An integrated and physically based nitrogen cycle catchment model

J. R. Hansen, J. C. Refsgaard, V. Ernstsen, S. Hansen, M. Styczen and R. N. Poulsen

ABSTRACT

This paper presents a modelling approach where the entire land-based hydrological and nitrogen cycle from field to river outlet was included. This approach is based on a combination of a physically based root zone model (DAISY) and a physically based distributed catchment model (MIKE SHE/MIKE11). Large amounts of data available from statistical databases and surface maps were used for determination of land use and management practises to predict leaching within the catchment. The modelling approach included a description of nitrate transformations in the root zone, denitrification in the saturated zone, wetland areas and the river system within the catchment. The modelling approach was applied for the Odense Fjord catchment which constitutes one of the pilot river basins for implementation of the European Water Framework Directive. The model simulated overall nitrogen fluxes in the river system consistent with the observed values but showed some discrepancies between simulated and observed daily discharge values The results showed significant differences of denitrification capacities between larger areas such as sub-catchments. This approach has great potential for optimal planning of the establishment of wetlands and further land use legislation with respect to high denitrification rates.

Key words | catchment, integrated, model, nitrate, non-point sources, physically based

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INTRODUCTION

It is generally recognised that excess nitrogen from agricultural fertilisers and manure constitutes an environmental problem. Elevated nitrogen levels in aquifers are a major concern in relation to drinking water standards for areas that have based their drinking water supply on groundwater. Furthermore, nitrate is, in particular, a problem in the aquatic environment as it contributes to eutrophication of freshwater bodies and coastal waters.

Various processes influence the fate of nitrogen from its application in the fields to its appearance as nitrate in groundwater or surface water. Denitrification in the soil (e.g. Schaffer & Liwang Ma 2001), the saturated zone (e.g. Korom 1992), riparian zones (e.g. Brüsch & Nilsson 1993; Hill 1996) and hyporheic zones (e.g. Christensen & Sørensen 1988) constitutes an important sink in the nitrogen cycle at the catchment scale.

The EU Water Framework Directive (European Union 2000) requires that water resources management is carried out at the scale of a hydrological catchment and that surface water and groundwater resources are seen in an integrated context. This paper presents a modelling approach that includes the entire hydrological and nitrogen cycle at the catchment scale in a simplified but physically sound manner. The present model can address nitrate transport pathways within the catchment, in contrast to most models reported previously.

doi: 10.2166/nh.2009.035

Examples of integrated nitrogen cycle catchment models reported in the literature are INCA (Whitehead *et al.* 1998), SHETRAN-NITS (Birkenshaw & Ewen 2000) and SWAT (Arnold *et al.* 1998). INCA and SWAT can be characterised as lumped conceptual catchment models whereas SHETRAN is an example of a physically based catchment model. Models may be characterised by the level of complexity of their process descriptions as being either black box, lumped conceptual or physically based (Refsgaard 1996). The INCA and SWAT models are successfully used to simulate discharge and nitrogen transport in rivers but neglect denitrification in the saturated zone and riparian zone. The SHETRAN model neglects nitrate reduction by pyrite and iron oxidation in the saturated zone, which can be important processes in the nitrogen cycle at the catchment scale.

Other catchment models use a combination of model codes to simulate flow and transport from field to stream. Often a leaching model is used to simulate water and nitrogen leaching from the root zone at the point scale. A catchment model is used to distribute the root zone output and handle the flow and transport below the root zone to the surface water. Examples of the combination approach are: NL-CAT (Schoumans & Silgram 2003) and SWAT-MODFLOW (Perkins & Sophocleous 1999; Conan *et al.* 2003). HVB-N (Arheimer & Brandt 2000) is an example of a hybrid where a physically based leaching model SOIL-N (Johnson *et al.* 1987) is used together with a lumped catchment model HBV (Bergström 1995). Arheimer & Wittgren (2002) reported a version of HBV-N that accounts for nitrate removal in wetlands.

An example of combining a leaching and a spatially distributed catchment model is the DAISY MIKE SHE approach (Styczen & Storm 1993*a*,*b*) that constitutes a coupling of a root zone model DAISY (Hansen *et al.* 1991) and a distributed catchment model MIKE SHE (Refsgaard & Storm 1995). The catchment model in the present paper uses the DAISY MIKE SHE approach in a complex hydrogeological setting. Statistical databases and surface maps were used in combination for determination of land use and management practices to set up the root zone model and predict leaching within the catchment. In addition to simulation of denitrification in the saturated zone this approach also describes denitrification in wetlands and sediments at the river bottom. The denitrification concept for the saturated zone and wetlands could ideally point out areas of low and high denitrification potential for optimal catchment management of land use and wetland establishment. This modelling work was initiated as a part of planning the *3rd Water Environment Protection Act* in Denmark. The objective here was to provide input to a water quality model for the Odense Fjord for different catchment management scenarios (Nielsen *et al.* 2004). The results presented in the present paper are a recalculation of the results reported by Nielsen *et al.* (2004). The objective of this paper is to describe the modelling approach but mainly to analyse potential strengths and limitations of its application.

STUDY AREA

The study area is the catchment area of Odense Fjord on Funen Island, Denmark (Figure 1). The Odense Fjord is a shallow estuary with an area of 64 km^2 and a residence time of around 20 d. The topographical area of the catchment is approximately 1,046 km^2.

Three major and several minor ice advances and subsequent ice retreats during the Weichselian glaciation have formed the present landscape and geology (Houmark-Nielsen & Kjær 2003). It was found that the topographical catchment of the Odense Fjord did not coincide with the groundwater divides of the middle and lower aquifers (Figure 1) simulated with the Danish National Water Resource Model (Henriksen *et al.* 1997, 2003). The union of the topographical boundary and the simulated groundwater boundaries was chosen as a delineation of the model area. The model area including the fjord is 1,312 km^2. The average annual precipitation in the catchment is about 840 mm (10-year period 1992–2001).

METHODOLOGY

Modelling framework

In this study a combination of the DAISY leaching model and MIKE SHE catchment model was applied. The catchment model was based on the existing National Water

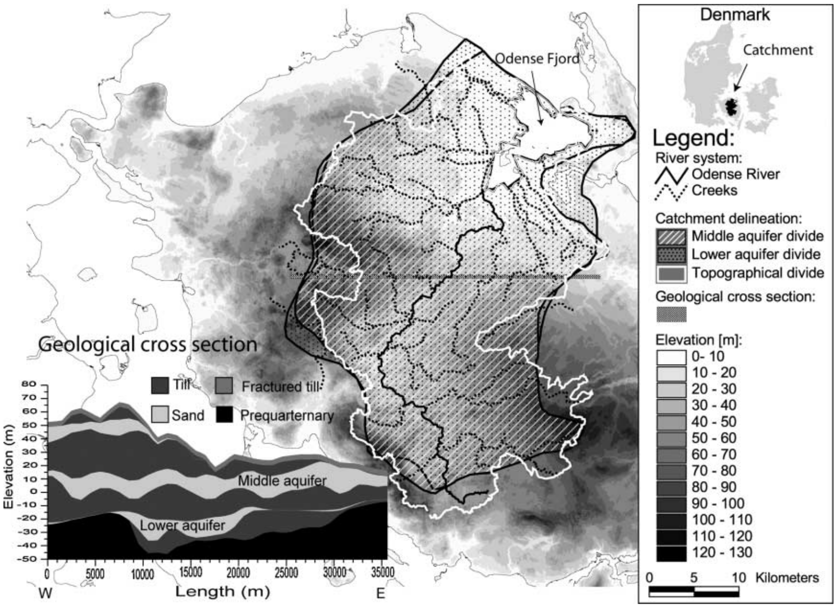

Figure 1 | Odense Fjord catchment on Funen Island, Denmark.

