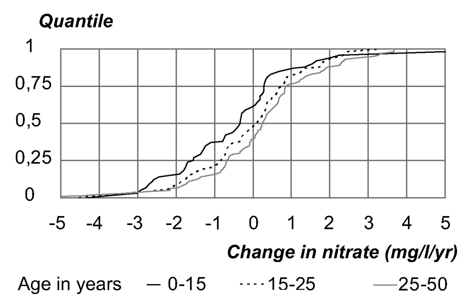

FIGURE 5. Quantile plot of changes in groundwater nitrate concentration (mg/L/yr) on a monitoring point level grouped by recharge age. The change in nitrate concentration is equivalent to the slope of the linear regression lines of nitrate versus sampling year seen in Figure 4.

TABLE 1. Amount (%) of Statistically Significant Nitrate Trends on a 95% Confidence Level of Oxic CFC Dated Groundwater According to the Age of the Groundwater Recharge

recharge age in years	upward	downward	no trends	total
0−50 (all)	50 (33%)	44 (38%)	58 (29%)	152 (100%)
0−15	10 (18%)	24 (44%)	21 (38%)	55 (100%)
15−25	19 (30%)	17 (27%)	28 (43%)	64 (100%)
25−50	21 (64%)	3 (9%)	9 (27%)	33 (100%)

monitoring points with downward trends than the older oxic groundwater. However comparison of the common trends in the three age groups demonstrated an only slight statistical significance ($p = 0.0394$).

Although the general trend (Figure 3) shows at trend reversal around 1980, the trends from the individual monitoring points show a more complex picture. According to Table 1, a significant downward trend was demonstrated in approximately 44% of the youngest oxic groundwater (0−15 years old), 27% of the medium old oxic groundwater (15−25 years old), and 9% of the oldest oxic groundwater (25−50 years old). In comparison, a significant upward trend was found in approximately 18% of the youngest oxic groundwater (0−15 years old), 30% of the medium old oxic groundwater (15−25 years old), and 64% of the oldest oxic groundwater (25−50 years old).

4. Discussion

Long-term groundwater quality monitoring with up to 20-year time-series provides optimal opportunities for investigating and understanding the impact of pressures and political action plans on groundwater quality. When addressing trends of pollutants in groundwater, it is fundamental to have long-term time-series of data, thereby being able to combine general trends and trends for individual monitoring points as shown in this study. This requires a consistent national monitoring program. Due to economic and political adjustments of the monitoring system, many time series are too short or abrupt, which reduces the payoff of monitoring investment.

This study demonstrates that groundwater recharge ages can be included as an essential component of groundwater trend investigations and that their inclusion may help to correlate changes in land use and management practices with changes in groundwater quality. Groundwater recharge age determination allows concentrations of nitrate to be related to the time of recharge instead of the time of sampling (e.g. refs *13−15 and 17)*, which, in turn, makes comparison between nitrate in groundwater and N loss from agriculture possible. In this study using the CFC method on oxic groundwater it is assumed that infiltration water maintains equilibrium with the unsaturated zone air during recharge and that degradation of CFC does not occur under the oxic redox conditions. Deep unsaturated zone of up to 36 m and small niches with anoxic redox conditions might increase the uncertainty in the determination of the groundwater recharge year using the CFC method. However, previous studies of sandy aquifers in Denmark have shown that the residence time of water in the unsaturated zone using tritium dating is similar to that of air diffusion through the unsaturated zone determined by CFC-gases on pore-space gases (*13, 26*).

In the Danish groundwater monitoring program it was decided to use the CFC method for dating groundwater due to successfully preliminary results under Danish hydrogeological conditions. Dating relative young (<20 years old) groundwater is a very important tool when evaluating the effect of agricultural action plans on the environment. However, atmospheric concentrations of CFCs were rapidly increasing before the 1990s, but as a result of the Montreal Protocol on Substances that Deplete the Ozone Layer adopted in 1987, atmospheric concentrations are now declining, which makes it impossible to use the CFC method for dating groundwater younger than 1990 (*34*). Therefore, there is a need for developing, testing, and implementing new methods suitable for dating young groundwater (e.g. refs *24, 34, and 35)*.

A trend in groundwater quality is defined as a change over a specific period in time within a given region that is related to land use or water quality management (*36, 37*). Both temporal variations due to climatic and meteorological factors and spatial variability may complicate trend detection (*27*). Important in this context is the period of time under consideration. Periods of 8 to 30 years have been recommended, depending on the sampling frequency for water analysis (*28*). This study demonstrates that preprocessing of data (oxic redox condition, 8 years time-series, stabile redox conditions, and no outliers) and selection of a subgroup for trend analyses are very important for the interpretation of the data.

