Modelling the effects of changing climate and nitrogen deposition on nitrate dynamics in a Scottish mountain catchment

M. N. Futter, R. C. Helliwell, M. Hutchins and J. Aherne

ABSTRACT

The effect of changing climate and N deposition on montane ecosystems is a topic of considerable importance. Mountains are vulnerable environments and their ecosystems are often in a delicate balance. An application of the INCA-N model is presented to simulate current-day nitrate dynamics in a Scottish mountain lake and to project the possible future effects of climate change and reductions in N deposition on lake nitrate concentration ($[NO_3^-]$). The INCA-N model is calibrated using data from 1996–2006 in an attempt to determine the controls on $[NO_3^-]$ in Lochnagar and process sensitivities to changing climate. Predictions were sensitive to hydrologic, vegetation-related and in-soil processes. Over the longer term, surface water $[NO_3^-]$ in this mountain ecosystem is expected to increase. From 2020 to 2100, when N deposition is modelled at a constant rate, warmer temperature exerts a stronger effect on N losses to the lake surface than the N deposition. While the effects of a warming climate are projected to lead to increased surface water $[NO_3^-]$, concentrations are not projected to either return to, or exceed, historical levels.

Key words | climate change, Lochnagar, modeling, mountain lakes, nitrate, water quality

M. N. Futter (corresponding author)
R. C. Helliwell
Macaulay Institute, Craigiebuckler,
Aberdeen AB15 8QH,
UK
Tel.: +44 1224 395 148
Fax: +44 1224 311 556
E-mail: *m.futter@macaulay.ac.uk*

M. Hutchins
Centre for Ecology and Hydrology,
Wallingford, Oxon OX10 8BB,
UK

J. Aherne
Environmental and Resource Studies,
Trent University, Peterborough,
Ontario K9J 7B8,
Canada

INTRODUCTION

Both nitrogen (N) deposition and climate change can affect retention and loss of N from mountain catchments to surface waters. The last few decades have seen an exponential increase in the atmospheric concentration of reactive N (Galloway *et al.* 2008). This has led to concerns from scientists, land managers and politicians regarding a cascade of ecosystem impacts, and the potential for elevated atmospheric inputs to significantly alter nutrient-poor systems throughout North America, and increasingly in Asia (Galloway *et al.* 2008). At particular risk are fragile mountain ecosystems, which are extremely sensitive to environmental change and respond rapidly to perturbations in deposition and climate (Helliwell *et al.* 2009). The ability of mountain ecosystems to retain or immobilize N depends, in part, on past and future nutrient supplies from deposition (Fowler *et al.* 2007) and catchment characteristics (Helliwell *et al.* 2007) including soil type (Tipping *et al.* 2008). Soil N dynamics can also be altered by climate change and carbon enrichment. Atmospheric N deposition may interact with these global change factors over the coming century (Matson *et al.* 2002) to the detriment of montane biodiversity.

In montane environments the N accumulation capacity in soils is limited as soils are generally thin and poorly developed, and the vegetation is subject to much stronger climatic limitations than that at lower altitude, including a short growing season, high wind speeds and exposure to low winter temperatures (Britton & Fisher 2008). It is of prime importance to understand how long upland ecosystems will be able to retain N (Aber *et al.* 1998). The concentration of N, particularly as nitrate ($[NO_3^-]$), in upland lakes, streams and rivers is diagnostic of the

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vulnerability of upland ecosystems to increased atmospheric N deposition and saturation. Increasing N deposition may be a confounding factor in catchment recovery from the effects of anthropogenic acidification (Curtis *et al.* 2005). N enrichment of upland soils and plant biomass has been observed (Kristensen *et al.* 2004). Little is known about how sustainable this N accumulation may be in the long term. If the capacity of an ecosystem to assimilate extra N (through plant and microbial nutritional demand) is exceeded, the system will eventually become N saturated and leaching to surface waters will commence (Aber *et al.* 1998). Over recent years studies of N dynamics in semi-natural ecosystems have received considerable scientific attention; however, it is not yet possible to quantitatively assess the combined implications of N deposition and climate-induced processes in high altitude mountain ecosystems in the longer term.

Given that many of the key processes active in terrestrial ecosystems such as the release of N and C from soil organic matter by mineralization are temperature- and moisture-dependent, climate-induced changes in N retention and loss from semi-natural ecosystems may be expected (Kaste *et al.* 2004). A warmer climate can potentially enhance both acidification and eutrophication by increasing the release of N from soil organic matter to runoff (Wright & Schindler 1995). A review of the response of soil processes considering warmer global conditions was conducted by Rustad *et al.* (2001) with the findings that soil respiration, N mineralization and plant productivity will increase and that soils can both attenuate and buffer the effects of climatic change.

At present the climate in the eastern Cairngorm Mountains is characterized by long (5 months) cold winters with intermittent snow cover and ice cover over small lakes (Thompson *et al.* 2007). Snowmelt-induced spring floods usually dominate the annual hydrological pattern and can sustain base flow into the summer months, whereas less pronounced flow peaks often occur in autumn due to rainfall events. In this area, a major fraction of the annual NO_3^- loss occurs during these high flow periods. These temporal patterns may change considerably in the future, given the projections of a warmer and generally wetter climate in northern Europe. Of specific relevance to the Cairngorm Mountains is the projected reduction in the duration and extent of the snow pack in the future (UKCIP08, available at: http://www.ukcip.org.uk/index.php). There have been no climate change experiments in the Cairngorm Mountain region. However, the importance of snow cover in relation to N leaching has been investigated at a small manipulated headwater catchment in southern Norway (Kaste *et al.* 2008). They found that warmer soils during winter imply a greater risk for inorganic N leaching compared to the possible risk of increased soil frost events due to reduced snow cover. Given this evidence, research into the effects of climate and deposition change on water quality in mountain ecosystems in the UK is essential.

