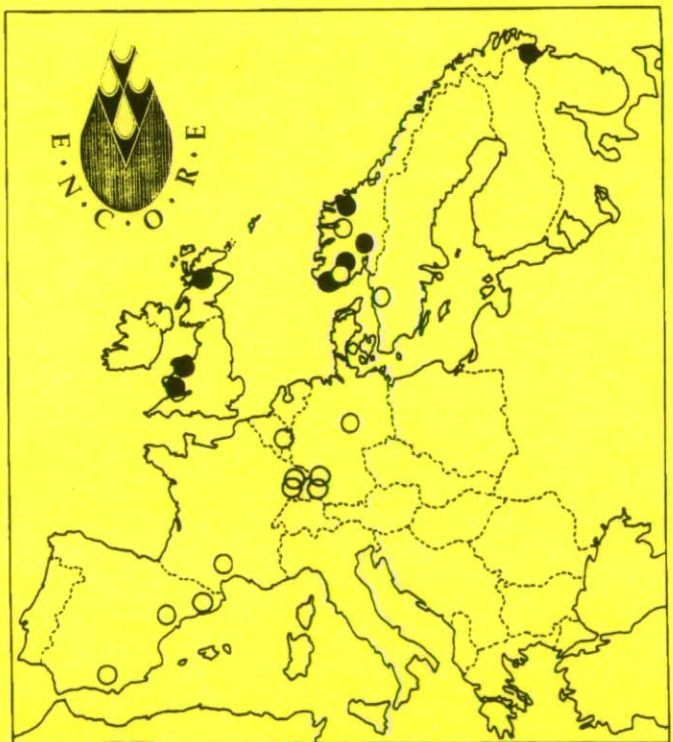


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Acid Rain Research

REPORT 35/1994

**Modelling Long-Term
Hydrochemical
Response at
ENCORE
Catchments in the
UK and Norway**



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Abstract: MAGIC, a catchment-scale model of soil and water acidification, is applied to 10 ENCORE catchments in the UK and Norway and used to examine the dynamic response to several scenarios of future land-use. The model is evaluated against catchment manipulation studies involving acid addition, acid exclusion, terrestrial liming and upland afforestation. Critical loads for sulphur are calculated.

At all sites MAGIC successfully simulates present-day observed stream and soil chemistry. The predicted response of soils and surface waters to the two standard future deposition scenarios is similar at all catchments. All catchments continue to acidify under the worst-case scenario (business as usual) and all catchments recover (or begin recovery) under the best-case scenario. Exceptions are related to situations with concurrent land-use change, or in the case of nitrogen saturation.

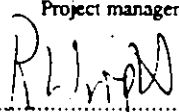
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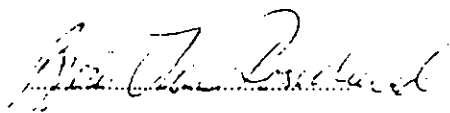
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Modelling long-term hydrochemical response at

ENCORE catchments

in

the UK and Norway

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ABSTRACT

Here we apply MAGIC, a catchment-scale model of soil and water acidification, to 10 ENCORE catchments in the UK and Norway. The model is used to examine the dynamic response to several scenarios of future environmental change including acid deposition and land-use. Critical loads for sulphur are assessed for forest and water at each of the catchments.

Deposition of sulphur is one of the major driving variables within the MAGIC model. The response of catchments to two possible deposition reduction scenarios is assessed. These are; (1) a 55% decrease in sulphur deposition by the year 2006, and (2) a business-as-usual scenario whereby we assume no change in sulphur deposition relative to deposition in 1990.

At all sites MAGIC successfully simulates present-day observed stream and soil chemistry confirming that the model is well suited for application to these types of areas. The predicted response of soils and surface waters to the two standard future deposition scenarios are similar at all catchments. All catchments continue to acidify under the worst-case scenario (business as usual) and all catchments recover (or begin recovery) under the best-case scenario. Exceptions are related to situations with concurrent land-use change, or in the case of nitrogen saturation.

The combined effect of catchment afforestation in the presence of high sulphate deposition loading has been shown to have an extreme acidifying effect on both soils and surface water. This is borne out by the model reconstructions.

Across the range of sulphate deposition loads considered the empirical critical load for water compares favourably with the critical load for water calculated using MAGIC in that both methods generally agree on whether each site is currently in exceedence or not.

Because the deposition of both sulphur and nitrogen compounds contribute to acidification, the critical load must be specified in terms of sulphur and nitrogen deposition. Changes in the fraction of incoming nitrogen retained by the catchment (nitrogen saturation) will also affect critical loads. All three factors must be specified to before critical loads for either S or N (or both) can be quantified.

The model is further evaluated against catchment manipulation studies involving acid addition, acid exclusion, terrestrial liming and upland afforestation.

The success of MAGIC illustrates its robustness and indicates that the major processes included in the model are correctly identified as the major mechanisms controlling catchment chemical response to acidic input.

1. INTRODUCTION

ENCORE (European Network of Catchments Organised for Research on Ecosystems) is an interdisciplinary project focusing on biological and chemical response to environmental change and the links between terrestrial and aquatic ecosystems (Hornung et al. 1990). ENCORE began in July 1991 and is part of the Commission of European Communities STEP

and ENVIRONMENT programmes.

In all, 29 catchments in 7 European countries are included in ENCORE (Figure 1). The sites span natural gradients in climate, vegetation and soils, as well as the present-day gradients of acid deposition and air pollution (Table 1a, 1b and 1c). At each of these catchments data are collected to permit calculation of input-output budgets of major chemical species at the catchment scale.

