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Modelling stream and soil water nitrate dynamics during experimentally increased nitrogen deposition in a coniferous forest catchment at Gårdsjön, Sweden

M. N. Futter, R. A. Skeffington, P. G. Whitehead and F. Moldan

ABSTRACT

Increased atmospheric deposition of inorganic nitrogen (N) may lead to increased leaching of nitrate (NO_3^-) to surface waters. The mechanisms responsible for, and controls on, this leaching are matters of debate. An experimental N addition has been conducted at Gårdsjön, Sweden to determine the magnitude and identify the mechanisms of N leaching from forested catchments within the EU funded project NITREX. The ability of INCA-N, a simple process-based model of catchment N dynamics, to simulate catchment-scale inorganic N dynamics in soil and stream water during the course of the experimental addition is evaluated. Simulations were performed for 1990–2002. Experimental N addition began in 1991. INCA-N was able to successfully reproduce stream and soil water dynamics before and during the experiment. While INCA-N did not correctly simulate the lag between the start of N addition and NO_3^- breakthrough, the model was able to simulate the state change resulting from increased N deposition. Sensitivity analysis showed that model behaviour was controlled primarily by parameters related to hydrology and vegetation dynamics and secondarily by in-soil processes.

Key words | acidification, experimental nitrogen addition, Gårdsjön, nitrogen leaching

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INTRODUCTION

There is increasing concern over adverse effects of nitrogen (N) in the environment. This has been particularly true of N-limited natural and semi-natural upland catchments, where anthropogenic emissions have led to an excess in N availability. This has resulted in nitrate (NO_3^-) leaching from forest and moorland systems (Dise & Wright 1995). As a result of international concern, the first protocol to limit N emissions was formulated in 1988 under the auspices of the UNECE and implemented in 1991 in the Sophia Protocol (Hornung & Langan 1999). Skeffington (2002) gives a history of N emissions and control strategies since 1988.

As N deposition levels increase, the uptake capacity of vegetation and soil biota can be exceeded, resulting in the release of excess N (Emmett *et al.* 1998). Similarly, as forests reach maturity, they take up less N and any excess may be leached. Climate change may alter patterns of N leaching. Changes in rainfall and temperature patterns will alter soil moisture conditions, leading to increased rates of mineralization and nitrification (Wright *et al.* 1998). If a changing climate leads to altered rates of biological uptake in the soil and vegetation, this may also affect catchment-scale carbon sequestration and dissolved organic carbon dynamics (Pregitzer *et al.* 2004). The excess N in rivers from enhanced leaching may lead to surface water acidification as NO_3^- is a strong acid anion. Increased eutrophication in streams, lakes and coastal waters may also result from excess N in surface waters. Both acidification and surface water eutrophication are of concern across Europe.

The mechanisms of N retention and possible timing of N breakthrough and increased leaching are subjects of practical and theoretical interest. A number of experimental N additions have been performed in an attempt to

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identify the mechanisms responsible and assess the possible magnitude of N leaching in forested catchments (Moldan *et al.* 1995, 2006; Currie *et al.* 1996; Gundersen 1998; Moldan & Wright 1998*b*; Wright & Rasmussen 1998; Pregitzer *et al.* 2004). Many of these experiments found that much of the added N was retained in the catchment, with only a small fraction leaching to surface waters. It is assumed that much of the added N remains in catchment soils and biomass. If this retained N were to be released, it would lead to N "breakthrough" and rapid re-acidification of surface waters.

This paper presents a model simulation of the experimental N addition at the Gårdsjön Experimental Catchment in Sweden during the NITREX experiment (Moldan *et al.* 1995, 2006). The *In*tegrated *Ca*tchments model for *N*itrogen, INCA-N (Whitehead *et al.* 1998; Wade *et al.* 2002) was used to simulate soil and stream water N dynamics in the Gårdsjön G2 catchment. This was done to explore the strengths and shortcomings of the INCA-N conceptual model of N-dynamics for explaining the observed patterns of $[NO_3^-]$ in the catchment during the course of experimental N addition and to see if the model could add to our under standing of the processes responsible for N leaching and retention in forested catchments receiving excessive N input.

There have been a number of previous attempts to model experimental N addition using more detailed process-based models. The MERLIN model has been applied to the Gårdsjön G2 catchment (Kjønaas & Wright 1998). Modelling results suggested that most of the experimentally added N was immobilised and incorporated into the soil organic matter pool. The MERLIN model was able to simulate the observed increase in N leaching from below the rooting zone. As MERLIN operates on an annual time step, it does not simulate any of the observed seasonal behaviour. Wright *et al.* (1998) used MERLIN to simulate changing N dynamics at an experimental catchment in Norway. Beier & Eckersten (1998) used SOILN in their simulations of N dynamics during fertilisation of a forested catchment in Denmark.

