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Nitrogen transformation component for SHETRAN catchment nitrate transport modelling

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Abstract

The capability to simulate nitrogen transformations has been added to the SHETRAN physically based, spatially distributed river catchment modelling system so that it can be used in 3D simulations of coupled flow and nitrate transport. In SHETRAN, the subsurface is a variably saturated heterogeneous region, comprising perched, unconfined, confined and unsaturated systems, and at the surface there is vegetation and water flow overland and in stream networks. Nitrate transport is modelled in SHETRAN using advection–dispersion equations with terms added for adsorption and a two-region (dynamic region and dead-space) representation. The nitrogen transformations taking place in and below the root zone are modelled using NITS (Nitrate Integrated Transformation component for SHETRAN), which was designed to be comprehensive, self-consistent and fully compatible with SHETRAN. NITS has pools for both carbon and nitrogen in manure, litter and humus, and further pools for ammonium and nitrate, and involves the simultaneous solution of seven ordinary differential equations plus several auxiliary equations. NITS and its integration in SHETRAN are described here, as are a series of successful verification simulations for the responses of the carbon and nitrogen pools when straw and manure are added to the soil, and a successful field validation for nitrate generation and leaching in a fertilised barley plot. The NITS equations strictly apply at a point, and are used in SHETRAN with distributed parameters (i.e. each finite difference cell in SHETRAN has its own set of transformation variables and parameters). The intention is that in addition to being used in simulations of nitrate pollution and the effectiveness of proposed remedial measures and changes in agricultural practice, SHETRAN will be used in studies of the ‘upscaling’ of the equations and parameters for nitrate transport using the ‘UP’ approach of Ewen [Ewen, J., 1997. Hydrol. Earth System Sci. 1, 125–136]. In Birkinshaw and Ewen [Birkinshaw, S.J., Ewen, J., 2000. Modelling nitrate transport in the Slapton Wood catchment using SHETRAN. J. Hydrol. 230, 18–33.] SHETRAN is used to simulate the generation of nitrate following the application of fertiliser in the Slapton Wood catchment, Devon, UK, and the subsequent leaching, lateral subsurface transport and discharge of nitrate to the ground surface and its transport in the Slapton Wood stream.

Keywords: Catchment modelling; Nitrate pollution; Nitrogen transformations; Fertiliser applications; SHETRAN

1. Introduction

Throughout the world, a variety of limits and targets have been set on nitrate concentrations in water (e.g. EC, 1991; U.S. EPA, 1991). Thus, the pollution of surface water and groundwater by nitrate is an international problem (Robert and Marsh, 1987; Meybeck et al., 1989; Spalding and Exner, 1993; Zhang et al., 1996), which in some countries has worsened in the recent years (Robert and Marsh, 1987; Betton et al., 1991). One source of nitrate is inorganic nitrogen fertilisers, and there is a wealth

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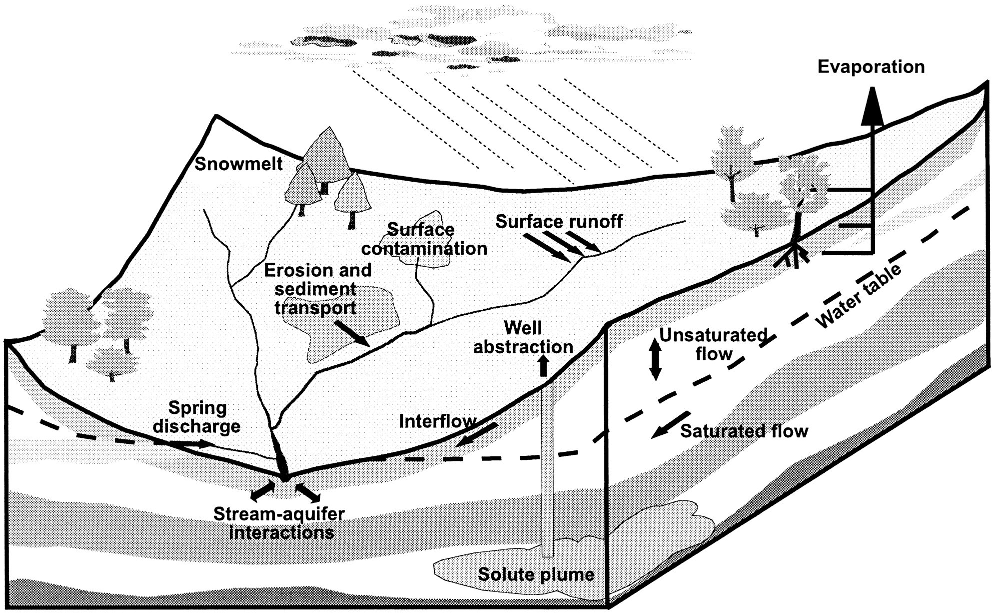

Fig. 1. Schematic showing some the main processes represented in SHETRAN.

of literature on the link between agriculture and nitrate pollution (e.g. Royal Society, 1983; National Research Council, 1993; Criado, 1996).

The behaviour of nitrogen in soil is known to be complex, and several models have been specifically developed for modelling nitrogen transformations and nitrate leaching in the root zone: e.g. ANIMO (Rijtema and Kroes, 1991), DAISY (Hansen et al., 1990), LEACHN, part of the LEACHM model (Wagenet and Hutson, 1989), SOILN (Johnsson et al., 1987) and WAVE (Vanclooster et al., 1995). Several programmes of intercomparisons of root zone nitrate models have been carried out (e.g. de Willigen, 1991; Diekkrüger et al., 1995) and recently there has been a comparison of the organic matter components of these models (Smith et al., 1997).

An important aspect of the agricultural nitrate pollution is the pollution of river water, so the natural scale for studying nitrate problems is often the river catchment scale. At this scale, river catchment modelling can be used in the study of the pollution resulting from the current, past and potential future applications of fertiliser, the effects of changes in agricultural practices and the effectiveness of possible remedial measures for existing polluted sites. Ideally, the river catchment model should allow an integrated analysis of surface and subsurface pollution, and so must be able to represent the application of nitrogen materials to the ground surface, the nitrogen transformations in the soil/rock which control the rate of production and loss of nitrate, and the transport of nitrate through the surface and subsurface zones of the catchment. A small number of models have the capability for use in studying nitrate pollution in river catchments, including: CATCHN (Cooper et al., 1994), CWSS (Reiche, 1994), DAISY/MIKE-SHE (Styczen and Storm, 1993; Refsgaard et al., 1999), NMS (Lunn et al., 1996) and INCA (Whitehead et al., 1998).

Considerable advances have been made in physically based spatially distributed (PBSD) river catchment modelling in the past few years, especially in relation to subsurface modelling, resulting in the development of SHETRAN Version 4 (Ewen et al., 2000), a PBSD coupled surface/subsurface modelling system for 3D water flow and multi-fraction sediment transport, and multiple, reactive solute transport (Fig. 1). The subsurface is represented in SHETRAN as a fully 3D variably saturated heterogeneous medium, allowing the representation of combinations of confined, unconfined and perched groundwater systems, and complex lithologies. SHETRAN is designed to allow detailed representation of a river

