

Modelling seasonal nitrate concentrations in runoff of a heathland catchment in SW Norway using the MAGIC model: I. Calibration and specification of nitrogen processes

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ABSTRACT

MAGIC (the Model of Acidification of Groundwater In Catchments) has been widely applied on catchments all over the world. The model has been used with annual time resolution to simulate the long-term effects of acidic deposition on surface water chemistry. Here MAGIC was applied using a monthly time step. The purpose was to simulate observed seasonal nitrate (NO_3) concentrations and fluxes at an upland heathland catchment in southwestern Norway during the period 1993–2004. The rates of the key ecosystem nitrogen (N) processes (mineralization, plant uptake, litterfall and immobilization) were assumed to be governed by temperature. A snow accumulation and melt routine was used. The rates were calibrated to obtain the best match between the observed and simulated NO_3 patterns. The best fit was obtained with standard yearly cycles for deposition and N parameters. The results show that MAGIC can explain 68 and 88% of the variation in seasonal NO_3 concentrations and fluxes, respectively. The calibrated model provides a tool for exploring the effects of future scenarios of climate change and N deposition on NO_3 in streamwater.

Key words | heathland, model, nitrate, nitrogen deposition, Norway, water

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INTRODUCTION

Large regions of Europe and eastern North America have experienced decades of high levels of nitrogen (N) deposition. N has contributed to acidification of surface waters and increased N loading to coastal marine waters (Jaworski *et al.* 1997; Wright *et al.* 2001). The deposition of N in Norway peaked around 1990, and thereafter it has stabilized or decreased slightly (Schöpp *et al.* 2003). Although N deposition has decreased, nitrate (NO_3) leaching to surface waters is still a widespread problem in Europe and eastern North America and causes acidification and eutrophication with subsequent damage to biota (Wright *et al.* 2001; Skjelkvåle *et al.* 2003).

Many years with high N deposition have resulted in a large accumulation of N in soil. At some sites this has

resulted in increased leaching of inorganic N (mainly as NO_3) to surface waters, a phenomenon termed “nitrogen saturation” (Ågren & Bosatta 1988; Aber *et al.* 1989; Stoddard 1994). In moderately affected soils (saturation stages 1 and 2, according to Stoddard (1994)), the net effect of catchment N sources (non-point sources, atmospheric deposition, direct effluent discharges, mineralisation) and sinks (plant uptake, microbial immobilisation, denitrification) is the commonly observed seasonal pattern in NO_3 surface water concentrations at temperate catchments (Reynolds & Edwards 1995; Mitchell *et al.* 1996). This pattern entails high values in winter and early spring, and low values during the summer due to increased biological activity.

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Water quality models such as the dynamic model MAGIC (Model of Acidification of Groundwater In Catchments) (Cosby *et al.* 1985a,b, 2001) can be valuable tools in understanding different catchment responses to changes in N deposition.

MAGIC was originally developed to simulate the long-term effects of acidic deposition on surface water chemistry (Cosby *et al.* 1985a,b, 2001). The model has been in use for more than 20 years and has been widely applied in North America and Europe (see Cosby *et al.* 2001).

Over the years MAGIC has been modified and extended. The most recent version now also provides a facility for simulating short-term (monthly) responses in lakes and streams (e.g. Cosby & Wright 1998) and process-based N dynamics in soils (Cosby *et al.* 2001). The following major N processes are incorporated either explicitly or implicitly into the MAGIC model: atmospheric deposition, plant uptake, decomposition, nitrification, denitrification, mineralisation, litterfall, immobilisation into soil organic matter and export in runoff.

Despite the extensive use of MAGIC on an annual basis, there apparently has only been one application based on a monthly time step (Collins & Jenkins 2001). In their study the same long-term mean monthly input files were used each year during calibration. In the present study the objectives were to reproduce the long-term (1993–2004) seasonal NO₃ pattern of an upland heathland catchment in southwestern Norway by applying MAGIC 7.77 using a monthly time step. This is the first study with in-depth focus on nitrogen using both long-term mean and year-to-year variability in input files to MAGIC.

MATERIALS AND METHODS

Site description

Øygardsbekken (2.55 km²) is a small, semi-natural upland catchment in the Bjerkreim river basin, Rogaland County, southwest Norway (Figure 1). There is one lake (Hedlevatn, 309 m a.s.l.) and several small ponds within the catchment that have a dampening effect on variations in NO₃ concentrations at the catchment outlet (see Figure 2 for a bathymetric chart of Lake Hedlevatn).

The catchment altitude ranges from 185–545 m a.s.l., with granitic–gneiss bedrock, thin and patchy podsolc soils mixed with areas of exposed bedrock. Dominant vegetation is *Calluna* heather, *Sphagnum* mosses, grasses and mountain birch. The climate is mild and humid with relatively high amounts of annual precipitation (2,053 mm yr⁻¹, mean 1993–2004) and with a mean annual air temperature of 6.3°C. Nitrogen deposition is about 20 kg N ha⁻¹ yr⁻¹ and inorganic N output (mostly as NO₃) is about 5 kg ha⁻¹ yr⁻¹ (Kaste *et al.* 1997).

MAGIC model description

General description

The MAGIC model is a lumped-parameter model of intermediate complexity (Cosby *et al.* 1985a,b, 2001). The model simulates soil solution and surface water chemistry to predict average concentrations of major ions. In the application here, MAGIC version 7.77 was used to simulate monthly mean concentrations and fluxes of inorganic N compounds in streamwater and calibrated by comparison with measured monthly data (1993–2004).

When applying MAGIC to a catchment normally one (or two) soil layer(s) and a surface water compartment are implemented. The soil characteristics are thus aggregated in space and time to encompass the whole basin and to monthly (or annual) time steps. MAGIC does not simulate runoff, thus it is determined externally and used as model input. The surface water compartment can be used to either simulate streams or lakes, either of which will receive deposition input directly from the atmosphere as well as drainage from the terrestrial portion of the catchment. Employing the lake alternative, the retention time of water and mixing within the lake must be specified. For monthly simulations the lake can be periodically stratified (for example, during summer and winter) with catchment inflows entering and lake discharge leaving the epilimnion. When the lake is not stratified (for example, during spring and late autumn), the entire volume of the lake is mixed with the terrestrial drainage.

Within each compartment of the model, mass balance is required for the total amount of ions (i.e. the difference between input and output of each ion must equal the rate of

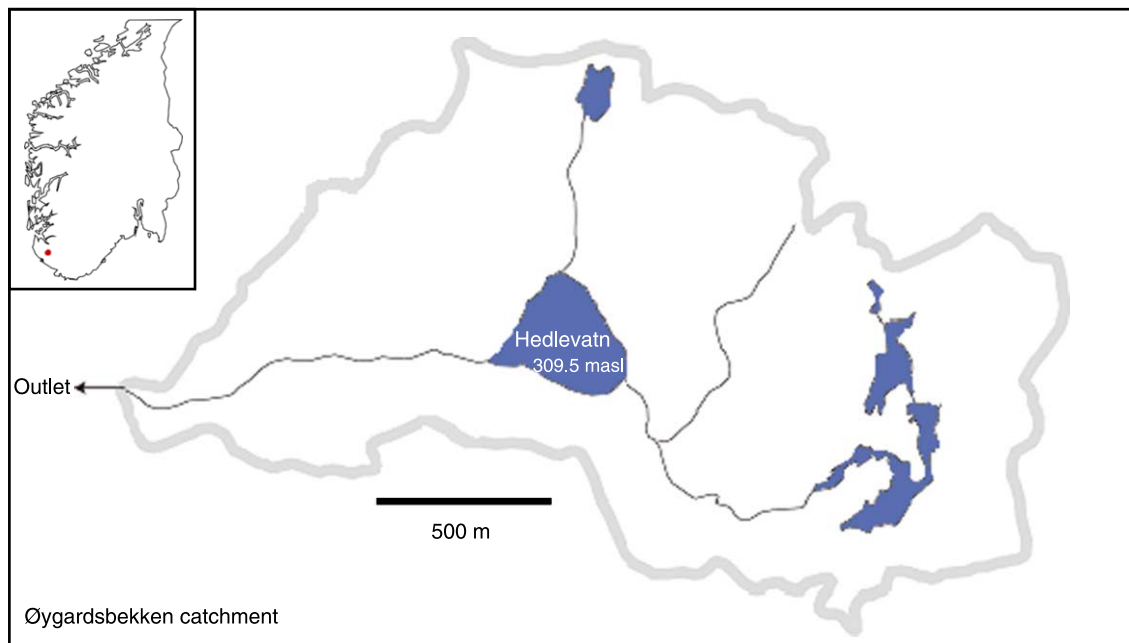


Figure 1 | Location and map of the Øygardsbekken catchment.

change of the total amount of that ion in each compartment of the model). Atmospheric deposition is an external input. Biological processes such as plant uptake, litterfall, organic matter decomposition, mineralisation and immobilisation withdraw or add dissolved nitrogen to the soil solution. Outputs from the soil and surface water compartments occur as water discharges or biological removal (uptake or immobilisation). For further elaboration and mathematical formulation of MAGIC see *Cosby et al. (2001)*.

