Acid deposition, land-use change and global change: MAGIC 7 model applied to Aber, UK (NITREX project) and Risdalsheia, Norway (RAIN and CLIMEX projects)

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Abstract

Nitrogen processes are now included in a new version of MAGIC (version 7), a process-oriented catchment-scale model for simulating runoff chemistry. Net retention of nitrogen (N) is assumed to be controlled by plant uptake and the carbon/nitrogen (C/N) ratio of soil organic matter, the latter as evidenced by empirical data from forest stands in Europe. The ability of this version of MAGIC 7 to simulate and predict inorganic N concentrations in runoff is evaluated by means of data from whole-ecosystem manipulation experiments at Aber, Wales, UK, (nitrogen addition as part of the NITREX project) and Risdalsheia, Norway (exclusion of acid deposition as part of the RAIN project and climate change as part of the CLIMEX project). MAGIC 7 simulated the changes in N leaching satisfactorily as well as changes in base cations and acid neutralising capacity observed at these two sites. MAGIC 7 offers a potential tool for regional assessments and scenario studies of the combined effects of acid deposition, land-use and climate change.

Introduction

The link between deposition of nitrogen (N) and sulphur (S) compounds from the atmosphere and acidification of soils and waters is now well documented (Rohde *et al.*, 1995). The chemical processes that drive the acidification process, particularly with respect to S, are also well understood, and process-based hydrochemical models have been developed to predict the response of soils and surface waters to changes in atmospheric deposition of S. More recently, attention has been focused on the impact of N deposition on soils and surface waters. Needed now are models capable of predicting total acidity impacts to provide the basis for international agreements on reduction in S and N emissions.

Unlike S, which is only marginally utilised and stored in the biota and is subject, essentially, to chemical control, N is tightly cycled and fluxes and storage are dominated by biological processes. Recent experimental results from the NITREX Project (Wright and van Breemen, 1995; Gundersen *et al.*, 1998; Emmett *et al.*, 1998a) and elsewhere provide understanding of the controls on N cycling and enable the formulation of models that incorporate the key processes to provide predictions of N leaching to surface water in response to changes in N deposition.

A complication in predicting future surface water chemistry in response to reductions in S and N emission is the potential interaction with, and impacts of, land use and climate change; this issue lies at the heart of the DYNAMO project (Ferrier, 1998). With respect to land use change, forestry practice, in particular deforestation and subsequent re-afforestation, exerts a major impact on surface water chemistry (Stevens *et al.*, 1994) largely attributable to changes in S and N deposition fluxes (Fowler *et al.*, 1989) and to changes in the biochemical cycling of N (Emmett *et al.*, 1993) as the forest grows. Experimental results also indicate that global climate change will have a significant effect on the N dynamics of terrestrial and surface water systems (van Breemen *et al.*, 1998) promoting increased losses of nitrate to surface waters as a result of increased decomposition of soil organic matter (Wright, 1998). The modelling challenge, therefore, lies in developing representations of the main ecosystem controls on N leaching to surface water which are sufficiently robust to allow assessment of the integrated impacts of S and N deposition, land use and climate change.

In addition, political and economic demands, stemming from the requirement for international agreement, dictate that the models produced be capable of application at large

spatial (regional) scale. This adds a further constraint on the structure of the models since fully mechanistic formulations of ecosystems require detailed data describing N storage and fluxes. Such data, whilst available for a few detailed plot- and catchment-scale studies, are not available for catchments and surface waters within a large region.

The original MAGIC model is based upon 5 chemical processes which determine the leaching of S to surface water and the resultant acid-base chemistry (Cosby et al., 1985a,b). Nitrogen processes were not included. The MERLIN model, on the other hand, links carbon (C) and N cycling with the specific aim of simulating leaching losses of inorganic N (Cosby et al., 1997). A new version of MAGIC (version 7) now includes a simplification of the N processes from MERLIN.

If this simplified model structure can capture observed surface water chemistry and changes in response to experimental manipulations, then the model has clear advantages at regional scale since mapped soil data, land use and deposition data can be utilised for calibration. Furthermore, simulated changes in plant uptake, litterfall, etc. from the MERLIN model calibrated at the plot scale can then be used to provide information on fluxes used as driving variables in MAGIC 7.

MAGIC 7 has been applied to data from two sites at which whole-ecosystem manipulations with acid deposition, land-use and climate change have been conducted. At Aber, Wales, UK, moorland was ploughed and planted with Sitka spruce in 1960, and in 1991–95 N deposition was increased experimentally as part of the NITREX project (Emmett et al., 1995a; Emmett et al., 1998). At Risdalsheia, Norway, N and S deposition were drastically reduced in 1985 as part of the RAIN project (Wright et al., 1993) and subsequently, in 1994, CO_2 and temperature were increased as part of the CLIMEX project (van Breemen et al., 1998; Wright, 1998). Extensive data on C and N cycles and pools are available from both sites and the MERLIN model has been applied previously at both (Emmett et al., 1997; Wright et al., 1998). This paper evaluates the ability of MAGIC 7 to predict responses of surface-water chemistry to the combined effects of changes in S and N deposition, land-use and climate, and compares simulated with observed response during the manipulations.

Model description

MAGIC is a lumped-parameter model of intermediate complexity, developed to predict the long-term effects of acidic deposition on surface water chemistry (Cosby et al., 1985a,b). The model simulates soil solution and surface water chemistry to predict average concentrations of the major ions. The time step is month or year. MAGIC calculates for each time step the concentrations of major ions on the assumption of simultaneous reactions involving sulphate (SO_4) adsorption, cation exchange, dissolution-precipitation-speciation of aluminium and dissolution-speciation of inorganic carbon. MAGIC accounts for the mass balance of major ions in the soil by bookkeeping the fluxes from atmospheric inputs, chemical weathering, net uptake in biomass and loss to runoff.

Central to MAGIC is the size of the pool of exchangeable base cations in the soil. As the fluxes to and from this pool change over time owing to changes in atmospheric deposition, the chemical equilibria between soil and soil solution shift to give changes in surface water chemistry. The degree and rate of change of surface water acidity thus depend both on flux factors and the inherent characteristics of the affected soils.

MAGIC has recently been extended to include functions for N retention and loss. The new version (version 7) incorporates a soil C and N pool. The changes in size of the C pool are specified external to the model. Net plant uptake of N and loss to the atmosphere by denitrification are specified for each time step. At each time step, leaching of N (N_{leach}) is the net result of N input in deposition (N_{dep}), net uptake by plants (N_{upt}), denitrification (N_{den}) and net immobilisation in the soil (N_{immob}).

$$N_{leach} = N_{dep} - N_{upt} - N_{den} - N_{immob}$$

If inputs in deposition are insufficient to satisfy N uptake and denitrification, the model assumes that the N required is taken from the soil N pool, thus increasing C/N ratio. This implies 'mining' of the soil N pool to provide the N necessary to grow a forest, for example.

Net immobilisation of N in the soil is assumed governed by the C/N ratio of the soil organic matter pool following the general relationship derived from empirical data for coniferous forests in Europe (Matzner and Grosholz, 1997; Gundersen et al., in press; Emmett et al., 1998b). At high C/N, immobilisation of N in soil solution is 100% and, at low C/N, immobilisation is 0% of N in soil solution. These upper and lower limits are set as part of the model calibration.

Ammonium (NH_4) and nitrate (NO_3) are treated separately. Nitrification rate is specified as the percentage of the soil NH_4 pool nitrified at each time step. Together, these parameters allow calibration to the measured concentrations of NO_3 and NH_4 in runoff or leachate as well as to the C/N ratio in the soil for the reference year.

Data inputs required for calibration of MAGIC 7 comprise input and output fluxes for water and major ions, soil chemical and physical characteristics, and net uptake fluxes for vegetation.