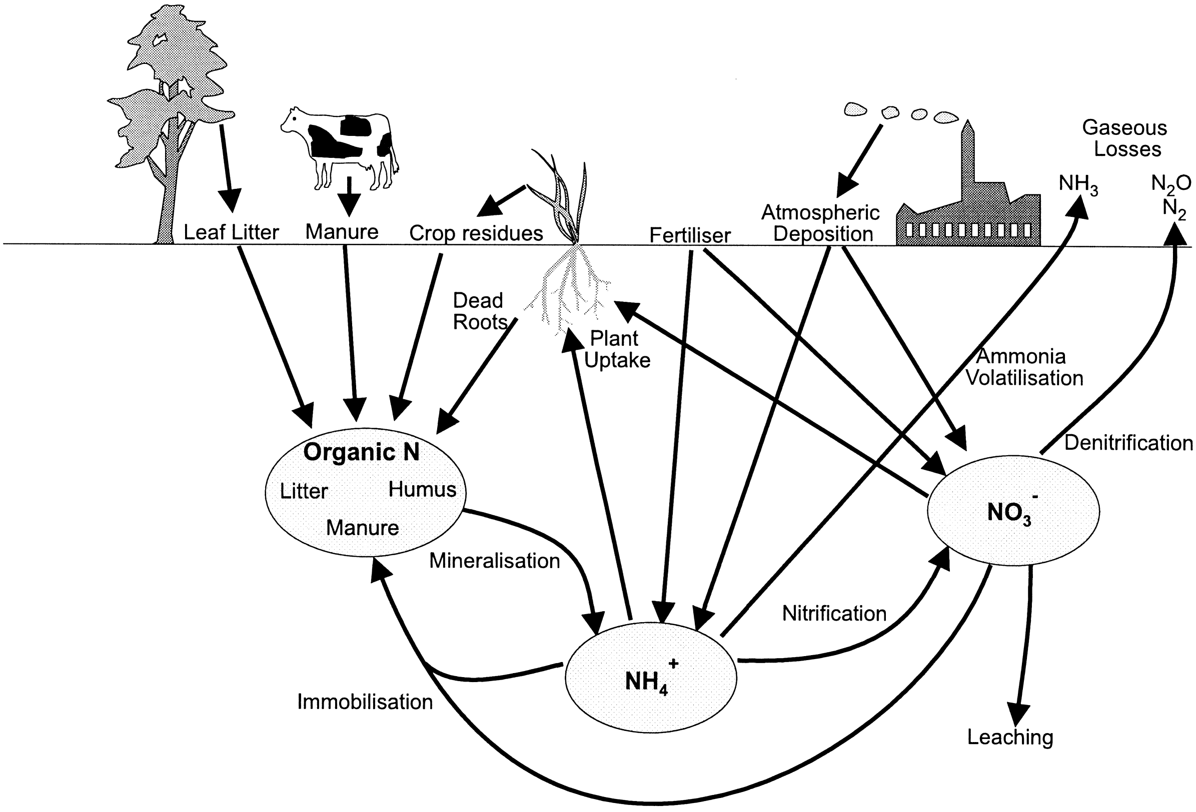

Fig. 2. The nitrogen cycle as represented in NITS.

catchment, including the simultaneous 3D surface/subsurface transport of a set of interacting solutes. It can therefore be used to represent the transport of leached nitrate through perched, phreatic, confined and unsaturated subsurface systems, and the ultimate discharge of the nitrate to seepage areas and into surface waters. To achieve this, within SHETRAN the subsurface is divided into finite-difference cells (typically 15,000 cells), and the changes in water content and solute concentrations over time are simulated for each cell on a timestep of 1 h or less. The main solute transport processes simulated by SHETRAN are advection, dispersion, adsorption, absorption into dead-space (e.g. small and dead-end soil pores and relatively stagnant regions in river banks), and plant uptake. In surface water, in addition to the above processes, solute may be transported adsorbed to the moving sediments. SHETRAN is driven by rainfall and meteorological data (usually hourly data), and it is common to run simulations of periods of a few years or decades.

A nitrogen transformation model, NITS, (standing for Nitrate Integrated Transformation component for SHETRAN) is developed here. This has been integrated within SHETRAN's solute transport component, so the concentrations of the nitrogen species (and carbon) are simulated for every finite-difference cell, and are updated, along with water flow and nitrate transport, every timestep. The result is a PBSD 3D coupled flow and transport surface/subsurface modelling system for nitrate generation and transport, which can be used, for example, to simulate nitrogen fertiliser application and the resulting nitrate leaching and the subsurface transport to the ground surface, then transport overland and through the river network, as demonstrated in the Slapton Wood catchment simulations in Birkinshaw and Ewen (2000).

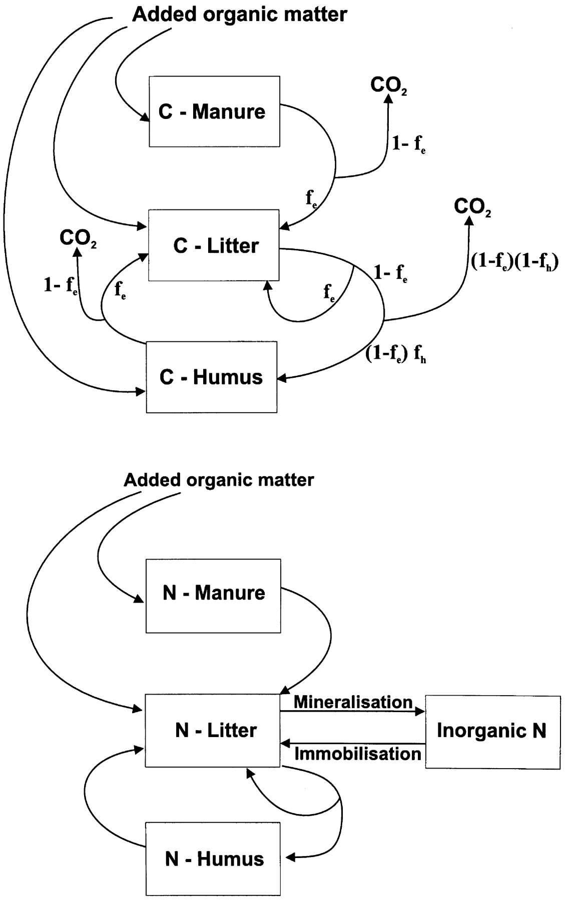

Fig. 3. Carbon and nitrogen transformations.

NITS is physically based (as far as is practical) and fully integrated into SHETRAN. The physical basis is important since it provides the link between the simulations and physical property measurements, whether new measurements or measurements reported in the literature, which apply to the current and, if relevant, possible future or post-remedial field conditions. Some of the existing catchment models for studying catchment pollution are physically based, but none are fully integrated models for flow and transport. Integration is an important feature of SHETRAN since it ensures that the distributed parameters for the nitrogen transformations and nitrate transport are entirely consistent with the very complex patterns of soil and rock which can be represented in SHETRAN. It also ensures that there is consistent treatment, for flow and transport, of vegetation dynamics and soil development and erosion, which are coupled aspects of flow and nitrate transport modelling which if the current plans are realised will be explored further in future versions of SHETRAN.

A point, which requires emphasis, is that NITS is a small scale (or point scale) model, and is used in SHETRAN with distributed parameters. There is now widespread understanding of the problems of scale (almost all of which remain to be solved) and of the need for appropriate parameterisation in models that have gridscales larger than the scale at which the available property or parameter values apply. The approach to scale problems being explored by the developers of SHETRAN, the so-called ‘UP’ approach, is outlined in Ewen (1997), Sloan and Ewen (1999) and Ewen et al. (1999). This involves ‘upscaling’ based on the output from PBSD models run with distributed small-scale parameters. The development of NITS as a small-scale model and its integration in SHETRAN is part of this effort, and SHETRAN will, if the current plans are realised, be used in ‘upscaling’ studies of catchment nitrate transport.

2. NITS

It is known that nitrogen transformations such as denitrification in saturated regions (Morris et al., 1988; Starr and Gillham, 1993) can occur outside the root zone, so the use of NITS within SHETRAN is therefore not restricted to the root zone. The nitrogen cycle as represented by the NITS component is shown in Fig. 2. Organic matter can comprise materials of different types which decompose at substantially different rates, so it is common in modelling to represent organic matter as if it occupies two or more pools (McGill et al., 1981; van Veen et al., 1985; Hansen et al., 1990; Jenkinson, 1990). Three main pools are used in NITS, one each for: very fast decomposing manure, comprising mainly animal wastes and faeces; fast decomposing litter, comprising mainly leaf litter, dead roots and microbial biomass; and slow decomposing humus, comprising stabilised decomposition products. The carbon dynamics associated with each of the above nitrogen pools is also modelled, using three carbon pools, since it is known that the rate of decomposition of carbon materials control the rates of turnover of organic nitrogen, mineralisation of organic nitrogen to ammonium, and immobilisation of ammonium and nitrate to organic nitrogen (Harris, 1988).