The N cycle and long-term N dynamics

In MAGIC the N processes are calculated sequentially at each time step. First NH_4 and NO_3 from deposition and NH_4 from mineralisation are added to the soil solution. A specified fraction of the NH_4 is then nitrified, thus removing NH_4 and adding NO_3 to the soil solution. Next, the net uptake requirement of the plants is satisfied by removing inorganic N from soil solution (NH_4 is removed first, followed by NO_3). If the available inorganic N concentration in soil solution is not sufficient to satisfy the plant requirement, the additional N needed may be removed from the soil organic matter pool. Any inorganic N remaining in soil solution following plant uptake is either immobilised by microbes or

leached in runoff. This partitioning is controlled by two parameters: first by the C/N ratio (a measure of the N “richness” controlling the long-term N dynamics in soil in MAGIC) of the soil organic matter pool which sets the maximum fraction that is potentially immobilised, and then by a parameter termed % potential retention which specifies the % of this maximum amount that is removed by

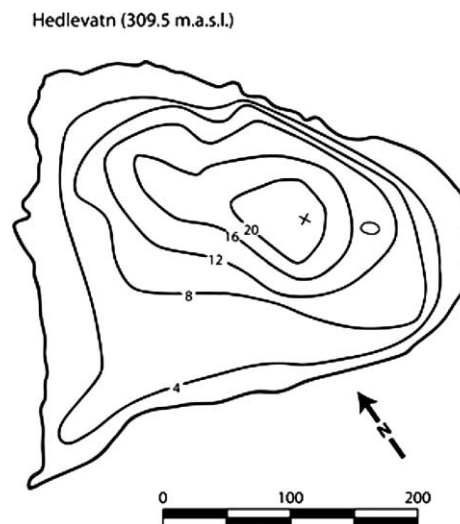


Figure 2 | Bathymetric chart of Lake Hedlevatn. Contour intervals are 4 m and maximum depth of 21 m is indicated by the cross. Adapted from *Sjøeng (1998)*.

microbial immobilisation. The immobilised N is added to the soil organic matter pool (Figure 3).

The concept of using the C/N ratio of the soil organic matter pool in controlling long-term immobilisation is based on the empirical relationship between the C/N ratio of the soil organic matter pool and N immobilisation (the “Gundersen curve”) as obtained from forested ecosystems (Gundersen *et al.* 1998), but also proven significant for heathland ecosystems (Curtis *et al.* 2004; Rowe *et al.* 2006). This is a linear function with an upper C/N threshold at which all inorganic N in soil solution remaining after plant uptake is immobilised, and a lower C/N threshold at which none of the inorganic N in soil solution is immobilised. In MAGIC this is described by a simple function only requiring specification of two parameters, the upper and lower C/N ratio at which immobilisation is 100% and 0%, respectively (Figure 4) (Cosby *et al.* 2001). The initial size and changes over time of the C pool must be specified. The inorganic N immobilised from soil solution is added to the soil organic matter pool, thereby lowering its C/N ratio. Thus chronically elevated levels of N deposition and N immobilisation cause a gradual decline in the C/N ratio of the soil organic matter pool. When the C/N ratio drops below the upper threshold, leaching of inorganic N begins and gradually increases as the C/N ratio declines further.

MAGIC also considers in-lake retention of N, assumed to be mainly due to denitrification at the sediment–water interface. This is based on an empirical relationship

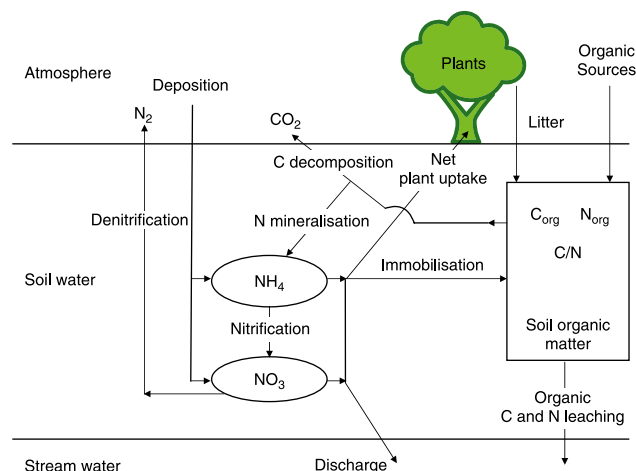


Figure 3 | Illustration of the N cycle in MAGIC. Adapted from Cosby *et al.* (2001).

between the hydrological flushing time and NO_3 and NH_4 concentrations in lake water (Dillon & Molot 1990; Kaste & Dillon 2003). Inputs to MAGIC required for this are the specification of the hydrological flushing rate, the seasonal stratification pattern of the lake and the rate constants.

Data

Atmospheric deposition and precipitation

The atmospheric deposition data were obtained from stations 42890 Skreådalen (474 m a.s.l., 50 km to the north-east, data from 1975–2004) and 877 Ualand (196 m a.s.l., 15 km to the southeast of the site, data from 1992–2000), both included in the Norwegian Monitoring Programme on long-range transported air pollutants (LRTAP) operated by the Norwegian Institute for Air Research (NILU) (Aas *et al.* 2004). Bulk deposition was sampled weekly, and the chemical composition and amount of precipitation were used to calculate wet deposition (Aas *et al.* 2002). Annual precipitation amount and its chemical composition were obtained by averaging data from Skreådalen and Ualand for the years 1992–2000 (when Ualand was in operation). Before and after this period, precipitation and deposition for individual components were extrapolated using data from Skreådalen and average annual ratios (1992–2000) from Ualand and Skreådalen.

Deposition data were adjusted to fit the Øygardsbekken catchment based on several assumptions using the data for 1993–1995. First the volume of precipitation was calculated from the chloride (Cl) balance for the catchment, under the assumptions that both the annual discharge and annual flux of Cl from the catchment were correctly measured, and that the measured volume-weighted concentration of Cl in deposition was correct. This gave a “Cl-correction factor” by which the measured precipitation volume was multiplied. Next the seasalt fraction of the sulfate (mSO_4) annual flux in deposition was calculated from the Cl flux and the assumption that the ratio of mSO_4/Cl in deposition is the same as that in seawater (0.103 eq/eq). Finally the deposition of the two nitrogen (N) components, oxidised N (NO_x) and reduced N (NH_y), were assumed to be equal to the non-marine SO_4 (SO_4^*) deposition multiplied by the ratio of the measured

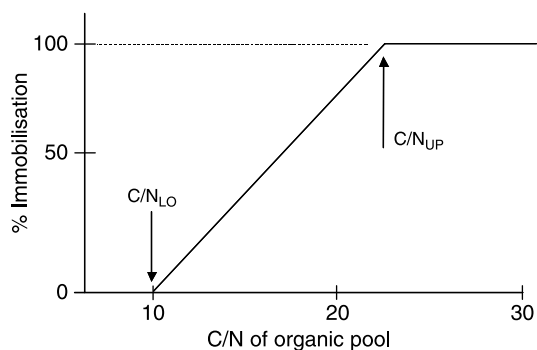


Figure 4 | Immobilisation of inorganic N (both NO_3 and NH_4) as a function of the C/N ratio of the soil organic pool. Immobilisation is 100% of input N whenever the C/N ratio is above the upper threshold (C/N_{UP}) and is 0% when the C/N ratio is below the lower threshold (C/N_{LO}). C/N_{UP} and C/N_{LO} are calibrated. Adapted from Cosby *et al.* (2001).

volume-weighted annual concentrations of NO_3 and NH_4 , respectively, to SO_4^* in deposition.

The long-term historical (for the hindcast period 1860–1995) and future N deposition (for the forecast period 1996–2100) were taken from estimates for southern Norway derived from N emissions in Europe and the EMEP transport and deposition model (Schöpp *et al.* 2003) and scaled to the N deposition for the calibration years at Øygardsbekken.

Meteorology, snow cover, discharge and streamwater chemistry

Daily air temperature data were obtained from station 43500 Ualand (1968–1997) operated by the Norwegian Meteorological Institute (met.no) (same location as the NILU station). This station was closed in 1997. After 1997, air temperature data were estimated from several nearby met.no stations using kriging (Tveito *et al.* 2005).