MAGIC 7 applied to Aber

SITE DESCRIPTION AND EXPERIMENTAL DESIGN

The Aber forest is located in the UK near the North Wales coast (53° 13′N, 4° 00′W) at an altitude of 300 m.

Table 1. Fixed parameters (measured or estimated) for Aber and Risdalsheia used in calibration of MAGIC 7. Data for Aber from Emmett *et al.* (1995) and unpublished; data for Risdalsheia from Wright *et al.* (1993) and Cosby *et al.* (1995).

	Aber	Risdalsheia	Units
Runoff parameters			
Discharge annual	0.568	1.53	m
Solubility Al(OH)$_3$	8.7	6.6	log10
Temperature	8.0	7.0	°C
CO$_2$ partial pressure	.0007	.0008	atm
Total organic acid	18	45	mmol m^{-3}
pK1	3.0	4.2	−log10
pK2	5.0	4.5	−log10
pK3	8.0	7.0	−log10
Soil parameters			
Soil depth	.53	.1	m
Porosity	50	50	%
Bulk density	655	620	kg m^{-3}
Cation exchange capacity	63	62	meq kg^{-1}
Ca saturation	1	11.2	%
Mg saturation	4	5.9	%
Na saturation	2	1.4	%
K saturation	3	2.8	%
SO$_4$ ads. half-saturation	500	60	meq m^{-3}
SO$_4$ ads. max-capacity	2.0	6.0	meq kg^{-1}
Solubility Al(OH)$_3$	8.7	7.6	log10
Temperature	8.0	7.0	°C
CO$_2$ partial pressure	.0066	.002	atm
Total organic acid	150	120	mmol m^{-3}
pK1	3.0	2.1	−log10
pK2	5.0	5.6	−log10
pK3	8.0	7.0	−log10

Originally under moorland vegetation, the site was planted in 1960 with *Picea sitchensis* (Bong. (Carr.)) following ploughing. In 1990, the stand had a high basal area of 60m^2 ha^{-1} with 2020 stems ha^{-1}. The stand had not been thinned due to windthrow risk. The trees are healthy with no obvious nutritional deficiencies. The regional geology is Ordovician mudstone and shales with extensive glacial deposits, and soils are poorly-developed ferric stagnopodzols (Emmett *et al.*, 1995a).

A nitrogen addition experiment was started in 1990 and consisted of a replicated block design with three replicate plots of three different nitrogen treatments and two control treatments. The additions were carried out using a spray system installed beneath the canopy. These applications were carried out weekly and were equivalent to a 1.91-mm event. Further details can be found in Emmett *et al.* (1995a, 1998b). The Aber site is one of 7 European sites in the NITREX project (Nitrogen saturation experiments; Wright and van Breemen, 1995).

MAGIC 7 was used to model the changes in soil solution chemistry in two of the five treatments. These were a zero-N control treatment (ZN) which received deionised water only, and an ammonium nitrate N application treatment (AN35) at 35 kgN ha^{-1} yr^{-1}.

MODEL DATA AND CALIBRATION

Mean annual discharge, soil temperature, soil depth, bulk density and cation exchange capacity were all measured at the site. Sulphate adsorption was estimated from values obtained from similar soils (Table 1).

Atmospheric inputs at Aber are measured as bulk deposition and throughfall (Table 2). Outputs are measured by chemical concentrations sampled monthly by porous ceramic cup lysimeters at 50 cm depth in the B horizon combined with water flux estimated using the SOIL model (Jansson, 1991). Both input and output estimates are uncertain and show large year-to-year variations. For this MAGIC 7 calibration, 5-year mean values for the control plots given by Emmett *et al.* (1998b) were used, and all uncertainty in the measurements was assumed to be in the estimation of dry deposition.

Table 2. Input-output fluxes for water and major ions at Aber control plots for the 5-year period 1990–95. Measurements are bulk deposition, throughfall and soil leachate at 50 cm (data from Emmett *et al.*, 1998b). For the MAGIC 7 calibration estimations of dry and total deposition (measured bulk plus estimated dry) were used. A^- = organic anions; SBC = sum base cations; SSA = sum strong acid anions; ANC = acid neutralizing capacity. Units: meq m^{-2} yr^{-1}; water m yr^{-1}.

	Deposition bulk (meas.)	throughfall (meas.)	dry (est.)	total (est.)	Leachate (meas.)
water (m)	1.877	0.706		1.877	0.568
H^+	29	33	10	39	29
Ca	22	41	4	26	17
Mg	50	110	19	69	73
Na	194	276	83	277	281
K	5	78	2	7	10
NH_4	37	45	111	148	6
Al^{n+}	0	0	0	0	141
SO_4	60	191	98	158	158
Cl	229	353	97	326	326
NO_3	39	59	33	72	61
A^-	9	−20	0	9	12
SBC	308	550	218	526	387
SSA	328	603	228	556	545
ANC	−20	−53	−10	−30	−158

Chloride (Cl) inputs were assumed to be equal to Cl outputs, and dry deposition is thus set as the difference between Cl flux in leachate and Cl flux in bulk precipitation (Table 2). It is assumed that this dry deposition is of marine origin and that the dry deposition of the base cations calcium (Ca), magnesium (Mg), sodium (Na) and potassium (K) is proportional to dry deposition of Cl and the ionic ratios in seawater. For Na, this estimate gives total deposition close to that measured in throughfall. For Ca, Mg, and K, however, the throughfall fluxes are much larger than calculated total deposition, probably because of recycling through the canopy (Table 2).

Dry deposition of SO_4 was also estimated as the difference between leachate and bulk deposition. This assumes that there is no net source or sink of SO_4 in the forest, and that the soil is in steady-state with respect to sulphate adsorption. These assumptions are justified because the soil does not contain significant amounts of S-bearing minerals and does not have large sulphate adsorption capacity.

Dry deposition of nitrogen was estimated from fluxes in bulk precipitation plus dry deposition estimates using a modelling approach and concentrations recorded in NO_x and NH_3 diffusion tubes (D. Bojanic, pers. comm.). Historical rates of deposition were assumed proportional to estimates of historical emissions of S, NH_4 (UKRGAR, 1990) and NO_3 (Simpson *et al.*, 1997) (Fig. 1).

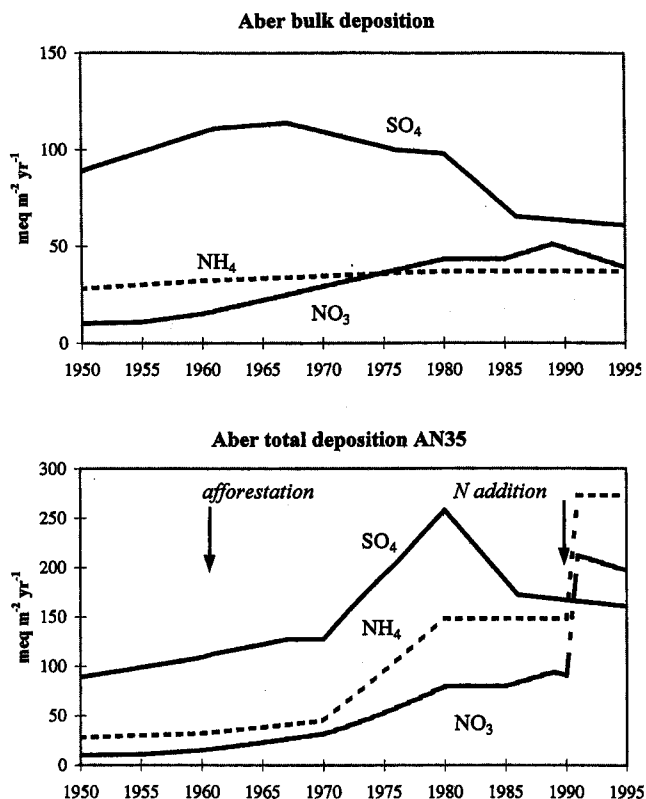The net uptakes of base cations and nitrogen into the biomass in 1990 were estimated from regressions of bio-