Other studies have used INCA-N to model the effects of changing N deposition (Langusch & Matzner 2002; Whitehead *et al.* 2002; Kaste *et al.* 2004). The work presented here draws on previous work by Whitehead *et al.* (2002) who used INCA-N simulations to explore the possible causes of excess N leaching at a catchment scale. The work presented here is novel as it is the first application of INCA-N to simulate an experimental N addition. The process representation in INCA-N is simpler than that in either MERLIN or SOILN. Unlike the other two models, INCA-N does not include any carbon dynamics and assumes an infinite pool of organic N in the soil. Unlike MERLIN, INCA-N does not model adsorption/desorption of NO_3^- or NH_4^+ in the soil. SOILN has a more detailed representation of the plant–nitrogen interactions than either MERLIN or INCA-N.

The goals of this study were: (i) to assess whether INCA-N is able to simulate the stream and soil water N dynamics observed during experimental N addition, (ii) to determine which parameters controlled model performances and (iii) to evaluate the suitability of the INCA-N conceptual model for describing the long-term effects of chronic N addition to forested catchments.

STUDY SITE

The Gårdsjön catchment in southern Sweden has been the site of numerous large scale experimental studies designed to improve understanding of the effects of atmospheric deposition on forest biogeochemistry (Moldan *et al.* 1995, 2006; Hultberg & Skeffington 1998). The Gårdsjön region has been described previously by Andersson & Olsson (1985) and Andersson *et al.* (1998). Briefly, the Gårdsjön study area is located 15 km from the west coast of Sweden in the Svartedalen region. The region is dominated by mature coniferous forests comprised mainly of Norway Spruce (*Picea* abies (L.) Karst.) with some Scots Pine (*Pinus* sylvestris L.) The understory vegetation is predominantly dwarf shrubs and mosses. Soils are shallow and are derived from tills of a local origin. Dominant soil types in the catchment include Carbic Podsols, Gleyic Podsols and Lithic Leptosols (Vestgarden & Kjønaas 2003). Rainfall and runoff average 1,150 and 580 mm yr^{-1}, respectively. There are three intensively monitored small catchments in the Lake Gårdsjön area: F1, a control catchment; G1, the site of a roof experiment (Moldan *et al.* 2004) and G2, which has been set up for the experimental precipitation additions (Hultberg & Skeffington 1998). The 0.52 ha G2 catchment is

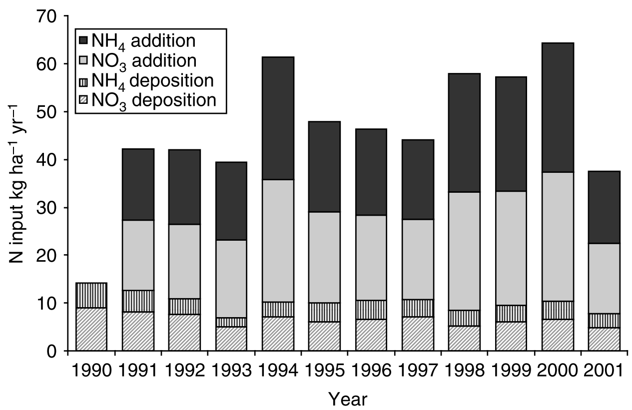

Figure 1 | Inputs of NO_3^- and NH_4^+ from deposition and experimental addition.

too small to support a natural permanent stream. However, a weir has been built at the foot of the catchment to facilitate flow monitoring.

The G2 catchment was used as part of the NITREX project (Wright & Rasmussen 1998) to investigate N mobilisation and transport in catchments. During the course of the experiment, a spraying mechanism in the catchment was used to add N to the G2 catchment. The experiment began in 1989 and N addition started in April 1991. Nitrogen as NH_4NO_3 was sprayed on average 20 times a year at a target rate of 40 kg N ha^{-1} yr^{-1}, adding to the background atmospheric N deposition of approximately 11 kg N ha^{-1} yr^{-1} (Moldan & Wright 1998*a*; Moldan *et al.* 2006). There was some inter-annual variability in both atmospheric deposition and experimental N addition (Figure 1). During the course of the experiment, a wide range of environmental variables were monitored, including hydrology and chemistry of runoff (Moldan & Wright 1998*a*), runoff episodes (Moldan & Wright 1998*b*), groundwater and soil water chemistry (Stuanes & Kjønaas 1998), soil processes (Kjønaas *et al.* 1998), mycorrhizae (Brandrud & Timmermann 1998), fine roots (Persson *et al.* 1998), tree growth, litter and needles (Kjønaas *et al.* 1998).