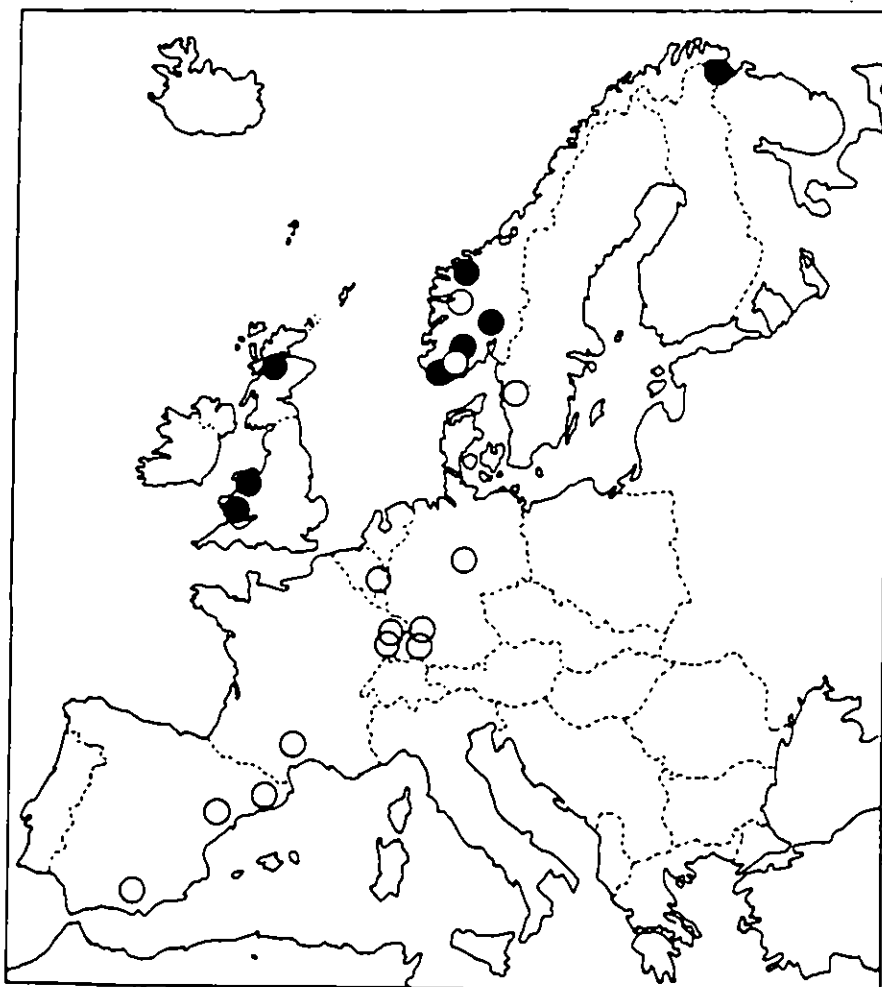


Figure 1. Location of the ENCORE sites. Several sites have more than one catchment. Sites with MAGIC applications included in this report are indicated by solid circles.

Table 1a. Physical characteristics of ENCORE catchments in UK and Norway at which MAGIC was calibrated.

Name	Area km ²	Vegetation	Soil type	Mean soil depth m	Geology
UK catchments					
Allt a Mharcaidh	9.98	grassland	peat, peaty podsol	0.83	biotite granite
Afon Gwy (Plynlimon)	3.88	grassland	peat, brown earth, stagnopodsol, stagnogley	0.81	mudstone, shale, sandstone
Afon Hafren (Plynlimon)	3.7	48% Sitka spruce, 52% grassland	peat, brown earth, stagnopodsol, stagnogley	1.02	mudstone, shale, sandstone
C16 (Llyn Brianne)	0.72	grassland	peat, gley, podsol	1.0	mudstone, shale, sandstone, greywacke
L11 (Llyn Brianne)	2.55	Sitka spruce	peat, gley, podsol	1.0	mudstone, shale, sandstone, greywacke
Norwegian catchments					
Birkenes	0.41	spruce, pine, birch	podsol, brown earth	0.4	biotite granite
Storgama	0.60	sparse pine, birch, heather	podsol, peat	0.32	granite, gneiss
Langtjern	4.56	pine, birch	podsol, peat	0.40	granite, gneiss
Kaarvatn	25	heather	podsol, peat	0.29	granite, gneiss
Dalelva	3.2	birch, heather	podsol, peat	0.46	granite, gneiss

Table 1b. Hydrochemical characteristics of ENCORE catchments in UK and Norway at which MAGIC was calibrated.

Name	Data period	Rainfall mm/yr	SO ₄ * deposition meq/m ² /yr	Cl deposition meq/m ² /yr	Stream pH	Soil base saturation %
UK catchments						
Allt a Mharcaidh	1989	1066	32	110	6.3	4.6
Afon Gwy (Plynlimon)	1989	2500	129	350	4.9	21.0
Afon Hafren (Plynlimon)	1989	2391	126	407	5.0	8.3
C16 (Llyn Brianne)	1989	1765	114	286	5.9	20.9
L11 (Llyn Brianne)	1989	1981	209	428	5.0	27.7
Norwegian catchments						
Birkenes	1973-88	1471	146	146	4.4	17.7
Storgama	1975-88	1009	69	31	4.5	6.9
Langtjern	1975-88	725	44	10	4.6	8.9
Kaarvatn	1978-88	2000	15	93	5.6	16.3
Dalelva	1978-88	770	55	66	5.6	21.1

Table 1c. Data sources for ENCORE catchments in UK and Norway at which MAGIC was calibrated.

Name	Input chemistry	Output chemistry	Soils data
UK catchments			
Allt a Mharcaidh	Ferrier et al. 1990, Warren Spring Laboratory	UK Acid Waters Monitoring Network, Jenkins et al. 1989	Nolan et al. 1985, Jenkins et al. 1989
Afon Gwy (Plynlimon)	Reynolds et al. 1988, 1989	Reynolds et al. 1988, 1989	Reynolds et al. 1988, 1989
Afon Hafren (Plynlimon)	Warren Spring Laboratory	UK Acid Waters Monitoring Network	Reynolds et al. 1988, 1989
C16 (Llyn Brianne)	Warren Spring Laboratory	UK Acid Waters Monitoring Network	Reynolds and Norris 1990
L11 (Llyn Brianne)	Warren Spring Laboratory	UK Acid Waters Monitoring Network	Reynolds and Norris 1990
Norwegian catchments			
Birkenes	Norwegian State Pollution Control Authority (SFT 1990)	Norwegian State Pollution Control Authority (SFT 1990)	A.O. Stuanes (NISK), Reuss 1989
Storgama	Norwegian State Pollution Control Authority (SFT 1990)	Norwegian State Pollution Control Authority (SFT 1990)	A.O. Stuanes (NISK), Reuss 1989
Langtjern	Norwegian State Pollution Control Authority (SFT 1990)	Norwegian State Pollution Control Authority (SFT 1990)	A.O. Stuanes (NISK), Reuss 1989
Kaarvatn	Norwegian State Pollution Control Authority (SFT 1990)	Norwegian State Pollution Control Authority (SFT 1990)	A.O. Stuanes (NISK), Reuss 1989
Dalelva	Norwegian State Pollution Control Authority (SFT 1991)	Norwegian State Pollution Control Authority (SFT 1991)	A.O. Stuanes (NISK), Reuss 1989

In the natural sciences the usual approach is to set up an hypothesis and then design an experiment to test the hypothesis. The ecosystem-scale effects of future environmental changes such as acid deposition and land-use, however, are both long-term and multifarious and thus it is difficult to carry out the appropriate experiments. We are thus forced to use mathematical models to simulate future change. To a large extent such models can also be used to test hypotheses.