Fig. 1. *Measured bulk (top panel) and estimated total (bottom panel) deposition of SO_4, NO_3 and NH_4 at Aber over the period 1950–1995. Total deposition for the years 1991–1995 includes the N addition at the AN35 plots.*

mass on basal area following the destructive sampling of five trees and diameter at breast height (dbh) measurements for all trees in the experimental area. Changes in uptake during stand maturation were estimated for bolewood using production forestry yield class tables and for crown biomass using the assumption that the crown/tree ratio changed from 50% to 15% as the stand matured (Miller and Miller, 1993) (Fig. 2).
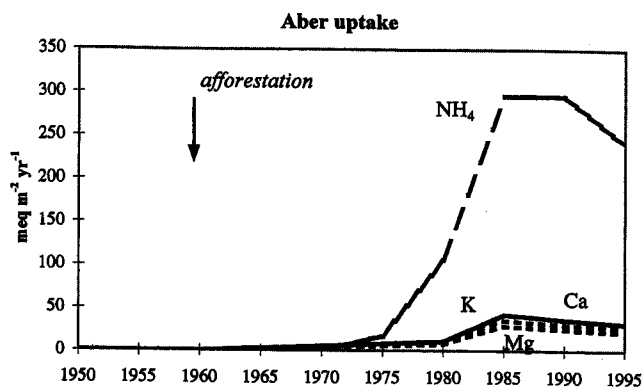

Aber uptake

Fig. 2. *Net uptake of base cations and nitrogen in the vegetation at Aber over the period 1950–1995. The large uptake since 1975 reflects the accumulation of elements in biomass of the growing forest.*

The soil C pool at Aber in 1990 was 302 mol m^{-2} in the forest floor and 1641 mol m^{-2} in the mineral soil (Emmett *et al.*, 1997). The 1-box version of MAGIC 7 calls for one soil C pool, and the C/N ratio of this pool largely controls the retention and release of N to leachate. A pool size of 302 mol m^{-2} is too small to retain the N deposited over the past 100 years with realistic C/N ratios over time, yet a pool size of 1850 mol m^{-2} is too large to allow for the significant changes in C/N and thus N loss over time. As an intermediate value for this calibration, a C pool size of 850 mol m^{-2}, about 1/2 of the total C pool (Table 3) was chosen.

Measurements of soil C and N pools under moorland and forest of varying ages indicate that afforestation results in building of forest floor (Emmett *et al.*, 1997). At Aber, the increase in C from 1960 (moorland) to 1990 (forest) amounts to about 120 mol m^{-2}, and this increase was included in the MAGIC 7 calibration.

The model was calibrated to observed average annual volume-weighted concentrations of ions in soil leachate of the B-horizon (50-cm depth) in the zero nitrogen control plots for the 5-year period 1990–95 (Table 2). This included both changes in historical acid deposition and afforestation of the site in 1960. The calibrated model was then used to predict the response of the 30-year-old forest to the five years of experimental NH$_4$NO$_3$ treatment (1990–1995).

The parameters for the C/N curve were calibrated, roughly, to match the empirical relationships between N leaching and forest floor C/N from the ECOFEE dataset (Gundersen, in press). For the forest in 1990, this gave 100% retention at C/N of 36 and 0% retention at C/N of 28 (Fig. 3). For moorland conditions prior to 1960, however, a different C/N curve was necessary, because moorland at Aber has C/N of 26 yet very little N is leached. Thus, a C/N curve with 100% retention at C/N of 30 and 0% retention at C/N of 14 was used (Fig. 3). These C/N curves and total C pool in soil fit the combined conditions that, in 1960 under moorland, the C/N of soil is 26 with <10 µeq l^{-1} inorganic N in soil leachate and, in 1990 under forest, the C/N of soil is 29 with about 120 µeq l^{-1} inorganic N in leachate.

NH$_4$ was calibrated by adjusting the % nitrification such that the NH$_4$ concentration in leachate in 1990 and 1960 was <10 µeq l^{-1}. Because plant uptake of NH$_4$ in 1990 at 296 meq m^{-2} yr^{-1} greatly exceeds NH$_4$ deposition at 129 meq m^{-2} yr^{-1}, the remaining NH$_4$ must come from 'mining' the soil N pool, thus acting to increase soil C/N. This process accounts in part for the increase in soil C/N from 26 under moorland in 1960 to 29 under forest in 1990. The
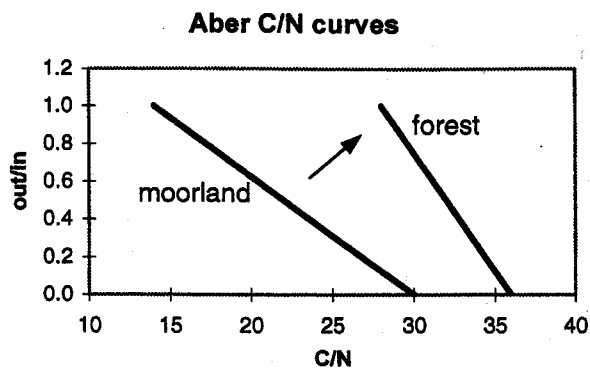
Table 3. Soil carbon and nitrogen parameters for Aber estimated for 1960 (moorland) and measured for 1990 (forest) used in calibration of MERLIN and MAGIC 7. LOM = labile organic matter; ROM = refractory organic matter. Data from Emmett *et al.* (1995a) and Emmett *et al.* (1997).

moorland 1960	C mol m^{-2}	N mol m^{-2}	C/N mol mol^{-1}
MERLIN			
LOM	186	7.2	26
ROM	1641	109	15
MAGIC 7	750	28.9	26

forest 1990	C mol m^{-2}	N mol m^{-2}	C/N mol mol^{-1}
MERLIN			
LOM	302	10.4	29
ROM	1641	109	15
MAGIC 7	850	29.3	29

Aber C/N curves

Fig. 3. *The C/N curves used in calibration of MAGIC 7 to Aber for the moorland in 1960 and the forest in 1990.*

Aber ZN control

model assumes that plant uptake is preferentially NH_4, and thus always simulated no NH_4 in leachate. Measured concentrations in 1990–95 were 11 µeq l^{-1}. Since NH_4 is a minor ion in soil solution and comprises <10% of output flux of inorganic N, the non-fit of NH_4 in the calibration had negligible influence on the calibration of the other ions.

Results

Prior to 1960, nitrogen leaching was low due to both high C/N ratios in the soil and low rates of nitrogen deposition. After afforestation, nitrogen inputs increase due to both increases in N concentrations in dry and wet deposition and the greater capture of pollutants by the tree canopy. As N retention rates decline rapidly despite an increase in the soil C/N ratio, it was necessary to change the N retention response function calibrated for the moorland to achieve a successful simulation using MAGIC 7. A similar change was found necessary during application of the MERLIN model to the Aber site (Emmett *et al.*, 1997).