The treatment using the three main pools is based on the SOILN (Johnsson et al., 1987), LEACHN (Wagenet and Hutson, 1989), and WAVE (Vanclooster et al., 1995) models. However, there are significant differences between NITS and the other three models. In SOILN, LEACHN and WAVE, all the decomposed nitrogen in the humus pool is mineralised and all the decomposed carbon is lost as CO_2. In NITS, however, for self-consistency and similarity between pools, organic matter in the humus pool is assumed to decompose as a result of biomass activity with a fraction f_e of the decomposed carbon assumed to supply biosynthesis and fraction $1 - f_e$ to supply energy (producing CO_2 as a byproduct), and some of the decomposed nitrogen is taken up for biosynthesis, with the remainder available for mineralisation (Fig. 3). Also, in NITS the microbial biomass is contained within the litter pool, while in SOILN, LEACHN and WAVE some of the biomass is contained in the soil litter pool and some in the soil manure pool.

To account for the nitrogen and carbon in the three main pools, and also for ammonium and nitrate, eight pools in total are used in NITS to represent the state of carbon and nitrogen at a single point in space, i.e. one pool each for carbon litter, carbon manure, carbon humus, ammonium, nitrate, nitrogen litter, nitrogen manure and nitrogen humus. The behaviour of the first seven of these pools is represented by a coupled set of seven ordinary differential equations, each equation representing mass balance in a single pool. A differential equation is not required for the nitrogen humus pool since the carbon/nitrogen (C/N) ratio in humus for a particular soil is generally constant (Jenkinson, 1988). The development of NITS was carried out in a systematic way to ensure that there is as much similarity as possible between the treatments of the various pools, and to ensure that the fate of every gram of mass is explicitly accounted for.

As is the common practice (backed by the experimental evidence of van Veen and Paul (1981) the decomposition processes for the carbon litter (concentration c_l), carbon humus (c_h) and carbon manure (c_m) are assumed governed by first-order kinetic equations (the full notation is described in Tables 1 and 2):

$$\frac{\mathrm{d}c_l}{\mathrm{d}t} = -k_l e_o^T e_o^\psi c_l + f_e k_l e_o^T e_o^\psi c_l + f_e k_h e_o^T e_o^\psi c_h + f_e k_m e_o^T e_o^\psi c_m + c_{al} \tag{1}$$

$$\frac{\mathrm{d}c_h}{\mathrm{d}t} = (1 - f_e) f_h k_l e_o^T e_o^\psi c_l - k_h e_o^T e_o^\psi c_h + c_{ah} \tag{2}$$

and

$$\frac{\mathrm{d}c_m}{\mathrm{d}t} = -k_m e_o^T e_o^\psi c_m + c_{am} \tag{3}$$

The rates of nitrogen transfer between pools depend on the rates of carbon transfer. Therefore, to develop the NITS equations in a systematic fashion, the nitrogen transformations (Fig. 3) are assumed similar to the carbon transformations, giving the following equations for nitrogen litter (n_l) and nitrogen manure (n_m) (there is not, as noted earlier, an ordinary differential equation for nitrogen humus):

$$\frac{\mathrm{d}n_l}{\mathrm{d}t} = -k_l e_o^T e_o^\psi n_l + f_e k_l e_o^T e_o^\psi \frac{c_l}{(\mathrm{C/N})_b} + f_e k_h e_o^T e_o^\psi \frac{c_h}{(\mathrm{C/N})_b} + f_e k_m e_o^T e_o^\psi \frac{c_m}{(\mathrm{C/N})_b} + \frac{c_{al}}{(\mathrm{C/N})_{al}} \tag{4}$$

$$\frac{\mathrm{d}n_m}{\mathrm{d}t} = -k_m e_o^T e_o^\psi n_m + \frac{c_{am}}{(\mathrm{C/N})_{am}} \tag{5}$$

It can be seen from these equations that the response of the nitrogen litter and manure pools to added materials is controlled by the carbon/nitrogen ratios $(\mathrm{C/N})_{al}$ and $(\mathrm{C/N})_{am}$ for added litter and manure, respectively. These, in turn, depend on the nature and composition of the materials added. The corresponding ratio for the biomass in the litter pool, $(\mathrm{C/N})_b$, is assumed to be constant. The two remaining ordinary differential equations, for ammonium (n_{NH_4}) and nitrate (n_{NO_3}), are very similar to those used in SOILN (Johnsson et al., 1987) and WAVE (Vanclooster et al., 1995). These involve sums of the rates (ξ) of generation and loss through processes such as

Table 1
Nomenclature for Constants and Variables

Symbol	Meaning
a	External additions of nitrogen (g N m^{-3} day^{-1})
A	[a]Plan area of a column (m^2)
b	[a]Mass adsorbed per unit volume of soil (g N m^{-3})
c	Carbon concentration (g C m^{-3})
C/N	Carbon to nitrogen ratio (dimensionless)
d	[a]Dry deposition rate (g N m^{-2} day^{-1})
d_a	[a]Width of column (m)
d_b	[a]Width of column (m)
D	[a]Dispersion coefficient (m^2 day^{-1})
e	Environmental reduction factor (dimensionless)
f_e	[a]Efficiency fraction (dimensionless)
f_h	[a]Humification fraction (dimensionless)
k	[a]Decomposition parameters (day^{-1})
K	[a]Distribution coefficient (dimensionless)
L	[a]Leaching rate (day^{-1})
n	Nitrogen concentration (g N m^{-3})
p	Plant uptake of inorganic nitrogen (g N m^{-3} day^{-1})
P	Rainfall (mm day^{-1})
P^*	Potential plant uptake rate for nitrogen (g N m^{-3} day^{-1})
Q_{10}	[a]Temperature factor (dimensionless)
R	[a]Retardation factor (dimensionless)
s	Source rate for nitrate generation as a result of nitrogen transformations (g N m^{-3} day^{-1})
S	Degree of saturation (dimensionless)
t	Time (day^{-1})
u	Velocity of flow (m day^{-1})
v	Volumetric lateral flow rate, per unit depth, into a face of a column (m^2 day^{-1})
w	[a]Wet deposition rate (g N mm^{-1})
z	[a]Length of a soil column (m)
α	[a]Denitrification factor (dimensionless)
β	[a]Nitrate diffusion constant (day^{-1})
χ	Volumetric rate of water flow into dead-space (day^{-1})
γ	Net mineralisation rate (g N m^{-3} day^{-1})
δ	[a]Coefficient for exchange between the dynamic region and dead-space (day^{-1})
θ	Moisture content (dimensionless)
ψ	Matric potential (m)
ϕ	[a]Fraction of pore water which is in the dynamic region (dimensionless)
ξ	Rate of process (g m^{-3} day^{-1})
μ	Fertiliser application rate (g N m^{-2} day^{-1})

[a] Indicates constant.

mineralisation (subscript min) and immobilisation (subscripts in and ia):

$$\frac{\mathrm{d}(R_{\mathrm{NH_4}} n_{\mathrm{NH_4}})}{\mathrm{d}t} = \xi_{\mathrm{min}} - \xi_{\mathrm{ia}} - \xi_n - \xi_{\mathrm{v}} + a_{\mathrm{NH_4}} - p_{\mathrm{NH_4}} \tag{6}$$

Table 2
Nomenclature for general superscripts and subscripts

Symbol	Meaning
ah	Added to humus pool from external source
al	Added to litter pool from external source
am	Added to manure pool from external source
b	Microbial biomass
CO_2	Carbon dioxide production
d	Denitrification
ds	Dead-space
dy	Dynamic region
h	Humus
i	Total immobilisation
i^*	Potential immobilisation
ia	Immobilisation of ammonium
in	Immobilisation of nitrate
l	Litter
lch	Nitrate leaching
m	Manure
min	Mineralisation
n	Nitrification
NH_4	Ammonium (or ammonium pool)
NO_3	Nitrate (or nitrate pool)
o	Organic matter turnover
p,NO_3	Maximum plant uptake of nitrate
p,NH_4	Maximum plant uptake of ammonium
T	Temperature
u,NO_3	Maximum uptake for immobilisation of nitrate
u,NH_4	Maximum uptake for immobilisation of ammonium
v	Ammonia volatilisation
θ	Moisture
ψ	Matric potential
*	Dead-space
$\bar{\ }$	Evaluated at the face of a column
$\lvert\gamma\rvert$	Absolute value of variable γ

and

$$\frac{\mathrm{d}n_{\mathrm{NO_3}}}{\mathrm{d}t} = -\xi_{\mathrm{in}} + \xi_{\mathrm{n}} - \xi_{\mathrm{d}} + a_{\mathrm{NO_3}} - p_{\mathrm{NO_3}} - \xi_{\mathrm{lch}} \tag{7}$$

where the rates (a) of input of nitrogen depend on the dry deposition rate, the wet deposition rate and the rate of input of fertiliser.