Models play a central role in the ENCORE project. Integration and exploitation of the results from catchment studies are achieved by the development of mathematical models. Much of the catchment-based work provides data and information about processes that form the basis for models. Over the past 10 years several catchment-scale models have been developed. These vary in complexity, conceptual basis, and time scale at which they are applied. The models generally fall into one of two categories -- "event" and "long-term" models (Whitehead 1992). Event type models are designed to explain the response of catchments at the hourly-to-daily time scale, while long-term models focus on trends over years-to-decades. Both types of models are necessary to account for biological effects of environmental change in terrestrial and aquatic ecosystems.

MAGIC (Model for Acidification of Groundwater In Catchments) (Cosby 1985a, 1985b) is one of the more-widely used long-term process-oriented models operating at the catchment scale. MAGIC is an intermediate-complexity process-oriented model for constructing acidification history and predicting future acidification over time periods of decades. MAGIC makes use of lumped parameters on a catchment scale and focuses on chemical changes in the soil caused by atmospheric deposition, vegetation, and leaching to runoff.

Here we apply MAGIC to 10 ENCORE catchments in Europe representing a wide range of acid deposition and physical-chemical characteristics. Several of these applications build upon MAGIC calibrations and data previously reported. At these sites the model is used in predictive mode to assess the catchment response to several scenarios of future environmental change including acid deposition in conjunction with land-use and land-use change. Critical loads for sulphur for forest and water are calculated at each of the catchments, and use the model for comparison with empirical calculation techniques and to illustrate the dynamic response to critical loads.

The model is also applied to 4 ENCORE catchments at which ecosystem manipulation experiments have been carried out. These include exclusion of acidic deposition from an impacted site (Risdalsheia, Norway), addition of acid deposition to a pristine site (Sogndal, Norway), terrestrial lime application to remediate acidification (Storgama/Tjønnsstrand, Norway) and catchment scale afforestation (LI8 Lynn Brianne, UK). The model application to the experimental data from these experiments provides a thorough test of the model structure and also provides a robust evaluation.

2. DESCRIPTION OF THE MAGIC MODEL

The MAGIC model combines a number of key soil chemical processes lumped at the catchment scale to simulate soil and surface water chemistry. MAGIC consists of: 1) soil-soil solution equilibria equations in which the chemical composition of soil solution is

assumed to be governed by simultaneous reactions involving sulphate adsorption, cation exchange, dissolution and precipitation of aluminium, and dissolution of inorganic carbon; and 2) mass balance equations in which the fluxes of major ions to and from the soil and surface waters are assumed to be governed by atmospheric inputs, mineral weathering, net uptake in biomass, and loss in runoff (Cosby et al. 1985a, 1985b) (Figure 2).

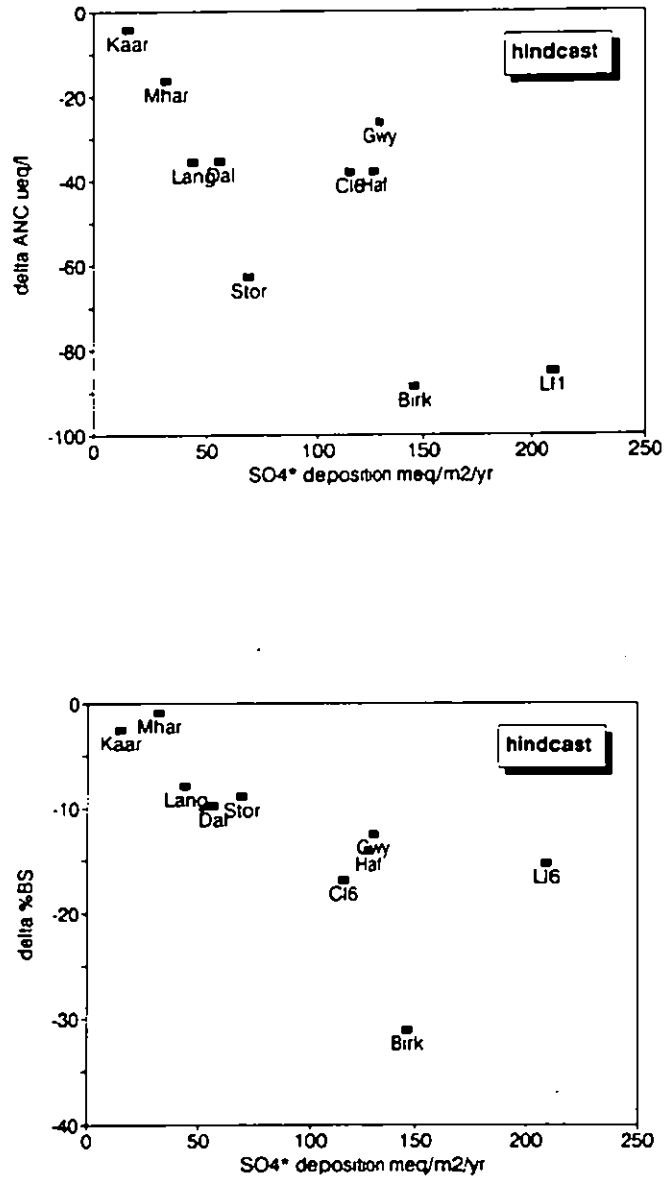


Figure 2. Change in streamwater acid neutralising capacity (ANC) (upper panel) and soil % base saturation (lower panel) from pre-acid deposition (about 1840) to the present as reconstructed by MAGIC, and present-day excess sulphate deposition at 10 ENCORE catchments.

MAGIC has been extensively used in a variety of applications at sites in both North America and Europe. Application of MAGIC to the whole-catchment experimental manipulations of the RAIN project shows that this intermediate-complexity lumped model predicts the response of water and soil acidification to large and rapid changes in acid deposition (Wright et al. 1990a). These results reinforce other evaluations of MAGIC such as comparison with paleolimnological reconstructions of lake acidification (Jenkins et al. 1990a, Neal et al. 1988) and changes in regional lake chemistry in southern Norway (Wright et al. 1991). In addition several of the assumptions in MAGIC have been tested experimentally (Grieve 1989). MAGIC is one of several dynamic models included in the UN-ECE Handbook on Mapping Critical Loads (Sverdrup et al. 1990).