Snow cover data used to estimate soil temperature were obtained from met.no station 44520 Helland, in the township of Gjesdal (280 m a.s.l., 15 km to the northwest of the catchment, operated since 1962).

Daily discharge measurements were available for Øygard (1992–2005) from the gauging station at the catchment outlet operated by Norwegian Institute for Water Research (NIVA).

Streamwater was sampled fortnightly at the outlet, during 1993–1995, as part of the research project “Nitrogen from Mountains to fjords” (Henriksen & Hessen 1997) and from 1996 within the framework of the Norwegian

LRTAP programme (SFT 2004). Samples were analysed unfiltered for major ions and nutrients by standard methods at NIVA (NIVA 2004). Only NO_3 , NH_4 , SO_4 and Cl data were used here.

Catchment soils and vegetation cover

Soil data were obtained from samples collected during 1999 and 2000 within six sub-catchments of Øygardsbekken, each of which were dominated by heather, peat and bare-rock/grasses respectively (Sjøeng *et al.* 2007). At each sub-catchment 9–27 soil pits were dug and sampled from the surface (0–20 cm) of the organic horizon and from the mineral soil. Analyses used here comprise bulk density, depth and total content of carbon (C) and N. The soil data were mass-weighted to aggregate to one value for the whole Øygardsbekken catchment.

Daily soil temperature data were estimated from air temperature, using a simple sine function relating air and soil temperature:

$$T_{\text{soil}} = T_{\text{air}} - C_{16} \sin\left(\frac{3}{2} \pi \frac{\text{day no.}}{365}\right) \quad (1)$$

(Whitehead *et al.* 1998), where T_{soil} is soil temperature ($^{\circ}\text{C}$), T_{air} is air temperature ($^{\circ}\text{C}$) and C_{16} is a parameter ($^{\circ}\text{C}$) to be calibrated, which adjusts the maximum difference between summer and winter conditions. The daily soil temperature was assumed to equal 1°C when snow was present in the catchment. This is based on measurements of soil temperature and snow accumulation during winter at Storgama, a similar upland catchment in southern Norway (Kaste *et al.* 2008). Storgama has a mean annual (1993–2004) air temperature of 5.9°C .

GDD (growing degree days) was defined as the accumulated sum of degrees Centigrade between the daily mean temperature (air or soil) and a threshold temperature of 5°C (Gudem & Hovland 1999):

$$\text{GDD} = \Sigma(\text{daily mean air temperature} \\ - \text{threshold temperature } (5^{\circ}\text{C})) \quad (2)$$

When daily mean temperature was less than the threshold temperature, GDD for that day was set to zero. GDD is a good estimate of cumulative heat and is therefore

a useful index of energy available for biological growth, especially in areas such as Norway where temperature is a growth-limiting factor (Gudem & Hovland 1999). The threshold temperature of 5°C is the temperature regarded as the threshold for the growing season by the agricultural sector in Norway.

Annual C and N process rates

Due to a lack of direct measurements, annual rates for plant N uptake and litterfall were taken from Risdalsheia, an experimental catchment in southern Norway (Wright *et al.* 1998), and are assumed to represent the long-term mean annual rates (1993–2004) at the Øygardsbekken catchment (Table 1 and Figure 5). This assumption is reasonable because the catchments Øygardsbekken and Risdalsheia are both situated in the southern part of Norway (about 130 km apart), are relatively undisturbed, upland heather-dominated ecosystems on thin soils and have approximately the same climate and N deposition.

Year-to-year variations in plant N uptake and litterfall N were estimated by multiplying the long-term mean annual

rates (e.g. 480 mmol N m⁻² yr⁻¹ for both) with relative annual soil growing degree days (soilGDD) (“relative” refers to the ratio of annual/long-term mean (1993–2004) annual GDD).

The size of the C pool was assumed constant (see the model calibration section). Long-term mean annual rate for decomposition C was calculated as the difference between litterfall C and measured TOC leaching to surface water (Figure 5, right panel). The annual N balance for each pool is given in Equations (3)–(6):

$$\Delta = N_{\text{dep}} - \text{DIN}_{\text{lea}} - \text{DON}_{\text{lea}} \quad (3)$$

$$\Delta = N_{\text{up}} - N_{\text{lit}} (\text{assumed } \Delta = 0) \quad (4)$$

$$\Delta = N_{\text{dep}} + N_{\text{min}} - N_{\text{immob}} - N_{\text{up}} - \text{DIN}_{\text{lea}} (\text{assumed } \Delta = 0) \quad (5)$$

$$\Delta = N_{\text{lit}} + N_{\text{immob}} - N_{\text{min}} - \text{DON}_{\text{lea}} \quad (6)$$

where Δ = net annual change, N_{dep} = N deposition, DIN_{lea} = inorganic N leached, DON_{lea} = organic N

Table 1 | Long-term measured or estimated soil parameters, C and N pools (mmol m⁻²) and fluxes (mmol m⁻² yr⁻¹) at Øygardsbekken used during calibration of MAGIC 7.77. for the calibration period 1993–2004

Parameters				Reference	
<i>Soil</i>					
Mean depth (m)	0.22			Measured	Mulder unpublished
Porosity (fraction)	0.50			Measured	Mulder unpublished
Bulk density (kg m ⁻³)	351			Measured	Mulder unpublished
<i>Water fluxes (mean 1993–2004)</i>					
Annual precipitation (m)	2.053			Measured	This study
Annual discharge (m)	1.960			Measured	This study
<i>C and N pools and fluxes</i>					
	<i>C</i>	<i>N</i>	<i>C/N</i>		
Deposition inorganic N (mean 1993–2004)		117.1		Measured	This study
Runoff inorganic N (mean 1993–2004)		22.6		Measured	This study
Plant uptake	21,600	480		Estimated	Wright <i>et al.</i> (1998)
Litterfall	21,600	480	45	Estimated	Wright <i>et al.</i> (1998)
Plant-pool change	0	0		Assumed	
Soil organic matter-total	2,571	101	25.5	Measured	Mulder unpublished
Soil organic matter - pool change	0	80		Assumed	
Decomposition-gross	21,400	840	25.5	Calculated	
Decomposition-net		390		Calculated	
TOC/TON export	230	13	18	Measured	This study

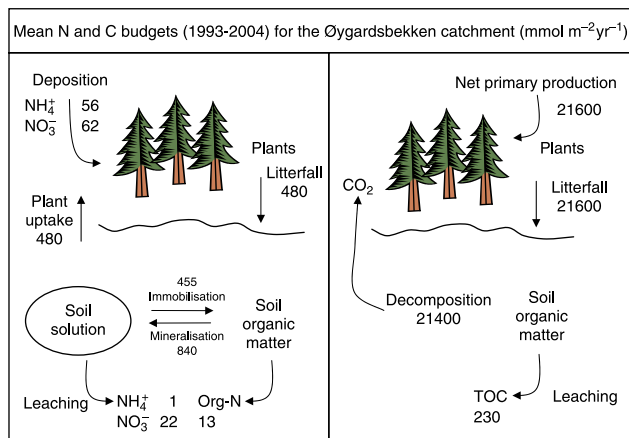


Figure 5 | Mean annual N and C budgets ($\text{mmol m}^{-2}\text{yr}^{-1}$) for the Øygardsbekken catchment. Rates for leaching and deposition are measured values; gross immobilisation, decomposition C and mineralization N (= gross N mineralization) are calculated from measured values and estimated rates from Wright *et al.* (1998).

leached, N_{up} = N uptake in plants, N_{lit} = N litterfall, N_{min} = gross N mineralisation and N_{immob} = gross N immobilisation.

N_{min} (mineralisation in Figure 5, left panel) was estimated from decomposition C and the measured soil C/N ratio. Long-term mean annual rates for immobilisation were then calculated by the difference in Equation (5) from the other rates in Figure 5 assuming no N accumulation in plant or soil solution on annual basis. This gives a net annual mineralisation of 385 and a net N accumulation in soil organic matter (SOM) of $82 \text{ mmol m}^2 \text{ yr}^{-1}$.