Resource Model of Funen Island (Henriksen *et al.* 1997, 2003). The model was run for 14 years using climate data from 1989–2002. In this period the land use and nitrogen use in the catchment was set up to represent the historical development during these years.

DAISY

DAISY is a one-dimensional crop model describing soil water dynamics, soil temperature, and the carbon and nitrogen cycle of the root zone (Hansen *et al.* 1991; Abrahamsen & Hansen 2000). Flow and leaching via three possible pathways–matrix, macropores and drain pipe–is simulated for a set of computational nodes in a soil column.

MIKE SHE

MIKE SHE is a physically based integrated catchment model. It includes flow and transport modules for all land-based phases of the hydrological cycle at the catchment scale. The model can perform numerical solutions of 1D unsaturated flow, 2D overland flow and 3D saturated flow and transport (Refsgaard & Storm 1995). In the model applied in this paper the unsaturated flow module of MIKE SHE is replaced with the DAISY model. The MIKE SHE model also has a forward particle tracking procedure where the flow path of particles can be recorded.

MIKE11

MIKE11 is a one-dimensional river model designed for simulation of flow, transport and water quality (Havnø *et al.* 1995). In addition to transport calculations MIKE11 has a submodule for ecological simulations 'Ecolab'. With the Ecolab module it is possible to include various in-stream processes, e.g. denitrification, nitrification and degradation of organic matter. Furthermore, it is possible to apply user-defined processes such as denitrification in wetlands adjacent to the river system.

Coupling of the models

In this study DAISY and MIKE SHE were coupled sequentially without any feedback from the groundwater and river to the root zone. DAISY first calculated the water and nitrogen budget of the root zone for all field blocks within the catchment for the entire simulation period. The simulated percolation and total nitrogen leaching components below the root zone were aggregated to daily net values and applied as input to the top layer in the MIKE SHE model. The DAISY column simulations were aggregated into the size and layout of model grid blocks using a weighting area procedure. The catchment transport simulations were carried out after execution of the flow calculations and based on the stored flow results and the nitrate leaching simulated by DAISY. The river reaches in the MIKE11 model were coupled to MIKE SHE, allowing exchange of flow and transport between the river and the saturated zone. The surface water model received water and nitrogen from three components from the groundwater model: overland flow, drainflow and baseflow. In the MIKE SHE modelling context baseflow accounts for groundwater that discharges into the river system through the river bottom. Hence baseflow is not used as a term for low flow situations in the rivers here because some areas will also contribute to the total discharge as drainflow even in very dry periods. Hansen *et al.* (2007) described the coupling of the root zone and catchment models in detail.

Code and model modifications

A post analysis of the modelling results reported in Nielsen *et al.* (2004) revealed that the coupled modelling scheme was not mass conserving. This was corrected before the model runs were repeated in the present study.

During the calibration process it was found that the solution of the advection dispersion equation in the MIKE11 river model was not quite mass conserving even with computational time steps as small as 1 min. Approximately 4% of the nitrogen input to the river from the saturated zone and point sources is lost during transport in the river system because of numerical errors. A further analysis showed that depletion of mass occurred during high flow periods whereas a small increase of mass was occurring during low flow periods. It was not possible for us to correct the mass balance error and implement improvements in the commercial MIKE11 model code.

In addition to nitrate Nielsen *et al.* (2004) also included transport and processes for ammonium, oxygen and organic matter from sewage in the river model simulations. The nitrogen content of the organic matter was set to 29%. However, this resulted in computational times of several days for simulation of just one year. Therefore, the river model was changed to account for transport and denitrification of total nitrogen as nitrate only. It was assumed that ammonium and organic nitrogen from sewage changed to nitrate form instantaneously when entering the rivers. This simplification had a negligible influence on the model results but allowed a considerably faster computation.

Calibration and validation

The same parameters that Nielsen *et al.* (2004) used were initially used in this study. So the calibration and validation was basically carried out by Nielsen *et al.* (2004).

The root zone model

Standard parameter values mostly from Styczen *et al.* (2004) were used. It was not possible to calibrate the simulated percolation of individual DAISY columns. However, some manual calibrations of the parameters were made after evaluation of catchment simulations in an attempt to improve the performance of the simulated discharge at the catchment scale (Nielsen *et al.* 2004). Simulated nitrogen balances were calibrated against agricultural crop yield statistics in the period 1991–2000.

The catchment model

A calibration and validation of the original National Water Resource Model was carried out using a split sample test for the performance of discharge and groundwater head simulation by Henriksen *et al.* (1997). The periods 1988–1990 and 1991–1996 were assigned for calibration and validation, respectively.

In this study simulated heads from a stationary model run of the period 1991–2000 were compared with all available observed heads within the catchment. Furthermore, water balances at 10 discharge gauging stations (Figure 2) were evaluated during a calibration period (1991–2000). Nitrogen balances at four water quality stations (Figure 2) were evaluated only in the last part of the calibration period (1998–2000) to allow for a warming-up period of the DAISY columns.

New observed discharge and nitrogen data from the period 2001–2002 that were not included in the calibration process by Henriksen *et al.* (1997) or Nielsen *et al.*

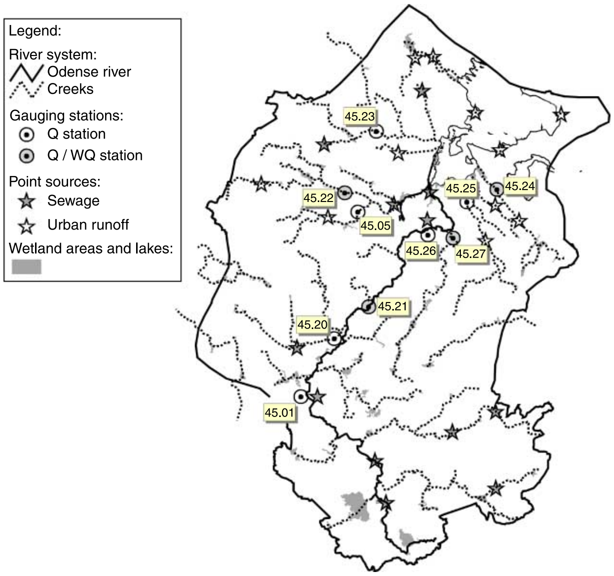

Figure 2 | Identification of discharge (*Q*) and water quality (WQ) gauging stations; sewage and run off point sources; and wetland areas.

(2004) were used in this study to validate the capability of the model.