MAGIC uses a lumped approach in two ways: (1) a myriad of chemical and biological processes active in catchments are aggregated into a few readily-described processes, and (2) the spatial heterogeneity of soil properties within the catchment is lumped to one set of soil parameters.

Whereas standard precipitation and throughfall gauges provide adequate estimates of integrated inputs to catchments and the outputs in runoff are integrated at the weir, corresponding estimates of soil parameters characteristic for an entire catchment are more difficult to obtain. Key soil parameters required by the model include depth, bulk density, porosity, cation exchange capacity (measured at soil pH), and the fraction of exchange sites occupied by Ca, Mg, Na, and K. We estimate these from soils data collected annually. Values were aggregated both spatially and with depth at each catchment to obtain single values for each parameter.

In the applications here we use an optimisation procedure to calibrate MAGIC (Jenkins and Cosby 1989). For each catchment we use precipitation data, soil and soil solution data together with estimated acid deposition and net uptake histories to produce a calibrated model (Table 2). The optimisation routine determines the set of initial saturation and weathering rates for each of the 4 base cations for the assumed pre-acidification condition (assumed to be the 1840's). This set of initial values when run forward 140 years in time to the present (1980's) produces the best fit to the present-day measured soil chemistry and runoff chemistry. The calibrated model at each site is then used to predict future soil and water acidification 0-50 years into the future given various deposition and uptake scenarios.

Table 2. Catchment and soil parameters used in application of MAGIC to ENCORE catchments in the UK and Norway.

Parameter	Units	Ailt a Mharcaidh	Afon Gwy (Plynlimon)	Afon Hafren (Plynlimon)	Cl6 (Llyn Brianne)	LJ1 (Llyn Brianne)	Birkenes	Storgama	Langtjern	Kaarvatn	Daletva
area	km ²	9.98	3.88	3.47	0.72	2.55	0.41	0.60	4.56	25.00	3.20
precipitation	mm/yr	1066	2500	2391	1765	1981	1470	1010	725	2000	770
runoff	mm/yr	961	2170	2042	1601	1580	1190	970	605	1830	540
soil depth	m	0.83	0.81	1.02	1.00	1.01	0.40	0.32	0.40	0.29	0.46
porosity	ratio	0.50	0.45	0.45	0.45	0.45	0.50	0.50	0.50	0.50	50.00
bulk density	kg/m ³	924	1073	950	527	991	936	503	828	764	1179
CEC	meq/kg	428	73	115	109	111	46	121	63	91	27
SO4 ads. half-sat.	meq/m ³	1103	151	600	538	400	110	80	100	60	100
SO4 ads. max-cap	meq/kg	2.90	1.00	4.58	4.48	4.00	0.90	1.00	1.00	6.00	1.00
solubility Al(OH) ₃	log	9.05	7.95	9.02	9.05	9.06	8.20	8.10	8.20	8.80	8.10
select. coeff. Al-Ca	log	6.70	1.49	2.53	5.27	-1.04	0.50	0.20	1.40	1.10	3.50
select. coeff. Al-Mg	log	6.70	1.67	4.88	5.33	-0.70	0.60	-0.50	1.60	0.70	5.00
select. coeff. Al-Na	log	2.37	-1.26	-0.20	0.39	-2.72	-1.90	-1.70	-2.20	-0.50	-0.20
select. coeff. Al-K	log	-1.52	-5.97	-3.44	-2.13	-5.14	-5.80	-4.30	-6.00	-5.00	-4.00
total organic C, water	mmol/m ³	12	20	13	20	75	65	90	60	20	60
organic pK1	-log	4.5	4.5	4.5	4.5	4.5	4.5	4.7	4.5	4.0	4.4
organic pK2	-log	10.3	10.3	10.3	10.3	10.3	8.0	8.0	8.0	8.0	8.0
CO2 soil air	atm	.0066	.0120	.0066	.0066	.0150	.0050	.0050	.0050	.0060	.0036
soil temp.	oC	5.0	9.6	5.0	5.0	5.0	5.0	5.0	5.0	6.6	1.0
CO2 stream	atm	.0007	.0012	.0007	.0007	.0007	.0007	.0007	.0007	.0025	.0007
stream temp	oC	5.0	9.6	5.0	5.0	5.0	5.0	5.0	5.0	6.6	2.0

3. CALIBRATION TO ENCORE SITES

MAGIC can be used in predictive mode to assess the water and soil chemistry changes that may occur in response to prescribed changes in the driving variables through time. This predictive capability provides a powerful tool for the formulation and assessment of different management strategies. The management options considered here include changes in atmospheric deposition of sulphur (sulphur emission control), changes in land use, future afforestation policy, and changes in the rate of nitrogen leakage from the terrestrial phase to the aquatic phase of the catchment system. We calibrate MAGIC to 10 ENCORE sites in the UK and Norway and then evaluate the effects of these various scenarios on soil and water acidification.

Increased atmospheric deposition of sulphur, above natural background levels, is responsible for the historical acidification of soils and surface waters in Europe and eastern North America. The recognition of this link between acidic deposition and soil and water acidification has prompted the formulation of deposition reduction strategies in an effort to reverse, or at least halt, the acidification process. Deposition of sulphur is one of the major driving variables within the MAGIC model and here we assess the response of catchments to two possible deposition reduction scenarios. These are; (1) a 55% decrease in sulphur deposition by the year 2006; this scenario represents an optimistic strategy given the rate at which new technology can be implemented to achieve the planned reductions; (2) a business-as-usual scenario whereby we assume no further cuts in sulphur deposition relative to 1990; clearly, this represents a pessimistic strategy. The actual future deposition may be expected to fall somewhere between the two. These applications assume a linear relationship between sulphur emissions and deposition.

Nitrogen deposition is assumed to remain constant into the future for the worst-case scenario and to decrease to 60% of present levels by year 2006 for the best case. This decrease reflects ongoing discussions within UN-ECE extrapolated forward to 2040 at the same rate. We assume that a similar best case is possible for the UK sites, and that there is no change in NH_4 deposition through the forecast period in either of the scenarios.

The major potential land-use change in upland UK catchments is management strategies associated with commercial plantation forestry. Coniferous trees enhance soil and water acidification through three mechanisms; increased ability of the canopy to scavenge acidic compounds, often referred to as occult deposition, uptake of base cations from the soil as the forest grows, and increased water use by the growing forest leading to greater concentration of the chemical throughputs. The effect of these three mechanisms are modelled explicitly within MAGIC by describing historical and future sequences for forest filtering, runoff and uptakes (Cosby et al. 1991).