MAGIC 7 simulates present-day levels of NO_3 in leachate (Fig. 4). Nitrate concentrations in soil and streamwater in upland Wales are increased with four key variables; areal cover of trees, the maturity of the forest, amount of N deposition and the N status of the forests (Stevens *et al.*, 1994; Reynolds *et al.*, 1994; Emmett *et al.*, 1995b; Emmett *et al.*, 1998a). The greater N leaching from forests is in part due to greater scavenging of pollution from the atmosphere by the trees. The relationship with forest age is due to reduced net uptake of N from the soil store as the stand matures. In mature forests, nitrogen losses increase as the C/N ratio of the forest floor decreases due to increased mineralisation and nitrification rates (Emmett *et al.*, 1995b). Several studies have indicated that N leaching from mature stands can be predicted using an empirical relationship between the C/N ratio or %N of the forest floor (Emmett *et al.*, 1998a; Matzner and Grosholz, 1997; Gundersen *et al.*, 1998; Gundersen *et al.*, in press). MAGIC 7 takes account of the stand age, depo-
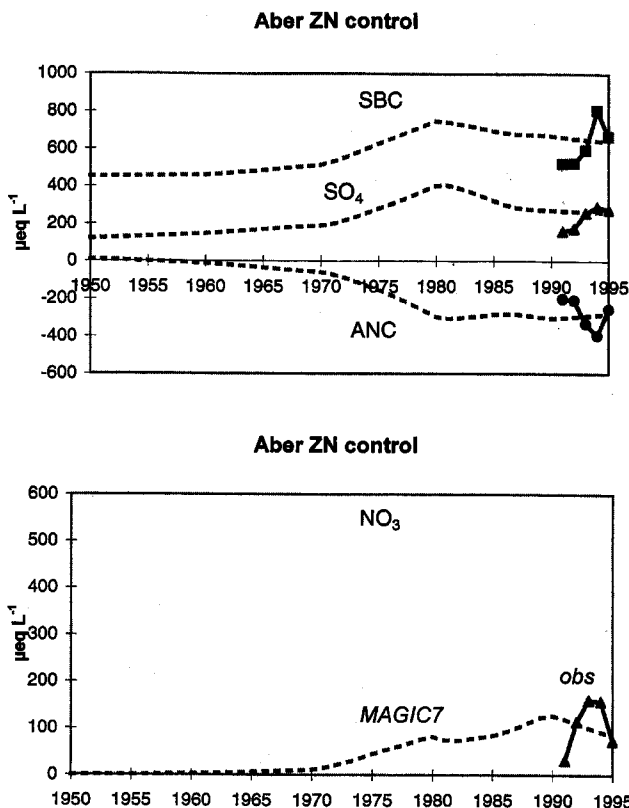
Aber ZN control

Fig. 4. *Aber control. Annual volume-weighted concentrations of key components in leachate at Aber (ZN control plots) as modelled by MAGIC 7 (1950–95) and measured (1990–95). Top panel: Sum base cations (SBC), SO_4, and acid neutralising capacity (ANC). Bottom panel: NO_3. Measurements from Emmett et al. (1998b).*

sition flux and the turnover and retention rate in the soil using the C/N ratio in the soil.

The nitrogen-addition treatment (AN35) provides an independent test of the model. The MAGIC 7 calibration simulated well the observed increase in NO_3 leaching in the treatments (Fig. 5). The observed data show large year-to-year variation, but are in the same range as the simulated concentrations.

The historical reconstruction of soil water chemistry indicates a gradual increase in base cations and a decrease in acid neutralising capacity (ANC) during the period 1950–1980 in response to the increased acid deposition, leaching of strong acid anions SO_4 and NO_3, and the planting and growth of the forest in 1960 (Fig. 4). The model simulation indicates that ANC decreases from –15 µeq l^{-1} in 1960 to –300 µeq l^{-1} in 1990 (Fig. 4).

MAGIC 7 simulates well the observed increase in base cations and decrease in ANC for the 5 years of treatment at the AN35 plots (Fig. 5). The model also predicts an increase in aluminium and a decrease in pH in line with observed data at the AN35 plots (not shown).
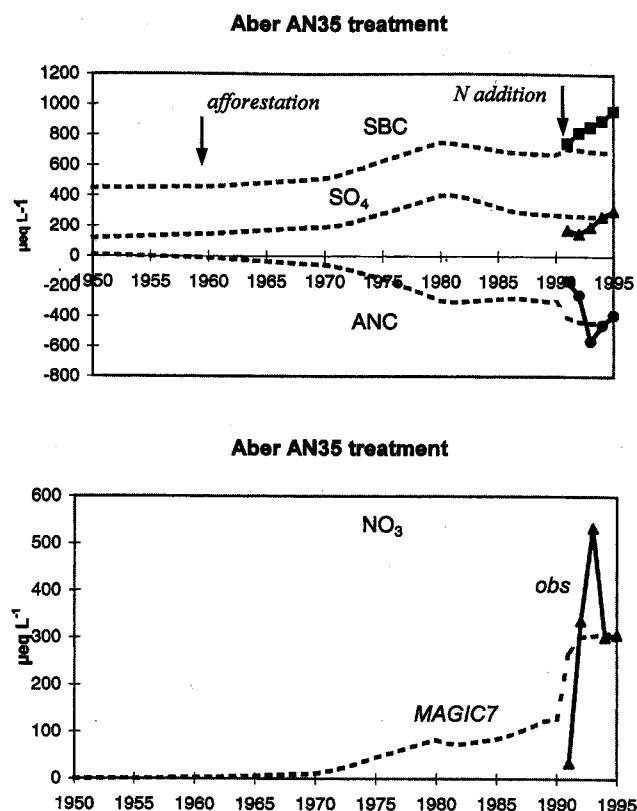
Aber AN35 treatment

Aber AN35 treatment

Fig. 5. *Aber AN35. Annual volume-weighted concentrations of key components in leachate at Aber (AN35 nitrogen addition plots) as modelled by MAGIC 7 (1950–95) and measured (1990–95). Arrows indicate planting of the forest and start of the N addition experiment. Top panel: Sum base cations (SBC), SO₄, and acid neutralising capacity (ANC). Bottom panel: NO₃. Measurements from Emmett et al. (1998b).*

MAGIC 7 applied to Risdalsheia

SITE DESCRIPTION AND EXPERIMENTAL DESIGN

Risdalsheia is located near Grimstad, Norway, (58°23′ N, 8°19′E) about 20 km inland from the North Sea. The site is 300 m a. s. l., and is typical of large areas of upland southern Norway. Risdalsheia has a maritime climate with mean annual precipitation of about 1400 mm, runoff 1200 mm, and mean annual temperature of about 5°C (mean of −3°C in January and +16°C in July). Vegetation is mainly a sparse cover of pine (*Pinus sylvestris* L.) and birch (*Betula pubescens* L.) with heather (*Calluna vulgaris* L.) and blueberry (*Vaccinium myrtillus* L.) as dominant ground species. Bedrock is biotite granite covered by thin (about 10 cm) and patchy podsolic and peaty soils.

Risdalsheia receives high levels of acid deposition. Mean values of total deposition (wet and dry) for the 8-year period 1984–92 were 226 mmol m⁻² yr⁻¹ S, 132 mmol m⁻²

yr^{-1} N (59 as NH_4^+ and 73 as NO_3^-), and 106 mmol m⁻² yr^{-1} H⁺ (Wright *et al.*, 1993).

The first set of experiments at the site (the RAIN project; Reversing Acidification In Norway) involved exclusion of ambient N and S deposition. These experiments comprise several headwater catchments of which KIM catchment (860 m²) was covered by roof above the canopy and received clean rain and ROLF catchment (220 m²) served as untreated reference (Wright *et al.*, 1993). Manipulation of the precipitation (termed 'clean' precipitation) at KIM catchment began June 1984 and has continued uninterrupted through 1997. Incoming precipitation is collected from the roofs by gutters, led to storage tanks, filtered, passed through a mixed-bed ion-exchange resin, dosed with natural levels of sea salts (at about 1:8000 in summer and 1:5000 in winter) and distributed back automatically out under the roofs through a sprinkler system.