The results of a modelling exercise to simulate current hydrology and N dynamics in a montane catchment and to project the possible effects of changing climate and N deposition on future hydro-climatology and water chemistry are presented here. The main processes responsible for the long term release of NO_3^- to surface waters have been identified using output from a hydrological model (HBV) as an input to INCA-N (the *In*tegrated *Ca*tchments Model for Nitrogen); a process-based, catchment-scale model of N dynamics in soils and surface waters. Future impacts of deposition and climate change on $[NO_3^-]$ at Lochnagar are simulated under two N deposition scenarios: the Current Legislation Emissions (CLE) and the Maximum Feasible Reductions (MFR) scenario. Climate projections were based on the SRES A2 scenario which was statistically downscaled for the period 1961–2099, as described below.

STUDY SITE AND DATA SOURCES

The Lochnagar catchment (NO 252 859) has been monitored for 18 years as part of the UK Acid Waters Monitoring Network (UKAWMN; Monteith & Evans 2005; Rose 2007*b*). The catchment is located in NE Scotland on the eastern edge of the Cairngorm Mountains (Figure 1). It has an area of 102 ha with an altitudinal range of 790–1,150 m, most of which is covered by montane vegetation. A particularly prominent feature of this catchment is a steep north-facing corrie that comprises about 30% of the catchment area. Geologically the catchment is composed of biotite granite. The soils are derived from the

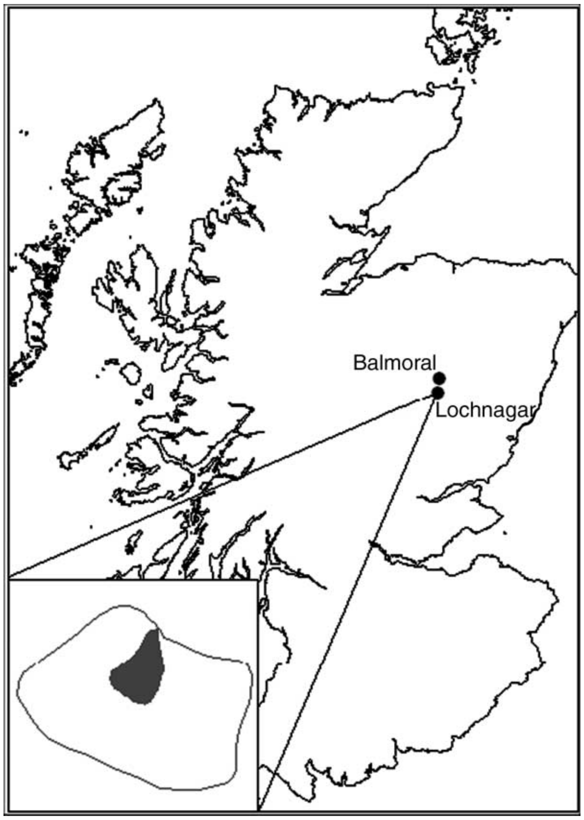

Figure 1 | Map of Scotland with location of Lochnagar. The inset map shows the location of the lake within the catchment.

Countesswells Association and range from poorly developed alpine podsols on the steeper slopes (33% of catchment area) to deep peats at lower altitudes surrounding the lake (5%). Rock and lithosols (32%) and shallow peat (20%) comprise the other dominant soil types. The lake has an area of about 10 ha (10% of the total catchment area) and has no identifiable input streams. The magnitude of acid deposition at Lochnagar is minor relative to other areas of the UK with average (2003–2005) N deposition inputs of 19 kg ha^{-1} yr^{-1} (Air Pollution Information Systems, available at: http://www.apis.ac.uk/index.html).

Concentrations of inorganic N in wet and dry deposition were obtained from the UKAWMN precipitation collector (operated by University College London) at Lochnagar. These data have been collected on a monthly basis since 1996. Chemical analyses were performed by the Fisheries Research Services (FRS) Laboratories at Pitlochry. Additional deposition time series were available from Glen Dye (UK Grid Reference NO 627 838) for 1987–2005.

Meteorological data are available from Balmoral (NO 254 950) and Lochnagar (Figure 1). The Balmoral site, located in the grounds of Balmoral Castle, has been in continuous operation since 1918. The Lochnagar site has been fully operational since 1996. The Review Group on Acid Rain (RGAR) began monitoring rainfall at the site in November 1977. Balmoral is at a much lower elevation (283 m.a.s.l.) than Lochnagar (790 m.a.s.l.), but a continuous data record is available. The Lochnagar site is probably more representative of conditions in the catchment but the data record has many gaps, especially in the winter months. There has been evidence in recent years of less snow cover in the Lochnagar catchment (Rose 2007*a*).

Surface water chemistry was sampled as part of the UKAWMN from 1988 through 2008. From 1988 to 1996, samples were collected quarterly. After that, they were collected fortnightly (Jenkins *et al.* 2007). For the purpose of this study, the period from October 1996 to October 2006 has been analyzed.

The Lochnagar outflow is an unconstrained natural channel. Stage height in the outflow is recorded continuously by a data logger; stages are transformed to flows using a rating curve generated by the salt dilution method (Jenkins *et al.* 2007). There are a number of issues with the discharge measurements at Lochnagar. Anecdotal evidence suggests that stage height can be affected by the direction of prevailing wind (personal communnication from Jo Porter). When the wind is blowing down the lake, water builds up near the outflow. When wind is blowing the other way, flow reversals have been observed where water moves into the lake from downstream of the outflow. During the winter, channel geometry is altered by ice build up in the outflow.

MODEL DESCRIPTION

Rainfall–runoff modelling

The HBV rainfall–runoff model is a lumped, conceptual catchment-scale model of runoff generation. The model uses descriptors of catchment topography, vegetation and land cover with daily time series of precipitation and air temperature to simulate catchment hydrological processes by calibrating to observed daily stream flows. Model fit was assessed with Nash–Sutcliffe (NS) statistics comparing both untransformed and log-transformed streamflow. This was done to ensure the model fit over the periods of high and low flow. The model was developed in Sweden (Bergström 1992) and has been used extensively in the Nordic countries for rainfall–runoff and flood modelling (Sælthun 1996). Subroutines of the HBV model simulate snow dynamics including accumulation, sublimation and altitude-dependent melting. By using climate data from one site to calibrate streamflow at another, HBV has been used to simulate temperature, precipitation and snow cover at sites where meteorological data are unavailable. This works best when high-quality stream flow data are available at the site of interest. The HBV model can also be used to estimate soil moisture deficits (SMD) and the components of a water balance, including hydrologically effective rainfall (HER), or the fraction of precipitation falling on a catchment that contributes to runoff.