Land-use scenarios are carried out at LII (Llyn Brienne) and Afon Hafren (Plynlimon) to assess the interaction of the growing forest under different future deposition scenarios. The two deposition strategies are utilised in conjunction with two future forest management scenarios; to replant a felled forest immediately and to leave a felled forest as moorland. In all cases the forest is assumed to follow a 50- year rotation between planting and felling with maturity, and by inference canopy closure, occurring after 15 years. Occult deposition and

evapotranspiration are assumed to increase linearly from planting to maturity. Base cation uptake is assumed to increase to a maximum at 15 years age and then decrease slowly until the stand is felled (Cosby et al. 1991).

Observations from surface waters in Norway indicate that during the past 20 years nitrate concentrations have increased although nitrogen deposition has not changed appreciably (Henriksen et al. 1988). This is potentially the result of nitrogen saturation; the terrestrial ecosystems are retaining less and less of the incoming nitrogen. The reasons for this incipient nitrogen saturation are as yet speculative. Whatever the mechanism, the increased nitrate flux represents a potentially serious acidification factor in ecosystems already heavily impacted through decades of sulphur deposition.

Due to the uncertainty regarding the causes of nitrogen saturation, this process is not explicitly modelled within MAGIC. The net retention of ammonium and nitrate inputs to the catchment system is represented by a first-order uptake coefficient which is adjusted to match observed input and output fluxes. By varying this uptake factor, the effect of nitrate saturation on soils and runoff can be simulated. Here we demonstrate the effect of nitrogen saturation for the catchment at Birkenes, Norway.

Nitrogen saturation is assumed to double every 12 years until nitrate output equals nitrate input. This follows the observed pattern of doubling over the 12-year period 1974 to 1986 observed in the 1000-lake survey (Henriksen et al. 1988). The retention of ammonium is assumed unchanged at 95%.

3.1. THE CATCHMENTS

Allt a Mharcaidh

Allt a Mharcaidh is an unacidified upland moorland site in the Cairngorm Mountains of Scotland, UK. Total sulphur deposition is relatively low and there is less of a sea-salt influence than at the other UK sites considered in this report. The catchment area comprises a Site of Special Scientific Interest within the Cairngorm National Nature Reserve and land-use is confined to deer grazing. The site was identified as a 'transitional' catchment in 1985 for the Surface Waters Acidification Programme and hydrochemical monitoring has continued since that date. The stream is essentially unacidified but is characterised by severe acid pulses associated with rainstorms and snowmelt and as such was chosen to represent a site which might become chronically acidified with continued or higher acidic deposition. Future sampling at this site will continue until least 1995 under the UK Acid Waters Monitoring Network.

MAGIC has previously been applied to Allt a Mharcaidh to assess model sensitivity to soil physical and chemical parameters (Jenkins et al. 1988). Sulphate adsorption characteristics were identified as being important with respect to long-term. A subsequent calibration was carried out to assess the impact of including two-layer soil representation and flow routing upon the long-term predictions (Jenkins and Cosby 1990). The results of this analysis show that long-term stream chemistry response is unaffected by this refinement but soil chemistry, particularly the upper layer, may become more acidic in the long term. Here we have completely re-calibrated MAGIC using multiple optimisation techniques and more recent

chemistry data. A single soil layer was employed although it is clear that at this site at least two layers would improve estimates of soil critical loads and calibration to a monthly or weekly time-step might provide a useful basis for assessing short-term responses.

Afon Gwy (Plynlimon)

Afon Gwy is an acidified upland moorland catchment at Plynlimon in central Wales, UK. The area receives substantial sulphur input, much of which is associated with neutral sea-salt. The catchment supports rough sheep grazing throughout the year and cattle grazing in the lower portion in summer. The stream has been monitored by the Institute of Hydrology since the early 1970's as part of a major study into the water resources impacts of upland afforestation. Chemical sampling commenced in the mid 1980's and will continue until at least 1995 within the framework of the UK Acid Waters Monitoring Network.

The MAGIC model has previously been applied to this site in an attempt to assess the hydrochemical impact of afforestation (Whitehead et al. 1988) although using only a crude representation of the forest effects. Here we have completely re-calibrated MAGIC using multiple optimisation techniques and more recent chemistry data. Problems were encountered in matching observed stream nitrate concentrations since these are appreciably higher than observed nitrate concentrations in wet deposition. The source of the additional nitrate may be gaseous and dry deposition, but may also reflect nitrate generation through soil mineralisation. High concentrations have also been found in shallow soil lysimeters (Reynolds et al. 1989). Since MAGIC utilises only a simple first order uptake to relate nitrate input and output flux, for this application additional nitrate was added to the soil to enable a match with observed stream flux.

Data from this site has recently be used in an attempt to link long and short term hydrochemical responses by linking MAGIC with an end-member mixing model (Robson et al. 1991, Neal et al 1992).

Afon Hafren (Plynlimon)

Afon Hafren is an acidic forested catchment at Plynlimon in upland Wales, UK. The large fluxes of sea-salt derived ions and excess sulphate are due to the high rainfall and the enhancement deposition associated with the forestry. Planting of conifers took place over 50% of the catchment area in two phases; between 1948 and 1950 and between 1963 and 1964. The other fifty percent of the catchment is utilised for rough sheep grazing and prior to afforestation the catchment was entirely exploited as upland sheepwalk. The stream has been monitored by the Institute of Hydrology since the early 1970's as part of a major study into the water resources impacts of upland afforestation. Chemical sampling commenced in the mid 1980's and will continue until at least 1995 within the framework of the UK Acid Waters Monitoring Network.

An earlier version of the MAGIC model has been previously applied at this site to assess the impact of upland afforestation (Neal et al. 1986, Whitehead et al. 1988) incorporating only increased occult deposition as the major forestry driven process. Here we have completely recalibrated MAGIC using more recent chemistry data, multiple optimisation techniques and explicitly incorporating the ion uptake, pollutant filtering and increased water use of the

growing forest. The mid-years of the planting periods were taken to simplify the designation of uptake, hydrology and deposition sequences.

CI6 (Llyn Brianne)

CI6 is an unacidified moorland catchment at Llyn Brianne the Cambrian Mountains of mid-Wales. The catchment has a long history of utilisation for rough sheep grazing. Monitoring of the stream commenced in the early 1980's as part of the Llyn Brianne Acid Waters Study within which scheme this site represented the unacidic moorland control. This programme was completed in 1990 and only monthly chemical sampling is currently undertaken.

MAGIC has been previously applied to this site to assess the effect of upland afforestation (Whitehead et al 1988) although increased occult deposition was the only forest process considered. Here we have completely recalibrated MAGIC using multiple optimisation techniques and more recent chemistry data.