To evaluate the model performance of the simulated groundwater heads, discharge and nitrogen flux the following numerical criteria were used:

- RMSE–the root-mean-square error between observed and simulated stationary heads.
- ME_Q–the difference between observed and simulated discharges averaged over the calibration and validation periods.
- ME_N–the difference between observed and simulated fluxes of total nitrogen averaged over the calibration and validation periods.
- $R^2_{Q,\text{daily}}$–the model efficiency or explained variance calculated on the basis of observed and simulated daily discharge values (Nash & Sutcliffe 1970).
- $R^2_{N,\text{daily}}$–the model efficiency or explained variance calculated on the basis of observed and simulated daily total nitrogen flux (Nash & Sutcliffe 1970).

Description of model set-up

Unsaturated zone

The parametrisation of the DAISY model was a straightforward approach where all the available information was used for root zone calculations. A more detailed description is given by Nielsen *et al.* (2004).

Climate. 14 interpolated 10 km × 10 km precipitation grids from the Danish Meteorological Institute were used. The temperature used in the simulations was based on 20 km × 20 km grid values. A global radiation value from a single observation point in the central part of the catchment was applied. The reference evapotranspiration, which is used for calculation of the actual evapotranspiration in the DAISY model, was calculated by a modified version of Makkink's Equation (Hansen 1984).

Soil. The dominating soil types in the area are: sandy loam (74%), coarse sand (21%), clay (1.5%) and peat (3.5%). Based on the dominating soil types four soil profiles were applied in the DAISY calculations. Hydraulic parameters for the soils were estimated by HYPRES pedotransfer functions (Wösten *et al.* 1999) based on textural analysis data available within the catchment. Default parametrisation of macropores in the DAISY model was applied.

Land use, farm type and crop rotations. Agricultural statistics from databases and GIS maps of land use were used to categorise the agricultural areas into six main types: cereal, pig, cattle, mixed, pasture, fallow or unidentified (Table 1). The average animal density in the area is 0.9 Danish animal units/ha (Nielsen *et al.* 2004)

Table 1 | The distribution of land use in the catchment

Land use	Percentage of catchment area
Agriculture	67
Cereal farming	7
Pig	17
Cattle	11
Mixed	3
Pasture	5
Fallow	4
Unidentified	20
Forest (coniferous and deciduous)	11
Urban areas	14
Lakes and wetlands	4
Other vegetation (low)	4

which is equivalent to 100 kg N/yr. For representation of different application amounts of manure and fertilisers some of the farming types were divided further into 7 cattle, 6 pig, 6 mixed and 2 cereal rotations. The rotation schemes for the individual farming types were constructed as rotations of typical crops with respect to the nitrogen available within the given categories.

Once the land use and nitrogen load of all areas were identified 30 crop rotation schemes were constructed. The rotation schemes were permutated to represent each crop in the rotation every year. The permuted simulation outputs were averaged to represent a mean output of the scheme each year. The procedure is described in detail by Hansen *et al.* (2007). The mean scheme was then distributed within field blocks characterised by that particular farming practice. The rotation schemes are not able to predict the nitrate leaching at farm level. Nevertheless, the distribution and levels are statistically correct for larger areas such as sub-catchments.

Non-agricultural areas. 50% of the urban areas were assumed to be covered by pavement or buildings. The precipitation here was routed to the stream as surface runoff with an initial loss to evaporation of 2 mm/d. The generated runoff was routed to the MIKE11 network and distributed as point sources (Figure 2). DAISY simulations of permanent grass represented the remaining 50% of the urban areas.

In non agricultural areas the leaching simulated by DAISY was replaced by standard leaching figures from the literature. The leaching from forest was set to annual values of 12 kg N/ha/yr, areas with other vegetation 3.5 kg N/ha/yr and urban areas $1/2 \times 3.5$ kg N/ha/yr due to the assumption of 50% paved areas.

Lower boundary condition. Owing to the sequential coupling of the DAISY and MIKE SHE models a lower boundary condition must be specified manually in the DAISY column. Three different boundary condition options in DAISY were applied in the present study: A constant groundwater level, a gravitational gradient and a time-varying groundwater level using a drain pipe option in DAISY. Since the actual depth to the phreatic surface is not measured the spatial distribution of lower boundary conditions had to be estimated. To get an idea of the lower boundary to use in the whole catchment the simulated water tables from the National Water Resource Model (Henriksen *et al.* 1997) were applied. Based on this the drain pipe option was applied at a depth of 1 m in all DAISY columns where the simulated mean water table depth is shallow. Where the average water table is deeper than 3 m the lower boundary condition was set to the deep groundwater level option, which corresponds to a gravitational gradient. For wetland areas the lower boundary condition was a fixed water table approximately 45 cm below the ground.

Aggregation procedure from field blocks to MIKE SHE model grids. A total of 6,061 DAISY column simulations were made. After averaging the permutations of rotation schemes, 2,095 mean rotation schemes were distributed within corresponding field blocks. The field blocks were then aggregated to grid values for application in the groundwater model.

Saturated zone

Conceptual hydrogeological model. The hydrogeological model is characterised by 9 geological layers (Figure 1). The top layer is characterised as fractured till, while the succeeding layers (2–8) are of alternating aquitard (till) and aquifer (sand) material, starting and ending with an aquitard. Sandy units in aquitards are included as sand lenses in the geological model. The lower ninth layer constitutes Palaeocene marl and clays and older limestone. The model is discretised into 500 m × 500 m grid blocks.

Drainage and pumping. Drainage was handled using the built-in drain routing option in MIKE SHE. If the groundwater level in the upper layer exceeds a specified threshold of 1 m below the surface the excess water is routed to the nearest river reach by a first-order rate specified by the so-called drain time constant (s^{-1}).

Pumping wells within the catchment were distributed spatially in the model according to the location of waterworks.

Boundary conditions. Zero-flux conditions were assumed on the boundary of the model area. Discharge generated as drainwater and baseflow in areas outside the topographical area were routed in river branches flowing out of the model area and not discharging into the fjord (Figure 1).

Delineation of redox interface. Danish as well as foreign studies suggest that nitrate is not reduced in the oxidised part of the saturated zone but is rapidly reduced in an anaerobic environment (Korom 1992; Ernstsen 1996). The transition from oxidised to reduced conditions (the redox interface) in young glacial sediments usually occurs within a vertical distance of decimetres to a few metres. In this study a concept where no nitrate is reduced above the redox interface whereas all nitrate transported below the interface is removed instantaneously was applied. It was assumed that the depth to the redox interface is related to soil types 1 m below the surface. The rationale for this was that sandy areas are assumed to have higher infiltration rates than more clayey areas and therefore deeper redox interfaces. The average depths were interpreted from colour descriptions in lithological borehole logs. The dominating soil type within the model grids was used to distribute the redox interfaces. The redox interface was assumed to be located 2 m below the surface in clay and organic soil areas, and 3.5 or 8 m below the surface in till areas below and above an elevation of 45 m, respectively. The division between till above and below this elevation was a distinction between areas with shallow and deep groundwater tables. A deeper unsaturated zone will result in a deeper redox interface, owing to faster diffusive transport of oxidising agents, especially oxygen, above the water table. Finally, the redox interface in sandy areas was set to 16 m below the surface. In addition to the presence of a redox interface it is known that local anaerobic zones exist in the upper oxidised zone (Pedersen *et al.* 1991). In order to account for this Nielsen *et al.* (2004) applied a first-order decay removal in the uppermost model layer of the oxidised zone with a calibrated half-life of 2 yr. The half-life was subject to further calibration in this study after the correction of the coupling between DAISY and MIKE SHE.