$$a_{\mathrm{NH_4}} = \frac{d_{\mathrm{NH_4}}}{z} + \frac{P w_{\mathrm{NH_4}}}{d_{\mathrm{a}} d_{\mathrm{b}} z} + \frac{\mu_{\mathrm{NH_4}}}{z} \tag{8}$$

and

$$a_{\mathrm{NO_3}} = \frac{d_{\mathrm{NO_3}}}{z} + \frac{Pw_{\mathrm{NO_3}}}{d_a d_b z} + \frac{\mu_{\mathrm{NO_3}}}{z} \tag{9}$$

and the rates of plant uptake (p) are given by

$$p_{\mathrm{NH_4}} = \min\begin{cases} P^* n_{\mathrm{NH_4}}/(n_{\mathrm{NO_3}} + n_{\mathrm{NH_4}}) \\ k_{P,\mathrm{NH_4}} n_{\mathrm{NH_4}} \end{cases} \tag{10}$$

and

$$p_{\mathrm{NO_3}} = \min\begin{cases} P^* n_{\mathrm{NO_3}}/(n_{\mathrm{NO_3}} + n_{\mathrm{NH_4}}) \\ k_{P,\mathrm{NO_3}} n_{\mathrm{NO_3}} \end{cases} \tag{11}$$

The above equations for plant uptake are based on the substantial literature on the uptake of nitrogen by plants (e.g. Haynes, 1986; Wild, 1988). The uptake rate is known to depend both on a plant's requirements and the availability of nitrogen in the soil to meet those requirements. For the purpose of verifying and validating NITS, the plant requirements will be specified. (In SHETRAN the requirements are calculated using a plant model, and depend on the rate of increase of the mass of the plants and also on the fraction of nitrogen within the new plant material). Based on the literature review of Haynes (1986), and following the approach used in other models (e.g. NTRM, Shaffer et al., 1983; SOILN, Johnsson et al., 1987), as shown in Eqs. (10) and (11), it is assumed that if sufficient mineral nitrogen is available then ammonium in solution and nitrate will be taken up in proportion to their concentrations.

In SHETRAN, the leaching of nitrate is controlled by the existing solute transport component, which simulates 3D advection and dispersion of solutes. For the purpose of verifying and validating the NITS equations, however, a 1D advection model is used.

$$\xi_{\mathrm{lch}} = -K_{\mathrm{lch}} L n_{\mathrm{NO_3}} \tag{12}$$

2.1. Auxiliary equations

Following standard approaches (e.g. Hansen et al., 1990; Rijtema and Kroes, 1991; Vanclooster et al., 1994; Rodrigo et al., 1997) environmental reduction factors are used to account for the effects of temperature and soil moisture.

$$e_o^T = (Q_{10,0})^{(T-30)/10} \tag{13}$$

and

$$e_o^\psi = \begin{cases} 0.6 & \psi \geq -0.01\ \mathrm{m} \\ 1.05 + 0.225\log(-\psi) & -0.01\ \mathrm{m} \geq \psi \geq -0.6\mathrm{m} \\ 1 & -0.6\ \mathrm{m} \geq \psi \geq -3\ \mathrm{m} \\ 1.136 - 0.284\log(-\psi) & -3\ \mathrm{m} \geq \psi \geq -10{,}000\ \mathrm{m} \\ 0 & -10{,}000\ \mathrm{m} \geq \psi \end{cases} \tag{14}$$

where the time-varying matric potential, ψ, is a flow state variable in SHETRAN, and so is calculated simultaneously with the nitrogen transformation state variables. Environmental reduction factors similar to the above are used in the representation of nitrification (Rijtema and Kroes, 1991; Vanclooster et al., 1994).

$$\xi_n = k_n e_n^T e_n^\psi n_{\mathrm{NH_4}} \tag{15}$$

and in the representation of ammonia volatilisation (Vanclooster et al., 1994).

$$\xi_v = k_v e_v^T n_{\mathrm{NH_4}} \tag{16}$$

The biomass in the litter pool requires a certain amount of nitrogen for growth, and the rate of mineralisation of organic nitrogen, ξ_{min}, and the potential rate of immobilisation of nitrate and ammonium, ξ_i^*, depends on the difference between the amount being taken up and that needed for growth (Harris, 1988). If this difference is γ and

$$\begin{aligned} \gamma = {} & k_l e_o^T e_o^\psi \left(n_l - \frac{c_l(1-f_e)f_h}{(\mathrm{C/N})_h} - \frac{c_l f_e}{(\mathrm{C/N})_b} \right) \\ & + k_h e_o^T e_o^\psi c_h \left(\frac{1}{(\mathrm{C/N})_h} - \frac{f_e}{(\mathrm{C/N})_b} \right) \\ & + k_m e_o^T e_o^\psi \left(n_m - \frac{c_m f_e}{(\mathrm{C/N})_b} \right) \end{aligned} \tag{17}$$

then

$$\xi_{\mathrm{min}} = \frac{1}{2}(\gamma + |\gamma|) \tag{18}$$

$$\xi_i^* = \frac{1}{2}(-\gamma + |\gamma|) \tag{19}$$

Both ammonium and nitrate can be immobilised, so the total rate of immobilisation, ξ_i, is $\xi_{ia} + \xi_{in}$. It is assumed that ammonium is immobilised in preference to nitrate, and the rates of immobilisation are limited by supply.

$$\xi_{\mathrm{ia}} = \min\begin{cases} \frac{1}{2}(-\gamma + |\gamma|) \\ k_{u,\mathrm{NH_4}} n_{\mathrm{NH_4}} \end{cases} \tag{20}$$

and

$$\xi_{\mathrm{in}} = \min\begin{cases} \frac{1}{2}(-\gamma + |\gamma|) - \xi_{\mathrm{ia}} \\ k_{u,\mathrm{NO_3}} n_{\mathrm{NO_3}} \end{cases} \tag{21}$$

If the potential rate of immobilisation, ξ_{i}^{*}, is not being achieved, decomposition of the litter and manure pools ceases until sufficient nitrogen has been mineralised from the humus pool to satisfy the discrepancy.

Denitrification in the root zone is mainly due to biological denitrification. In many models of nitrate transformations in the root zone (e.g. SOILN, Johnsson et al., 1987 and WAVE, Vanclooster et al., 1994), it is assumed that organic matter is present in sufficient quantities so that the rate of denitrification is not limited by the supply of organic matter. However, it is known that in saturated regions in the field the biological denitrification rate may be limited by the supply of organic matter (Korom, 1992). NITS is designed to be used in SHETRAN both within and below the root zone and therefore uses an approach similar to DAISY (Hansen et al., 1990). The denitrification rate depends on the availability of degradable organic matter and the effeciency with which anaerobic conditions develop, if the availability of these limits denitrification. It depends on the nitrate concentration if the supply of nitrate limits denitrification.

$$\xi_{\mathrm{d}} = \min(\alpha e_{\mathrm{d}}^{T} e_{\mathrm{d}}^{\theta} \xi_{\mathrm{CO_2}}, \beta n_{\mathrm{NO_3}}) \tag{22}$$

where the rate of CO_2 production, $\xi_{\mathrm{CO_2}}$, is assumed to be a measure of the availability of degradable organic matter.

$$\begin{aligned} \xi_{\mathrm{CO_2}} = {} & (1 - f_{\mathrm{e}})(1 - f_{\mathrm{h}}) k_{\mathrm{l}} e_{\mathrm{o}}^{T} e_{\mathrm{o}}^{\psi} c_{\mathrm{l}} + (1 - f_{\mathrm{e}}) k_{\mathrm{h}} e_{\mathrm{o}}^{T} e_{\mathrm{o}}^{\psi} c_{\mathrm{h}} \\ & + (1 - f_{\mathrm{e}}) k_{\mathrm{m}} e_{\mathrm{o}}^{T} e_{\mathrm{o}}^{\psi} c_{\mathrm{m}} \end{aligned} \tag{23}$$

and e_{d}^{θ} is the soil moisture reduction factor for denitrification.

$$e_{\mathrm{d}}^{\theta} = \begin{cases} 0 & S \le 0.8 \\ -1.6 + 2S & 0.8 < S \le 0.9\,, \\ -7 + 8S & 0.9 < S \le 1 \end{cases} \tag{24}$$

where S is the degree of saturation, i.e. the ratio of the volumetric moisture content to the porosity, and is calculated in SHETRAN from the matric potential. Chemodenitrification can be also important in the saturated zone in aquifers with high metal loadings (Postma et al., 1991; Ottley et al., 1997), but this process is not included in the model.