LII (Llyn Brianne)

LII is an acidified forested catchment at Llyn Brianne in the Cambrian Mountains of mid-Wales. Conifers were planted between 1961 and 1963 to cover the entire catchment area. Prior to afforestation the catchment was under moorland vegetation and land use comprised rough sheep grazing. Monitoring of the stream commenced in the early 1980's as part of the Llyn Brianne Acid Waters Study within which scheme this site represented an acidic mature forest control. This programme was completed in 1990 and monthly chemical sampling is currently undertaken in conjunction with continuous flow measurement using a steep stream flume.

MAGIC has been previously applied to this site to assess the effect of upland afforestation (Whitehead et al. 1988) although increased occult deposition was the only forest process considered. Further analysis of forestry impacts was carried out using the modified model incorporating changes in deposition, hydrology and uptake as the forest grows and utilising multiple optimisation techniques (Waters and Jenkins 1992). The results presented here utilise the calibrated model from this latter application.

Birkenes

The Birkenes catchment lies in the region of southern Norway receiving the highest loading of acid deposition. Runoff is acidified with annual volume-weighted pH levels of 4.4 and high concentrations of inorganic aluminium. The stream at Birkenes supported brown trout until about 1950.

Birkenes has been a calibrated catchment and research site since the early 1970's, with continuous monitoring of air, precipitation and runoff. Birkenes has been included in several national and international monitoring networks. It is also the site of several detailed studies of soil chemistry and hydrology.

MAGIC has previously been calibrated to Birkenes and used to estimate critical loads for the catchment (Wright et al. 1990). We use this calibration here in conjunction with several acid

deposition scenarios and to explore the interaction between critical loads for sulphur, nitrogen and nitrogen saturation.

Storgama

Storgama is an acidified catchment receiving moderate amounts (for Norway) of acid deposition. The site is located at about 600 meters above sealevel in sparse and unproductive forests and moorlands. Brown trout populations in lakes in the regions were lost in the 1950's.

Storgama has been a calibrated research site since 1974 and included in the Norwegian national environmental monitoring program since 1980. An adjacent catchment, Tjønnsstrond, is the object of a whole-catchment liming experiment carried out in 1983, with subsequent monitoring of runoff chemistry and the restocked fish population.

MAGIC has previously been calibrated to Storgama and used to estimate critical loads for the catchment (Wright et al. 1990). These are used in this calibration in conjunction with several acid deposition scenarios.

Langtjern

Langtjern is an acidified lake receiving moderate amounts (for Norway) of acid deposition. The lake is typical of inland forest lakes in southern Norway. It is 0.25 km² in area, mean depth of about 3 m and water-retention time of only 2-3 months. Brown trout population in the lake was lost in the 1960's due to recruitment failure. The lake is marginally acidic (pH 4.7).

Langtjern has been a calibrated research site since 1974 and included in the Norwegian national environmental monitoring programme since 1980. Monitoring points for runoff include the 2 major inflowing streams and the outlet of the lake. Due to the short-water retention time, the chemistry of the outflow water is very similar to that of the inflow water.

MAGIC has previously been calibrated to Langtjern (outlet) and used to estimate critical loads (Wright et al. 1990). We use this calibration here in conjunction with several acid deposition scenarios.

Kaarvatn

Kaarvatn is a pristine but acid-sensitive catchment receiving only negligible amounts (for Norway) of acid deposition. The site is located in the mountains of west-central Norway. Lakes and streams in the area support healthy brown trout populations.

Kaarvatn has been a calibrated research site since 1978 and included in the Norwegian national environmental monitoring programme since 1980.

MAGIC has previously been calibrated to Kaarvatn and used to estimate critical loads for the catchment (Wright et al. 1990). We use this calibration here in conjunction with several acid deposition scenarios.

Dalelva

Dalelva is an acid-sensitive catchment receiving only moderate amounts (for Norway) of acid deposition. The site is located in northernmost Norway only 30 km from the major copper-nickel smelters in Nikel, Russia. Here emissions of SO₂ began in the late 1930's and peaked in 1980 at about 400 000 tons SO₂/yr. Most of the acid input at Dalelva is thus as dry-deposition of SO₂ gas.

The chemical composition of runoff at the weir indicates water quality on the verge of becoming acidic. Lakes in the headwaters regions of the Dalelva catchment are already chronically acidic with pH < 5 and have damaged fish populations.

Dalelva has been a calibrated research site since 1989 and is included in the Norwegian national environmental monitoring programme.

MAGIC has previously been calibrated to Dalelva and used to estimate critical loads for the catchment (Wright and Traaen 1992). We use this calibration here in conjunction with several acid deposition scenarios.

3.2 Discussion -- MAGIC calibrations

The present state of acidification of soils and surface waters is the result of many decades of acid deposition. The response and rate of response of terrestrial and aquatic ecosystems to these acid inputs depend on many factors including intrinsic properties such as soil thickness and mineralogy, local factors such as forest harvesting, and of course the amount and history of acid deposition. Similarly the degree and rate recovery of acidified systems following reduction in acid deposition will vary from catchment to catchment.

At all sites the model successfully simulates present-day observed stream and soil chemistry confirming that the model is well suited for application to these types of areas. The sites included represent mainly cool, temperate climates and are characterised by acidic soils overlaying slowly weathering bedrock which consequently, has little acid buffering capacity. Excess sulphate deposition covers a wide range from 15 to 209 meq/m²/yr across all the sites. Chloride deposition also varies considerably between the sites from 10 to 428 meq/m²/yr (Table 1), the highest levels being in the UK sites where sea-salts dominate the input flux. Organic acid concentrations vary by a factor of 10 across all the sites studied. Mean soil depth at the UK sites is generally about double (c. 1m) the Norwegian sites and in most cases, particularly the Welsh sites, have greater rainfall inputs. This is reflected in the relatively high excess sulphate deposition loads at the UK sites.

The success of the model across this range of conditions illustrates its robustness and indicates that the major processes included in the model are correctly identified as the major mechanisms controlling catchment chemical response to acidic input.

The effect of anthropogenic sulphate deposition on soil and water acidification is well illustrated by the model reconstructions at the 10 sites (Table 3, Figure 3). As expected, the

Table 3. Results of MAGIC calibration to ENCORE catchments.