The second set of experiments at the site (the CLIMEX project; Climate change experiment) began April 1994 and involves manipulation with CO_2 and air temperature at KIM catchment (Van Breemen *et al.* 1998; Wright 1998). This new treatment is superimposed on the clean rain treatment. In the winter of 1993–94, KIM catchment was enclosed completely with airtight transparent walls. An airtight transparent dividing wall was installed across the catchment such that the uppermost 20% of the catchment (termed control, KIM-c) receives the clean rain treatment only and not higher CO_2 and temperature. KIM-c serves as control area for plant and soil studies which are conducted on small plots of about 4 m². Runoff from KIM-c is sampled weekly for chemical composition; it flows into the treated 80%, and thus runoff from the treated section (KIM-t) contains water from both KIM-c and KIM-t.

In the treatment section (KIM-t), CO_2 is added to the air during the growing season (defined as 1 April–31 October) at target concentration of 560 ppmv. The air is warmed by means of a central electric heating system in which heated fluid (maximum 60°C) circulates through 3 ranks of 6-cm diameter steel pipes mounted on the insides of the walls. The target for air warming is +5°C above KIM-c in January and +3°C in July, with intermediate temperatures in the intervening months. Average air temperature rise achieved during the first 3 years of treatment was 3.7°C.

Results from the RAIN and CLIMEX experiments at KIM catchment (roof, clean rain, CO_2 and temperature) and ROLF catchment (untreated reference) have been used in the modelling.

MODEL DATA AND CALIBRATION

Ambient bulk precipitation is collected by funnel and volume measured weekly at the meteorological station located in an open area at Risdalsheia (Table 4). At KIM and

Table 4. Input-output fluxes for water and major ions at Risdalsheia untreated reference catchment ROLF for the calibration year 1986 (May 1985 – April 1986). Bulk precipitation and runoff are measured and dry and total deposition estimated (data from Wright *et al.*, 1993). Total deposition is A^- = organic anions; SBC = sum base cations; SSA = sum strong acid anions; ANC = acid neutralizing capacity. Units: meq m^{-2} yr^{-1}; water m yr^{-1}.

	Deposition bulk (meas.)	dry (est.)	total (est.)	Runoff (meas.)
water (m)	1.253		1.253	1.008
H^+	76	16	92	89
Ca	12	2	14	17
Mg	12	9	21	25
Na	47	41	88	78
K	5	1	6	3
NH_4	55	6	61	15
Al^{n+}	0	0	0	9
SO_4	82	15	97	94
Cl	51	48	99	99
NO_3	47	12	59	26
A^-	27	0	27	17
SBC	131	59	190	138
SSA	180	75	255	219
ANC	−49	−15	−64	−81

EGIL catchments, the volume of sprinkled water is metered and read at minimum weekly intervals. Dry deposition of S and N is estimated from measured daily concentrations for S and N species in air at the nearby EMEP station at Birkenes and assumed deposition velocities. Dry deposition of sea salts is estimated from the mass balance for Cl (Wright *et al.*, 1993). Rates of historic deposition used for the period prior to the start of measurements are based on estimates for emissions of SO_2 (Mylona, 1996) and NO_x in Europe (Simpson *et al.*, 1997).

Runoff (Table 4) is collected at the bottom of each catchment and led by hose to 0.5-m^3 tanks, which empty automatically when full. Discharge is measured by logging the number of tanks emptied. Samples for chemical analysis are collected automatically at about weekly intervals from each full tank (or a pre-set selection of tanks). These systems at Risdalsheia have been in continuous operation since March 1984 (KIM) and October 1984 (ROLF). Precipitation samples are analysed for pH, Ca, Mg, Na, K, NH_4, NO_3, Cl, and SO_4. Runoff samples are analysed in addition for aluminium species (reactive-Al and organic-Al), Total Organic C (TOC) and Total N. Details are given by Wright *et al.* (1993) and Wright (1998).

The total C and N pools in the soil are estimated from measurements of C and N content in bulk soil, 13.5% and 0.65%, respectively, bulk density of the soil (0.66 g cm^{-3}) and an average soil depth of 10 cm (Wright *et al.*, 1993). These values are used for all catchments (Table 5). The total amount of organic matter is assumed to be constant

over time at the control catchment ROLF and until onset of CLIMEX at KIM catchment. Values for all other soil parameters are taken from previous MAGIC calibrations (Cosby *et al.*, 1995) (Table 1).

At KIM catchment, the CLIMEX treatment has apparently resulted in increased mineralisation of soil organic matter (Verburg and van Breemen, in press). The decomposition rate of soil organic matter is temperature dependent (Kirschbaum, 1995). Measurements at Risdalsheia indicate that fresh litter does not decompose faster at elevated temperatures and, therefore, probably increased decomposition of 'old' organic matter accounts for the observed increase in N mineralisation at KIM catchment (Verburg and van Breemen, in press).

As the ecosystems at Risdalsheia are undisturbed and not subject to forest practices, it was assumed that the

Table 5. Measured soil carbon and nitrogen parameters for Risdalsheia in 1990 used in calibration of MERLIN and MAGIC 7. LOM = labile organic matter; ROM = refractory organic matter. Data from Wright *et al.* (1993) and Wright *et al.* (1998).

	C mol m^{-2}	N mol m^{-2}	C/N mol mol^{-1}
MERLIN			
LOM	45	2.1	21
ROM	698	33	21
MAGIC 7	760	36	21

system is at steady state with no net accumulation biomass, and hence no net uptake of base cations or nitrogen by the vegetation.

Results

The decline in S deposition at Risdalsheia resulted in decreased concentrations of SO_4 in runoff. MAGIC 7 values closely track the observed at the untreated ROLF catchment (Fig. 6), as well as the sharp decline due to the clean rain treatment at KIM catchment (Fig. 7). At ROLF catchment, concentrations of sum of base cations (SBC) remained roughly constant and, thus, most of the decline in SO_4 is reflected in increased ANC (Fig. 6). At KIM catchment also an increase in ANC (Fig. 7) accompanied the sharp decline in SO_4. MAGIC 7 simulated all these trends as well as the year-to-year variations at both catchments. The calibration for all ions except for N species was nearly identical to the application of the earlier version of MAGIC (Cosby et al., 1995).

MAGIC 7 simulates concentrations of NH_4 and NO_3 in runoff. The combination of i) 14-year record of fluxes of N in runoff at the untreated reference catchment (ROLF), ii) the observed response in experimentally-changed N deposition at KIM catchment, and iii) the subsequent response to superimposed changes in CO_2 and air temperature at KIM catchment provide a very strict set of conditions to which the MAGIC 7 model can be calibrated and tested. The observed changes in runoff N flux include:

1. In 1984 at the start of measurements at Risdalsheia, runoff from all catchments contained elevated concentrations of both NH_4 and NO_3 with N flux in runoff about 30–40% of N flux in deposition.
2. During 14 years of measurements at ROLF catchment, annual deposition and runoff of N varied from year-to-year by about a factor of 2, but there was no time trend (Fig. 6).
3. During the 11 years of the RAIN experiment at KIM catchment (roof, clean rain), the 90% reduction of N deposition caused immediate and persistent reduction in N flux in runoff (Wright et al., 1993) (Fig. 7).
4. During the 3 years of CLIMEX treatment at KIM catchment (CO_2 and warming), the flux of N in runoff increased by about 5 mmol N m^{-2} yr^{-1} relative to the immediate previous 3-year clean rain period and to runoff from the control section KIM-c (Wright, 1998) (Fig. 7).