Nitrogen deposition modelling

Inorganic N deposition fluxes were estimated using UKAWMN deposition concentration data from Lochnagar and the HBV-estimated precipitation depths. Rainfall obervations from Balmoral were utilized as a more reliable data time series than the Lochnagar raingauge, as the Balmoral data is available over a much longer time period and had fewer gaps in the record compared to the Lochnagar data. The Balmoral rainfall was adjusted for altitude using the HBV model to ensure a mass balance with the flow data for Lochnagar.

Daily time series of N deposition data for use in INCA-N modelling were created in the following manner. N deposition data was adjusted for snowmelt and timing of precipitation to create daily time series of N input to the catchment. It was assumed that all N falling in snow remained in the snow pack, and that N inputs during snowmelt were proportional to the amount of N in the snow pack. No attempt was made to simulate preferential elution of N during early stages of snowmelt. Modelled N deposition included both wet and dry components. It was assumed that accumulated dry deposition entered the lake and soil during precipitation events.

INCA-N modelling

INCA-N, the *In*tegrated *Ca*tchments Model for Nitrogen, is a catchment-scale, process-based dynamic model of N dynamics in terrestrial and freshwater aquatic environments (Whitehead *et al.* 1998; Wade *et al.* 2002). The model simulates catchment and lake inorganic N dynamics. While the model has been applied numerous times to rivers and catchments containing lakes, this is the first application of INCA-N specifically to a lake and its surrounding catchment. The model operates on a daily time step and can be used to model temperature and soil wetness to investigate climate effects. INCA-N simulates a number of N-transformation processes in the soil including nitrification, denitrification, mineralization and immobilization. Vegetation-related processes have been described in more detail in Futter *et al.* (2009). All in-soil process rates are soil temperature- and moisture-dependent. The model simulates nitrification and denitrification in surface waters.

INCA-N was calibrated using UKAWMN data from 1996–2006 in an attempt to determine the controls on [NO_3^-] in Lochnagar and sensitivities of in-catchment N processes to changing climate. The catchment was modelled as a single reach containing three land-cover classes representing bare rock, peat and podsols and rankers. The bare rock part of the catchment simulated hydrologic N; all modelled N processes were turned off for this land cover class during simulations. Vegetation-related and in-soil processes were simulated for both the peat and podsol land cover types. Model fit was assessed using Pearson product moment correlation coefficients (r^2) comparing observed to modelled time series of flow, [NO_3^-] and [NH_4^+]. Parameter sets were further constrained to ensure that modelled lake volume was within ±10% of the observed lake volume.

Sensitivity analysis

A sensitivity analysis was performed to assess the effect of varying parameter values on model goodness of fit. Parameters were allowed to vary between 85 and 115% of their values from the best performing model calibration ($r^2 = 0.86$, $NS = 0.65$ for [NO_3^-]). The parameter space was sampled 10,000 times and INCA-N was run with each parameter set. Model fit was assessed using the r^2 statistic comparing modelled to observed time series. Cumulative distribution functions (cdfs) of parameters from the best performing 2% of model runs were compared to cdfs of the remaining model runs. Parameter sensitivity was defined as the difference in cdf between the top performing 2% of model runs and the remaining 98%. The statistical significance of this difference was assessed using a Kolmogorov–Smirnov (KS) statistic for comparing distributions. Significance values of the KS tests were adjusted for multiple comparisons. The top-performing 100 model runs were used to assess the effect of parameter uncertainty on current-day model behaviour. The top-performing 20 model runs were used to provide an assessment of INCA-N parameter uncertainty during model projection.

SCENARIO DATA

Climate projections

Climate projections were obtained using the Statistical DownScaling Model (SDSM) developed by Wilby *et al.* (2002) to statistically downscale outputs from the Hadley Centre Global Circulation Model (GCM) version HadCM3 model using the climate change A2 scenario (Nakicenovic *et al.* 2000). Downscaled data were available for 1961 to 2099. Downscaling is a means of relating regional-scale atmospheric predictors to local weather (Wilby *et al.* 2002). Here, it was used to develop a transfer function relating regional climate estimates from the National Center for Environmental Prediction/National Center for Atmospheric Research (NCEP/NCAR) 50-year reanalysis database (Kistler *et al.* 1999) to observed weather at Balmoral. The NCEP/NCAR reanalysis database is a mixture of observed and modelled data representative of current climate. It is not meant to reproduce the short-term variability in year-to-year climate but has similar statistical properties and long-term trends to those in the observational record.

The SDSM weather generator was used to generate 20 daily time series of temperature and precipitation from the downscaled NCEP reanalysis data for Balmoral. The time series were adjusted from 360 d to calendar years by duplicating every 72nd record (to give a 365 d year). Leap years were simulated by duplicating the 60th record every four years. This was necessary, as INCA-N is set up for years with the same number of days as a calendar year.