Parameter	Units	Alit a Mharcaidh	Afon Gwy (Plynlimon)	Afon Hafren (Plynlimon)	C16 (Llyn Brienne)	L11 (Llyn Brienne)	Birke- nes	Stor- gama	Lang- gjern	Kaar- vatn	Datelva
Soil 1983/4											
Ca	%	1.6	5.8	3.7	7.8	11.7	9.1	3.3	3.7	5.9	11.7
Mg	%	1.2	7.5	0.9	7.3	8.2	4.0	2.2	1.6	5.3	3.6
Na	%	0.8	3.7	2.3	4.1	6.6	1.6	0.7	1.0	0.8	3.3
K	%	1.1	4.0	1.4	1.7	1.2	2.8	0.7	2.6	1.8	2.5
total BS	%	4.6	21.0	8.3	20.9	27.7	17.5	6.9	8.9	13.8	21.1
Soil 1844											
Ca	%	1.9	9.5	8.8	14.9	18.6	26.3	9.0	8.8	7.2	15.8
Mg	%	1.4	12.9	5.8	14.1	12.9	14.7	4.4	3.3	6.3	7.2
Na	%	1.0	6.4	5.2	6.6	8.9	3.8	1.0	1.9	0.9	5.4
K	%	1.2	4.2	2.6	2.2	2.6	3.8	1.1	2.8	1.9	2.7
total BS	%	5.6	33.8	22.4	37.8	43.0	48.6	15.5	16.8	16.3	31.1
Weathering											
Ca	meq/m ² /yr	22.2	20.9	5.9	79.8	5.5	12.4	10.4	12.0	23.2	9.3
Mg	meq/m ² /yr	1.5	3.2	57.2	41.9	0.0	0.4	0.3	2.3	2.9	10.7
Na	meq/m ² /yr	38.9	8.7	30.6	28.9	41.2	5.9	0.0	6.5	8.0	7.8
K	meq/m ² /yr	4.6	0.0	6.8	7.1	0.0	1.0	0.0	0.0	2.2	0.9
total	meq/m ² /yr	67.2	44.7	100.5	157.7	46.7	19.7	10.7	20.8	36.3	28.7
Deposition											
Ca*	meq/m ² /yr	4.0	11.0	12.0	9.0	49.0	16.8	10.0	6.5	7.3	8.1
Mg*	meq/m ² /yr	0.0	-2.0	-2.0	0.0	0.0	0.0	0.5	0.9	0.2	3.3
Na*	meq/m ² /yr	-1.0	-19.0	-13.0	-1.0	-17.0	2.2	2.0	0.0	0.0	0.0
K*	meq/m ² /yr	1.0	0.0	2.0	1.0	9.0	7.6	2.8	3.3	1.6	0.0
total BC*	meq/m ² /yr	4.0	-10.0	-1.0	9.0	41.0	26.6	15.3	10.7	9.1	11.4
BC* weath.+ dep	meq/m ² /yr	-71.2	34.7	99.5	166.7	95.7	46.3	26.0	31.5	45.4	40.1
SO ₄ * deposition change BS	meq/m ² /yr %	32.0 -1	129.0 -12.8	126.0 -14.1	114.0 -16.9	209.0 -15.3	146.0 -31.1	69.0 -8.6	44.0 -7.9	15.0 -2.5	55.0 -10

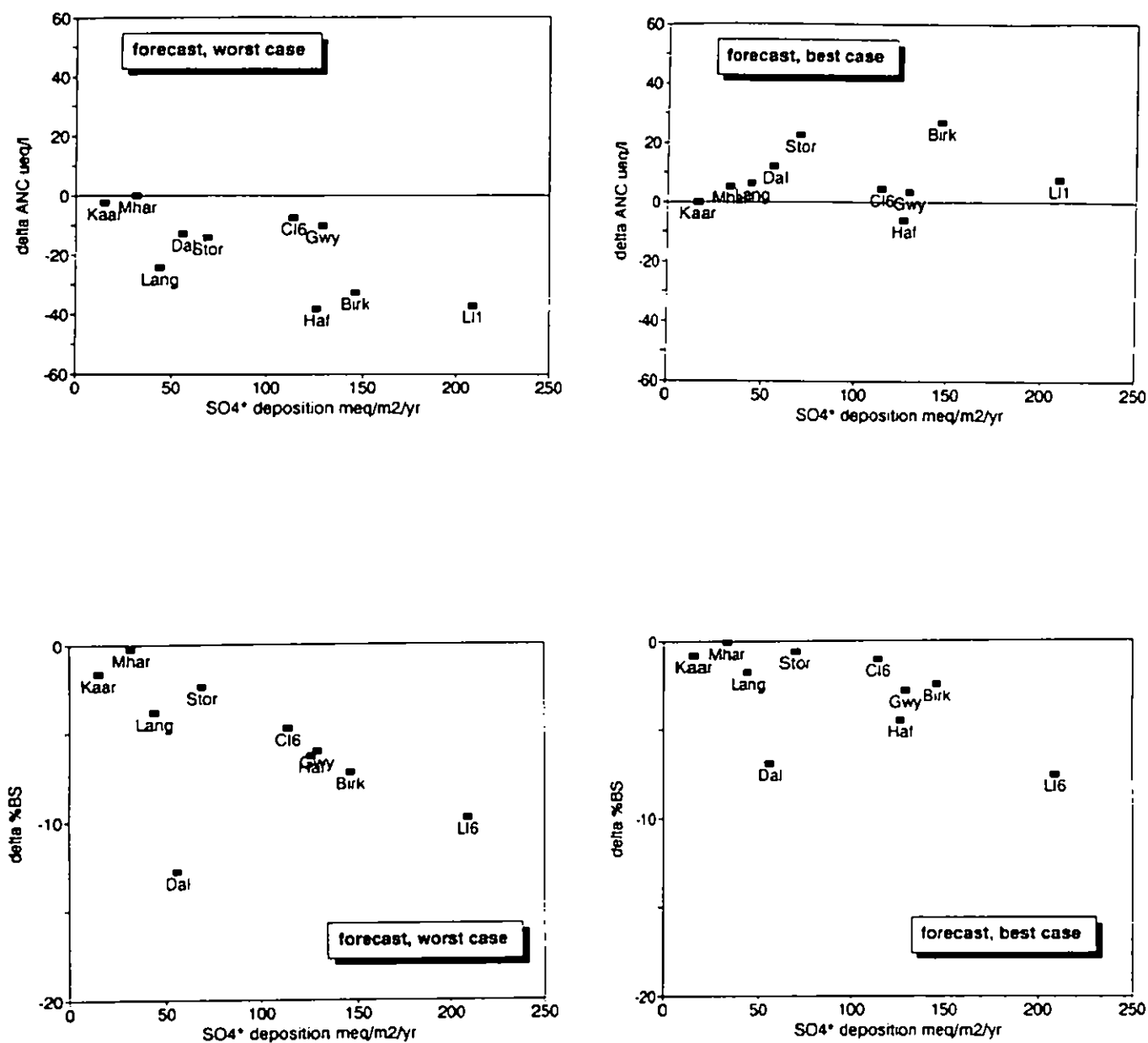


Figure 3. Predicted changes in streamwater acid neutralising capacity (ANC) (upper panels) and soil % base saturation (lower panels) from present-day to 50 years in the future under worst case (left-hand panels) and best case (right-hand panels) sulphur deposition scenarios.

sites which receive the highest sulphate load have suffered the greatest loss of soil base saturation and surface water alkalinity and vice versa. This cause and effect relationship is, however, far from linear since the degree of acidification at any site depends crucially upon other catchment physicochemical parameters. These include soil sulphate adsorption capability, soil depth, soil type and flux of base cation weathering.