Ammonia in solution is readily adsorbed to the microscopic surfaces of soil, rock and sediment, and this has a significant effect on the transformations within the soil, as the adsorbed ammonium does not readily undergo decomposition and is not easily absorbed by plants (Wild, 1988). The simple approach used to account for this is to assume a linear adsorption isotherm.

$$b_{\mathrm{NH_4}} = K_{\mathrm{NH_4}} n_{\mathrm{NH_4}} \tag{25}$$

where $K_{\mathrm{NH_4}}$ is assumed to be constant. The total concentration of ammonium, both in the soil solution and adsorbed, is then

$$n_{\mathrm{NH_4}} + b_{\mathrm{NH_4}} = (1 + K_{\mathrm{NH_4}}) n_{\mathrm{NH_4}} = R_{\mathrm{NH_4}} n_{\mathrm{NH_4}} \tag{26}$$

For the purpose of verification of the NITS equations, they were first solved using the computer simulation package ModelMaker (SB-Technology, 1993), before integration into and further testing in SHETRAN. The NITS equations form a complicated set, as can be seen from the link chart for the ModelMaker version of NITS (Fig. 4). The NITS equations are solved in SHETRAN using an implicit finite-difference approach.

3. SHETRAN

In SHETRAN, the concentrations in the eight pools are simulated for every finite-difference cell, and updated along with the water flow and nitrate transport state variables, timestep-by-timestep. The solute transport component of SHETRAN (Ewen, 1995) models 3D advection, dispersion, adsorption, absorption into dead-space and plant uptake, using an approach based on the advection–dispersion equations for non-steady flow conditions in unsaturated

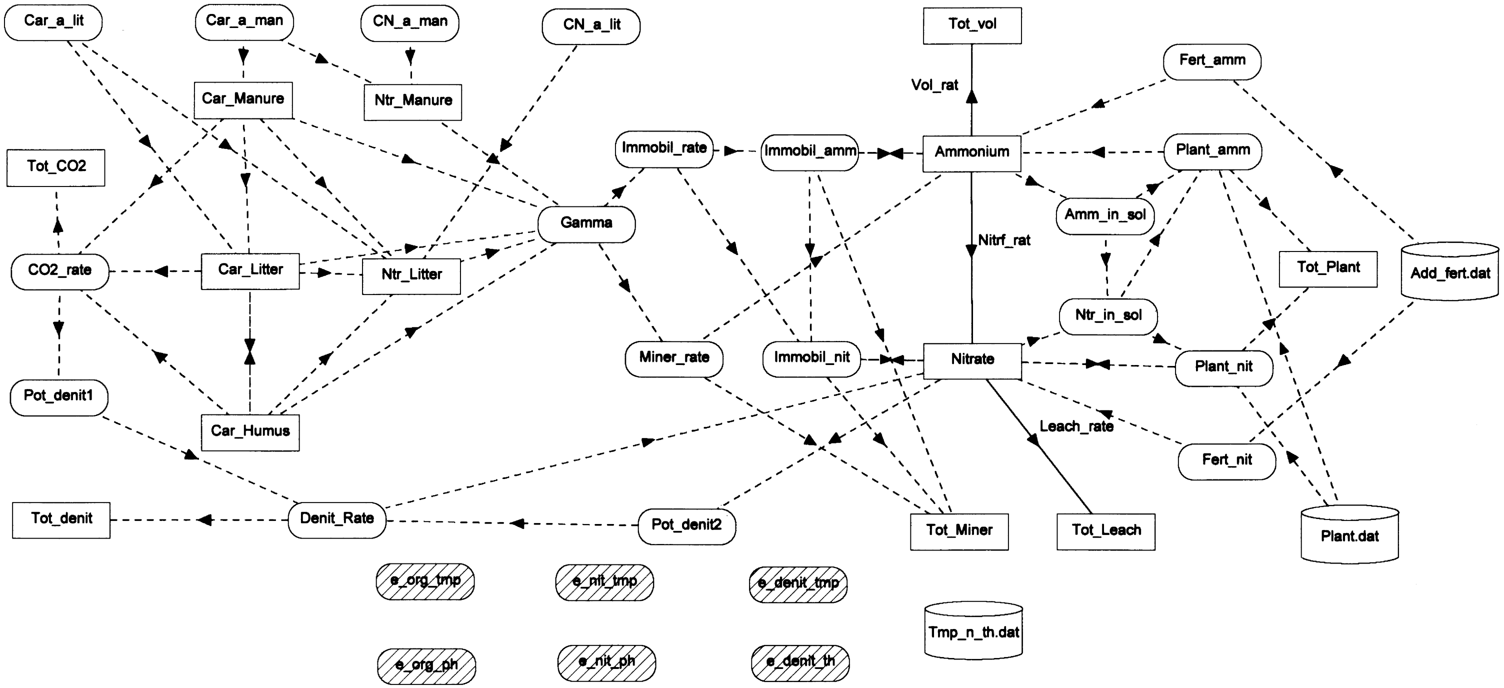

Fig. 4. Model Maker link diagram for NITS. The following symbols are used: ⛀ input data; ▭ compartment for differential equation; ⬭ variable; ▨ global variable; – – – influence; — flow. variable and component names that are not intuitively obvious are: *a*—external addition; CN—carbon to nitrogen ratio; *e*—environmental reduction factor; *gamma*—net mineralisation/immobilisation rate; org—organic matter turnover; ph—matric potential; pot—potential rate of a process; th—moisture content; tmp—temperature; tot— total for a process.

porous media (van Genuchten and Wierenga, 1976). The inclusion of dead-space is an important feature as it allows for the effects of the wide range of flow velocities seen at the pore scale. In the simulation of solute transport (including nitrate transport), each finite difference cell in SHETRAN is, in effect, assumed to have two pore regions, a 'dynamic region' in which the velocities can be high, and 'dead-space', which contains small and dead-end pores, in which the velocity is low or zero. The result is that the simulated solute transport undergoes a form of mechanical dispersion associated with the preferential flow through the dynamic region (i.e. the dispersive effect seen in laboratory breakthrough experiments where the outlet concentration plot for a pulse of solute injected into the flow through a sample of soil or rock shows early breakthrough associated with high pore velocities and a long tail associated with low pore velocities). For a SHETRAN nitrate transport simulation, therefore, there are two nitrate concentrations for each SHETRAN finite-difference cell. This implies that Eqs. (10), (11), (21) and (22), which depend on the nitrate concentration, are modified when included in SHETRAN. These now contain a term for the nitrate concentration in the dynamic region multiplied by the fraction of pore water in the dynamic region and a term for the nitrate concentration in the dead-space region multiplied the fraction of dead-space pore water.