Very little NH_4^+ is observed in the stream. Almost all the added NH_4^+ is either nitrified or rapidly taken up by the vegetation and soil biota. At the beginning of the experiment, the catchment was N-limited, as shown in Figure 2, with no detectable NO_3^- leaching in runoff or groundwater. By 1995, there was some NO_3^- in stream water year round. Figure 2 shows the rising N release from the catchment during the course of experimental addition. There is a slow build up in stream NO_3^- concentration over the course of the experiment but the release of N into the stream amounts to approximately 10% of the N deposited. Increased inorganic N deposition was expected to increase NO_3^- concentrations in the upper soil from 1992 onwards and in the lower soil from 1993 onwards (Stuanes & Kjønaas 1998; Moldan *et al.* 2006).

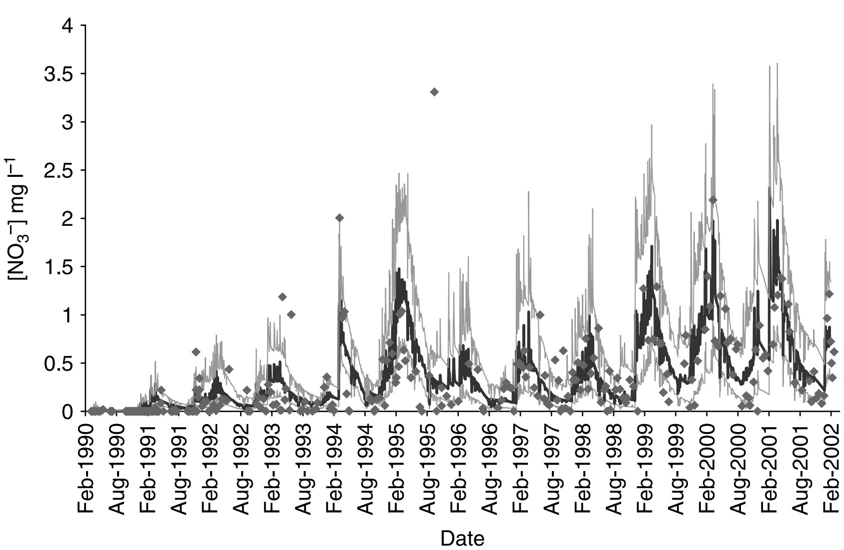

Figure 2 | Observed (dots) and INCA-N simulated stream water nitrate at the Gårdsjön G2 catchment outflow. The thick line represents the median modelled $[NO_3^-]$ for the day while the thin lines are the maximum and minimum modelled behavioural values.

THE INCA-N MODEL

The INCA-N (*In*tegrated *Ca*tchments Model for Nitrogen) is a catchment-scale, process-based dynamic model of nitrogen dynamics in terrestrial and freshwater aquatic environments (Whitehead *et al.* 1998; Wade *et al.* 2002). The model has primarily been applied to agricultural catchments but there have been some applications to near-natural systems (i.e. Kaste *et al.* 2004). INCA-N operates on a daily time step and thus is ideal for modelling effects of soil temperature and wetness as well as investigating weather and climate influences on biogeochemical processes. One of the main differences between INCA-N and other models such as MAGIC (Cosby *et al.* 2001), MERLIN (Wright *et al.* 1998), SOILN (Beier & Eckersten 1998) and WANDA (Tietema 2004) is that soil C/N ratios are not used in predicting N dynamics.

In INCA-N, mass balance equations are solved for NO_3^- and NH_4^+ in both the soil and groundwater zones. The key processes modelled in the soil zone are nitrification, denitrification, N fixation, NH_4^+ mineralisation and immobilisation. Within the model, all biological uptake of NH_4^+ and NO_3^- is assumed to be controlled by vegetation in the catchment. Biological uptake of NH_4^+ and NO_3^- by the soil biota is not explicitly modelled within INCA-N. The land phase model accounts for all the inputs affecting each land use including dry and wet deposition of NH_4^+ and NO_3^- and fertiliser addition for both NH_4^+ and NO_3^- (e.g. as ammonium nitrate). In addition, temperature and soil moisture controls process rates for mineralisation, nitrification and denitrification. In the groundwater zone, it is assumed that no biochemical reactions occur and that there are mass balances for NH_4-N and NO_3-N. The output generated by INCA-N includes daily time series of flows, $[NO_3^-]$ and $[NH_4^+]$ at the catchment outflow, daily fluxes associated with NO_3^- and NH_4^+ leaching and each of the N processes included in the model. Within the model code, all processes are represented as a series of linked first-order differential equations.

The processes represented in INCA-N have been documented elsewhere (Whitehead *et al.* 1998; Wade *et al.* 2002). The following is a brief review of the overall structure and a detailed description of the vegetation sub-model of INCA-N, given its importance in the results presented later.