In addition, daily output from Regional Climate Models (RCMs), which are available at 0.5 degree resolution of latitude and longitude (http://prudence.dmi.dk), were assessed for comparative purposes by selected outputs from a cell appropriate to Balmoral. The model output used was generated by the regional atmospheric model RCAO (Döscher *et al.* 2002), repeated for two GCMs:

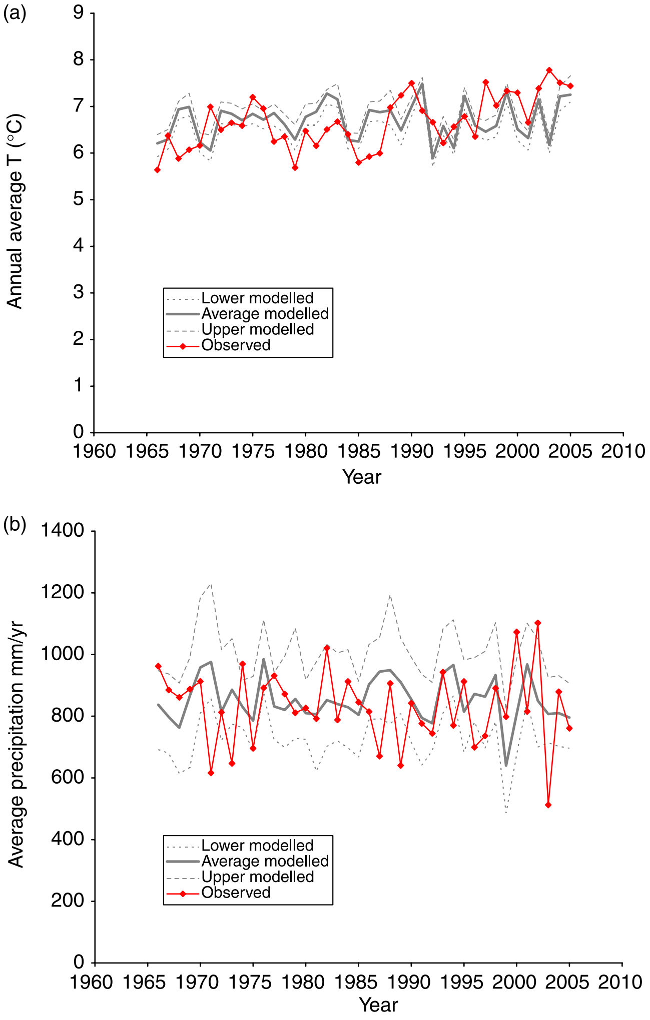

Figure 2 | (a) Observed, minimum, average and maximum NCEP-reanalysis-derived annual average temperatures for Balmoral. (b) Observed, minimum, average and maximum NCEP-reanalysis-derived annual precipitation values for Balmoral.

ECHAM4 (Roeckner *et al.* 1996) and HADAM3 (Pope *et al.* 2000). These outputs represent dynamic downscaling of GCMs (rather than the statistical downscaling techniques of SDSM). A control period (1961–1990) was assessed in conjunction with projected data for 2071–2099 under the SRES A2 scenario. In both cases correspondence with observations during the control period was generally less good than for the SDSM-based data. Compared with SDSM, the projected changes differ, increases in temperature being greater. The RCMs also predict increases in winter rainfall which are not predicted by SDSM.

There was good correspondence between annual measured and downscaled temperature and precipitation at Balmoral (Figure 2(a, b)). Both the instrumental and modelled data show a slight increase in annual average temperatures (Figure 2(a)) and the downscaled precipitation was within the range of observed values (Figure 2(b)).

N deposition

Two future N deposition scenarios were employed: CLE, or Current Legislated Emissions, and MFR, or Maximum Feasible Reductions (Figure 3). As the N deposition scenarios provided values at 5 year intervals, intermediate values were obtained by linear interpolation. Daily N deposition scenarios were created for each instance of the downscaled GCM data. Deposition time series were created by assuming an equal concentration of N species in precipitation within a year. Daily deposition amounts were obtained by multiplying the annual average deposition for 2000 by the annual multiplier from the deposition scenarios and the fraction of annual precipitation falling on that day in the downscaled time series.

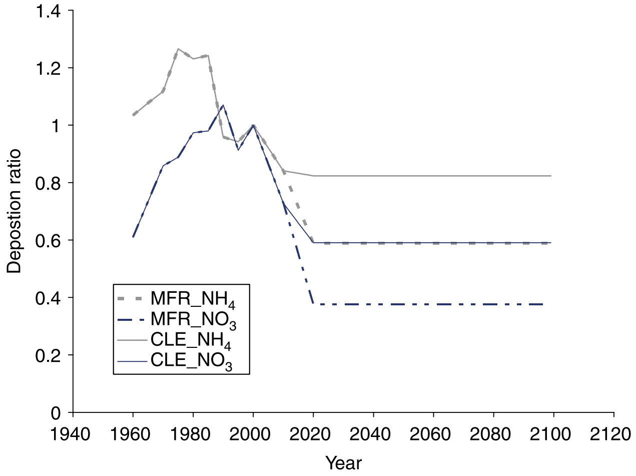

Figure 3 | Modelled N deposition for Lochnagar from the Current Legislated Emissions (CLE) and Maximum Feasible Reductions (MFR) scenarios. Emissions are scaled to a value of 1 in the year 2000.

RESULTS

Hydrological simulation

Stream flow at the Lochnagar outflow was modelled using HBV with observed flows from the Lochnagar outlet and temperature and precipitation data from Balmoral. Calibration was performed for the period April 1999 to December 2003. Stream flow data were not available outside those date ranges. An ensemble of HBV parameter sets was generated, each of which had NS statistics for observed and log-transformed model fits of greater than 0.7 The HBV model calibration was able to capture the seasonal and inter-annual pattern of flow (Figure 4). Observed stream flows were generally within the range of modelled stream flow for any given date.

Modelled present day inorganic nitrogen deposition

Time series of daily deposition of NO_3^- and NH_4^+ for April 1996 through December 2005 were simulated. There was a pronounced seasonal pattern in inorganic N deposition that was driven by the amount of precipitation falling in any given month. The highest deposition values were simulated for April, May and October (average DIN of 1.76, 1.48 and 1.34 kg N/ha/month, respectively). There was no evidence of a long-term trend in deposition over the time period of the simulation.