These changes in runoff flux of NO_3 and NH_4 are well simulated by MAGIC 7 at both ROLF catchment (reference) and KIM catchment (treatment) (Figs. 6 and 7). The model calibrated to ROLF catchment transfers remarkably well to KIM catchment, and the response to reduced N deposition was well simulated. The MAGIC 7 simulations are similar to those of the MERLIN model (Wright et al., 1998) despite the fact that MAGIC 7 contains only one soil
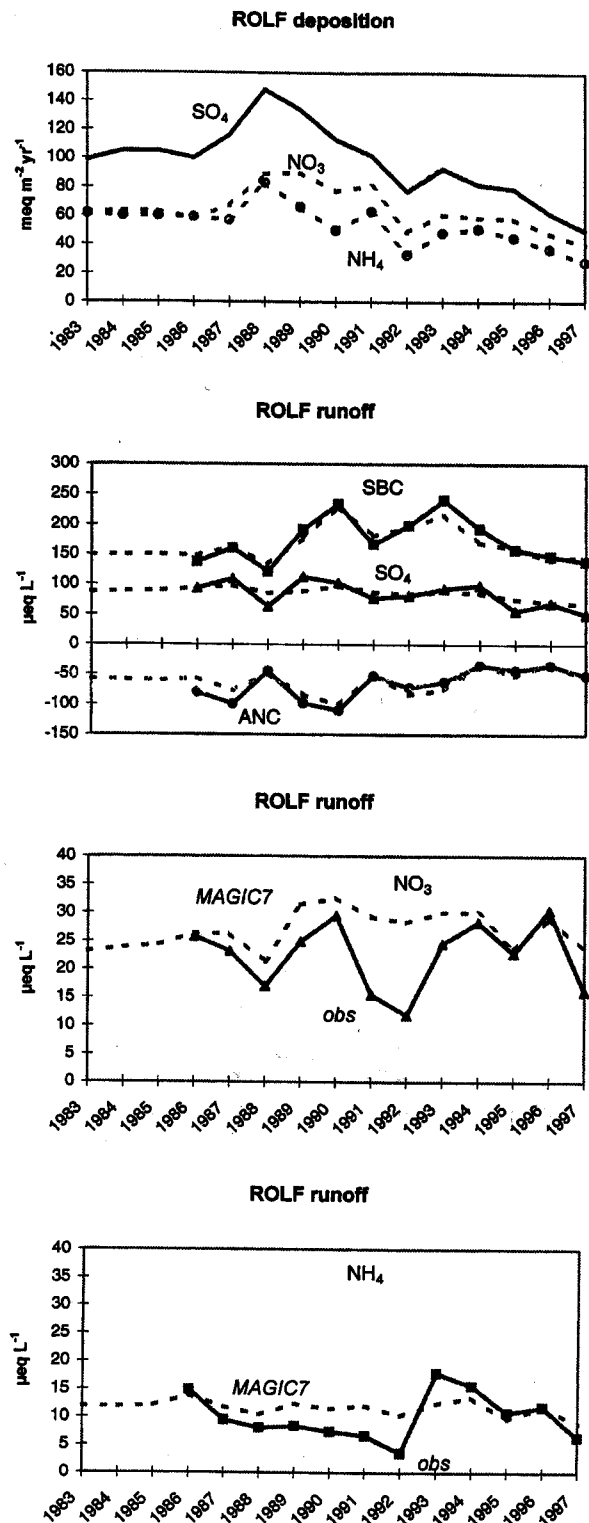

Fig. 6. ROLF. Deposition and runoff of key components at ROLF catchment (untreated reference) at Risdalsheia for the period 1983–1997 as modelled by MAGIC 7 and measured. First panel: Total deposition of SO_4, NO_3 and NH_4. Second panel: Sum base cations (SBC), SO_4, and acid neutralising capacity (ANC). Third panel: NO_3. Fourth panel: NH_4. Measurements from Wright et al. (1993) and Wright (1998).
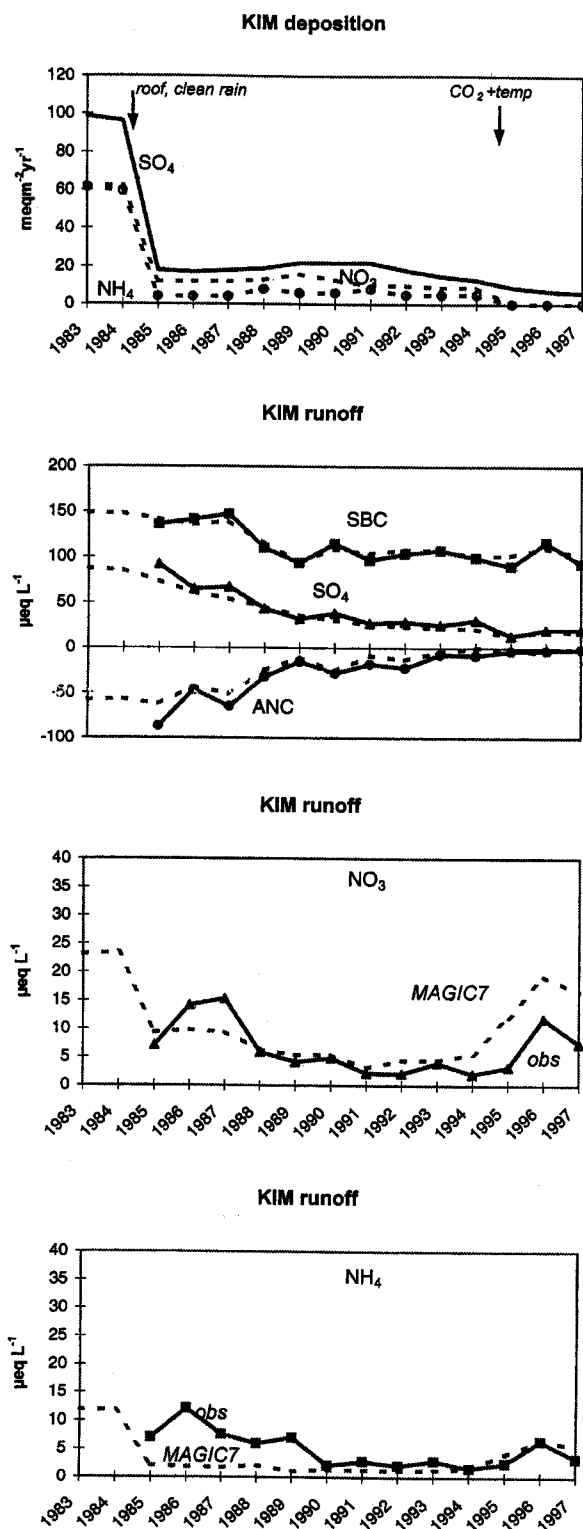
Fig. 7. *KIM. Deposition and runoff of key components at KIM catchment (roof, clean rain, climate change) at Risdalsheia for the period 1983–1997 as modelled by MAGIC 7 and measured. Arrows indicate start of the clean rain and climate change experiments. First panel: Total deposition of SO_4, NO_3 and NH_4. Second panel: Sum base cations (SBC), SO_4, and acid neutralising capacity (ANC). Third panel: NO_3. Fourth panel: NH_4. Measurements from Wright et al. (1993) and Wright (1998).*

C pool whereas MERLIN has both a labile organic matter pool (LOM) and a refractory organic matter pool (ROM).

The model indicates that the ecosystem accumulates N over the 50 years of increasing N deposition, and that most of the N is retained in the soil. The system begins to leak a larger and larger fraction of the incoming N as the C/N molar ratio in LOM decreases below about 23. This fits with the empirical relationships from coniferous forest ecosystems in Europe (Matzner and Grosholz, 1997; Wilson and Emmett, in press; Gundersen et al., in press) and in North America (van Miegroet et al., 1992) which indicate that N retention is correlated to both N deposition and C/N ratio in the upper soil horizons, and with the experiments of the NITREX project (Tietema and Beier, 1995; Gundersen et al., 1998, Emmett et al., 1998a). At Risdalsheia when the roof at KIM catchment in 1984 excludes the N deposition, the system stops leaking N, but still is full of N.

