The effect of nitrogen mitigation measures evaluated by monitoring of nitrogen concentrations and loadings in Danish mini-catchments – 1990–2015
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ABSTRACT
Monitoring of agricultural mini-catchments has been part of the Danish national monitoring programme (NOVANA) since 1989. Thus, nitrogen (N) concentrations and loads have been monitored in soil water, tile drains, and streams within five agricultural mini-catchments. Moreover, extensive monitoring of N concentrations and loads in streams draining 46 mini-catchments has been conducted every year since 1989. This has resulted in two national datasets on trends in flow-weighted N concentrations relative to factors such as groundwater age and management history. We analyzed these datasets and found that the intensively monitored micro-catchments generally showed a strong signal with significant downward trends in flow-weighted N concentrations in monitored soil water (−22% to −68%), tile drains (−38% to −59%), and streams (−19% to −53%). The 46 micro-catchments monitored for N in streams also exhibited downward trends in flow-weighted N concentrations, which can mainly be ascribed to the introduction of mandatory national regulation of N in agriculture in Denmark in the mid-1980s. However, classification of the mini-catchments according to the age of the oxidized groundwater revealed significant differences in N trends between the groups of mini-catchments. Thus, the strongest downward trend in flow-weighted N concentrations was as follows: <1 year (−52%), 1–3 years (−44%) and >3 year (−38%).

Key words | agriculture, groundwater age, mini-catchments, nitrogen

INTRODUCTION
Losses of nitrogen (N) from diffuse sources to groundwater and surface water bodies have attracted great attention in recent decades (Riemann et al. 2016). Significant losses of N from agriculture have long been recognized as the main source of diffuse pollution, and the excess N inputs to rivers, lakes, and estuaries create detrimental ecological effects in consequence of eutrophication (Riemann et al. 2016).

Implementation of land management measures, such as introduction of different mitigation tools to combat the N problem in surface waters, demands in-depth knowledge about the N continuum (Sutton & Howard 2011). The N continuum ranges from: (i) sources (fields) where N is mobilized; (ii) the travel and retention of N forms along different pathways (tile drainage, surface runoff, groundwater); (iii) retention and fate of N in the impacted receptors (streams,
rivers, wetlands, lakes, and estuaries) (Hinsby et al. 2012; Windolf et al. 2012; Blicher-Mathiesen et al. 2014a).

The link between policy, management, and the response of water bodies to N is not straightforward because of socio-economic and biophysical attenuation and lags (Jordan et al. 2012; Wulff et al. 2014). Therefore, monitoring of mini-catchments mimicking the field and farm scale at which farmers operate within river basins may produce valuable information at an early stage about the responses of receptors to various land management changes (McGonigle et al. 2015).

In Denmark, long-term monitoring of N concentrations, discharge, and N transport in smaller streams draining a number of different mini-catchments has been used as a means of quantifying the effectiveness of agricultural mitigation measures in reducing the N load to the aquatic environment. Mitigation measures include higher manure storage capacity, rules for timing for application of manure, limits for the maximum amount of N which may be applied to different crops and better cover of catch crops in autumn and winter (Kronvang et al. 2015). The monitoring includes measurements in 46 small agriculture-dominated catchments included the National Monitoring Programme for Water and NAture (NOVANA), which was implemented to document the effect of agricultural mitigation measures on the load of N to the aquatic environment. The aims of this study were to analyze the trends in N concentrations and loads from source to stream along a gradient of farming and biophysical properties in a subset of five intensively monitored agricultural mini-catchments and in a larger set of 41 mini-catchments following implementation of different regulations and land managements.