Modelled present-day $[NO_3^-]$ in Lochnagar

INCA-N was calibrated using UKAWMN data from 1996–2006. An ensemble of behavioural model runs (Figure 5) was generated in which r^2 exceeded 0.5, 0.85 and 0.575 for flow, $[NO_3^-]$ and $[NH_4^+]$, respectively. With some exceptions, the INCA-N calibration was able to capture the seasonal and inter-annual patterns in $[NO_3^-]$ in Lochnagar (Figure 5). There was a relatively narrow range of daily predicted values

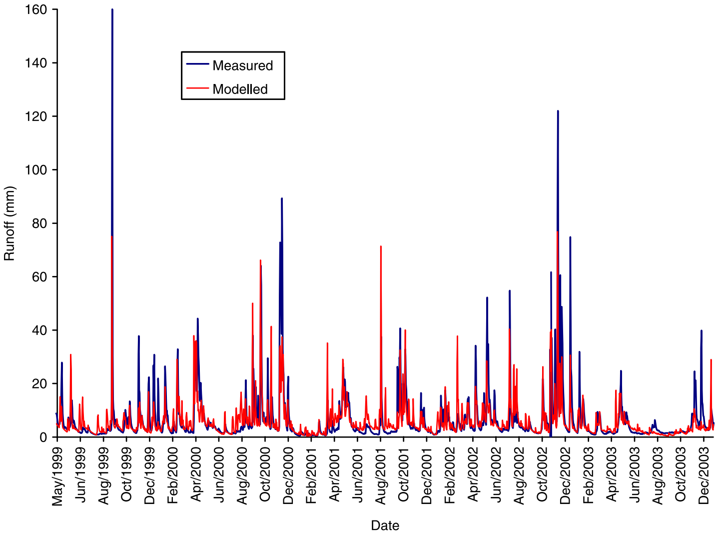

Figure 4 | Observed and HBV-modelled runoff at Lochnagar.

from behavioural parameter sets. There was no clear monotonic trend in either the modelled or observed [NO_3^-] time series between 1996 and 2006. The model under-predicted [NO_3^-] during the first half of 2001 and 2003 and over-predicted for the winter of 2001/2002. Modelled fluxes of NO_3^- through the lake outflow were about half the modelled inorganic N deposition (Table 1). There were only negligible fluxes of NH_4^+ from the lake.

Model predictions were sensitive to parameters related to hydrology, vegetation dynamics and in-soil N processes. Parameters with statistically significant (adjusted $p \leq 0.05$) KS statistics and the associated KS d statistic are shown in Table 2. Virtually all of the sensitive parameters are affected by climate, either directly through changing temperatures or indirectly through the effects of climate change on hydrology. These results suggest that, even if N deposition remains relatively constant at Lochnagar, changing climate may have large and potentially serious effects on the N dynamics in the catchment, especially if these changes lead to increases in the rates of in-soil processes.

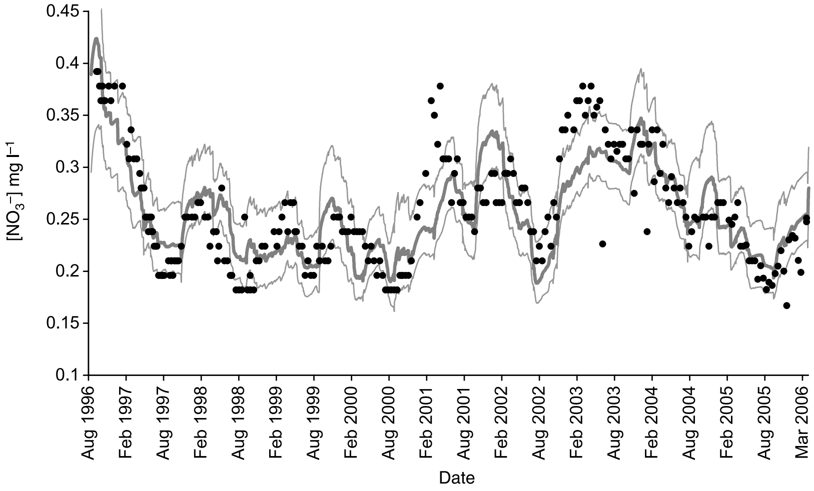

Figure 5 | Observed (dots) and INCA-N modelled [NO_3^-] in Lochnagar. The thick line is the average modelled value from behavioural simulations. Thin lines show the maximum and minimum daily predicted [NO_3^-].

Table 1 | Modelled fluxes of nitrate through the outflow (NO_3^- Out) and deposition onto the catchment of nitrate (NO_3^- In) and ammonium (NH_4^+ In). All figures are in units of kg N ha^{-1} yr^{-1}

Year	NO_3^- Out	NO_3^- In	NH_4^+ In
1997	5.13	5.13	5.15
1998	5.63	5.04	5.34
1999	4.35	5.12	4.55
2000	6.12	6.17	5.18
2001	5.81	7.74	5.85
2002	7.51	7.31	5.29
2003	4.16	5.70	4.70
2004	6.49	6.49	4.34
2005	4.20	4.31	3.67

Future climate at Balmoral

The projected future climate at Balmoral (Figure 6) is warmer and drier under the SRES A2 scenario. There is still considerable variability in year-on-year projected climate. Projected annual average temperatures differ by an average of 0.5°C from year-to-year while there is a year-to-year difference of approximately 120 mm in projected precipitation. Increased rates of warming are projected from 2020 onwards. Precipitation is not projected to change substantially until about 2040, after which large declines are projected.

Table 2 | Sensitive INCA-N model parameters for which the KS *d* statistic was statistically significant (*p*-adjusted ≤ 0.05), ranked in order of increasing sensitivity

Parameter name	*d*
Flow “b”	0.39
Podsol plant growth period	0.36
Podsol plant growth start day	0.31
Flow “a”	0.30
Rock and scree ratio of total to available water in soil	0.29
Podsol mineralization response to a 10° change in temperature	0.27
Base flow index	0.24
Rock and scree NH_4 uptake base temperature response	0.23
Initial groundwater nitrate	0.23
Peat plant growth start day	0.22
Podsol denitrification response to a 10° change in temperature	0.21
In-stream nitrate initial conditions	0.21

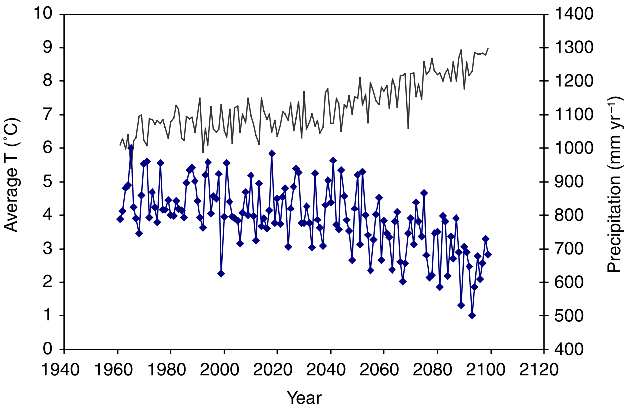

Figure 6 | Annual average temperature (line) and precipitation (dots and line) projected for Balmoral under the SRES A2 scenario.