Model calibration

Assumptions regarding the nitrogen cycling processes and soil organic matter

Several assumptions regarding the N soil processes in the catchment were made. During calibration 100% nitrification in both soil and surface water was assumed as observed NH_4 concentrations in stream and lake water at the site rarely exceeded $1 \mu\text{mol N l}^{-1}$. Furthermore, denitrification in soil was assumed negligible in accordance with measurements in heathland soils in the UK (Curtis *et al.* 2000, 2006). Moreover, peatland covers only 6% of the catchment (Kaste *et al.* 1997), thus supporting the assumption. Net annual uptake of N in vegetation was assumed to be matched by annual litterfall (i.e. no increase in N in biomass over time). This means that

the two processes may vary independently each month, but sum up to the same rate annually. This assumption is reasonable as there is no management or removal of biomass in the catchment. In the absence of any direct measurements over time of the size of the soil organic C pool, the amount of C stored in the SOM pool was assumed constant for the whole period (1860–2004). This implies that total annual decomposition of organic matter in the soil plus the annual loss of organic C in runoff equalled the yearly litterfall (Figure 5, right side). Conceivably the ecosystem could be slowly accumulating C, and possibly the higher N deposition during the past 50 years could have increased C sequestration. Evans *et al.* (2006) have used a simplified version of MAGIC under assumptions of increasing, constant and decreasing C storage, and shown that future N leaching (yearly) is sensitive to this assumption.

Soil and surface water compartments

The catchment soil and surface waters were aggregated into one compartment each, with the surface waters constituting 7% of the catchment area. Thus the largest part (93%) of precipitation was assumed to pass through the soil before entering the lake, while the remaining fraction (7%) entered the lake unchanged by soil processes (Figure 6). Monthly deposition and runoff were specified as fixed input files to the model.

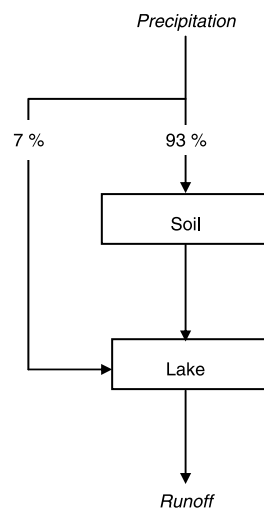


Figure 6 | General set-up of MAGIC showing the fraction of water from precipitation that is assumed to pass through the soil before entering the lake (93%) and the fraction entering the lake unaltered by soil processes (7%).

Lake physical characteristics (volume and residence time of Lake Hedlevatn, the largest lake in the catchment) were taken from Sjøeng (1998) and the rate constant for N retention within the lake from (Kaste & Dillon 2003). Due to lack of seasonal lake stratification measurements the same monthly distribution of % epilimnion volume was used each year during model calibration. This distribution was calibrated and based on lake stratification measured during May 1995 (A.M.S. Sjøeng, unpublished data 1995) and a general seasonal depth-time diagram of isotherms (Wetzel 1983, p 75). The calibrated lake stratification pattern entailed two periods of circulation (i.e. the months May and December with epilimnion volume equal to 100%), a very thin epilimnic layer in the winter when the lake was assumed ice-covered and a gradually increasing epilimnion throughout the summer and autumn (Figure 7).

General description of the calibration procedure

Monthly MAGIC calibration of Øygardsbekken catchment was accomplished using annual calibration (Kaste *et al.* 2006) as the starting point. The model was calibrated to reconstruct the observed runoff chemistry at the Øygardsbekken catchment during the period 1993–2004.

In the calibration several ways of estimating monthly rates for each of the N and C processes included in MAGIC were tested; gross N mineralisation (based on estimates of decomposition C and soil C/N ratio), plant N uptake, litterfall N and microbial immobilisation (in MAGIC based on a term called % potential retention). The estimated annual rates for plant N uptake and litterfall N and the

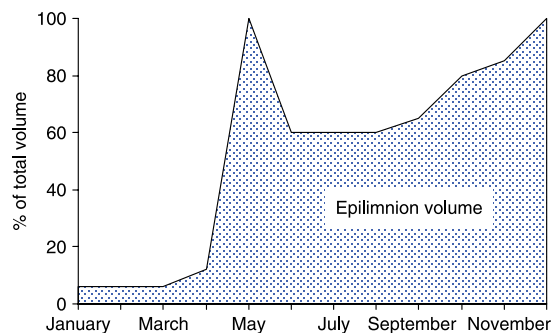


Figure 7 | Monthly lake stratification pattern (% epilimnion volume) used during calibration. 100% epilimnion volume implies complete mixing of the lake.

long-term mean rate for mineralisation provided the basis for estimates of monthly rates for these processes. In estimating the different N processes several trials (Table 2, trials 1–4) were run as further explained below. Based on the best set-up of trials 1–4 the effect of including a snowmelt routine was tested (trial 5). Then the effect of using either all or some of the input and parameter files was tested with all years alike (i.e. input with long-term (1993–2004) monthly mean values for each year) both with (trials 6.1snowm and 6.2snowm) and without (trials 6.1 and 6.2) the snowmelt routine (suffix snowm) included.

The relative success of each trial was judged on the basis of three statistical measures:

1. $EFF = 1 - (MSE)/var(obs)$
 $= 1 - (sumsq(sim - obs)/n)/var(obs)$
2. $RMSE = \sqrt{sumsq(sim - obs)/n}$
3. $r^2 = \frac{\sum(obs - \overline{obs})^2 \sum(sim - \overline{sim})^2}{\sum(obs - \overline{obs}) \sum(sim - \overline{sim})^2}$

where EFF = efficiency, MSE = mean square error, var = variance, sumsq = sum of squares, obs = observed data, sim = simulated data, \overline{obs} = mean of observed data, \overline{sim} = mean of simulated data, RSME = root mean squared error and r^2 = coefficient of determination.

The best trial was judged as that with the highest EFF and r^2 (i.e. closest to 1) and lowest RMSE (i.e. closest to 0).

Calibrating monthly N and C processes as model input

In trials 1–4 (Table 2) first plant N uptake based either on airGDD (trial 1.1) or soilGDD (trial 1.2) was tried. Monthly plant N uptake was thus estimated by multiplying the estimated annual rates for plant N uptake with monthly relative airGDD or soilGDD, respectively. Here relative airGDD and soilGDD refer to the ratio of monthly to annual airGDD or soilGDD, respectively.

Second, soil temperature (relevant for C decomposition, N mineralisation and plant N uptake) was estimated from air temperature using values for the parameter C_{16} (maximum difference between summer and winter conditions) set at 6 (trial 2.1), 3 (trial 2.2) or 4.5 (trial 1.2).

Table 2 | The different trials during MAGIC calibration of Øygardsbekken. During trials 1–4 we tested for best estimates of monthly plant N uptake (air- or soilGDD), decomposition (soil temperature estimate using $C_{16} = 3, 6$ or 4.5), litterfall (1 or 3 peaks) and % potential retention (high, almost flat vs. approximately sinusoidal). During trial 5 we used the best of trials 1–4 and included a snowmelt routine. Trial 6 tested the effect of using input files and N parameter files with all years equal, based on the best trial with and without the snowmelt routine. Trial 7 tested no change in monthly lake epilimnion volume (100% each month, i.e. complete mixing)

Trials	Plant N upt	Decomposition	Litterfall	% potential retention
Trial 1. Monthly plant N uptake estimates				
1.1	AirGDD	Estimated soil temp. $C_{16} = 4.5$	AirGDD and monthly distribution with one autumn peak	Approximately sinusoidal distribution $C_{16} = 4.5$
1.2	SoilGDD $C_{16} = 4.5$		SoilGDD, $C_{16} = 4.5$ and monthly distribution with one autumn peak	
Trial 2. Soil temperature estimates (plant uptake and decomposition)				
2.1	SoilGDD $C_{16} = 6$	Estimated soil temp. $C_{16} = 6$	SoilGDD, $C_{16} = 6$ and monthly distribution with one autumn peak	Approx. sinusoidal distribution, $C_{16} = 6$
2.2	SoilGDD $C_{16} = 3$	Estimated soil temp. $C_{16} = 3$	SoilGDD, $C_{16} = 3$ and monthly distribution with one autumn peak	Approx. sinusoidal distribution, $C_{16} = 3$
Trial 3. Monthly litterfall distribution estimates				
3	SoilGDD $C_{16} = 3$	Estimated soil temp. $C_{16} = 3$	SoilGDD, $C_{16} = 3$ and monthly distribution with 3 peaks	Approx. sinusoidal distribution, $C_{16} = 3$
Trial 4. Monthly % potential retention distribution (immobilisation) estimates				
4	SoilGDD $C_{16} = 3$	Estimated soil temp. $C_{16} = 3$	SoilGDD, $C_{16} = 3$ and monthly distribution with 3 peaks	High, almost flat distribution, $C_{16} = 3$
Trial 5. Including a snowmelt routine (snowm) using the best set-up (3)				
5_snowm	SoilGDD $C_{16} = 3$	Estimated soil temp. $C_{16} = 3$	SoilGDD, $C_{16} = 3$ and monthly distribution with 3 peaks	Approx. sinusoidal distribution
Trial 6. All years alike in all input files (6.1 and 6.1_snowm) or with interannual variability in runoff file only (6.2 and 6.2_snowm), using the best set-up (3) with and without snowm				
6.1	SoilGDD $C_{16} = 3$	Estimated soil temp. $C_{16} = 3$	SoilGDD, $C_{16} = 3$ and monthly distribution with 3 peaks	Approx. sinusoidal distribution
6.1_snowm	SoilGDD $C_{16} = 3$	Estimated soil temp. $C_{16} = 3$	SoilGDD, $C_{16} = 3$ and monthly distribution with 3 peaks	Approx. sinusoidal distribution
6.2	SoilGDD $C_{16} = 3$	Estimated soil temp. $C_{16} = 3$	SoilGDD, $C_{16} = 3$ and monthly distribution with 3 peaks	Approx. sinusoidal distribution
6.2_snowm	SoilGDD $C_{16} = 3$	Estimated soil temp. $C_{16} = 3$	SoilGDD, $C_{16} = 3$ and monthly distribution with 3 peaks	Approx. sinusoidal distribution
Trial 7. All months alike in the monthly distribution of lake epilimnion volume (100%, i.e. complete mixing) using setup from trials 6.2 and 6.2_snowm				
7	SoilGDD $C_{16} = 3$	Estimated soil temp. $C_{16} = 3$	SoilGDD, $C_{16} = 3$ and monthly distribution with 3 peaks	Approx. sinusoidal distribution
7_snowm	SoilGDD $C_{16} = 3$	Estimated soil temp. $C_{16} = 3$	SoilGDD, $C_{16} = 3$ and monthly distribution with 3 peaks	Approx. sinusoidal distribution