Within INCA-N, uptake of NO_3^- and NH_4^+ by vegetation is modelled as a time-varying function of a potential N uptake, U. Potential uptake of NO_3^- or NH_4^+ is modelled as a modified sine-function in the following manner (Equation (1)). Uptake can only occur during the growing season, indicated by k_1. This parameter is set to a value of 1 during the growing season and 0 otherwise. The shape of the uptake curve is described by k_2 and k_3. These are empirical parameters that define the offset and amplitude, respectively, of a sine curve describing potential uptake. The J and k_4 parameters are required so that the maximum and minimum potential uptake values occur at the appropriate time of year:

$$U = k_1\left(k_2 + k_3 \cdot \sin\left(2\pi\frac{[J-k_4]}{365}\right)\right). \tag{1}$$

The change in mass of NO_3^- taken up by plants (dNO_3^-/dt) is modelled as follows (Equation (2)):

$$\frac{dNO_3^-}{dt} = U \cdot k_5\left(\frac{NO_3^-(S)}{V}\right) \tag{2}$$

where U (from Equation (1)) defines the time-varying potential N uptake rate and k_5 is the NO_3^- uptake rate (d^{-1}), $NO_3^-(S)$ is the mass of nitrate in the soil and V is the total volume of water in the soil. Change in mass of NH_4^+ is modelled in a similar manner.

APPLICATION OF INCA-N TO GÅRDSJÖN

INCA-N was used to simulate NO_3^- surface water concentrations and fluxes from the Gårdsjön G2 experimental catchment from 1 March 1990 to 10 February 2002. The model was set up to simulate a single reach with a single land-cover type (forest) within the catchment. Air temperature and precipitation data were obtained from the nearby Gårdsjön meteorological observation site. Water chemistry analyses were performed by the IVL analytical laboratory.

Monthly estimates of wet and dry N deposition data were collected at the Gårdsjön F1 catchment. These data were entered into the model as deposition time series. Daily deposition estimates were obtained by multiplying the daily depth of precipitation by the monthly deposition concentration. The mass of NH_4NO_3 added to the catchment in each experimental spraying was input to the INCA-N model as a fertiliser time series.

Soil moisture deficits (SMD) and hydrologically effective rainfall (HER) were estimated using the HBV rainfall–runoff model (Sælthun 1996). This was done using temperature and precipitation from the Gårdsjön meteorological site and observed outflow from the G2 weir. An iterative Monte Carlo calibration procedure (Futter *et al.* 2007) was used to calibrate HBV to observed flows. The calibrations were performed to maximise the Nash–Sutcliffe (NS) statistics for both untransformed and log-transformed modelled and observed flow. The best-performing parameter set was then used to generate time series of SMD and HER. After performing in excess of 100,000 HBV model runs, it was not possible to obtain untransformed and log-transformed NS statistics greater than 0.29 and 0.26.

Daily time series of observed temperature, stream flow and $[NO_3^-]$, as well as modelled HER and SMD, were used to drive INCA-N. The HER is an estimate of the precipitation falling on the catchment that contributes to runoff. The SMD estimates were used to simulate the effects of soil moisture on process rates. The hydrological sub-model in INCA-N was calibrated to fit observed to modelled flows. Parameter sets with a Pearson product moment correlation coefficient $(r^2) \geq 0.25$ between modelled and observed flow were considered acceptable. It was not possible to obtain correlations greater than 0.3 between modelled and observed flows.Possible reasons for this are discussed later. High flows were underestimated and low flows were simulated during periods at which no flow was observed.

The biogeochemical component of INCA-N was calibrated to simulate the in-stream $[NO_3^-]$ before and after the start of the experiment. Correlations ≥ 0.6 between modelled and observed $[NO_3^-]$ were considered acceptable. The median, maximum and minimum predicted daily $[NO_3^-]$ from this ensemble of parameter sets is shown in Figure 2. The model successfully simulated a change in the seasonal pattern of surface water $[NO_3^-]$ (Figures 2 and 3) and the observed increase in shallow (5–10 cm) soil water $[NO_3^-]$ (Figure 4). The model was unable to duplicate the observed pattern in deeper (>10 cm) soil water $[NO_3^-]$. Modelled values were generally higher than those observed (Figure 5).

Sensitivity analysis was used to aid in model calibration and to determine which processes may have been responsible for the observed N dynamics. Sensitivity analyses conducted for model calibration were performed using a Monte Carlo approach similar to that described by Futter *et al.* (2007). Parameter values were set at default values