Projected hydrology at Lochnagar

The projected temperature and precipitation data at Balmoral were used with the best-performing HBV parameter set, obtained during calibration to current conditions, to project future patterns of runoff at Lochnagar (Figure 7). The trend in projected annual runoff is largely driven by projected precipitation changes. Little change is projected in annual runoff until around 2040, after which runoff starts to decline. The large inter-annual variability in projected runoff is driven by the year-on-year variability in projected precipitation. The large within-year variability in runoff is a function of the variability introduced by the weather generator in SDSM.

The projected increase in temperature and decline in precipitation will lead to changes in the snow pack (Figure 8). While there is high year-on-year variability in depth of the snow pack, there is an overall trend towards less snow. As well as a lower average depth of snow, there are projected to be fewer days with snow cover. This has implications for flow generation. Currently, base flows are sustained by snow melt until June or July. Over the next 100 years, it is projected that April and May flows will be substantially reduced as a result of the decreased snow cover.

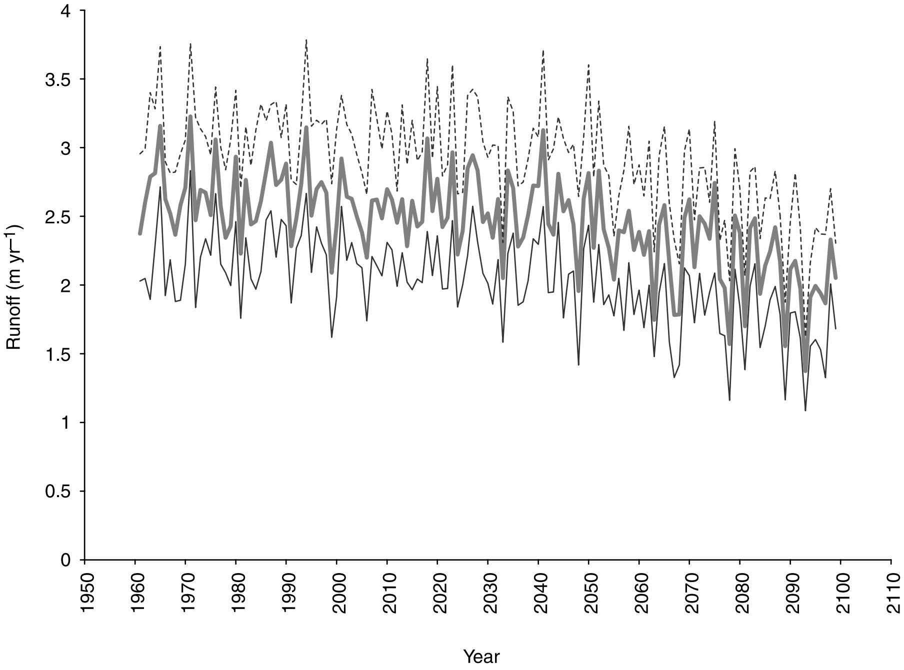

Figure 7 | Annual runoff at Lochnagar simulated using INCA, HBV and GCM data. The thick line is the average and the thin lines are the minimum and maximum projected values.

Projected nitrate concentrations

Concentrations of NO_3^- in the outflow of Lochnagar (Figure 9) were simulated using emission data from the two deposition scenarios and projected hydrological data obtained by running HBV on the downscaled Balmoral climate data. Two ensembles of projections were created. One used a single downscaled climate scenario and the 20 top-performing INCA-N parameter sets obtained during calibration to current conditions. The other used the single best-performing INCA-N parameter set and the 20 climate time series created by the weather generator. There was slightly greater within-year variability in the simulations using the ensemble of time series from the weather generator (not shown) but the results are essentially the same as those from the ensemble of INCA-N parameter sets (Figure 9). Projected [NO_3^-] do not diverge until after 2010 as the two deposition scenarios are identical up to that point. Post-2010, there are larger declines under the MFR than the CLE scenario. From about 2030 onwards, [NO_3^-] increases under both scenarios. This increase in concentration is occurring at a time when projected deposition levels are stable.

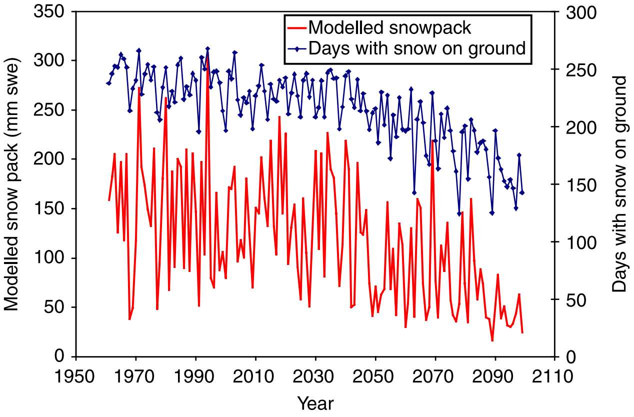

Figure 8 | Modelled days with snow cover and mean depths of snow in the Lochnagar catchment.