In SHETRAN the leaching and transport of nitrate is modelled using the 3D solute transport equations. This is achieved by modifying Eq. (7) to give

$$s_{\mathrm{dy}} = -\xi_{\mathrm{in}}^{\mathrm{dy}} + \theta k_{\mathrm{n}} e_{\mathrm{n}}^{T} e_{\mathrm{n}}^{\psi} n_{\mathrm{NH_4}} - \theta \min(\alpha e_{\mathrm{d}}^{T} e_{\mathrm{d}}^{\theta} \xi_{\mathrm{CO_2}}, \beta n_{\mathrm{NO_3}}^{\mathrm{dy}}) - p_{\mathrm{NO_3}}^{\mathrm{dy}} + a_{\mathrm{NO_3}} \tag{27}$$

$$s_{\mathrm{ds}} = -\xi_{\mathrm{in}}^{\mathrm{ds}} + \theta k_{\mathrm{n}} e_{\mathrm{n}}^{T} e_{\mathrm{n}}^{\psi} n_{\mathrm{NH_4}} - \theta \min(\alpha e_{\mathrm{d}}^{T} e_{\mathrm{d}}^{\theta} \xi_{\mathrm{CO_2}}, \beta n_{\mathrm{NO_3}}^{\mathrm{ds}}) - p_{\mathrm{NO_3}}^{\mathrm{ds}} + a_{\mathrm{NO_3}} \tag{28}$$

where s_{dy} is the net source rate for nitrate generation as a result of nitrogen transformations in the dynamic region, and s_{ds} the corresponding rate in the dead-space. These rates are used in the 3D transport equations, which for nitrate transport have the form

$$\frac{\partial}{\partial t}\{\theta[\phi R n_{\mathrm{NO_3}}^{\mathrm{dy}} + (1-\phi)R^{*} n_{\mathrm{NO_3}}^{\mathrm{ds}}]\} = \frac{\partial}{\partial z}\left(\phi\theta D \frac{\partial n_{\mathrm{NO_3}}^{\mathrm{dy}}}{\partial z}\right) - \frac{\partial(\phi\theta u n_{\mathrm{NO_3}}^{\mathrm{dy}})}{\partial z} + \sum_{j=1}^{4} (v\bar{n}_{\mathrm{NO_3}}^{\mathrm{dy}})_j/A + \phi s_{\mathrm{dy}} + (1-\phi)s_{\mathrm{ds}} \tag{29}$$

$$\frac{\partial}{\partial t}[(1-\phi)R^{*} n_{\mathrm{NO_3}}^{\mathrm{ds}}] = \delta(n_{\mathrm{NO_3}}^{\mathrm{dy}} - n_{\mathrm{NO_3}}^{\mathrm{ds}}) + (\chi + |\chi|)n_{\mathrm{NO_3}}^{\mathrm{dy}}/2 + (\chi - |\chi|)n_{\mathrm{NO_3}}^{\mathrm{ds}}/2 + (1-\phi)s_{\mathrm{ds}} \tag{30}$$

The terms on the right-hand side of Eq. (29), which is for the dynamic region are, respectively, for vertical dispersion, vertical advection, lateral transport and nitrate generation in the dynamic region and dead-space. The terms on the right-hand side of Eq. (30), which is for dead-space are, respectively, for exchange of nitrate between the dynamic region and dead-space, gain of nitrate with water moving from the dynamic region to dead-space, loss of nitrate with water moving from dead-space to the dynamic region, and nitrate generation in dead-space. It is through these equations that the nitrogen transformations are coupled to the nitrate transport and water flow equations.

The plant demand for nitrogen depends on the rate of increase of mass of the plants and also on the fraction of nitrogen within the new plant material, which is a method similar to that used by Shaffer et al. (1983). The mass of plant material on each grid square depends on two storage compartments, one of which grows and decays in size with the canopy leaf area index prescribed for the plant type (Ewen, 1995). The fraction of nitrogen in the new plant material depends on the time since the emergence of the plant and decreases as the plant becomes older. The plant root profile is specified and the plant demand for nitrogen is assumed to be distributed over depth in the same fashion. The temperature of the soil is calculated using the heat conduction equation, with air temperature data and with a zero flux plane at a specified depth.

The nitrogen transformation equations are solved

Table 3
Parameters in the verification simulations

Parameter	Value
$a_{\mathrm{NH_4}}$	0.0011 g N m^{-3} day^{-1}
$a_{\mathrm{NO_3}}$	0.0011 g N m^{-3} day^{-1}
$(C/N)_b$	8.0
$(C/N)_h$	12.0
f_e	0.5
f_h	0.2
k_h	0.003 day^{-1}
k_l	0.25 day^{-1}
K_{lch}	0.00003
k_m	0.11 day^{-1}
k_n	0.6 day^{-1}
$K_{\mathrm{NH_4}}$	20.0
$k_{p,\mathrm{NH_4}}$	0.1 day^{-1}
$k_{p,\mathrm{NO_3}}$	0.1 day^{-1}
$k_{u,\mathrm{NH_4}}$	0.1 day^{-1}
$\mathrm{k}_{\mathrm{u,NO_3}}$	0.1 day^{-1}
k_v	0.1 day^{-1}
α	0.05
β	0.1 day^{-1}

for every timestep, using an iterative finite difference scheme which is stable and converges extremely rapidly. The transformation calculations are carried out after the water flow calculations have been completed, but before the calculations for nitrate transport. The equation for the carbon manure concentrations is solved first, then the equations for carbon litter and humus pools (these concentrations depend on each other, so must be calculated together), then the equations for the nitrogen manure pool, the nitrogen litter pool, the mineralisation/immobilisation rate and the ammonium pool. The nitrate generation strengths are calculated the last.

3.1. Verification of NITS equations

The verification of the NITS equations involved testing solutions from NITS for self-consistency and physical reasonableness. The validation of NITS directly against field data is discussed in Section 3.2, and the validation of the full SHETRAN system is described in Birkinshaw and Ewen (2000).

The parameter values for carbon and nitrogen transformations vary considerably from soil to soil and situation to situation (Dendooven, 1990; Molina, 1998), so the values used in the verification simulations were chosen to be average, representative, values for surface soils (Table 3). The initial conditions assumed were: 500 g C m^{-3} of potentially mineralisable humus; 100 g C m^{-3} litter with a C/N ratio of 10; no manure; 10 g N m^{-3} nitrate; and 1 g N m^{-3} ammonium. The simulations were run for one year with a timestep of one day (when the NITS equations are solved within SHETRAN they are solved using the same timestep as SHETRAN, which is usually 1 h or less), and the overall mass balance errors for all the simulations were found to remain below 0.01% of the added nitrogen at all times. A large number of sets of simulations were run, all successfully, but only two sets are described here. These are for the addition of manure and the addition of straw.

The effect of an addition of manure was studied by running four simulations in which manure was applied on day number 100 at rates of 0, 1, 2 and 4 t ha^{-1}. The manure is readily decomposed, and there is a rapid growth of biomass as it decomposes (the biomass is contained in the litter pool) (Fig. 5). As the manure concentration falls, the biomass population cannot be sustained, so the litter concentration soon begins to fall. The small rise in the concentration of humus after day 100 is the result of humification of material taken up by the biomass. The manure is rich in nitrogen, so there is net mineralisation and no immobilisation, resulting in a rise in the ammonium concentration, then a rise in the nitrate concentration as the ammonium undergoes nitrification. This is typical of the response expected when poultry manure or pig slurry is applied in the autumn (a practice strongly discouraged; MAFF/WOAD, 1991); the nitrate concentration rises quickly, leading to nitrate leaching.

The above simulations were repeated for the addition of straw with a C/N ratio of 80 added on day number 100 at rates of 0, 1, 2 and 4 t ha^{-1}. Adding straw in the autumn is recommended (MAFF/WOAD, 1991), and the reason for this can be seen clearly in Fig. 6. The nitrate concentration is greatly reduced by the addition of the straw, as the result of immobilisation. The increase in humus is more marked than it was for the addition of manure. There is more litter, resulting in greater humification. At the end of the straw simulations the nitrate concentration is highest for the simulation in which no straw is added, but the