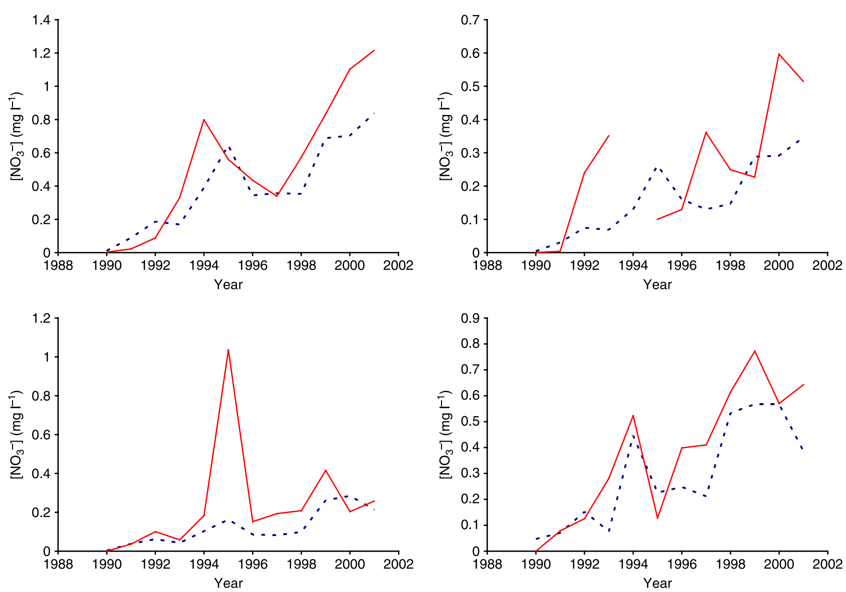

Figure 3 | Modelled (dashed) and observed (solid) seasonal volume weighted NO_3^- concentrations for spring (March–May, upper left), summer (June–August, upper right), autumn (September–November, lower left) and winter (December–February, lower right) in the G2 stream.

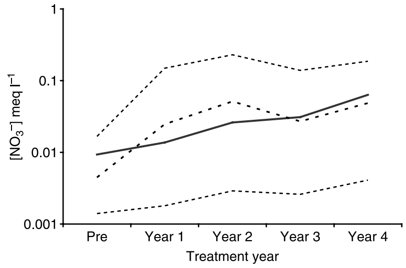

Figure 4 | Plot of annual average INCA-N simulated (solid) and observed (dashed) $[NO_3^-]$ concentrations from the upper soil layer. The INCA simulations are volume weighted $[NO_3^-]$ from the upper soil box. The dashed lines represent the minimum, maximum and average soil water $[NO_3^-]$ reported by Stuanes & Kjønaas (1998) from the G2 catchment for depths less than or equal to 10 cm.

suggested by Wade *et al.* (2002). A sensitivity analysis was run in which parameters were allowed to vary between 75 and 125% of their default values. Sensitive parameters were identified by comparing the cumulative distributions (cdf) of parameters from models within the best 1% of Pearson produce-moment correlations between observed and modelled $[NO_3^-]$ to the other 99% of model runs. Sensitivity was assessed using the Kolmogorov–Smirnov (KS) statistic. In the event that a statistically significant KS statistic was obtained, parameter ranges were adjusted and the process repeated until it was no longer possible to obtain significant differences between the parameter cdfs of the top performing 1% and the remainder of model runs.

The final sensitivity analysis was performed to identify parameters that might represent processes which were important in controlling the observed N dynamics. This analysis was performed by taking the parameter set which had provided the best fit between modelled and observed

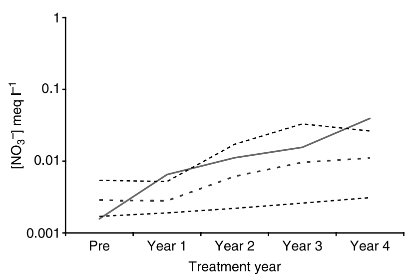

Figure 5 | Plot of annual average INCA-N simulated (solid) and observed (dashed) $[NO_3^-]$ concentrations from the lower soil layer. The INCA simulations are volume weighted $[NO_3^-]$ from the lower soil box, which is assumed to represent groundwater. The dashed lines represent the minimum, maximum and average soil water $[NO_3^-]$ reported by Stuanes & Kjønaas (1998) from the G2 catchment for depths greater than 10 cm.

$[NO_3^-]$ and allowing the biogeochemical parameters to vary between 75 and 125% of their initial values. It was not possible to obtain credible simulations of either flow or NO_3^- unless the stream velocity parameters and soil water residence times were correctly specified. Failure to constrain these parameters within an acceptable range led to unrealistic simulated $[NO_3^-]$. The only biogeochemical parameters to have significant KS statistics when adjustments were made for multiple comparisons were the base flow index, which is a measure of the relative contribution of groundwater to stream flow; the maximum N uptake rate (U) and the date on which plant growth started.

Calibrated parameter values were consistent with those reported by Andersson *et al.* (1998). The modelled growing season length of 229 d is within the range of 210–240 d they reported. The simulated growing season starts on day 77 (March 17), which is approximately one month earlier than that reported by Andersson *et al.* (1998). The maximum N uptake of 46 kg N ha^{-1} yr^{-1} is less than half the vegetation uptake of 0.899 mol m^{-2} (126 kg N ha^{-1} yr^{-1}) reported by Kjønaas & Wright (1998) for the G2 catchment in 1990 prior to the start of fertilisation.