DISCUSSION

Flow dynamics have been successfully simulated at Lochnagar using the HBV rainfall–runoff model and data from the Balmoral meteorological site. This implies that the amount of precipitation and the snow pack dynamics in

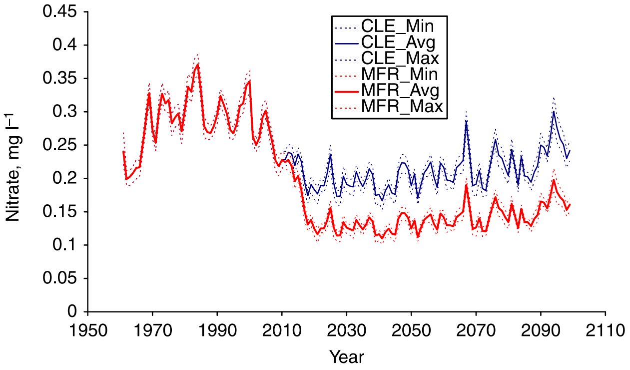

Figure 9 | Projected annual average [NO_3^-] under two deposition scenarios.

Lochnagar have been represented in a credible manner. Therefore instrumental records from lower altitudes can be used to make inferences about climate and weather patterns at higher altitude sites. This is extremely important for modelling montane catchments where limited data are available.

The INCA-N results presented here are consistent with the "best case" scenario presented by Jenkins *et al.* (2001) in their NO_3^- modelling at Lochnagar. In this scenario, they assumed that uptake coefficients remained constant and that deposition reductions were achieved consistent with the Gothenburg protocol.

The model application presented here demonstrates that INCA-N can be applied to lakes and their catchments. The model application is able to capture the overall pattern of NO_3^- dynamics in the lake. The exceptions were in the first half of 2001 and 2003 and in the winter of 2001/2002 where the INCA-N calibrations under- and over-estimated surface water [NO_3^-], respectively. There were a series of periods with extreme weather conditions between 1996 and 2006. The latter half of 2000 was unusually wet, as was the early part of 2003; the winter 2000–2001 was unusually cold and the summer of 2003 was unusually dry. These contrasting years provide an opportunity to evaluate the ability of INCA-N to model catchment scale N-dynamics under extreme weather conditions. The winter of 2000–2001 was unusually cold, with a prolonged and deep (~50 cm) snow pack in the catchment. It is possible that wetter conditions resulted in more rapid flushing of the catchment, with more N being flushed directly from the snow pack to the lake, without having passed through soils in the catchment. This "hydrological" NO_3^- bypasses biological retention mechanisms in the soil/vegetation system via overland flow as a result of saturation, and impermeable areas of rock and frozen soil (plus direct deposition to the lake surface). The high [NO_3^-] in the spring of 2001 may be due in part to a snowmelt-induced N pulse. Refinements to the snowmelt model might have resulted in improved INCA-N simulations for 2001. The results presented here suggest that warmer winters in Scotland will have significant effects with less snow cover, so that preferential elution of N from the snow pack will be a relatively minor process in catchment N dynamics. INCA-N slightly but consistently under-estimates [NO_3^-] during 2003. This was an unusually dry summer. Changes in hydrology may drive peat cracking and, if water bypasses the peat, then solutes will not be retained by the soil and will flush more rapidly into surface waters. These changes in soil hydrology are not represented in INCA-N. In the drier periods of 2003, soil water [N] may have increased in response to drought. Following rewetting, waters with higher [N] may be released to the lake.

Following the rapid simulated decline in surface water NO_3^- in response to the decline in deposition from 2000 to 2020, a slow and gradual increase in NO_3^- is simulated until 2100. This gradual increase in NO_3^- can be attributed to the small increases in temperature that are likely to stimulate soil microbial activity, increasing the turnover rate of both C and N (Nadelhoffer *et al.* 1992). Stimulated biomass production as a result of the projected increases in temperature has the ability to contribute to the organic N pool and, through nitrification processes, lead to enhanced NO_3^- leaching. The extent of N leaching would depend on the degree of N saturation of vegetation and microbial sinks. As discussed previously, experimental evidence suggests that changes in climatic factors will affect N availability and NO_3^- leaching. For example, the results from a soil warming experiment (CLIMEX) in southern Norway where the soil was warmed to 3–5°C above ambient showed a significant increase in [NO_3^-] in runoff (Lükewille & Wright 1997). The catchment was not N-limited and presumably unable to utilize all the additional N produced by the increase in microbial activity. This response is consistent with other results from soil warming studies which have generally shown an increase in

N availability (Mitchell *et al.* 1996; Ineson *et al.* 1998; Jandl *et al.* 2008). However, there are some exceptions where the design of climate change experiments have resulted in drying of the soil and impaired microbial/enzyme activity. The authors acknowledge that such experiments obviously produce a rapid increase in soil temperature compared with global warming where changes occur gradually over decadal time scales, allowing some selection and adaptation in the soil flora and fauna.

Modelled annual average soil temperature increased by close to 2°C between 1961 and 2100. This generated increases in the modelled rate of N mineralization and increased leaching of NO_3^- from the terrestrial parts of the basin.

Nitrogen transformation processes in catchments are temperature- and moisture-dependent, and a few degrees increase in air (and thereby soil) temperature may induce a significant increase in N process rates. Both laboratory experiments and large-scale experiments have suggested that decomposition and N mineralization show a faster response to a temperature increase than the corresponding N retention processes, at least during an initial phase of the warming process (Kirschbaum 1995; van Breemen *et al.* 1998). This may have important implications for N mineralization and subsequent leaching of N to surface waters as climate changes.

The long term trend in NO_3^- presented at Lochnagar illustrates that climate change might accelerate N release mechanisms from the terrestrial system and thus offset the effects expected from the CLE and MFR protocols. To what extent this might happen, however, depends on several uncertain factors. Among these are: (i) the ability of catchment vegetation and microbes to adapt to changing climate and pollution pressures, (ii) the size of the soil N pool available for mineralization and (iii) the amount of additional carbon sequestered due to climate change (and vegetation demands) which alters the soil C and N stocks.