Significant upward or downward trends can be determined either with statistical, linear methods (e.g., linear regression), or with nonparametric methods (e.g., based on Mann-Kendall) (*28, 29*). This study deployed a standard linear regression model for trend analysis of the nitrate concentration at each monitoring point in which normality was established. More complex statistical models were avoided in order to make the analyses as simple as possible. This study shows that the simple statistical analyses of the Danish groundwater monitoring data as required by the EU Water Framework Directive (*28, 33*) are adequate.

The nitrate concentration of the monitoring points at each groundwater recharge year demonstrates much variation, and it exceeds 50 mg/L in groundwater recharged after 1950 at many monitoring points (approximately 40%). This variation in the nitrate content is due to local and regional variation mainly in land use, application of fertilizer, and complex geological settings of the surface layers and aquifers in Denmark.

Trend reversal with a single change point can be determined for instance by a two-section linear model (*14, 28*). In this study, such a model successfully described a statistically significant trend reversal in 1980 (±3.4 years) of the nitrate concentration of Danish oxic groundwater. A trends reversal around 1980 in the N concentrations and loads at a hydrological catchment scale has also recently been documented in the Odense river in Denmark (*38*).

The trend reversal around 1980 of the nitrate concentrations in oxic groundwater coincided with the clear leveling out of the N surplus in agriculture after a period of strong increase, which actually occurred before the initiation of the first Danish environmental action plan in 1985, and the following action plans in 1987, 1991, 1998, 2000, 2001, 2004, and forward (*20*). All these plans have focused on the reduction of N-pollution from agriculture, being far the most important source for nitrate leaching in Denmark (*20*). However, especially in the beginning of the action plan period, and around the overall nitrate leaching turning point in the 1970s and 1980s, reduction of N-losses from point sources in the form of better wastewater storage and treatment facilities in the rural areas, and reduced runoff from livestock houses, silage clamps and manure heaps had a significant effect.

Since the initialization of the first Danish environmental action plan in 1985, the turnover of N has declined owing to several initiatives, the most important one being restrictions imposed on the application of N in the form, for example, of maximum N norms for specific crops and minimum thresholds for utilization of the N content of animal manure (*20*). The N surplus in the agricultural sector has therefore deceased by 40% since the mid 1980s. In addition, the nitrate leaching from agriculture has decreased by on average 33% and N concentrations and loads in surface waters have fallen by an average 29−32% (*20*). At the same time, the utilization (output/input) of N rose from 20 to 38% from 1980 to 2005 to maintain crop yields. In spite of the better utilization of nitrate, the environmental impact from agriculture remains high given current environmental objectives due mainly to the relatively high nutrient surplus levels.

The Danish findings are comparable to the results from other countries as the US (*15, 24*), Belgium (*29*), and The Netherlands (*14*) although differences exist. Thus, the increasing nitrate concentrations in the US groundwater since 1950 are likely the results of increasing fertilizer use, and highest nitrate concentrations are found in shallow, oxic groundwater beneath areas with high N inputs (*15, 17, 39*). In The Netherlands, concentrations of conservative pollutants increased in groundwater recharged before 1985 and decreased after 1990 (*14*).

Thus, the Danish data strongly indicate that a reduction in the N surplus and the nitrate leaching from the Danish agriculture have a significant effect on the groundwater nitrate concentration. However, the decrease in the nitrate concentration of oxic groundwater may also be influenced by climatic and meteorological factors. The fact that the monitoring points with the youngest oxic groundwater have seen the more pronounced significant downward nitrate trends (44%) than the older oxic groundwater (9−27%) supports the existence of the anticipated effect on groundwater of a reduced nitrate leaching following a lowering of the N surplus in Danish agriculture.

Although this study shows clear evidence of an effect of reduced N leaching on the groundwater nitrate concentrations the last evaluation of the Danish action plans showed that the measures have not had the expected and required effect on all parts of the environment. For example, Danish coastal waters are among the coastal water most frequently experiencing hypoxia, globally (*40*). In addition, groundwater nitrate concentrations still have to be lowered significantly in order to ensure good ecological status of Danish estuaries and good chemical status of groundwater according to EU legislation (*12*).

Geologic and hydrological information about the groundwater wells and the chemical composition of the Danish groundwater is available free of charge via the Internet at http://geus.dk in the database JUPITER.

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