MATERIAL AND METHODS

Study of mini-catchments

The 46 studied agricultural mini-catchments (ACMs) are situated in different georegions of Denmark and have been part of the NOVANA monitoring programme since 1990 (Figure 1). The age of oxidised groundwater percolating to the 46 streams was modeled using the MIKE-SHE model with a coupled particle tracer as described in Højbjerg et al. (2015). Five of the 46 ACMs are intensively monitored (IAMCs) and the remaining 41 are extensively monitored (EAMCs). The IAMCs are grouped according to dominant soil type and the entire group of AMCs (IAMCs & EAMCs) has been categorized relative to the age of oxidized groundwater, the age at which 95% of the percolating water with dosed particles is recaptured at the outlet stream monitoring station (see Table 1). 95% age was chosen as the grouping parameter for the IAMCs and EAMCs as lag times are expected to greatly affect the response time in catchments following the introduction of land management measures (McGonigle et al. 2012). The mini-catchments generally cover less than 20 km² and have a high proportion of agricultural land use (>60%) (Table 1), and mean annual water runoff measured at the stream gauging stations in the catchment and average livestock Units per hectare for the period 1990–2015 are also shown in this table.

Field monitoring methods

Intensively monitored agricultural mini-catchments

Field monitoring in the intensive agricultural mini-catchments (IAMCs) included in the Danish Agricultural Monitoring Programme includes monitoring of percolating water in the root zone (1 m depth) in a number of fields, in upper groundwater (1.5–5.0 m) and a number of tile drains, and at a stream gauging station at the outlet of the five catchments.

The monitoring in each IAMC encompasses intensive collection of information on agricultural practices at field and farm level via interviews with farmers. Direct measurements are made of soil water, drainage water, upper groundwater, and stream water. Two of the catchments are mainly located on sandy soils and three mainly on loamy soils (Table 1). A detailed description of the monitoring stations within each of the five catchments can be found in Table 2 and details are given in Grant et al. (2011) and Blicher-Mathiesen et al. (2014b).

A soil water station consists of 10 suction cups installed in a V-shape pattern into the soil app. 1.0 m below the surface (see Rasmussen, 1995). During the leaching season, weekly water samples from the suction cups of a station.
are pooled for nitrate analysis. Leaching and percolation are calculated as described in Blicher-Mathiesen et al. (2011).

**Extensively monitored agricultural mini-catchments**

Each mini-catchment has an established stream monitoring station instrumented with equipment for continuous recording of water stage, and discharge is measured at fortnightly to monthly intervals to enable establishment of a stage/discharge relationship. The N concentrations in streams are measured in water samples collected at fortnightly to monthly intervals, the interval being longest in baseflow-dominated streams (Kronvang and Bruhn, 1996). At all monitoring stations, the daily N transport is calculated using linearly interpolated daily N concentrations multiplied with daily discharge (recommended in Kronvang and Bruhn (1996) as the most robust transport estimator).
Laboratory methods

For all water samples, total N and nitrate-N were analysed for concentrations of total N (TN) or nitrate-N using standard methods (Danish Standards Association 1975).

Statistical methods

The Mann-Kendall method (Hirsch et al. 1982) is a well-established method to test for a monotone trend in a time series. It is non-parametric and based on Kendall’s tau, which is a measure of the correlation between two different variables. The method is robust towards outliers and a few missing data. If the trend is linear, Mann-Kendall’s method has slightly less power than ordinary regression analysis. The second part of trend analysis is the task of estimating the size of the trend or the change per year. The Theil-Sen slope estimator (Hirsch et al. 1982) is a non-parametric estimator that is resistant towards outliers. The method assumes a linear trend and estimates the change per year, and the estimator fails if the trend is non-linear, and if the time series shows time reversal. The simplest method is using the start and end values in the time series of flow-normalized are used for monitoring nutrient inputs, but if start and/or end values are too distant from the general trend, this method is not reliable. We applied the Mann-Kendall and Theil-Sen slope estimator to soil water and tile drain water (Equation (1)) because these data includes high inter-annual variations, and the start and end values in time series for stream water for trend analysis (Equation (2)), which are assumed to be a more robust method for these time-series.