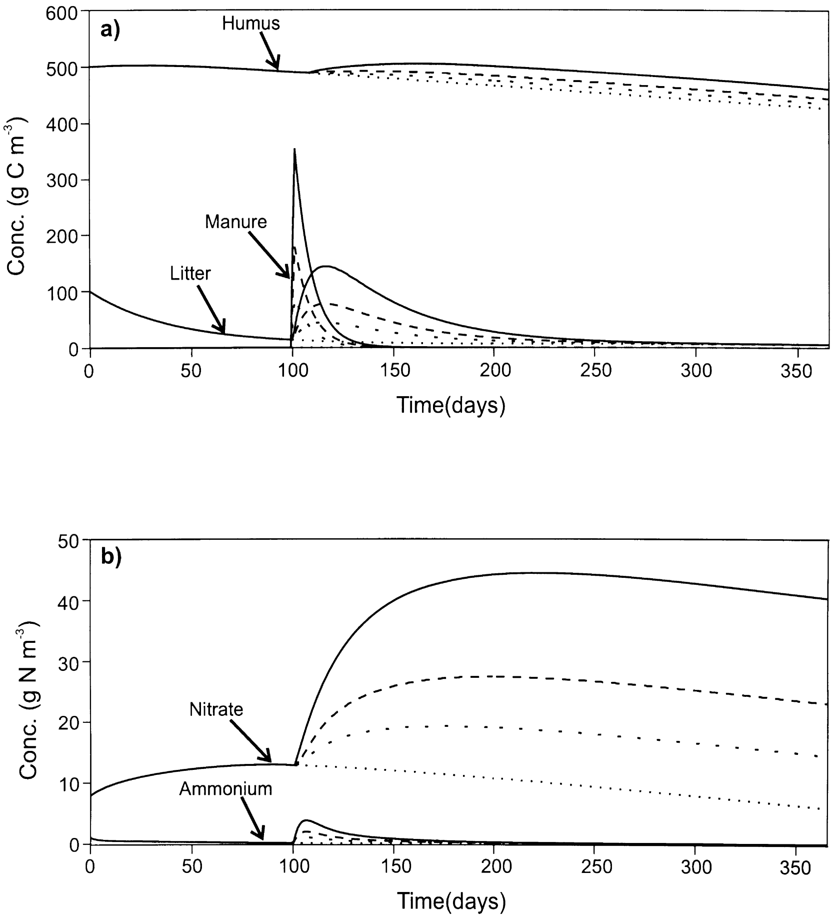

Fig. 5. Simulated response to additions of manure on day number 100 at four rates (— 4 N t ha^{-1}; – – 2 N t ha^{-1}; - - 1 N t ha^{-1};· · · 0 N t ha^{-1}). (a) Carbon concentrations in humus, litter and manure pools. (b) Ammonium and nitrate concentrations.

concentration of humus is highest for the simulation with the highest addition of straw. Since the rate of mineralisation increases with the humus concentration, this result is consistent with field results (Powlson et al., 1987) which show that the addition of materials with high C/N ratios result in an initial fall in the nitrate concentration, but also result in greater mineralisation in the long term.

3.2. Validation of the NITS equations

The data set used to validate NITS is for a 0.54 ha fertilised barley plot at the Kjettslinge experimental site in central Sweden. The site and data are described by Steen et al. (1984), Bergström (1986, 1987) and Johnsson et al. (1987). The annual average temperature at the site is 5.4°C and the average annual rainfall 520 mm. For the years considered, 1981–1983, the summer of 1981 was warm and wet, while the summers in 1982 and 1983 were warm and had prolonged dry spells. A thick snowpack in the winter of 1981–1982 prevented soil freezing. The barley was sown, fertilised and cropped on the same days each year: 6 May, 20 May and 25 August, respectively. The application rate for fertiliser, the same each year, was 120 kg N ha^{-1} of calcium nitrate fertiliser.

There are the layers of soil in the plot: 0.27 m mean thickness of clay loam topsoil, a sand layer with thickness varying between 0 and 0.5 m, an oxidised clay layer typically reaching down to 0.75 m below

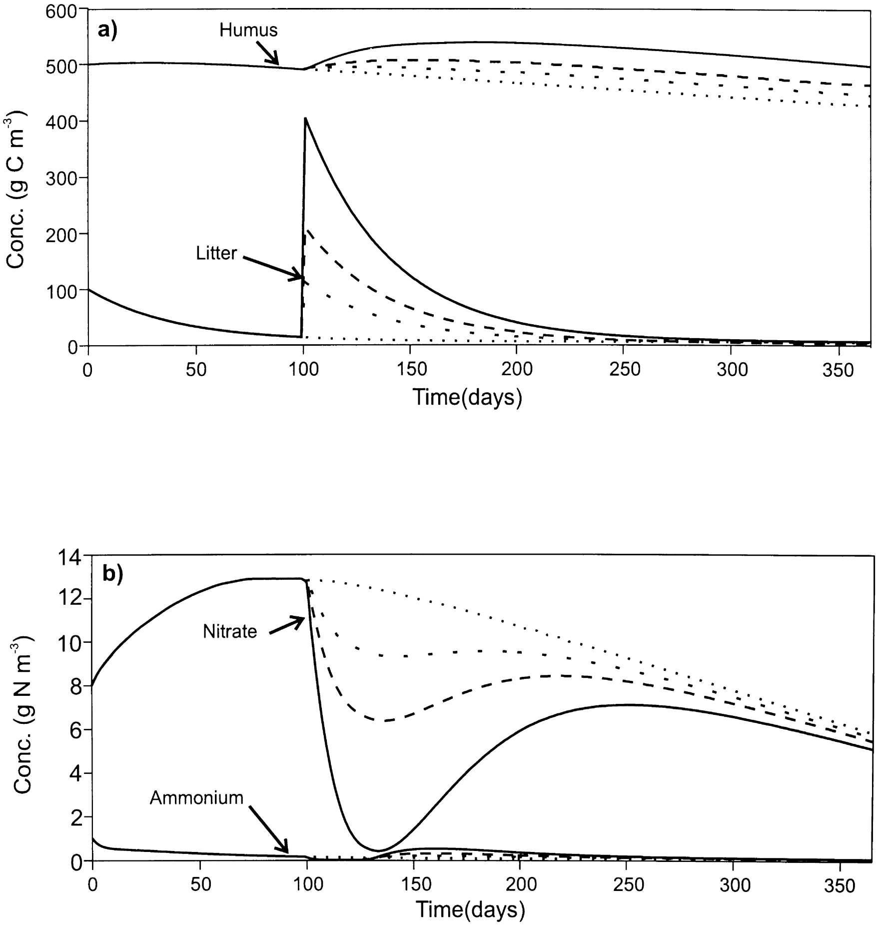

Fig. 6. Simulated response to additions of straw (C/N 80) on day number 100 at four rates (— 4 N t ha^{-1}; – – 2 N t ha^{-1}; - - 1 N t ha^{-1}; ··· 0 N t ha^{-1}). (a) Carbon concentrations in humus and litter pools. (b) Ammonium and nitrate concentrations.

ground, and a non-oxidised clay layer which lies below the oxidised layer. A single 1 m thick cell is used in the NITS validation, and is assumed to contain a mixture of all four soil types.

The parameter values for the validation simulations are listed in Table 4. Many of the values are based on Johnsson et al. (1987), who validated SOILN against the data for the plot. The following parameters were calibrated by trial and error for an adjacent barley plot which received no fertiliser: the parameters for the decomposition rates for the humus and litter pools, the parameter for the nitrification rate and the ammonium adsorption distribution coefficient. The potential rate for plant uptake of nitrogen was calculated as $20/(1 + 19\,e^{-0.12t})$ g N m^{-3}day^{-1}, where t is the day number after 3 June, which marks the start of the growing season. The potential uptake rate increases from 0.11 g N m^{-3} day^{-1} on 3 June to a maximum of 0.6 g N m^{-3} day^{-1} on 28 June and reduces to zero on 25 August. This is based on the cumulative demand equation used by Johnsson et al. (1987). The data for temperature, soil moisture and soil water potentials are taken from Johnsson et al. (1987) and used as input to NITS (when NITS is incorporated into SHETRAN, these data are calculated within SHETRAN).

One of the most encouraging features of the validation is the way that NITS, without calibration, correctly simulates the different behaviours seen from year to year (Fig. 7). For example, there is a

Table 4
Parameters for the fertilised barley simulation at Kjettslinge

Parameter	Value
a_{NH_4}	0.0011 g N m^{-3} day^{-1}
a_{NO_3}*	0.0011 g N m^{-3} day^{-1}
$(C/N)_b$	8.0
$(C/N)_h$	12.0
f_e	0.5
f_h	0.2
k_h	0.003 day^{-1}
k_l	0.25 day^{-1}
K_{lch}	1.8
k_m	0.11 day^{-1}
k_n	30.0 day^{-1}
K_{NH_4}	60.0
k_{p,NH_4}	0.1 day^{-1}
k_{p,NO_3}	0.05 day^{-1}
k_{u,NH_4}	0.1 day^{-1}
k_{u,NO_3}	0.1 day^{-1}
k_v	0.001 day^{-1}
α	0.05
β	0.1 day^{-1}

* Value does not include fertiliser additions.

fall in nitrate concentration during the wet autumn of 1981, but a rise during the dry autumns of 1982 and 1983.