Particle tracking

The Particle Tracking (PT) module (DHI 1999) in the MIKE SHE model was used to assess the transport pathways in the saturated zone for each model grid in the catchment. Initially 10 particles were placed randomly in the first layer of each model grid. The PT module then simulated the flow path of the particles, which were moved three-dimensionally in the saturated zone. The particles were displaced according to the local groundwater velocity previously calculated by MIKE SHE. The simulated saturated flow velocities from a ten-year period (summer 1990 – summer 2000) were used and repeated five times in a 50-year simulation period. During the particle movement it was recorded if the particle moved below the regional redox interface and if it ended up in drains, wells or baseflow to the river. The birth coordinates of the individual particles are known and the fate of particles from each grid within the model could be determined.

Surface water

All main water courses within the catchment were included in the MIKE11 model. Major sewage treatment plants and urban runoff were included in the river model as point sources at the locations shown in Figure 2.

Denitrification in the sediments at the river bed and wetlands is included in the MIKE11 Ecolab module as a temperature-dependent first-order reaction. A maximum denitrification capacity of 700 kg N/ha/yr for all wetlands was assigned to wetland areas along the river system. Wetland areas (a lumped definition of meadows, bogs, lakes and similar) along the river system receive water and nitrate from MIKE SHE as overland flow or drainwater. The extent of wetlands has been based on GIS maps (Figure 2). The areas of wetlands are linked to the nearest calculation point in the river model. The nitrate that discharges via overland and drainflow at this calculation point will partly be denitrified in the wetland area connected to that point. The total area of wetlands in the model area is approximately 36 km^2.

A maximum denitrification capacity rate at 20°C where neither temperature nor nitrate concentration limit the process is specified for the wetland and river denitrification processes.

RESULTS

Calibration and validation results

Root zone model

Simulated crop yields were selected from DAISY columns situated within a single 10 km × 10 km climate grid with a precipitation value close to the average of the catchment. After calibration of the crop modules the simulated harvested nitrogen from the represented crops was within the range of −39% to +11% of the statistical measures of harvested nitrogen from the same crops (Nielsen *et al.* 2004). Average measured harvested yields for the crops were available from statistics for Funen Island and the nitrogen content in the harvested crops was based on national average values.

Catchment model

The same parameters as used by Henriksen *et al.* (1997) were used in the groundwater model except for the drain time constant, which was changed. The stationary model run with DAISY input in the period 1991–2000 (Table 2) shows that the catchment model simulates groundwater heads with the same level of accuracy as the original model.

The water balance ME_Q for individual sub-catchments are under–and overestimated during the calibration period within the range −16% to +18% whereas the water balance during the validation period is generally underestimated (Table 3). The overall water balance ME_Q for the total gauged area is underestimated by about 2% and 8% in the calibration and validation periods, respectively. This appears quite satisfactory. However, an examination of the low model efficiency coefficients (R^2_Q) indicates that the model has some problems with the simulation of the daily discharge variation. At gauging station 45.21 an underestimation of daily discharge during the validation period is seen, especially during the autumn and an overestimation during wet winter and spring periods (Figure 3). This was also seen as a bias in overestimation in wet years and underestimation in dry years for all discharge stations during the period 1991–2002 (not shown). Similar results for nitrogen fluxes for water quality gauging stations are shown in Table 4 and Figure 4. The half-life of the first-order degradation in the saturated zone was changed to one year during the calibration process because the simulated nitrogen fluxes were overestimated after the correction of the model coupling. The differences between the simulated and observed average nitrogen fluxes range from −3% to 79% in the last part of the calibration (1998–2000) and from −22% to 15% in the validation period. The simulated nitrogen balance for the main branch of the Odense River appears satisfactory in the calibration period whereas the validation period appears underestimated. The problems experienced in the dynamics of the discharge simulations is seen to progress to the simulations of nitrogen fluxes by the low model efficiency coefficients (R^2_N) to an extent that the predictive capability of the model for simulating seasonal and inter-annual dynamics is somewhat limited (Figure 4).

Table 2 | The performance criteria for the simulated heads of the original model (Henriksen *et al.* 1997) and the simulated heads of this study

Identification	Henriksen *et al.* (1997)	This study
Maximum RMSE value in layer (m)	7.8	7.2
Weighted RMSE average all layers (m)	5.7	5.8
Simple RMSE average all layers (m)	5.4	5.4
Simple RMSE average all aquifers (4 layers) (m)	4.6	5.2

Catchment water and nitrogen balance

An advantage of the distributed modelling system applied here is that water balances can be retrieved for any simulation period for a single grid, a sub-catchment or the entire catchment. The water balance for the land area within the model domain during the period 1998–2002 is shown in Figure 5. Almost 80% of the water from percolation and point sources flows through the river system and discharges into the fjord. It is noted that the dominating flow component according to the model is drainflow. This number should be interpreted with caution and not transferred to the actual field condition, because the drainflow component is known to be overestimated in a large grid model due to scale problems. The drain routing in the groundwater model represents not only water in tile drains but also the small water courses not included in the

Table 3 | Performance criteria for simulation of river discharge in the calibration and validation period

		Calibration period 1991–2000				Validation period 2001–2002			
Gauging station	Catchment area (km^2)	Obs mm/yr	ME_Q mm/yr	ME_Q %	R^2_Q –	Obs mm/year	ME_Q mm/year	ME_Q %	R^2_Q –
45.01*, Odense River	302	320	15	−5	0.60	354	38	−11	0.58
45.20*, Holmehave Creek	32	266	−30	11	0.26	306	0	0	0.38
45.21*, Odense River	486	297	7	−2	0.51	336	34	−10	0.45
45.05†, Ryds Stream	42	240	38	−16	0.64	NA	NA	NA	NA
45.22, Stavis Stream	78	243	−4	2	0.52	279	32	−12	0.48
45.23†, Lunde Stream	42	188	−15	8	0.73	NA	NA	NA	NA
45.24, Geels Stream	27	269	12	−4	0.78	292	47	−16	0.81
45.25†, Vejrup Stream	41	216	−38	18	0.44	NA	NA	NA	NA
45.26, Odense River	535	329	8	−2	0.63	354	21	−6	0.54
45.27, Lindved Stream	65	228	19	−9	−0.04	272	63	−23	0.11
Area weighted average of grey	830 (calibration) 705 (validation)	294	6	−2	0.57	336	27	−8	0.50

*Gauging station exits further downstream; therefore this station is not included in catchment average.
†Only observed data until 31.12.1997 therefore not available (NA) in validation period.