If we seek to identify the total change in nutrient inputs over the whole time series expressed as a percentage, we can use the two methods below. Estimated linear slope:

\[
100 \cdot \frac{(n-1) \cdot \hat{\beta}}{\alpha}
\]

(1)

where \( n \) is the length of the series, \( \hat{\alpha} \) is the estimated input at start year minus one year, and \( \hat{\beta} \) is the estimated slope. Formula 1 is based on the Theil-Sen slope estimator, and \( \alpha \) is estimated using the estimator suggested by Conover (1980). When using start and end values we have the formula:

\[
100 \cdot \frac{\text{end-start}}{\text{start}}
\]

(2)

### Table 1
- Characteristics of soil type, proportion of agriculture, and mean of runoff, age of oxidized stream water, and Livestock Units (L.U.) for the period 1990–2015 in the monitored catchments

| Soil type       | Catchment area (km²) | Agri. Area (%) | Mean annual runoff (mm) | 95% age Oxidized water (year) | L.U. (LU ha⁻¹) |
|-----------------|----------------------|----------------|-------------------------|------------------------------|----------------|
| Højvads Rende   | Loamy                | 9.8            | 60                      | 156                          | 2.33            | 0.15           |
| Lillebæk       | Loamy                | 4.4            | 85                      | 240                          | 1.02            | 0.77           |
| Horndrup Bak    | Loamy                | 5.1            | 68                      | 297                          | 1.01            | 0.75           |
| Odderbæk       | Sandy                | 11.4           | 83                      | 225                          | 9.11            | 1.26           |
| Bolbro Bak      | Sandy                | 7.8            | 85                      | 503                          | 2.25            | 1.16           |

### Table 2
- Number of monitoring stations within each of the five intensive agricultural micro-catchments (IAMCs)

| Monitoring stations/ IAMC | Højvads Rende | Odderbæk | Horndrup Bak | Lillebæk | Bolbro Bak |
|---------------------------|---------------|-----------|--------------|-----------|------------|
| Soil water stations      | 4             | 6         | 4            | 6         | 7          |
| Tile drain stations      | 4             | 1         | 0            | 2         | 0          |
| Stream stations          | 1             | 1         | 1            | 1         | 1          |
RESULTS AND DISCUSSION

Intensively monitored agricultural mini-catchments

The flow-weighted concentrations of nitrogen (N) were generally highest in soil water at the bottom of the root zone (1 m depth) and lowest in stream water in all the five monitored agricultural catchments (Figure 2). Total N concentration in tile drainage water was monitored in the two loamy catchments Lillebæk and Højvads Rende and was nearly similar to the N concentration measured in soil water (Figure 2(a) and 2(c)). This finding was expected as most tile drains in agricultural fields are installed at the bottom of the root zone at 1–1.2 m depth below the soil surface. However, in the sandy catchment Odderbæk, the concentration of total N in tile drainage water was more similar to the total N concentration found in stream water (Figure 2(b)). The larger tile drain in Odderbæk functions as a piped stream draining both groundwater and soil water from a larger sub-catchment in the Odderbæk catchment as a whole. The two sandy catchments (Figure 2(e) and 2(f)) showed a much higher difference between the concentration of N in soil water and stream water N than the three loamy catchments (Figure 2(a)–2(c)). The difference can both be explained that increased utilization of N in manure has higher impact in catchment with higher L.U. and the fact that oxidized pathways dominate in the loamy catchments, while groundwater pathways dominate in the sandy catchments. Thus, reduction of N in anaerobic groundwater is much greater in sandy than in loamy catchments. N retention in groundwater was modeled to 95% (Bolbro Bæk) and 83% (Odderbæk) in the two sandy catchments compared with 50% in Højvads Rende, 60% in Lillebæk, and 65% in Horndrup bæk in the three loamy catchments (Højbjerg et al. 2015).

Nitrogen in soil water, tile drains, and the streams within the IAMCs showed a general downward trend during the period 1990–2015 (Table 3). This was expected as the national management plans have included more efficient use of N in animal manure, leading to a nearly 50% reduction of the use of chemical fertilizers in Danish agriculture during 1989–2015 (Windolf et al. 2012;
Blicher-Mathiesen et al. (2014). Several other national mandatory regulations of Danish agriculture have been adopted, such as a ban against use of animal manure in autumn and winter, lowering the use of N to crops under economic optimum fertilization rates, catch crops, etc.