C decomposition was first used to estimate monthly gross N mineralisation rates. Decomposition of soil organic matter is temperature-dependent and the temperature response is often described by Q_{10} -based formulations (Jenkinson *et al.* 1991; Tian *et al.* 1999; Schimel *et al.* 2000). The Q_{10} function assumes an exponential relationship with temperature in which Q_{10} is the factor by which respiration is multiplied when temperature increases by 10 K (i.e. the ratio of the rate at a given temperature to that at a temperature 10 K lower) (Chen & Tian 2005). Laboratory incubations and field warming studies suggest that the temperature dependence generally decreases with increasing temperature (Kirschbaum 1995; Winkler *et al.* 1996; Rustad *et al.* 2001), i.e. that Q_{10} values are higher (i.e. more sensitive) at lower than at higher temperature (Kirschbaum 1995, 2000). An exponential function for soil respiration (in terms of the respiration rate at 10°C) (Lloyd & Taylor 1994) was thus used to describe the rates of decomposition of organic material (and thus N mineralisation):

$$R = R_{10} \exp\left(E_0 \left(\frac{1}{283.15 - T_0} - \frac{1}{T - T_0}\right)\right) \quad (7)$$

where R_{10} is the respiration rate at 10°C, E_0 is a parameter loosely related to the concept of activation energy and T_0 is a temperature value (K) that has to be less than any measured soil temperature, T (K). According to Lloyd & Taylor (1994) Equation (7) provides an accurate unbiased estimate of soil respiration rates across a wide range of ecosystem types and soil temperatures, using $E_0 = 308.56$ K and $T_0 = 227.13$ K.

Utilising these numbers (and temporarily using $R_{10} = 1$) the long-term mean monthly soil temperatures estimated for 1993–2004 was inserted in Equation (7) and monthly respiration rates calculated. By trial and error R_{10} was estimated assuming that the monthly rates calculated should sum up to $21,400 \text{ mmol C m}^{-2} \text{ yr}^{-1}$, which is the decomposition rate taken from Wright *et al.* (1998) less the measured mean TOC leaching from Øygardsbekken (Table 1 and Figure 5). This resulted in the following equation for estimated monthly C decomposition rates (same as Equation (4) but with the inserted constants):

$$R = 2459.6 \exp\left(308.56 \left(\frac{1}{56.02} - \frac{1}{T - 227.13}\right)\right) \quad (8)$$

Equation (7) can be transformed to calculate a Q_{10} as

$$Q_{10} = \exp\left(10E_0 \left(\frac{1}{(T - T_0)(T - T - 10)}\right)\right) \quad (9)$$

Monthly gross N mineralisation rates were estimated from monthly decomposition rates (using Equation (8)) and the measured soil C/N ratio of 25.5 mol/mol (i.e. replacing the estimated R_{10} in Equation (8) with $2459.6/25.5 = 96.5$).

Third, two alternatives were tried for the monthly distribution of litterfall. Annual litterfall N was assumed equal to the annual rate for plant N uptake. Monthly litterfall was distributed over the year, with either one peak in autumn or three peaks in spring, summer and autumn (Figure 8). The latter representation of litterfall (three peaks) is based on litter production measurements in the UK from 165 adult *Calluna* plants (Cormack & Gimingham 1964).

Finally, two different estimates were tried for the monthly distribution of % potential retention (in MAGIC a measure of seasonal gross microbial immobilisation). Immobilisation is the unknown quantity set to balance the terrestrial N budget. The calibration is thus by trial and error to portion the net immobilisation among the months such that monthly NO_3 flux and concentration have the highest agreement with measurements. The estimated value for a given month was related to monthly soil temperature

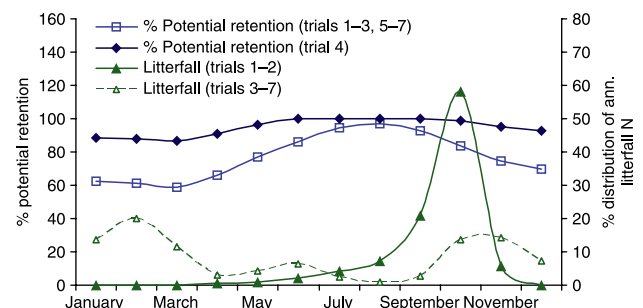


Figure 8 | Two different estimates for mean (1993–2004) monthly distribution of litterfall and % potential retention (estimate for seasonal immobilisation) tested during calibration. The solid line with solid triangles shows the distribution of litterfall tested during trials 1 and 2 and the dashed line with open triangles shows that tested during trials 3–7. The solid line with solid diamonds shows estimated % potential retention tested during trial 4 while the solid line with open rectangles shows that used during all other trials.

using a function similar to Equation (4) but replacing R_{10} and E_0 with factors obtained by trial and error using mean monthly soil temperature (Figure 9) in the equation. The monthly percent distribution for immobilisation was estimated by setting the % potential retention parameter to be continuously high, almost flat (trial 4), or approximately sinusoidal in shape with low values in winter months (minimum 59% in March) and high values in summer months (maximum 97% in August) (Figure 8). For the latter representation E_0 and R_{10} were estimated to be 100 and 88.2, respectively. The specification of these monthly rates gave the outcome that the monthly actual gross immobilisation is highest in April and November (Figure 10). This is because, although the potential immobilisation is, of course, highest in July (the month with the highest soil temperature), plant uptake in July has depleted the soil solution of NO_3 and thus there is little remaining for immobilisation.

For each of the trials the $\text{C}/\text{N}_{\text{up}}$ and initial organic N pool (initN) were adjusted in MAGIC to obtain the best match between simulated and observed mean (1994–2004) annual NO_3 streamwater concentration, C/N in soil and cumulative flux of NO_3 . These adjustments were necessary because each change in a seasonal N process affected the long-term retention and loss of N from the ecosystem. One requirement for each calibration trial was that present-day simulated C/N soil and NO_3 streamwater matched the observed.

Snowmelt routine (suffix snowm)

A simple snow accumulation and melting routine (calculated separately and incorporated in the MAGIC deposition

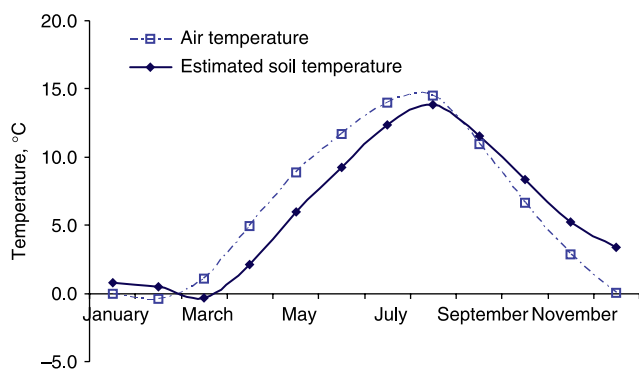


Figure 9 | Measured mean (1993–2004) air temperature (dashed line with open squares) and estimated soil temperature ($C_{16} = 3$) (solid line with solid diamonds) at the Øygardsbekken catchment.