The calibration process generated an ensemble of INCA-N parameter sets able to simulate seasonal stream water $[NO_3^-]$ dynamics before the start of fertilisation and during the experiment (Figure 2). The ensemble of INCA-N parameter sets produce modelled stream water $[NO_3^-]$ time series which match the dynamics of the observed data. The model predicts higher peak $[NO_3^-]$ in 1993–1994 than in 1995–1997. The model is also able to capture the peak values observed in 1999–2001. Summer $[NO_3^-]$ in 1993 and 1999 is over-predicted. With very few exceptions (notably the $[NO_3^-]$ value of 3.31 mg l^{-1} observed on 19 September 1995), the range of $[NO_3^-]$ values predicted by the ensemble of behavioural parameter sets encompasses observed concentrations in the stream.

The INCA-N model does a reasonable job of capturing the seasonal trends in $[NO_3^-]$ (Figure 3). The observed and modelled volume weighted spring (March–May, $r^2 = 0.89$) and winter (December–February, $r^2 = 0.92$) $[NO_3^-]$ are coherent. The poor fit for autumn values (September–December, $r^2 = 0.47$) is driven largely by the 3.31 mg/l NO_3^- recorded on 19 September 1995. Despite the poor correlation between modelled and observed volume weighted $[NO_3^-]$, which is largely the result of a poor fit between modelled and observed flows, the model still reproduces some of the inter-annual dynamics in autumn values. The model is unable to capture all the inter-annual variability in summer (June–August, $r^2 = 0.60$) $[NO_3^-]$ but does duplicate the long-term increase.

Stuanes & Kjønaas (1998) report soil solution N concentrations from the three Gårdsjön catchments. They state that the upper 10 cm of catchment soils consisted mainly of a mor layer. Lysimeters were placed at depths of between 5 and 70 cm (Stuanes & Kjønaas 1998). To facilitate comparison of their results with the model simulations presented here, it is assumed that data from lysimeters placed at depths of 5–10 cm corresponds to the INCA-N soil water box and that the lysimeters placed below 10 cm are sampling an environment below the rooting zone which corresponds to the INCA-N groundwater box. The simulated soil-water $[NO_3^-]$ in the upper soil box is corroborated by measured data from lysimeters placed at depths between 5 and 10 cm (Figure 4). The INCA-N simulations suggest that the groundwater box, which represents soil below the rooting zone, displays a gradual increase in $[NO_3^-]$.

The modelled pattern of $[NO_3^-]$ in the stream water was driven by a seasonal pattern of vegetative N uptake and inter-annual differences in modelled nitrification rates superposed on a long-term increase in soil and groundwater $[NO_3^-]$ (Figures 4 and 5). The INCA-N simulated annual average surface water concentrations are close to the average observed $[NO_3^-]$ between depths of 5 and 10 cm (Figure 4). However, the INCA-N simulated annual average ground water $[NO_3^-]$ (Figure 5) is generally higher than the maxima observed by Stuanes & Kjønaas (1998) from lysimeters placed at depths greater than 10 cm.

DISCUSSION

By 2001, runoff leaching of NO_3^- was between 5–10% of total N input, i.e. 90–95% retention. Therefore the catchment is still capable of retaining lots of N. At some sites in Europe, NO_3^- is now the most important anion in runoff. Increased nitrogen leaching may lead to re-acidification and has consequences for coastal and estuarine eutrophication.

In a regional survey of factors influencing N leaching from forests, Rothwell *et al.* (2008) showed that sites with historically high levels of N deposition did not leach inorganic N if current levels of deposition were low (< 3 kg N ha^{-1} yr^{-1}). Similarly, Oulehle *et al.* (2006) have shown that inorganic N leaching declines as atmospheric deposition is reduced. The INCA-N model application presented here is able to simulate the effects of declining N deposition on inorganic N leaching. Simulated temperature, precipitation, stream flow and atmospheric N time series were created by adding the observed data to the end of the period of record. This doubled the length of record by using the observed hydro-meteorological time series twice. The soil nitrogen concentrations at the end of the calibration period were used to set the initial N conditions and the model was re-run using the best performing parameter set. Without the added experimental N inputs, it took approximately one year for stream water $[NO_3^-]$ to return to pre-fertilisation concentrations. While this is an admittedly simplistic evaluation of recovery potential, it does corroborate observations at other sites and suggests that INCA-N may have a role to play in assessing changes in N leaching under different deposition scenarios.