MAGIC 7, however, somewhat overestimates the response to the 3 years of climate change (Fig. 7). Climate change is simulated in MAGIC 7 by assuming a net decrease in the C pool in soil by 1.1 mol m^{-2} yr^{-1} as is indicated by the mass budgets and the MERLIN calibration (Wright et al., 1998). The increased decomposition of soil organic matter is probably due to increased temperature. In MAGIC 7, the N associated with this carbon is largely released to soil solution and runoff, whereas in MERLIN about 1/2 of the released N is taken up by vegetation, LOM and ROM. The MERLIN calibration, thus, fits the observed increase in N runoff better for the 3 years of climate change.

Discussion

The major change in the new version of MAGIC used here (version 7) is the addition of processes regulating nitrogen retention and release. Previous versions of MAGIC required that net catchment N retention be calibrated to match present day observed concentrations of NO_3 and NH_4 in surface water. This percentage net retention was then usually assumed to remain constant throughout the simulation period, and so the model had no internal mechanism to simulate N saturation due to N deposition or changes in uptake by plants or soil. MERLIN, on the other hand, focuses entirely on N dynamics, and includes 2 plant compartments and 2 soil compartments with all the fluxes of N between the compartments either specified or modelled (Cosby et al., 1997). MERLIN provides a more rigorous treatment of N cycling and nitrogen saturation but requires a large amount of information on N and C pools and cycles in the ecosystem. Such information is generally lacking except for a few intensively studied research sites, such as Aber and Risdalsheia, addressed here.

MAGIC 7 now offers a compromise between the relatively complex and data-intensive nitrogen model

Table 6. Calibrated parameters for Aber and Risdalsheia obtained from MAGIC 7.

	Aber	Risdalsheia	Units
Cation exchange selectivity coefficients			
Al-Ca	−0.82	−3.79	log10
Al-Mg	−0.72	−2.25	log10
Al-Na	−1.01	−2.06	log10
Al-K	−5.85	−6.84	log10
Weathering rates			
Ca	8	5	meq $m^{-2}yr^{-1}$
Mg	14	1	meq $m^{-2}yr^{-1}$
Na	10	1	meq $m^{-2}yr^{-1}$
K	8	0	meq $m^{-2}yr^{-1}$
Initial base saturation			
Ca	3.3	13.3	%
Mg	6.5	9.2	%
Na	1.8	1.7	%
K	4.7	3.7	%
Initial soil C and N pools			
C	750	760	mol m^{-2}
N	27.1	30	mol m^{-2}
C/N	27.7	25.3	mol mol^{-1}

MERLIN and the simple empirical nitrogen functions in earlier versions of MAGIC. The new approach in MAGIC 7 appears to be satisfactory for simulation of response in N leaching, following afforestation and N addition at Aber, and reduced N deposition and climate change at Risdalsheia and allows for associated changes in acid base chemistry to be modelled.

MAGIC 7 does not replace MERLIN, however, because MERLIN can tackle the internal redistribution of N within the ecosystem, and point to changes in plant C/N and mineralisation in response to changes in land-use, N deposition or climate (Emmett *et al.*, 1997; Wright *et al.*, 1998). But MERLIN cannot be used directly to predict changes in acidification status of a site.

The comparison of simulated N leaching at Aber and Risdalsheia from MAGIC 7 and MERLIN suggests that MAGIC 7 provides a viable alternative to MERLIN for sites at which the extensive data required for MERLIN are not available. Further, now that MAGIC 7 includes a simple mechanistic description of N processes and can simulate changes in N leaching, the model can be used for scenario studies. Additional applications are necessary, however, of, for example, clearfelling and other forest management practices, and also other global change experiments at the ecosystem scale. The two applications presented here show that MAGIC 7 gives simulations consistent with the experimental data from whole-ecosystem experiments.

MAGIC 7 is about as complex a process-oriented model for simulation of runoff chemistry as is feasible for the amount of data generally available from individual sites. Incorporation of additional parameters, processes and complexity would be at the expense of 'transparency', and would require input data above and beyond that normally available on a regional scale. Previous versions of MAGIC have been used at the regional scale to predict future regional changes in surface water acidification given various scenarios of future acid deposition and land-use change (forest practices) (Wright *et al.*, 1991; Cosby and Wright, 1998; Helliwell *et al.*, 1998; Sefton and Jenkins, 1998; Collins and Jenkins, 1998; Evans *et al.*, 1998) These regional applications have been hampered by the lack of N dynamics in previous versions of MAGIC. Now that these are included, MAGIC 7 offers a potential basis for regional scenario studies of changes in surface water chemistry under scenarios of combined changes of S and N deposition, land-use and climate.

A major uncertainty that persists in the use of MAGIC 7 for regional or site-specific applications lies in the calibration to non-forested ecosystems. In contrast to coniferous ecosystems, the control of N leaching from moorlands, heathlands and grasslands is not well understood. No relationship between N leaching with deposition has been observed in the UK, although a few high deposition sites have been studied (Jenkins *et al.*, 1996). In addition, available data, although sparse, do not indicate clear empirical relationships between nitrate leaching and the C/N ratio of the soil. This may be due to the variability in drainage characteristics of different soil types, vegetation composition and management of moorland and grasslands. Grazing

intensity is an additional factor which can differ significantly between sites and can radically alter the rate of N cycling, productivity and thus, N available for leaching. More field data from non-forested sites with high levels of inorganic N in surface waters are urgently required before MAGIC 7 (or any other such process-based N model) can be applied to such areas with confidence.

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References

Collins, R. and Jenkins, A., 1998. Regional modelling of acidification in Wales: Calibration of a spatially distributed model incorporating land use change. *Hydrol. Earth System Sci.*, 2, 533–541.

Cosby, B.J., Ferrier, R.C., Jenkins, A., Emmett, B.A., Wright, R.F. and Tietema, A., 1997. Modelling the ecosystem effects of nitrogen deposition at the catchment scale: model of ecosystem retention and loss of inorganic nitrogen (MERLIN). *Hydrol. Earth System Sci.*, 1, 137–158.

Cosby, B.J. and Wright, R.F., 1998. Modelling regional response of lakewater chemistry to changes in acid deposition: the MAGIC model applied to lake surveys in southernmost Norway 1974–1986–1995. *Hydrol. Earth System Sci.*, 2, 563–576.

Cosby, B.J., Wright, R.F. and Gjessing, E., 1995. An acidification model (MAGIC) with organic acids evaluated using whole-catchment manipulations in Norway. *J. Hydrol.*, 170, 101–122.

Cosby, B.J., Wright, R.F., Hornberger, G.M. and Galloway, J.N., 1985a. Modelling the effects of acid deposition: assessment of a lumped parameter model of soil water and streamwater chemistry. *Wat. Resour. Res.*, 21, 51–63.

Cosby, B.J., Wright, R.F., Hornberger, G.M. and Galloway, J.N., 1985b. Modelling the effects of acid deposition: estimation of long-term water quality responses in a small forested catchment. *Wat. Resour. Res.*, 21, 1591–1601.

Emmett, B.A., Boxman, D., Bredemeier, M., Moldan, F., Gundersen, P., Kjønaas, O.J., Schleppi, P., Tietema, A. and Wright, R.F., 1998a. Predicting the effects of atmospheric nitrogen deposition in conifer stands: evidence from the NITREX ecosystem-scale experiments. *Ecosystems*, 1, 352–360.

Emmett, B.A., Brittain, A., Hughes, S., Görres, J., Kennedy, V., Norris, D., Rafarel, R., Reynolds, B. and Stevens, P., 1995a. Nitrogen additions (NaNO3 and NH4NO3) at Aber forest, Wales: I. Response of throughfall and soil water chemistry. *For. Ecol. Manage.*, 71, 45–59.