Significant parts of the discrepancies seen between the simulated and measured concentrations are likely to be associated with the restricted way NITS is set up for the validation exercise. The restrictions include representing leaching in a simple fashion and the use of a single 1 m thick cell to represent the four layers of the soil. It is known, for example, that 1980 was a fallow year, so the nitrate concentration in the deeper soil layers was quite high at the beginning of 1981. This resulted in a significant fall in the nitrate concentration during spring 1981, which was not properly captured by the simple representation of leaching used in the validation simulations.

The total flows of nitrogen over the three years are shown in Fig. 8. The substantial uptake by plants is mainly fed directly from the fertiliser, but there are also substantial inputs via crop residues that reach the plants through mineralisation and nitrification. All the flows vary in time, and the time of year at which each flow is at its maximum is different for each flow. The leached nitrate rate (14.8 kg N ha^{-1} year^{-1}) agrees well with the value measured by Johnsson et al. (1987) (13.7 kg N ha^{-1} year^{-1}).

The NITS model has a large number of parameters and to analyse the effect of these parameters on the nitrate concentration a sensitivity analysis was performed. The validation simulation was repeated many times gradually changing the value of one parameter while keeping the other parameters constant. Fig. 9 shows the most significant results of the sensitivity analysis. It can be seen that the nitrate concentration at the end of the simulation is quite sensitive to the decomposition rate in the humus pool, k_h and the maximum rate for the plant uptake of nitrate, $k_{p,NO3}$. It is likely that the sensitivity information will prove useful in future applications.

4. Conclusions

A nitrogen transformation model, NITS, has been

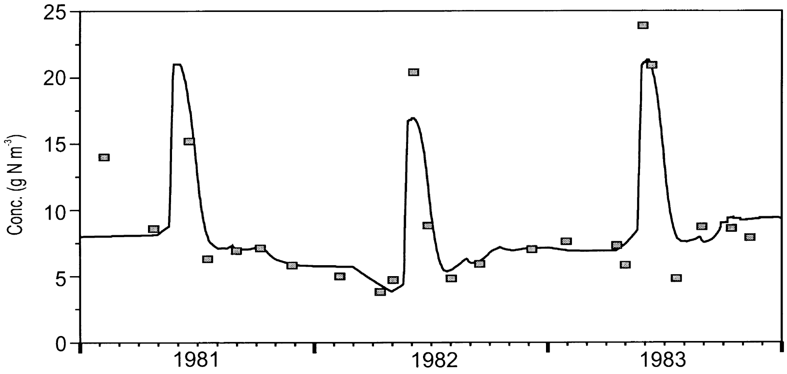

Fig. 7. Simulated (line) and measured (squares) nitrate concentrations for the top 1m of soil in the fertilised barley plot at Kjettslinge.

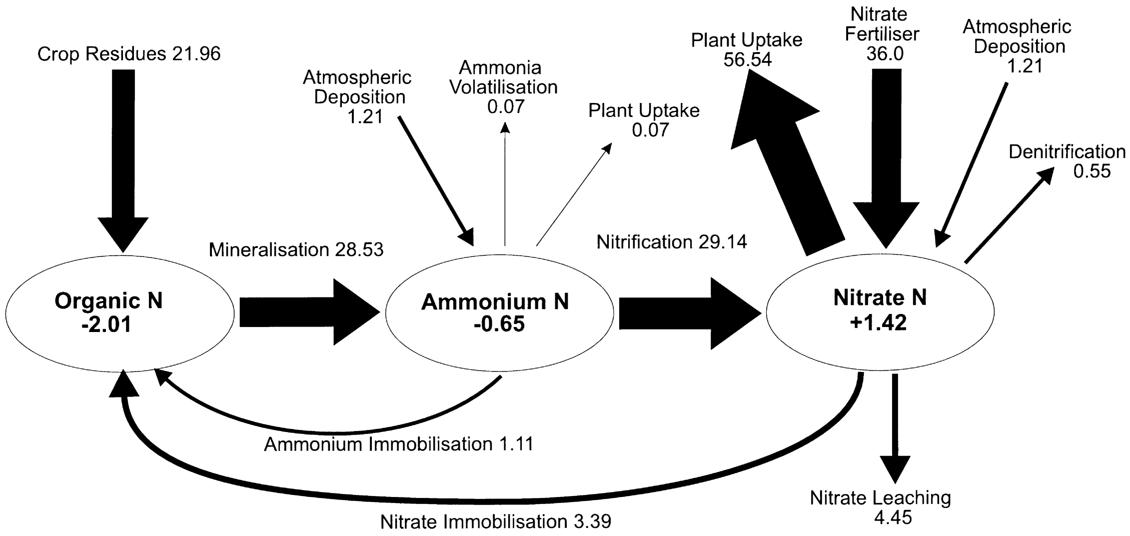

Fig. 8. Total nitrogen flows (g N m^{-3}) during the three year simulation of the fertilised barley plot at Kjettslinge.

developed and integrated into the physically based spatially distributed 3D coupled surface/subsurface flow and solute transport river catchment modelling system SHETRAN, giving the capability to simulate flow in perched, unconfined, confined and unsaturated systems, the associated leaching and transport of nitrate through the subsurface, and the ultimate discharge of nitrate to seepage areas into surface waters, and through river networks.

The NITS equations, which were developed specially for SHETRAN, are comprehensive, self-consistent, and fully compatible with the physically

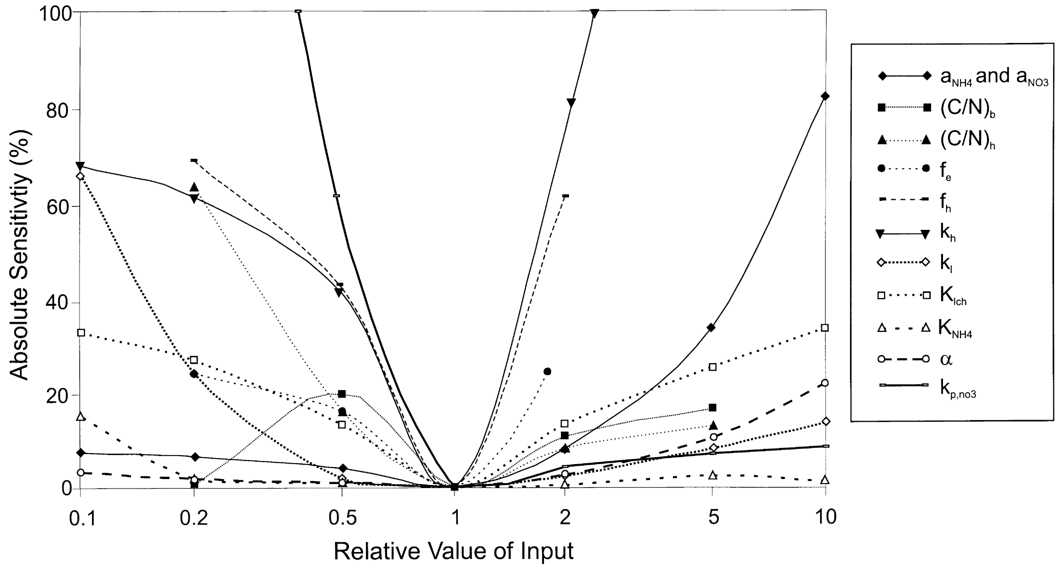

Fig. 9. Sensitivity Plot for the fertilised barley plot at Kjettslinge (absolute sensitivity is the absolute difference between the simulated and measured nitrate concentrations divided by the measured nitrate concentration).

based, distributed nature of SHETRAN, and were integrated fully into SHETRAN making it a uniquely flexible and powerful system for catchment nitrate modelling. Preferential flow and nitrate transport are allowed for using a two-region (dynamic region and dead-space) approach. It is intended that SHETRAN, as it stands, will be used in studies of the scaling of catchment nitrate modelling using the 'UP' approach of Ewen (1997), and the design of NITS is compatible with that approach. SHETRAN will also be used in the simulation of nitrate generation and transport in river catchments, as part of studies of past and present pollution and proposed remedial measures.

Several sets of verification simulations have been run to check the self-consistency and physical reasonableness of the NITS equations. These show that the solutions conserve mass and give physically reasonable results which agree, qualitatively, with field results reported in the literature. The NITS equations were also successfully validated directly against field data for nitrate concentrations measured in a fertilised barley plot. A validation test of the full SHETRAN system for a river catchment is described in Birkinshaw and Ewen (2000).

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