MIKE11 river model. A similar detailed description of the nitrogen transport and fate can be addressed at the catchment scale (Figure 6). The annual leaching for the entire land area is 6,404 tonnes per year, which corresponds to 52 kg N/ha. Almost all nitrate from leaching is transported to the river system via drains. 55% of the nitrogen in the catchment is denitrified in the saturated zone and another 1% in wetland areas, which corresponds to an average annual denitrification capacity of 20 kg N/ha. In addition 5% is lost to denitrification in the river system. A total of 2,127 tonnes/yr or 32% of the diffuse and point sources is transported out of the catchment to the Odense Fjord, of which only 2,034 tonnes/yr is recorded in MIKE11 owing to mass conservation problems.

The fate of nitrate

The simulated leaching from the bottom of the root zone for the period 1998–2002 is extracted for 14 sub-catchments within the topographical catchment (Figure 7).

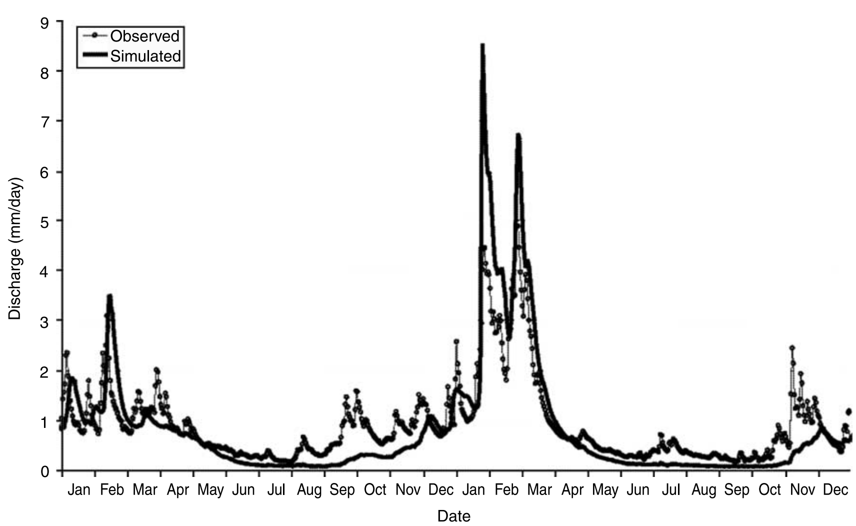

Figure 3 | Observed and simulated daily discharge at Odense River station 45.21 during the validation period.

Table 4 | Performance for simulation of nitrogen fluxes at the four water quality stations in the calibration and validation period

		Calibration period 1998–2000				Validation period 2001–2002			
Gauging station	Catchment area (km^2)	Obs Tonnes/yr	ME_N Tonnes/yr	ME_N %	R_N^2 –	Obs Tonnes/year	ME_N Tonnes/year	ME_N %	R_N^2 –
45.21, Odense River	486	1,291	38	−3	0.21	1,009	222	−22	0.57
45.22, Stavis Stream	78	177	−25	14	−0.25	123	11	−9	0.32
45.24, Geels Stream	27	48	−15	31	−0.50	42	−3	5	0.56
45.27, Lindved Stream	65	77	−61	79	−3.77	68	−10	15	−0.24
Area weighted average	656			9				−16	

The leaching ranges from 37 to more than 97 kg N/ha/yr. The average leaching for the topographical catchment is approximately 50 kg N/ha/yr. The average denitrification in the saturated zone is considered in the 14 sub-catchments by comparing the average input to the catchment with the river output from the individual catchments within the period 1998–2002 (Figure 7). The denitrification ranges from 47–94% in the individual sub-catchments without the wetland and river processes. The denitrification ranges from 53–94% in the individual sub-catchments when including wetland and river processes.

Two assumptions or limitations can be noted using this approach. The nitrogen transport across sub-catchment boundaries or to the model boundary is not accounted for. This could probably explain the apparently high denitrification in the small sub-catchments situated next to the fjord. Furthermore the time lag from the bottom of the root zone to the river systems is not considered in the calculations. However, this is not considered a significant issue for this catchment. If a pulse of nitrate is released from the bottom of the root zone 90% of the pulse will be found in the river system or degraded after approximately 2 years (Figure 8). After 10 years almost 99% of the nitrate pulse has either discharged into the river system (44%) or has been denitrified in the saturated zone (55%). This corresponds quite well to the average denitrification in the saturated zone during the period 1998–2002 (Figure 6). This indicates that the system has a short delay in development of nitrogen fluxes in the river system caused by changes in management practices.

A pulse of particles was released on the surface of each grid and their fate was recorded over the years. Based on the particle tracking, maps of areas that are susceptible to nitrate leaching can be constructed. This is possible by comparing a map of the fraction of particles that is transported below the redox interface with a map of the

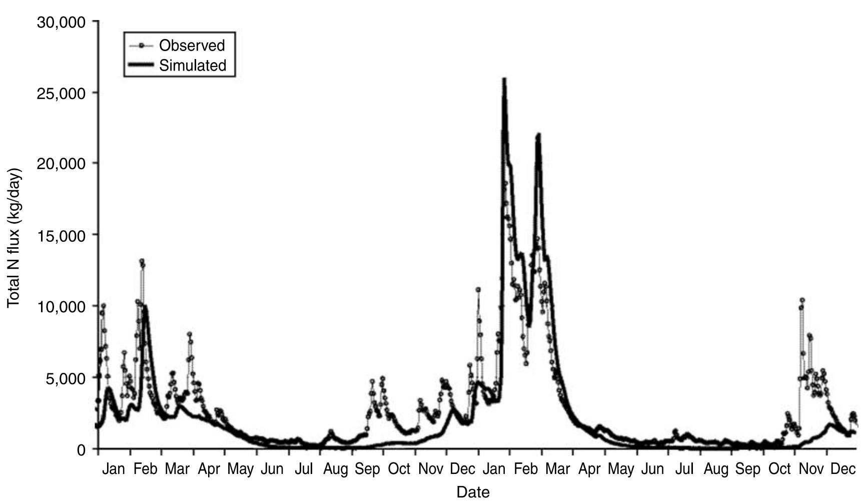

Figure 4 | Observed and simulated daily nitrogen flux at Odense River station 45.21 in the validation period.

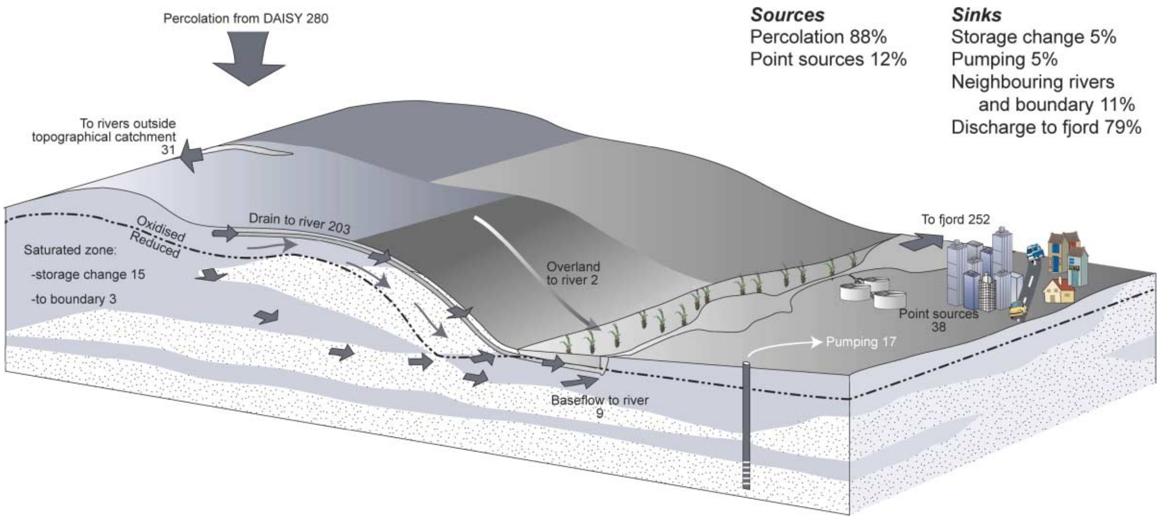

Figure 5 | Catchment water balance (mm/yr) for all land areas within the model area in the period 1998–2002.