Emmett, B.A., Cosby, B.J., Ferrier, R.C., Jenkins, A., Tietema, A. and Wright, R.F., 1997. Modelling the ecosystem effects of nitrogen deposition at the catchment scale: simulation of nitrogen saturation in a Sitka spruce forest, Aber, Wales, UK. *Biogeochemistry*, 38, 129–148.

Emmett, B.A., Reynolds, B., Silgram, M., Sparks, T.H. and Woods, C., 1998b. The consequences of chronic nitrogen additions on N cycling and soilwater chemistry in a Sitka spruce stand, N.Wales. *For. Ecol. Manage.*, 101, 165–176.

Emmett, B.A., Reynolds, B., Stevens, P.A., Norris, D., Hughes, S., Görres, J. and Lubrecht, I., 1993. Nitrate leaching from afforested Welsh catchments—interaction between stand age and nitrogen deposition. *Ambio*, 22, 386–394.

Emmett, B.A., Stevens, P.A. and Reynolds, B., 1995b. Factors influencing nitrogen saturation in Sitka spruce stands in Wales. *Wat. Air Soil Pollut.*, 85, 1629–1634.

Evans, C.D., Jenkins, A., Helliwell, R. and Ferrier, R.C., 1998. Predicting regional recovery from acidification: The MAGIC model applied to Scotland, England and Wales. *Hydrol. Earth System Sci.*, 2, 543–554.

Ferrier, R.C., 1998. Assessing the impact of environmental change on biogeochemical cycles through the use of dynamic models: the scientific challenges of the DYNAMO project. *Hydrol. Earth System Sci.*, 2, 375–383.

Fowler, D., Cape, J.N. and Unsworth, M.H., 1989. Deposition of atmospheric pollutants on forests. *Phil. Trans. Roy. Soc. Lond.*, B 324, 247–265.

Gundersen, P., Callesen, I. and de Vries, W., in press. Nitrate leaching in forest ecosystems is related to forest floor C/N ratios. *Environ. Pollut.*

Gundersen, P., Emmett, B.A., Kjønaas, O.J., Koopmanns, C.J. and Tietema, A., 1998. Impact of nitrogen deposition on nitrogen cycling in forests: a synthesis of NITREX data. *For. Ecol. Manage.*, 101, 37–55.

Helliwell, R., Ferrier, R.C. and Jenkins, A., 1998. A two layer application of the MAGIC model to predict the effects of land use scenarios and reductions in deposition on acid sensitive soils in the UK. *Hydrol. Earth System Sci.* 2.

Jansson, P.E., 1991. *Simulation model for soil water and heat conditions. Description of the SOIL model.* Report 165, Div. Agricultural Hydrotechnics, Dept. Soil Sciences, Swedish Agricultural University, Uppsala.

Jenkins, A., Renshaw, M. and Boorman, D., 1996. The UK Acid Waters Monitoring Network; an assessment of chemistry data. *Freshwat. Biol.*, 36, 169–178.

Kjønaas, O.J. and Wright, R.F., 1998. Nitrogen leaching from N limited forest ecosystems: the MERLIN model applied to Gardsjon, Sweden. *Hydrol. Earth System Sci.*, 2, 497–507.

Kirschbaum, M.U.F., 1995. The temperature dependence of soil organic matter decomposition, and the effect of global warming on soil organic C storage. *Soil Biol. Biochem.*, 27, 753–760.

Matzner, E., and Grosholz, C., 1997. Relationship between NO3- output, C/N ratios of the humus layer and N-input in Central European spruce forest (*Picea abies* Karst.) ecosystems. *Forstw. Cbl.*, 116, 39–44.

Miller, J.D. and Miller, H.G., 1993. A comparison of aboveground weights and element amounts in four forest species at Kirkton Glen. *J. Hydrol.*, 145, 419–438.

Mylona, S., 1996. Sulphur dioxide emissions in Europe 1880–1991 and their effect on sulphur concentrations and depositions. *Tellus*, 48B, 662–689.

Reynolds, B., Ormerod, S.J. and Gee, A.S., 1994. Spatial patterns in stream nitrate concentrations in upland Wales in relation to catchment forest cover and forest age. *Environ. Pollut.*, 84, 27–33.

Rohde, H., Grennfelt, P., Wisniewski, J., Ågren, G., Bengtsson, G., Johansson, K., Kauppi, P., Kucera, V., Rasmussen, L., Rosseland, B., Schotte, L. and Sellden, G., 1995. Acid reign '95?—conference summary statement. *Wat. Air Soil Pollut.*, 85, 1–14.

Sefton, C. and Jenkins, A., 1998. A regional application of the MAGIC model in Wales: calibration and assessment of future recovery using a Monte-Carlo approach. *Hydrol. Earth System Sci.*, 2, 521–531.

Simpson, D., Olendrzynski, K., Semb, A., Støren, E. and Unger, S., 1997. *Photochemical oxidant modelling in Europe: multi-annual modelling and source-receptor relationships.* EMEP/MSC-W Report 3/97, Norwegian Meteorological Institute, Oslo, Norway, 75 pp.

Stevens, P.A., Norris, D.A., Sparks, T.H. and Hodgson, A.L., 1994. The impacts of atmospheric N inputs on throughfall, soil and stream water interactions for different aged forest and moorland catchments in Wales. *Wat. Air Soil Pollut.*, 73, 297–317.

Tietema, A. and Beier, C., 1995. A correlative evaluation of nitrogen cycling in the forest ecosystems of the EC projects NITREX and EXMAN. *For. Ecol. Manage.*, 71, 143–151.

UKRGAR 1990. *Acid deposition in the UK 1986–1988.* Warren Spring Laboratory, Stevenage, UK.

Van Breemen, N., Jenkins, A., Wright, R.F., Arp, W.J., Beerling, D.J., Berendse, F., Beier, C., Collins, R., van Dam, D., Rasmussen, L., Verburg, P.S.J. and Wills, M.A., 1998. Impacts of elevated carbon dioxide and temperature on a boreal forest ecosystem (CLIMEX project). *Ecosystems*, 1, 345–351.

Van Miegroet, H., Cole, D.W. and Foster, N.W., 1992. Nitrogen deposition and cycling, p. 178–196, In: Johnson DW & Lindberg SE (Eds.) *Atmospheric Deposition and Forest Nutrient Cycling. Ecological Studies 91.* Springer-Verlag, New York, 707 pp.

Verburg, P.S.J. and van Breemen, N. Experimental manipulation of a forested catchment: litter decomposition and N mineralisation. *Biogeochemistry*, (in press).

Wilson, E.J. and Emmett, B.A. Factors influencing nitrogen saturation in forest ecosystems: advances in our understanding since the mid 1980's. In: *The Impacts of N Deposition on Natural and Semi-Natural Ecosystems.* (S.J. Langan and M.J. Wilson (Eds.)). Chapman and Hall, (in press).

Wright, R.F., 1998. Effect of increased CO_2 and temperature on runoff chemistry at a forested catchment in southern Norway (CLIMEX project). *Ecosystems*, 1, 216–225.

Wright, R.F., Beier, C. and Cosby, B.J., 1998. Effects of nitrogen deposition and climate change on nitrogen runoff at Norwegian boreal forest catchments: the MERLIN model applied to Risdalsheia, Norway (RAIN and CLIMEX projects). *Hydrol. Earth System Sci.*, 2, 399–414.

Wright, R.F., Cosby, B.J. and Hornberger, G.M., 1991. A regional model of lake acidification in southernmost Norway. *Ambio*, 20, 222–225.

Wright, R.F., Lotse, E. and Semb, A., 1993. RAIN project: results after 8 years of experimentally reduced acid deposition to a whole catchment. *Can. J. Fish. Aquat. Sci.*, 50, 258–268.

Wright, R.F. and van Breemen, N., 1995. The NITREX project: an introduction. *For. Ecol. Manage.*, 71, 1–5.