There is a strong seasonal pattern in runoff $[NO_3^-]$: low in summer, high in winter. However, in later years there is some NO_3^- present in runoff at practically all times. This suggests a change in catchment N dynamics and some form of breakthrough (Stoddard 1994). Prior to the start of the experiment, the catchment could be described by Stoddard's (1994) stage 0 of N saturation. There was a seasonal pattern in $[NO_3^-]$, with concentrations below detectable levels during the growing season and winter/spring concentrations of about 0.2 mg l^{-1} N. By 2001, the catchment had moved to Stoddard's (1994) stage 1 of N saturation. There was still a strong seasonal pattern but detectable levels of NO_3^- were observed throughout the growing season and winter peak concentrations exceeded 1 mg l^{-1}.

The changes are gradual: different parts of the system react at different rates and some are easier to monitor than others. After 12 years, there are changes in N concentrations in almost all parts of the catchment (Moldan *et al.* 2006). Detectable levels of NO_3^- in runoff during the growing season are indicative of N leaching. In the early part of the record, NO_3^- is not detected during the summer, suggesting that all inorganic N is being taken up by growing vegetation and biological activity in the soil. Some NO_3^- is present in runoff at almost all times in the latter part of the record. However, the INCA-N simulation reaches this condition much more quickly than occurs in reality. This suggests that there is an excess of inorganic N in the catchment in the early stages of the experiment above and beyond what can be used by vegetation and the soil biota. While it is not possible to unambiguously identify the source of N in the stream in the INCA-N simulations, it appears that the N being leached is a mixture of new N from precipitation which does not interact with the soil or vegetation during simulations (Kjønaas & Wright 2007) as well as "old" N (Moldan *et al.* 2006). It is also possible that N in the stream is "hydrological" N which has bypassed soil and vegetation sinks and entered the stream via macropore flow.

The results presented here are different from those of Whitehead *et al.* (2002). In their application of INCA-N to a forested catchment receiving excess N deposition in the southern UK, they found that N dynamics could be simulated by increasing the mineralisation rate which increased the simulated rate of nitrification. In the simulations presented here, N dynamics and the pattern of N leaching could be explained as a function of uptake by vegetation and inter-annual differences in nitrification. The simulated between-year differences in N dynamics presented here were the result of meteorological variability influencing rates of vegetation uptake and nitrification in the soil. The fact that different combinations of processes were able to explain N leaching in the application presented here rather than those of Whitehead *et al.* (2002) shows that INCA-N, like all complex process-based models, is underdetermined. The information available in the hydrochemical time series used for model calibration is not sufficient to identify a single best-performing parameter set. This has been noted previously by Wade *et al.* (2006) who showed that credible reproduction of in-stream N dynamics in INCA-N could be obtained by adjusting either in-soil or in-stream parameters.

The catchment appears to have a short-term capacity to take up N surplus to immediate requirements. Soil fungi may be able to sustain a "luxury" uptake for one to two years during which they take up inorganic nitrogen surplus to their current requirements (i.e. Ågren & Bosatta 1996, p 92). However, Brandrud & Timmermann (1998) did not observe any clear patterns in change in fungal biomass at Gårdsjön between 1990 and 1995.

Modelled potential N uptake by vegetation is much less than that observed prior to the start of experimental N addition (48 kg ha^{-1} yr^{-1} modelled vs. 126 kg ha^{-1} yr^{-1} observed). However, it is much higher than net N uptake by vegetation. Kjønaas & Wright (1998) noted that just over 2% of the N uptake by vegetation was retained and close to 98% was deposited during litterfall. Kjønaas & Wright (1998) ascribed much of the N uptake in their MERLIN simulations of the Gårdsjön G2 catchment to N incorporation into labile and refractory organic matter pools. This suggests that the vegetation dynamics in INCA-N actually represents the N uptake behaviour of plants and the soil fauna in forested catchments.

Modelled soil water $[NO_3^-]$ dynamics display a similar pattern to those observed by Vestgarden *et al.* (2001). After the start of fertiliser addition, they observed earlier changes in NO_3^- dynamics in the O and E soil horizons than were seen in the B horizon. This was consistent with the earlier modelled increase in the upper soil horizon in the INCA-N simulations.

The hydrological modelling approach presented here may not be optimal for small research catchments such as Gårdsjön G2. The generally poor fits between modelled and observed flows cannot be explained by the quality of the available data. The quality control checks on the hydrological data include inter-comparisons between the G1, G2 and F1 catchments. Chloride mass balances are calculated and inputs match outputs to within a few per cent. The close proximity of the meteorological site to the catchment suggests that the measured rainfall should be representative of that falling on the catchment. It is more likely that the HBV rainfall–runoff model does not accurately represent the stream flow generation processes operating in very small headwater catchments. While HBV is extremely successful for simulating flows in catchments with areas greater than about 100 ha, the conceptual model of flow generation may not represent the actual processes operating in catchments smaller than about 10 ha. HBV represents flow generation when a conceptual "bucket" fills and spills. In smaller catchments, this may not hold and runoff may be generated through either preferential flow paths or riparian contributing areas. There may be issues of temporal resolution. HBV operates on a daily time step. It will not successfully simulate runoff generation processes operating on a sub-daily time step.