fraction of particles that is transported to the river system via drains (Figure 9). The effect of management changes will be more evident on surface water quality in areas where the majority of particles are transported to rivers via drains but to a limited extent below the redox interface along their way. The effect of changes on management practices will be more limited or fail to appear in areas where the majority of particles are transported below the redox interface because the majority of nitrate leaching is already subject to denitrification before discharging into the river system. Some areas are characterised by a high fraction of particles in both drains and below the redox interface. This indicates that the particles are transported below the interface in recharge areas and then emerge as upward flows into the drains in areas where aquifers discharge to streams via drains. The first-order degradation of nitrate applied in the oxidised zone was not considered in the particle tracking so the results should be applied with some caution.

Simulated groundwater concentrations vs. observations

The simulated average nitrate concentrations during the period 1998–2002 in the middle sand aquifer which

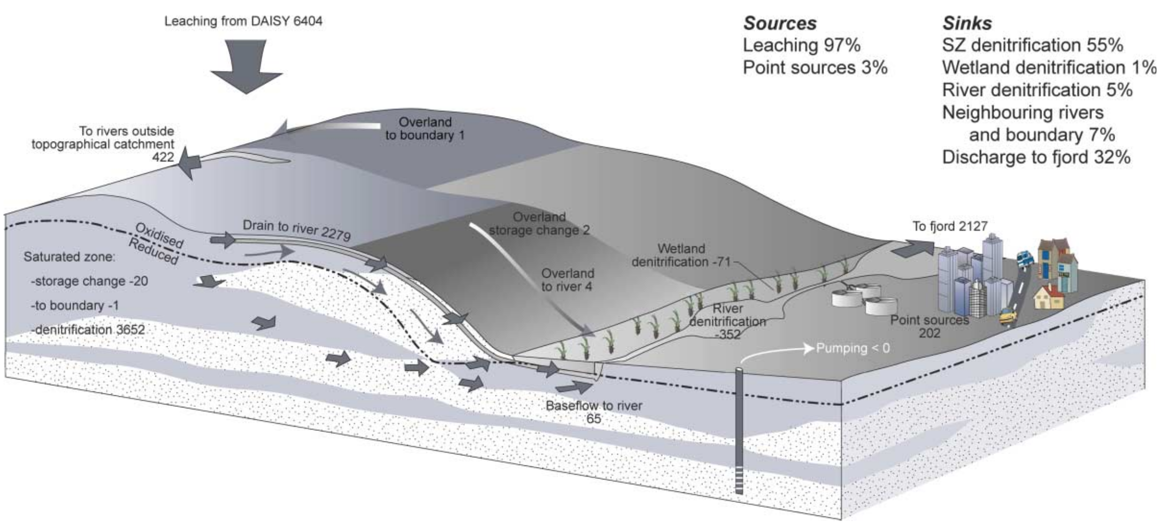

Figure 6 | Catchment nitrogen balance (tonnes N/yr) for all land areas within the model area in the period 1998–2002.

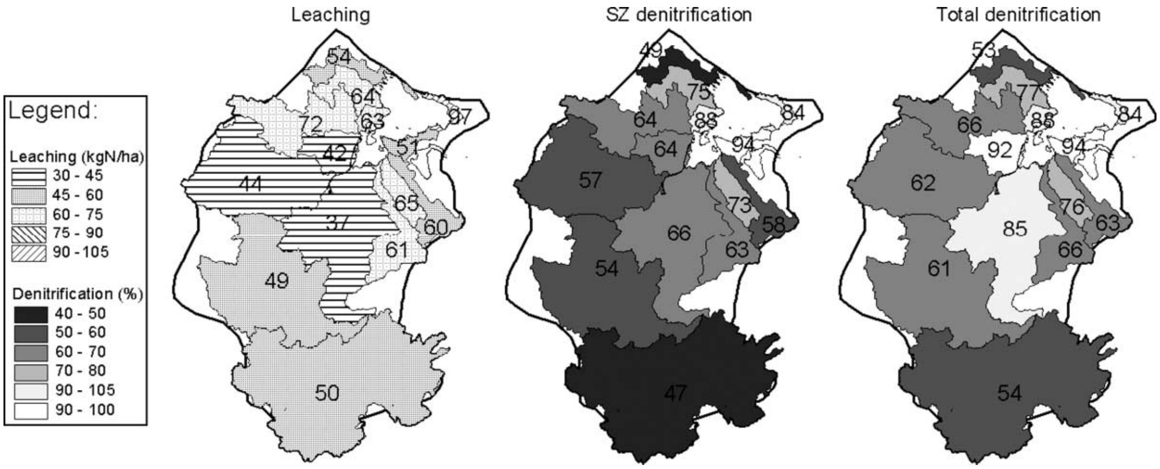

Figure 7 | Simulated leaching, denitrification in the saturated zone, and total denitrification for sub-catchments.

extends through the whole catchment (Figure 1) is shown in Figure 10. For comparison, measured nitrate concentrations during the same period are shown. Note that the nitrate concentrations are given in concentrations of mg Nitrate-N/l to be consistent with numbers used for total nitrogen-N fluxes and mass balances throughout this paper. There are some discrepancies between the location of simulated and observed elevated nitrate levels. The statistical cumulative distribution of simulated and observed nitrate concentrations in the middle aquifer (Figure 10 corner) shows that the (%) of areas where the simulated nitrate concentration is above 0 mg N/l (93%) is underestimated compared with the distribution of nitrate observations where approximately 81% of the observations are almost nitrate-free. The mean values of the observations is approx. 1 mg N/l whereas the simulated mean concentration is only 0.5 mg N/l. Approximately 2% of both the observed samples and the simulated concentrations exceed the drinking water quality demand of 11.28 mg N/l.

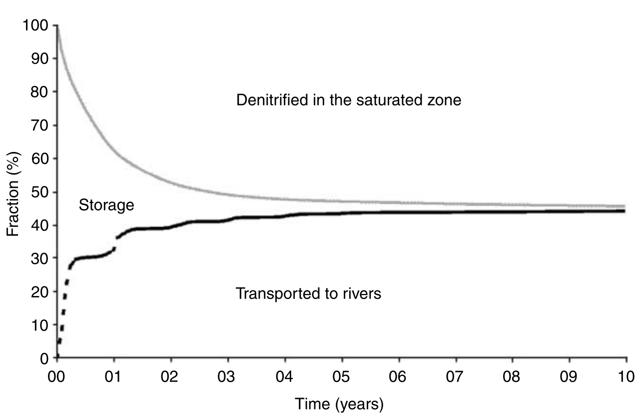

Figure 8 | The fate of a nitrogen pulse at the start of simulation as a function of time.