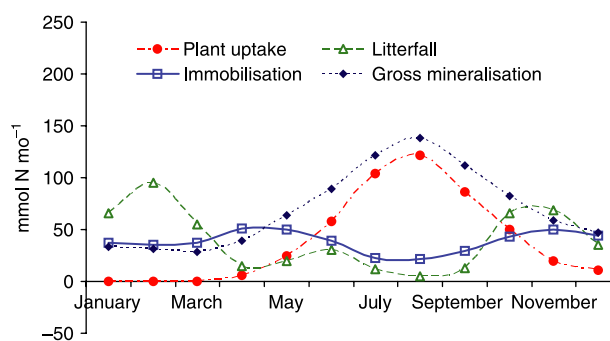


Figure 10 | Estimated long-term mean (1993–2004) monthly distributions of gross N mineralisation (dotted line with solid diamonds), plant N uptake (dashed line with solid circles), litterfall N (dashed line with open triangles) and immobilisation (solid line with open squares) at the Øygardsbekken catchment according to best trial.

input file) was used to modify the monthly deposition input of water and nitrogen. Both accumulation and melting were based on estimated (bulk) precipitation and linked to mean monthly air temperature. Snow was assumed to accumulate when the mean monthly air temperature was below the threshold of 2°C . The snowpack was assumed to melt by a fixed number of millimetres of water per month based on the air temperature. A linear function was used with lower threshold (mean monthly air temperature -6.5°C) and slope ($30\text{ mm}^\circ\text{C}^{-1}$). This threshold and slope gave the best fit to the measured monthly discharge during the winter months. (The threshold of -6.5°C implies that, even if the mean monthly air temperature is this low, one or more days will be sufficiently warm to give some melting.) In a given month if the temperature was low, snow was assumed to accumulate and thus the water (and ions) in deposition was added to the snowpack in that month. The snowpack was assumed to melt if the temperature was above the lower threshold for melting, by the calculated millimetres or by the millimetres in the snowpack, whichever was less. The remaining water (and ions) was then carried over to the snowpack the following month. No differential release of ions was assumed; for whatever fraction of the water was lost, the same fraction of the accumulated ion was removed.

Input files to MAGIC

Files to MAGIC consist of a general monthly parameter file and input files for monthly deposition, runoff and N parameters. The general parameter file requires information

for one year of mean monthly data from the catchment including: (1) hydrological routing, (2) deposition, (3) soils, (4) surface water, (5) the distributed N dynamics and (6) historical deposition sequence. Available data or estimates from the catchment were used for the hydrological routing, soils and surface water and used long-term mean (1993–2004) monthly data for bulk precipitation, deposition, runoff and distributed N dynamics. The historical deposition sequence was scaled to the annual N deposition for the calibration year 1995. When MAGIC was run with only the general parameter file, then the same monthly input for all years was assumed (i.e. all years alike). The exception to this is for N deposition, as the historical (annual) deposition sequence (Figure 11) predicts annual variation in N deposition (i.e. same monthly distribution each year, but with variable annual rates).

Monthly input files for precipitation, deposition and runoff were observed data for the periods 1975–2004 and 1990–2004, respectively. Furthermore, C and N process rates in the N parameter file were estimated and calibrated as previously described, and consisted of estimates for the period 1975–2004.

RESULTS

Seasonality in runoff data

Measured NO_3 concentrations at the Øygardsbekken catchment show a typical seasonal pattern with high values in winter and early spring and low values in summer.

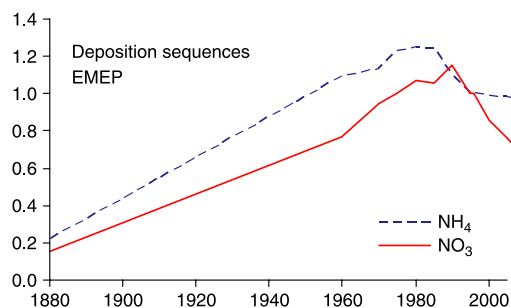


Figure 11 | Historic NO_3 (solid line) and NH_4 (dashed line) deposition sequences for Øygardsbekken scaled to year 1995. Data were obtained from N emissions in Europe and the EMEP transport and deposition model (Schöpp *et al.* 2003).

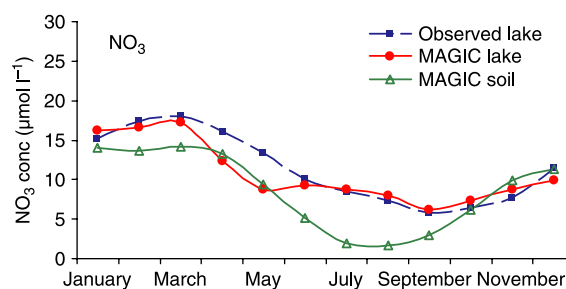


Figure 12 | MAGIC observed mean (1993–2004) monthly NO_3 surface water concentrations (dashed line with solid squares) and MAGIC simulated mean (1993–2004) monthly NO_3 concentrations for the lake (solid line with solid circles) and soil (solid line with open triangles) at the Øygardsbekken catchment.

At Øygardsbekken the summer minimum, however, does not completely decline to zero ($\approx 5 \mu\text{mol N l}^{-1}$) and the minimum period normally prevails for several months around September (Figure 12). Summer minima for mean monthly (1993–2004) soil solution NO_3 concentrations (as simulated by MAGIC), however, declines to near zero in July and increases again already in August (Figure 12).

Model calibration

Model evaluation of the different trials

The statistical evaluations of the different trials (Table 3) show that for the various N processes the best combined set-up was obtained with plant N uptake based on soilGDD, soil temperature estimates based on $C_{16} = 3$ (the most delayed soil temperature estimate) and annual litterfall with a monthly distribution of three peaks (trial 3). With this set-up MAGIC explained 32% and 81% of the variations in NO_3 concentrations and fluxes, respectively. For NO_3 fluxes this result was significantly better compared to trial 2.2, but there was no improvement in the explanation of NO_3 concentration. By including the snowmelt routine (trial 5_snowm), however, the explanation for NO_3 concentrations increased to 35%, while the explanation for fluxes remained unchanged. Moreover, using input and parameter files with all years alike (trial 6.1) the explanation for NO_3 concentration increased to 53% but at the expense of the explanation for fluxes, which decreased to 63% (Table 3). Only minor improvements were obtained by including the snowmelt routine (trial 6.1_snowm).

Table 3 | Statistical measures of NO₃ concentrations and fluxes during calibration for the different monthly N processes and lake stratification pattern. The resulting best set-ups are trials 3 and 6.2_snowm

Trial	Test parameter-description	NO ₃ concentrations			NO ₃ fluxes		
		EFF	RMSE	r ²	EFF	RMSE	r ²
1.1	Plant N uptake airGDD	0.20	4.81	0.28	0.74	0.66	0.80
1.2	Plant N uptake soilGDD	0.22	4.74	0.30	0.73	0.66	0.80
2.1	Soil temperature C ₁₆ = 6	0.17	4.91	0.27	0.71	0.70	0.78
2.2	Soil temperature C ₁₆ = 3	0.24	4.67	0.31	0.69	0.72	0.78
3	Litterfall 3 peaks	0.25	4.66	0.32	0.76	0.63	0.81
4	% potential retention. Almost flat, high	-0.03	5.46	0.07	0.66	0.74	0.69
Different trials with the best set-up – trial 3							
5_snowm	Trial 3 with snowmelt routine, inter annual variation in input and parameter files	0.30	4.51	0.35	0.77	0.61	0.80
6.1	Trial 3, all years equal in input and parameter files	0.49	3.84	0.53	0.63	0.78	0.63
6.1_snowm	Trial 3 with snow melt routine, all years equal in input and parameter files	0.52	3.73	0.55	0.63	0.78	0.63
6.2	Trial 3, all years equal in N parameter file and deposition file, with inter annual variability in runoff file	0.62	3.31	0.64	0.87	0.46	0.87
6.2_snowm	Trial 3 with snowmelt routine, all years equal in N parameter file and deposition file, with inter annual variability in runoff file	0.66	3.16	0.68	0.88	0.45	0.88
7.1	Trial 3, all years equal in N parameter file and deposition file, with inter annual variability in runoff file, lake epilimnion volume = 100% each month	0.35	4.33	0.40	0.79	0.58	0.80
7.1_snowm	Trial 3 with snowmelt routine, all years equal in N parameter file and deposition file, with inter annual variability in runoff file, lake epilimnion volume = 100% each month	0.28	4.56	0.29	0.76	0.63	0.78

Even better simulations were obtained when inter-annual variability of runoff and a snowmelt routine were included. The best trial was obtained when using all years alike for the deposition and nitrogen files (Figure 10), but with inter-annual variability in the runoff input file and with the snowmelt routine included (trial 6.2_snowm). Here C/N_{up} and C/N₁₀ were calibrated to 26.4 and 15.4, respectively. For this trial MAGIC was able to explain 68% and 88% of the variation in NO₃ concentration and fluxes, respectively (Figure 13).