The downward trend in the flow-weighted nitrate concentration in soil water (22%), and stream water (19%) were lowest for the catchments Højvads Rende, compared to the other four intensively monitored catchments. The Højvads Rende catchment also experiences the lowest amount of livestock (0.15 LU/ha) as compared to the much higher interval of 0.77–1.166 LU./ha found in the other four intensively monitored catchments. The lower trend found for nitrate-N in soil water and total N in the stream for this catchment was as expected as Danish regulation of agriculture has focused on a better utilization of N in manure. The downward trends in nitrate-N in soil water are generally stronger than in stream water, especially in the two sandy catchments where removal of nitrate in deeper groundwater is high, thus diluting the trend signal. The monitored tile drains also revealed a downward trend in the same order as that found in soil water (Table 3). In the loamy catchments, Lillebæk, only two of the six fields with soil water monitoring were monitored. Therefore, the different trend signals observed in soil and tile drain water could potentially be ascribed to the different number of paired observations.

### Extensively monitored agricultural mini-catchments

The three groups of AMCs show no major differences in catchment size, mean proportion of agriculture, and mean annual runoff (Table 1). The grouping according to age when 95% of the oxidized groundwater is discharged to the stream monitoring station at the catchment outlet shows relatively large differences in mean age, ranging from 0.5 years to more than 5 years (Table 1). Annual runoff and N losses vary from year to year and are slightly lower in the AMCs with the highest age of oxidized groundwater (Figure 3). The annual flow-weighted N concentrations have the same general level in the three groups of AMCs (Figure 3). However, the two groups with a low age of oxidized groundwater demonstrate a stronger response of total N concentration in periods characterized by an extreme climate, such as the drought year of 1995/96 and the wet year of 1993/94, than the group of AMCs with a longer residence time (Figure 3).

The overall trend in annual flow-weighted total N concentrations during the period 1990–2015 differed significantly between the three stream groups when classified according to age of oxidized groundwater (Table 4). The most significant downward trend in flow-weighted total N concentration was found in the group of streams receiving very young oxic groundwater (52%), whereas the streams with the oldest oxic groundwater exhibited the lowest downward trend (−38%) (Table 4). To some extent, this pattern proves the importance of lag times in groundwater, and the full effect of management plans implemented at catchment scale can therefore not be assessed immediately by managers and policy makers (Howden et al. 2011; Windolf et al. 2012).

### CONCLUSIONS

Our analysis of nitrogen data from soil water, tile drains, and streams within 46 agricultural mini-catchments in Denmark
showed the importance of scale, pressure of L.U., and groundwater age for measuring trends in nitrogen concentrations and loads over a relatively long monitoring period (1990–2015). Especially the time lag of oxidized groundwater was found to markedly influence the downward trend in nitrogen concentrations, and this knowledge is of high importance for catchment managers and policy makers.

**Figure 3** | Annual flow-weighted concentrations of total nitrogen, annual losses of total nitrogen, and annual runoff from 46 agricultural mini-catchments (AMCs) divided into three groundwater age classes: <1 year: (a,d,g); 1–3 years: (b,e,h); >3 years c,i).

**Table 4** | Mean trends in annual flow-weighted total N concentrations in streams draining extensively monitored agricultural mini-catchments (AMCs) when sub-divided into three groundwater age classes: <1 year; 1–3 years; >3 years for oxidized groundwater.

| Groundwater age class | Number of streams | Mean trend (%) (± s.e.) |
|-----------------------|-------------------|------------------------|
| <1 year               | 9                 | −52 (±3)a              |
| 1–3 years             | 22                | −44 (±2)b              |
| >3 years              | 15                | −38 (±4)c              |
ACKNOWLEDGEMENT

The authors are grateful for financial support granted from the Nordforsk research project BIOWATER and the data gathered under the National Water and Nature Monitoring Programme (NOVANA).

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First received 21 June 2019; accepted in revised form 29 November 2019. Available online 3 January 2020