The relatively poor fit between modelled and observed hydrology has implications for flux estimation. Fluxes during peak flows will tend to be under-estimated and the model will produce flux estimates with low flows during times when the stream is not flowing. Difficulties simulating low flows may have implications for process understanding. The INCA-N simulated NO_3^- is assumed to come from the deep soil solution or groundwater. It is possible that water from the lower soil horizon of the catchment leaches to the stream during periods of low or no flow. It is also possible that low flows are generated from soil water in the riparian zone. The semi-distributed nature of INCA-N means that it cannot easily be used to simulate catchment processes occurring exclusively in the riparian zone. Conceptually, INCA-N simulates the processes that are believed to occur below the rooting zone. However, modelled $[NO_3^-]$ in the INCA-N groundwater box is considerably higher than observed mean concentrations in the groundwater (Figure 5). This implies that the INCA-N groundwater pool is not the same as the real groundwater or lower soil horizon water but may in fact represent some other N store in the catchment.

It is clear that INCA-N does not simulate all processes occurring at Gårdsjön during the NITREX experiment. The lag between the start of fertilisation and the appearance of elevated $[NO_3^-]$ in soil and stream water is not captured by INCA-N. While the model does miss some aspects of the timing, the overall patterns in stream and soil water $[NO_3^-]$ are reproduced.

Given the dependence of model performance on vegetation-related processes, it seems reasonable to assume that better fits could have been obtained had climate-related parameters, such as growing season start and length, been allowed to vary between years. The model was sensitive to values of the parameter representing growing season start day, suggesting that timing of plant growth is an important control on N uptake.

The size of the soil carbon pool in the forest floor at Gårdsjön is increasing (Moldan *et al.* 2006). This is consistent with the findings from N additions at hardwood forests where large changes in soil C storage have been observed (Pregitzer *et al.* 2004). The forest floor C/N ratio has not changed during the experimental addition (Moldan *et al.* 2006), suggesting that much of the added N has been immobilised in the soil. The INCA-N simulations indicate that most of the added N has gone into the modelled vegetation pool. This almost certainly misrepresents the true situation in the catchment. The conceptual pool representing vegetation in INCA-N should probably be conceptualised as a pool representing both vegetation and the soil biota. Kjønaas *et al.* (1998) state that about 30% of the added dissolved inorganic nitrogen is taken up by the vegetation at Gårdsjön but that N assimilation by the soil pool is probably more important.

Unlike other models of catchment-scale N biogeochemistry, INCA-N does not use information about soil C stocks when simulating N dynamics. Soil C/N ratios are not always a good predictor of soil N leaching (Rothwell *et al.* 2008). Other factors including N deposition, climate and soil type are more important controls on N leaching in some situations. Changes in rates of N transformation are more dependent on soil temperature and moisture than the relative size of soil C and N pools (Bengtson *et al.* 2005). Catchment vegetation is also important. Nitrogen dynamics in hardwood-dominated catchments, such as those studied by Pregitzer *et al.* (2004), may be different than those dominated by coniferous vegetation.

Future modelling efforts should focus on improved representations of soil and vegetation N uptake and on linking catchment-scale C and N dynamics. A future version of INCA-N should separate uptake by soil biota from vegetation processes and should also account for nutrient returns to the soil system through litter inputs and enhanced N inputs through interception. A linked catchment-scale model of C and N dynamics might be developed by combining the organic carbon processes represented in INCA-C (Futter *et al.* 2007) with the inorganic N processes in INCA-N. Adding new processes to represent organic N dynamics to these two models would be a useful exercise that could lead to improved understanding of both C and N dynamics in forested catchments subject to excess inorganic N deposition.

Like the MERLIN simulations presented by Kjønaas & Wright (1998), the results presented here show that a process-based model can simulate some of the N dynamics observed in a forested catchment during experimental fertilisation. Like Kjønaas & Wright (1998), these results are consistent with increasing [NO_3^-] below the rooting zone and subsequent leaching. While models such as MAGIC or MERLIN show promise for long-term projections of future change, INCA-N can aid in understanding climate change effects on N leaching as it is driven by daily meteorology and hydrology.

It has been shown that the INCA-N model of catchment N-dynamics is able to successfully simulate soil and surface water NO_3^- dynamics ($r^2 > 0.6$) both before and during experimental inorganic N fertilisation at a small forested catchment. The fact that INCA-N was able to successfully simulate the behaviour of inorganic nitrogen in both the soil and stream water before and during experimental manipulations suggests that the simple conceptual representation of N dynamics embedded in the model may be able to provide credible annual to decadal scale projections of N dynamics under changing N deposition scenarios. Future work will assess the interactions between changing climate, deposition and leaching of both organic and inorganic N from forested catchments.

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