DISCUSSION

Temporal predictability: simulation of discharge and nitrogen fluxes

The overall water and nitrogen balances in the rivers were simulated satisfactorily with the applied model. However, the model was not able to predict inter-annual dynamics of flow and nitrogen transport. Furthermore, the results show that the model is not suitable for prediction of flow and nitrogen transport for extremely wet or dry years.

It is suspected that the poor dynamics of the model are caused by the lack of representation of heterogeneity in the parametrisation of the DAISY columns. Mostly standard soil and plant physical parameters were used as well as average interpolated 10 km × 10 km grid precipitation. Moreover, the sequential coupling of the DAISY and MIKE SHE calculations without any feedback from the saturated to the unsaturated zone could have had a significant effect on the dynamics of the simulations. Hansen *et al.* (2007) carried out an analysis of the importance of root zone heterogeneities in the parametrisation of DAISY columns for an improved simulation of discharge dynamics at the catchment scale.

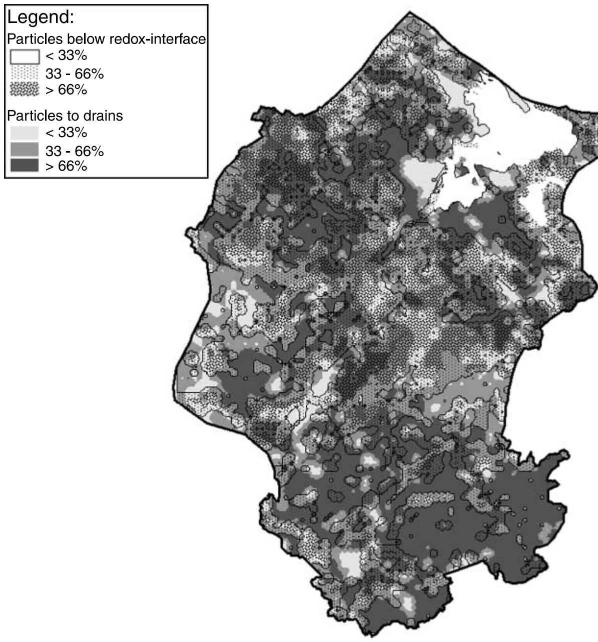

Figure 9 | Fractions of particles: (1) that are transported below the redox interface and (2) that are transported to the river via drains.

The simulation of daily discharge dynamics by nitrogen catchment models that have a lumped conceptual hydrological description generally seems to fit the observed values better than the pure physically based approach presented here. Many catchment nitrogen models are based on hydrological descriptions that were developed for rainfall–runoff models. For instance, the SWAT model (Arnold *et al.* 1998) uses the empirical curve number (CN) method (USDA-SCS 1972), the HBV-N (Arheimer & Brandt 2000) model uses the hydrological formulation of the rainfall–runoff model HBV (Bergström 1995) while the NL-CAT (Schoumans & Silgram 2003) model has a physically based root zone model but the catchment description is conceptual, with reservoirs with different residence times simplifying the flow and transport in the saturated zone. The modelling concept NL-CAT was applied in a part of the Odense River catchment (Dik & Groenendijk 2006). The outlet of the model area was equal to the location of the discharge and water quality station 45.21. Like the model applied in this paper the overall water and nitrogen balances were simulated satisfactorily but the simulated discharge and nitrogen dynamics were fitted better to the observations. However, it has been questioned whether this type of model is suitable for non-point source water quality modelling based on its empirical and conceptual hydrological descriptions (e.g. Refsgaard *et al.* 1999).

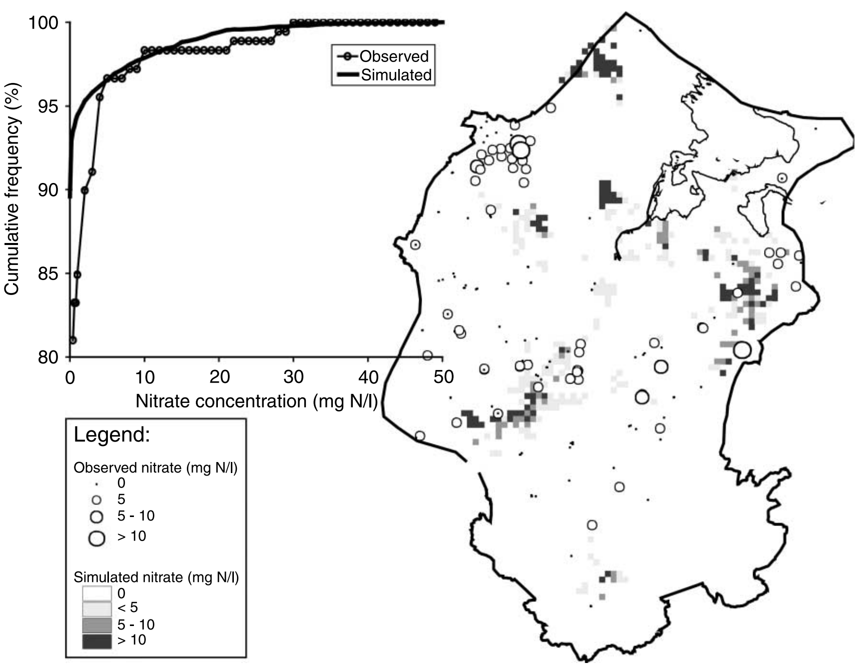

Figure 10 | Location and magnitude of observed and average simulated nitrate concentrations from 1998–2002 in the middle aquifer. The cumulative distribution of observed and simulated concentrations are shown for the same layer in the lower left corner.

Spatial predictability: the fate of nitrate

Saturated zone

Knowledge of the redox environments in glacial sediments was applied and upscaled to a catchment concept. The nitrate concentration was underestimated in the middle regional aquifer below the till aquitards. In most cases the bottom of the aquitard was deeper than the redox interface so that little nitrate was transported to the regional aquifer (Figure 10). This was partially caused by the use of general thicknesses of the oxidised zone but also the aquitard thicknesses in the geological model were treated as homogeneous within every model grid. The applied hydrogeological model and denitrification concept applied here do not properly account for the heterogeneities and sub-grid variation in this setting characterised by complex glacial geology. Nevertheless, the results indicate that there are differences between the sub-catchments within the model area. Also the results from the particle tracking procedure indicate that land use changes should be considered with the differences in denitrification potentials in mind.

A similar denitrification concept a presented here was applied in a sandy catchment by Styczen & Storm (1993*a*,*b*). The spatial predictability of the model was not examined except for comparison of observed and simulated groundwater concentration time series at a few locations. A later comparison between statistical cumulative distributions of simulated and observed shallow nitrate concentrations agreed quite well (Refsgaard *et al.* 1999) but all these concentrations were from the upper screens in the oxidised zone, so this tells us nothing about the goodness of the denitrification concept. Furthermore, these two studies neglected denitrification in wetlands and therefore did not report any comparison between mass balances for observed and simulated nitrogen fluxes.