To illustrate how epilimnion volume affected the results, one trial was performed using an epilimnion volume of 100% (complete mixing all year) each month using the best set-up from trial 6.2 and 6.2_snowm (Table 2, trials 7 and 7_snowm, respectively). The degree of variation explained in NO₃ concentrations and fluxes by MAGIC were reduced

to 0.40 and 0.80 (Table 3, trial 7), respectively, and 0.29 and 0.78 (Table 3, trial 7snowm), respectively. The reason for the poorer result was that the year-to-year variations in the simulated peaks disappeared (i.e. the same seasonal NO₃ pattern was repeated each year) (figure not shown).

Simulated versus observed data

During the best trial (6.2_snowm), MAGIC simulated both the timing and dynamics of observed NO₃ concentrations satisfactorily (Figure 13, top panel). MAGIC captured the late summer minimum better than the winter peaks. The concentrations during winter and early summer were generally underestimated (Figure 13). Generally, the month of May showed the largest difference between MAGIC simulated and observed (Figure 14), probably

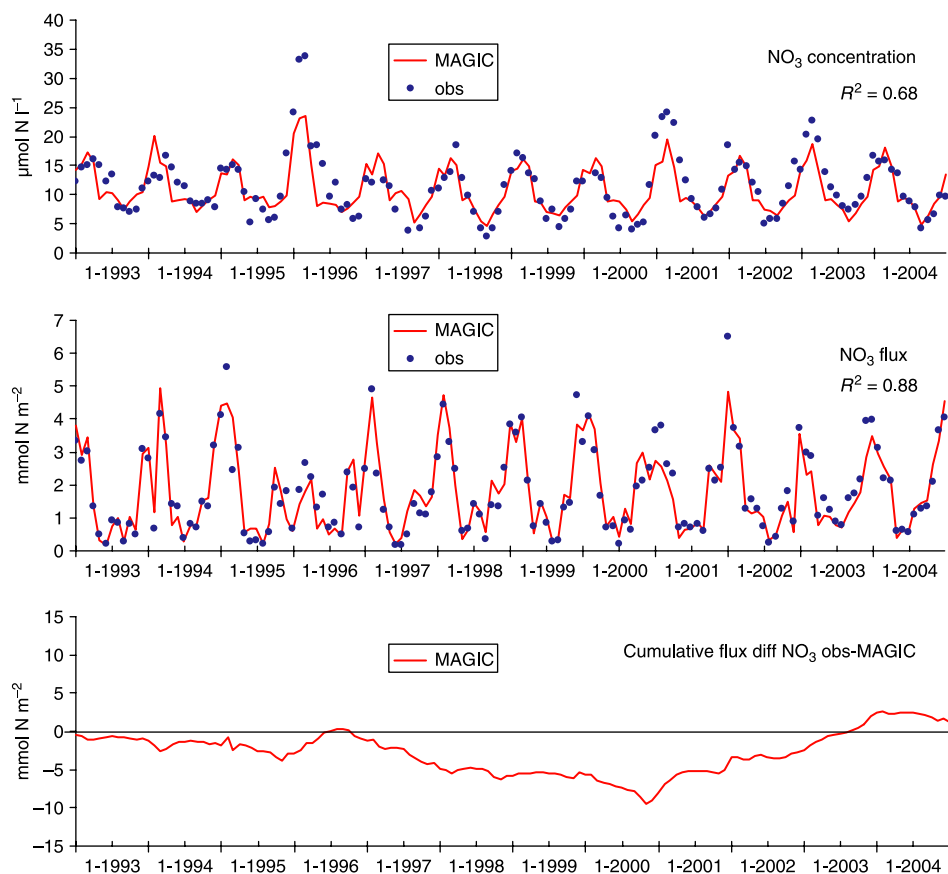


Figure 13 | Simulated (solid line) versus observed (solid circles) NO_3 concentrations (upper panel), fluxes (middle panel) and cumulative difference between observed and simulated fluxes (bottom panel) for the best set-up during calibration. No deposition or N parameter files were used (i.e. all years equal), whereas the inter-annual variable runoff file was used.

because the lake was calibrated to go from winter stratification (very small epilimnic volume) in April to complete mixing in May (Figure 7). The transition from April to May involves a large jump in the lake epilimnion volume as the entire volume of the lake is mixed with the terrestrial drainage, causing MAGIC to simulate higher NO_3 concentrations than is observed. By trial and error, the model showed to be quite sensitive to small changes in the epilimnion volume (not shown), but the set-up used gave the best results. Ideally it would be preferable to be able to change the date (i.e. month) for ice-on and ice-off each year, but due to lack of direct measurements this was not done.

The unusually high concentration peaks during the winters of 1996 and 2001 were poorly simulated. MAGIC simulated slightly higher peaks than observed during the winters of 1994 and 1997. MAGIC fluxes showed good agreement with measured NO_3 fluxes (calculated as

measured concentrations times runoff) (Figure 13, middle panel), but poorly captured the observed fluxes during the winters of 1996 and 2001.

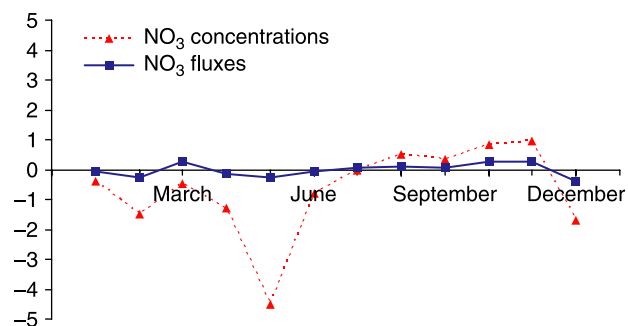


Figure 14 | Mean (1993–2004) difference between MAGIC simulation and observed data (i.e. a measure of the residuals) by month during the best trial (6.1_snowm). NO_3 concentrations ($\mu\text{mol l}^{-1}$) are shown as dotted line with solid triangles, and fluxes ($\text{mmol m}^{-2} \text{mo}^{-1}$) as the solid line with solid squares.

DISCUSSION

Seasonal NO₃ pattern

The observed seasonal NO₃ concentration pattern at the Øygardsbekken catchment, with high values during winter and spring (snowmelt) and low values during summer, is commonly observed in semi-natural, temperate ecosystems (Reynolds & Edwards 1995; Mitchell *et al.* 1996). The lakes at Øygardsbekken are probably responsible for the delay in the NO₃ seasonal pattern (highest and lowest concentration in March and September, respectively) compared to that observed in surface runoff from several small terrestrial sub-catchments established in the catchment and sampled during 1999–2001 (Sjøeng *et al.* 2007). Normally these sub-catchments showed highest and lowest NO₃ concentrations in January and July–August, respectively, with a summer minimum of nearly zero. Similar timing and with no NO₃ leaching during summer was simulated by MAGIC for soil water NO₃ concentrations (Figure 12). The dampening effects of large lakes have also been reported for several other sites within the same region (Kaste *et al.* 2003). Based on the bathymetric chart (Figure 2) the residence time for the largest lake, Lake Hedlevatn, was estimated to 2.4 months (Sjøeng 1998) and, together with the other ponds, clearly contributes to the delayed and damped variations in NO₃ concentrations observed.

Soil processes

The dampening effect of the lakes on NO₃ leaching from Øygardsbekken has implications for the parameters to be calibrated in the model. The temperature-dependent estimates of soil C and N processes had to be based on estimated soil rather than air temperature. Furthermore using Equation (1) in estimating soil temperature the C₁₆ factor was calibrated to 3 (most delayed) rather than 4.5 or 6. The same factor was used by Rankinen *et al.* (2004) in calibrating soil temperature data from a Finnish observation station although mean air temperature at that site was -1 compared to 6.3°C at Øygardsbekken. The estimated soil temperature pattern at Øygardsbekken was comparable to measured soil temperature data at Storgama in southeastern Norway (Kaste *et al.* 2008).