An alternative explanation for the gradual increase in surface water $[NO_3^-]$ after 2020 is the predicted change in snow cover in the catchment. The simulated increased air temperatures at Lochnagar are forecast to result in a significant decrease in snow accumulation (Figure 8). Besides increased winter flow and reduced spring melt flood, a reduction or even absence of snow cover may increase soil frost and also the frequency of freezing–thawing events. Freezing and subsequent thawing of soils often results in an initial flush of microbial respiration and transient N_2O effluxes. Laboratory incubation studies indicate that freeze–thaw cycles can lyse a substantial proportion of microbial cells (Christensen & Christensen 1991), resulting in C and N releases into the surrounding soil, although some nutrients may be immobilized by surviving microbes as they consume the enhanced supply of C substrate: this mechanism can result in severe losses to soils and surface waters (Grogan *et al.* 2004). Recent experimental studies and monitoring data have demonstrated that $[NO_3^-]$ in surface waters increased dramatically following periods of severe soil frost (Joseph & Henry 2008; Kaste *et al.* 2008). Freezing–thawing events might promote very high, episodic rates of mineralization, nitrification and denitrification, where the net effect on surface water N concentrations might vary with the hydrological flux and flow routing through the soil profile.

Significant differences in lake $[NO_3^-]$ are observed between the CLE and MFR deposition scenarios from 2010. There is projected to be a gradual increase in $[NO_3^-]$ between about 2050 and 2100. However, $[NO_3^-]$ is projected to remain lower than present-day levels even for the CLE deposition scenario, suggesting that the main influence on long term NO_3^- production at Lochnagar is deposition. The ecological implication of this combined effect of reduced deposition but increasing temperature (marginally declining discharge) is that it is unlikely that *calluna*-dominated communities would change to more grass-dominated communities. However, given the perceived longer growing season and less severe climatic conditions predicted at Lochnagar, the above-ground biomass will increase, which will have an effect on N leaching and the distribution of vegetation communities at Lochnagar.

Discussion and uncertainty

Modelling exercises, especially those projecting future conditions, should include an assessment of sources and possible magnitude of uncertainties. This is especially true when projecting future conditions. Beven (2009) provides a comprehensive review of uncertainty in environmental modelling. Uncertainty is closely tied to the difficult problem of determining parameters in a model. Often, environmental time series do not contain enough information to uniquely identify either model structure or parameter values. This problem can lead to equifinality (Beven 2009), where more than one parameter set provides equally credible model outputs. The effect on model projections of this uncertainty in parameter values was assessed by using ensembles of downscaled climate data and INCA-N modelled [NO_3^-] time series from ensembles of parameter sets. The relatively small uncertainty introduced by projections based on ensembles of model runs does not preclude the possibility of larger qualitative uncertainties introduced by uncertainties in model structure.

Uncertainty in measured data is especially problematic in montane catchments. Data about many environmental processes are unavailable at the required scale for hydrological and biogeochemical modelling. High quality climate data are difficult to obtain due to factors such as equipment failure in harsh environments and difficulties with site access during winter. At Lochnagar, ice jams alter channel geometry and high winds result in water backing up, adding to uncertainty in flow estimation.

Simulations of N deposition were obtained that are comparable to other modelled and observed datasets. Future work must focus on refining these estimates. Even though air temperature has a direct impact on snow accumulation, snowmelt, evapotranspiration and N transformation rates in soil and water, these processes are also affected by precipitation, wind, humidity and other catchment characteristics. Such complex interactions between factors make future projections difficult. Hence, there might be several chemical and biological outcomes from one single climate scenario, depending on the abiotic or biotic factors operating in the catchment.

Conceptual uncertainty arises from a lack of complete understanding of processes occurring in the natural environment. This may be a result of inadequacies in theory or data. Theories about N behaviour in natural and semi-natural environments are a topic of on-going debate (Galloway *et al.* 2008). The conceptual models of runoff generation and N dynamics implemented in HBV and INCA-N have been tested many times. HBV has been widely used for flow forecasting (Bergström 1992) and to generate hydrological time series for use in INCA-N modelling. The INCA-N model has been widely applied in lowland, agricultural and forested catchments. This is the first application of INCA-N to a lake-dominated montane catchment. Modelled in-lake N dynamics were most sensitive to parameters related to hydrology and vegetation dynamics. Wade *et al.* (2006) noted that either terrestrial or in-stream processes could explain the observed surface water N. A similar situation cannot be ruled out in the present study. While the modeling results show that the observed pattern on N dynamics can be explained by vegetation-related processes and soil moisture controls, it is possible that changes in the rate of N mineralization in catchment soils could have explained the observed results.

Previous models of N at Lochnagar have used information on catchment soil C:N ratios (Jenkins *et al.* 2001). INCA-N does not use soil C information when modelling N dynamics; instead the model assumes an infinite pool of organic N. This does not affect model projections in agricultural catchments or the model's ability to describe current behaviour in near-natural catchments but may affect long-term projections at sites like Lochnagar. Improved projections of long-term N dynamics could be obtained if INCA-N were to model organic N and soil C dynamics.

Projections of the long-term future inevitably involve a large measure of uncertainty. The constant N deposition in both the CLE and MFR scenarios post-2020 is probably more indicative of a lack of information about the future than a clear statement of predicted deposition. Using a single SRES emissions scenario constrains the possible effects of climate change. Despite these limitations and uncertainties, it now seems inevitable that temperatures will continue to warm for the foreseeable future and that N deposition in the eastern Cairngorms will continue to decline driven in part by high fossil fuel prices.

CONCLUSIONS

The observed present-day NO_3^- dynamics in the Lochnagar catchment are consistent with a catchment-scale model where N dynamics are controlled by deposition, hydrology and vegetative uptake. Future modelling work should examine the possible influence of changing rates of mineralization and changes in the C:N ratio on N dynamics. The results presented here suggest that the Lochnagar catchment and the Eastern Cairngorms will become warmer and somewhat drier over the next century. This will lead to less runoff and a much reduced snow pack. The modelling results presented here indicate that [NO_3^-] in Lochnagar will remain below present levels for the foreseeable future but that they will increase as a result of warmer temperatures even if deposition levels remain constant.

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