The comparison between observed and simulated nitrogen fluxes using an earlier version of the applied model showed that the simple on/off denitrification concept underestimated the overall denitrification (Nielsen *et al.* 2004). Therefore, a first-order degradation function was applied in the upper oxidised layer. The first-order degradation partly accounted for local anaerobic environments or redox-interface heterorogeneities not accounted for by the coarse concept. Using a somewhat similar denitrification concept for a part of the Odense Fjord catchment Refsgaard *et al.* (1999) found that the grid size of a model will significantly influence the number of flow lines crossing the reduction front and hence the nitrate concentrations. Therefore, the first-order degradation possibly also corrects for high levels of simulated nitrate leaching or erroneous flow path simulation, especially with the exaggeration of near-surface transport via drains in mind.

Dik & Groenendijk (2006) applied the NL-CAT model in the Odense River catchment. The hydrological catchment description is conceptual compared to the model approach in this paper. Percolation to groundwater and discharge to surface water is schematised by a pseudo-two-dimensional flow in a vertical soil column covering the whole unsaturated zone. Drainage and subsurface water discharges to surface water systems can be simulated with different residence times (Schoumans & Silgram 2003). In the NL-CAT model only the overland nitrogen and the different drainage components are transported to the river system. So the groundwater transport of nitrate is basically neglected and the denitrification in the saturated zone is implicitly equal to the difference between total transport out of the soil column and the amount that is transported into the river system. The model was run for the period 1990–2000. Average annual transport out of the soil column was only 43.6 kg N/ha in comparison with approx. 50 kg N/ha for the same area with the model applied in this study. However, the denitrification process as nitrate is transported from the bottom of the root zone to the rivers is not accounted for and the denitrification in the root zone is likely to be overestimated to compensate for this. The NL-CAT model and the model applied in this paper are conceptually different so the intermediate model results should be compared with some caution. Owing to the lower transport out of the soil column only 27%, which corresponds to the amount leaching to groundwater in the NL-CAT model, was removed in the saturated zone (Dik & Groenendijk 2006). Furthermore, if denitrification and biomass losses in the NL-CAT river system are considered, the total nitrate removal between the soil column output and the catchment outlet was 46%. In the model applied in this paper the denitrification for this catchment was 50% in the saturated zone and the total nitrate removal between the bottom of the root zone and the outlet of the catchment was 57%.

Wetland and river denitrification

Compared with the results reported by Dik & Groenendijk (2006) the model applied in this paper suggests limited wetland and river denitrification compared with the denitrification in the saturated zone. The maximum denitrification rate in the wetland areas was assumed quite high but the actual simulated denitrification was determined from the simulated amount of nitrate that was actually transported to these areas and the temperature at a given time. The delay of discharge in the autumn resulted in a delay of nitrate transport to the wetlands which could lead to low denitrification rates, owing to a temperature decline during the delay. The maximum denitrification rates in the individual wetlands along the river branches ranged from 70–690 kg N/ha/yr. These values are comparable with reported Danish monitored values (Paludan & Fuglsang 2000). Arheimer & Witgreen (2002) reported an application of the lumped conceptual catchment model HBV-N in a catchment in southern Sweden. Arheimer & Wittgren (2002) included a description for denitrification in wetlands as a first-order temperature-dependent degradation. The simulated wetland removal for eight individual wetland areas ranged from 29–1,186 kg N/ha/yr.

Data availability and uncertainties

The same methods for parametrising root zone, saturated zone and wetlands were applied in the whole model area. It could be claimed that there are not enough data available at the catchment scale to support the detailed and physically based approach in this study. Furthermore, the uncertainly of the input parameters and the simulation outputs was not investigated, which should be taken into account when making decisions based on such models. The leaching levels and denitrification (%) may not be correct at sub-catchment or even catchment scale. However, the relative difference between sub-catchments will not be as affected as the absolute results. Van der Keur *et al.* (2008) addressed the uncertainty in simulation of nitrate leaching at the field and catchment scale for the Odense River sub-catchment using a simplified version of the presented modelling approach.

Physically based models are sometimes criticised as being over-parametrised. In this study only a limited number of the parameters involved in the simulations were subject to calibration as suggested by Refsgaard (1997). For the percolation and leaching calculations from the root zone, standard values were applied with corrections to the soil physical parameters and the crops modules. In the calibration of the original National Water Resource Model about 10 free parameters were subject to calibration (Henriksen *et al.* 2003). During the calibration of the Odense Fjord model only the drain time constant was changed in an attempt to improve the discharge dynamics. There was no calibration of the concept for upscaling redox interface to the model area. However, the first-order degradation applied in the upper oxidised layer was recalibrated to obtain good results after correction of the model code. The first-order degradation processes can be argued to be a black-box concept with some physical explanation and not a true process description or a theoretically sound upscaling of point scale processes.

CONCLUSION

The model presented in this paper has been shown to have predictive ability at the catchment scale except for inter-annual flow and nitrogen flux dynamics. The model could potentially have predictive capabilities for nitrogen fluxes in rivers for smaller scales. However, this was not tested below the sub-catchment scale. In spite of a relatively detailed model (6,061 DAISY columns, 500 m × 500 m grid and nine geological layers) the model does not have predictive capabilities at the 500 m grid scale.

The applied model provides simulation results for nitrate leaching and surface water quality, as many other nitrogen models do. However, the detailed description of the saturated zone in the model also addresses the fate of nitrate transported from the bottom of the root zone to the catchment outlet. The model is able to simulate nitrate removal in the root zone, saturated zone, river systems and wetlands separately by use of mostly physically based process descriptions. In this way it has a larger potential applicability than most other models. However, it has not been possible to test the individual components, so the division of denitrification between groundwater and surface water has not been subject to a rigorous test. The NL-CAT and the presented DAISY MIKE SHE approach gave similar results for the Odense River catchment: however, the intermediate components were not the same. It is postulated that the results here are more correct, owing to the physical foundation of the model approach. However, this was not tested.

It is believed that the presented approach is the only available nitrogen catchment model that could possibly have predictive ability for conditions that are considerably different from the ones it was calibrated for. The physical formulation and integration of all hydrological domains ideally makes the concept applicable for scenario calculations for management and land-use changes under different flow regimes. Such a modelling tool is very useful for optimal planing and benefit of land-use changes and establishment of wetland areas within catchments to ensure as high a denitrification between field and recipients as possible.

ACKNOWLEDGEMENTS

The authors would like to thank the Ministry of the Environment and the Ministry of Agriculture that financed the original construction of the modelling approach. PhD funding from the Danish International Research School of Water Resources (FIVA) and the Geological Survey of Denmark and Greenland (GEUS) made it possible to recalculate and present the research results here.

We acknowledge Torsten Jakobsen, Karen Villholth, and Jørgen Krogsgaard (DHI Water & Environment) for technical assistance and Kristian Rasmussen (GEUS) for artwork assistance.

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First received 4 November 2007; accepted in revised form 7 December 2008