Model performance

The different trials in this modelling exercise illustrated that, for several of the parameters (i.e. deposition and N parameter file), the more complex the input files the lower degree of explanation was obtained by the model (Table 3). The best match between observed and simulated NO₃ concentrations was obtained by using inter-annual variation in the monthly runoff file but with all years alike (i.e. mean monthly data each year) for N and C processes and N deposition (i.e. inter-annual variability in annual N deposition according to the deposition sequence but with the same monthly distribution each year). Model results were slightly improved for NO₃ concentrations when a snow accumulation and melt routine was used. The implication is that good estimates of runoff volume are critical in modelling seasonal NO₃ leaching to surface waters with MAGIC. This is illustrated further when using all years alike (i.e. mean data) for runoff as well as deposition and N and C processes (trials 6.1snowm and 6.1) as the amount of variability explained by the model were reduced by as much as 13 and 25% for concentrations and fluxes, respectively (Table 3). It is the simulation of NO₃ concentrations that benefits the most by using simple (i.e. all years alike in N parameters and deposition, with inter-annual variability for runoff) rather than complex (i.e. inter-annual variation in N parameters, N deposition and runoff) input files, improving the degree of explanation from 35 to 68%. A possible explanation for this is that the soil N processes may not respond to short-term fluctuations in temperature. These results thus suggest that short-term temperature variations are not the key driver of NO₃ loss, whereas short-term variations in runoff are more important (Table 3, trial 6.2_snowm).

Uncertainties and limitations of model predictions

Variations in N concentrations in runoff from a catchment are the net result of complex interactions between processes on land and in surface waters. Models are simplified descriptions of natural systems with many inherent limitations and uncertainties. Model applications are limited by the availability of suitable data to describe the physical, chemical and biological characteristics of surface waters and their terrestrial catchment areas. It is often necessary to use

data from the literature for comparable catchments, without knowing to what extent these represent a good estimate of the catchment used in model applications. Furthermore, models require several parameters to be calibrated and there are numerous combinations of these that may give equally good matches between observed and simulated data. In the present study the bottleneck has been the lack of measurements in the catchment, particularly of soil and vegetation C and N process rates. There have been many assumptions necessary for this modelling exercise. Due to lack of direct measurements and the high annual amounts of precipitation (>2,000 mm) received by this catchment, no constraints on soil C and N processes due to very high or low soil moisture levels were modelled. Yet during dry periods in summer, the catchment could experience drought episodes that may disrupt the soil and vegetation C and N processes (e.g. Jensen *et al.* 2003). On the other hand, during high rainfall events soils may become water saturated inducing anaerobic conditions favourable for few N processes (i.e. denitrification). Thus, making the C and N processes dependent not only on temperature but also on soil moisture might improve model results slightly, particularly during the low NO₃ concentration periods during summer.

Generally, there are three major sources of uncertainty that potentially contribute to the lack of an exact match between simulated and observed NO₃ concentrations and fluxes in streamwater (Saloranta *et al.* 2003). First is uncertainty in the data. The streamwater samples were collected weekly or fortnightly and thus may misrepresent the peaks in NO₃ concentrations. The deposition data come from stations 15–50 km distant from the catchment and these had to be adjusted to estimate actual deposition at the catchment. The soil data were collected at a limited number of points and were assumed characteristic for the entire catchment soil. There are no direct measurements of the rates of the N processes in soil and vegetation in the catchment and therefore use data from other similar ecosystems. Finally, lake epilimnion volume proved critical for the timing of the seasonal NO₃ concentrations, but there are data from only one year. Since surface water measurements from the catchment are located downstream from the outlet of the lake, it is not possible to separate the effect of processes in the lake from that in the terrestrial part of the catchment.

The second source of uncertainty arises from time and space assumptions necessary to set up the model. MAGIC is run here with a monthly time step. A finer time step would help to describe short-term events such as those caused by hydrologic episodes (such as storms, snowmelt, timing of ice-on and ice-off), but there are few measurements on a finer time step available to confirm model results. MAGIC lumps spatial heterogeneity in soil properties into a single value for the entire catchment. In the absence of extensive measurements in the field these lumped values are necessary estimates with an unknown amount of uncertainty.

The third major source of uncertainty arises from the model structure itself. All models are necessarily simplified descriptions of nature. The Øygardsbekken catchment is a mosaic of small wetlands, well-drained heathlands, patches of birch, extensive areas of bare bedrock, and numerous small ponds and lakes. MAGIC simplifies all this heterogeneity into one vegetation type, one soil box, one lake and one stream, and specifies parameters and process rates for each of these. It is thus perhaps not surprising that the model calibration describes only 68% of the observed variance in concentration of NO₃ in streamwater.

Nevertheless the comparison of simulated with observed concentrations of NO₃ in streamwater clearly shows that the model works better in the summer months than in the winter months. This is perhaps due to short-term phenomena, such as hydrologic by-pass, that are not included in the current calibration. In the absence of monthly field data on these it is difficult to introduce these factors into the model.

The model misses several of the big peaks in the winter months, in particular those observed in the winters of 1996 and 2001 (Figure 13). The two winters were unusually cold and had periods of little or no snow cover. The large NO₃ concentration peak observed at Øygard during winter in 1996 appeared simultaneously in lakes and streams in the UK (Monteith *et al.* 2000). Hence, streamwater NO₃ dynamics at that time could be controlled by a large-scale climatic event. In this context, Monteith *et al.* (2000) found that variations in NO₃ concentrations at several UK sites showed a strong negative correlation with winter values for the North Atlantic Oscillation (NAO) index and mean winter temperature. High winter values for the NAO index are associated with relatively warm and wet winter

conditions in northwestern Europe, whereas low values coincide with colder and drier conditions (Hurrell 1995).

In 2001 the elevated winter NO₃ peak was also observed at several terrestrial sub-catchments of Øygardsbekken (Sjøeng *et al.* 2007). During the two years of surface water sampling (2000 and 2001) the NO₃ peak conditions were quite different, with a much broader and higher peak in 2001 compared to 2000. The two years also differed with respect to the relationship between discharge and NO₃ concentrations: positively correlated during 2000, while high concentrations appeared coincident with both low and high flow conditions in winter 2001 (Sjøeng *et al.* 2007). Since elevated NO₃ peaks were observed from both the total (including the lakes) and the terrestrial sub-catchments in 2001, this is likely to result from disruptions in the terrestrial rather than the aquatic part of the catchment. Similar peaks in NO₃ following exceptionally cold winters has earlier been reported at heathland sites in the UK (Reynolds & Edwards 1995) and in New York, USA (Mitchell *et al.* 1996). These sites all normally do not have extensive frost during the winter and soils are thus perhaps poorly adapted to occasional soil freezing events. Sjøeng *et al.* (2007) suggested that soil freezing might damage plant roots and cause microbial mortality, which in turn could lead to the release of NO₃ to soil solution and runoff as the dead roots and microbial cells are decomposed, mineralised and nitrified as soil thaws (Matzner & Borken 2008).

Since the elevated NO₃ peaks observed (in winters of 1996 and 2001) at the Øygardsbekken catchment were poorly simulated and can be explained by freeze–thaw events, it is tempting to speculate on how this could be represented in MAGIC. Perhaps an “additional mineralisation N” process could be added. The “additional mineralisation N” could, for example, be dependent on an upper soil temperature threshold that needs to be crossed for a prolonged period of time (Austnes & Vestgarden 2008), and the quantity of N that may potentially be mineralised could somehow be related to the SOM pool. There are few field data available from the literature to quantify this. Many of the studies addressing the relevance of freeze–thaw for N (and C) losses from soil are short-term laboratory-based, have no flux measurements or control treatments, and sometimes only focus on the thaw period rather than on the frost period (Matzner & Borken 2008).

Addition of the year-to-year variations in runoff gave a significant improvement in the explanation of the monthly fluxes of NO₃. This is because the complex trial includes the observed month-to-month variations in runoff volume, rather than the 12-year mean monthly runoff volumes used in the simple trial. The fact that the best trial gave an r^2 of 0.68 for NO₃ concentration but 0.88 for flux shows that the model simulates the NO₃ concentration better for months with low discharge than for months with high discharge. Some of the discrepancy can be accounted for by the winter months of the two “outlier” years, 1996 and 2001.

In this modelling exercise the combined set of equations and representations for the different C and N soil processes used could explain the variations in NO₃ concentrations and fluxes satisfactorily. There may, however, be other (unknown) descriptions that are equally good. Despite the inherent uncertainties, dynamic models like MAGIC are valuable tools in describing ecosystem function in a simplified manner. Most importantly they have a key role to play in the review of the latest (Gothenburg) Protocol for emission reductions (Jenkins *et al.* 2003) as they can be applied to project ecosystem response to future changes in N deposition and climate.

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