The model calibrations yield estimates for cation-exchange selectivity coefficients and base cation weathering rates (Tables 2 and 3). Both these sets of parameters are obtained by the optimising routine used in the calibrations of MAGIC. The cation-exchange selectivity coefficients vary by several log units among sites; this range is well-within that reported from field and laboratory measurements in soils and also are similar to values obtained from MAGIC application to other sites in Europe and North America.

The weathering rates estimated by the MAGIC calibrations are similar among sites. These sites are all characterised by soils derived mainly from crystalline parent material and are highly-resistant to chemical weathering. Within this narrow range the sites with thicker soils have higher weathering rates.

All the MAGIC applications here use a one-layer version of the model. This assumes that the catchment soil is uniform both spatially and vertically across the catchment. To achieve a model calibration, soil chemical and physical parameters are weighted to give mean values for the catchment. It is further assumed that all of the rainfall passes through this soil layer, except that which falls directly onto lake surfaces, and there is no flow routing represented in the model structures. Clearly, this is the most simplified representation of the catchment system. Previous modelling work, however, has indicated that the incorporation of additional soil layers and flow routing do not greatly influence the model predictions (Jenkins and Cosby 1990) since the model output describes annual average ionic concentrations. The model makes no attempt to infer short-term event in hydrochemistry; this would require a considerably shorter time step and more detailed physical representation of the catchment.

Model Predictions under standard scenarios

The predicted response of soils and surface waters to the 2 standard future deposition scenarios are similar at all catchments (Figure 3). All catchments continue to acidify under the worst case scenario (business as usual) and all catchments recover (or begin recovery) under the best case scenario.

Of the catchments investigated here Birkenes appears to have experienced the largest changes in ANC over the past, and the MAGIC predictions indicate that Birkenes will also exhibit the greatest response in the future. By contrast, Allt A Mharcaidh with its relatively thick soils and very low present-day sulphur deposition, has changed the least and is predicted to change little in the future under these 2 acid deposition scenarios.

Critical Loads Assessment

The concept of critical load is now widely used as a basis for decisions regarding future emissions of acidifying gases. Critical load for soil is of interest because soil acidification

affects biological organisms in terrestrial ecosystems (for example, trees). Negative effects in forest ecosystems include shortage of mineral nutrients, nutrient imbalance, and high concentrations of toxic aluminium compounds in soil solution (Nilsson and Grennfelt 1988).

Procedures for determination of critical load for a given ecosystem or region entails the use of models. Two types of models are available: steady-state and empirical models, and dynamic process-oriented models (Sverdrup et al., 1990). Much of the mapping work carried out to date is based on steady-state and empirical models (Henriksen et al. 1992). Although these models provide regional estimate of critical loads, they do not take into account the time aspect of acidification and recovery of terrestrial and aquatic ecosystems.

Criteria for "unacceptable change" are set in relation to effects on terrestrial and aquatic organisms. By itself soil is inanimate and the term "damaged" soil has no meaning. With respect to damage to terrestrial vegetation commonly used criteria include the concentration of inorganic aluminium in soil solution and the ionic ratio of aluminium to calcium in soil solution (de Vries 1988, Sverdrup et al. 1989), where the soil solution in rooting depth (0-50 cm) is of primary interest. With respect to aquatic organisms commonly used criteria are that the alkalinity of runoff water should have positive alkalinity and concentration of labile inorganic aluminium less than 50 $\mu\text{g/l}$ (Nilsson and Grennfelt 1988, Henriksen and Brakke 1988).

The dynamic aspects of acidification and the implications for critical and critical loads can only be assessed by using dynamic models such as MAGIC. Data for both water and soil chemistry at a catchment scale are used to derive estimates of soil acidification characteristic of the entire catchment. Critical loads are estimated by means of MAGIC and the empirical model of Henriksen et al. (1992) and are evaluated with respect to criteria for adverse effects to both soils and surface waters.

The critical loads for the 10 ENCORE catchments are calculated using MAGIC under the condition that deposition is suddenly changed to a new level and then held constant for 50 years. MAGIC is run repeatedly with different levels of deposition until the criterion of ANC (acid neutralising capacity) = 0 $\mu\text{eq/l}$ (fish) or $\text{Al/Ca} = 1.5$ (forest) is met. This deposition is the critical load for sulphur. For all cases it is assumed that the loading and retention of nitrogen compounds are not changed from present-day conditions.

The empirical model for calculating critical loads for waters is based on present-day water and precipitation chemistry (Henriksen et al. 1992). It is static in that it specifies the water chemistry resulting from a given change in deposition without specifying the time at which this new water chemistry will exist. The model thus does not provide information as to length of time required to achieve steady-state following change in acid deposition. A summary of the calculations for each catchment is given in Table 4.

Across the range of sulphate deposition loads considered the empirical critical load for water compares favourably with the critical load for water calculated using MAGIC in that both methods generally agree on whether each site is currently in exceedence or not (Figure 4). The absolute values at each site, however, show some differences. At the Afon Gwy the empirical critical load is significantly higher than the MAGIC critical load whilst at Allt a Mharcaidh the opposite occurs. The deep soils at the Allt a Mharcaidh are capable of

Table 4 . Calculation of critical load (fish) by the empirical model with variable F-factor. Units: $\mu\text{eq/l}$. Source (Henriksen et al. 1988).

	Allt a Mhar.	Afon Gwy	Afon Hafren	Cl16 (Llyn Brianne)	L11 (Llyn Brianne)	Birkenes	Storgama	Langtjern	Kaarvatn	Dalelva
runoff	0.96	2.17	2.04	1.6	1.58	1.19	0.97	0.61	1.83	0.54
SBC 1985	224	241	308	343	413	212	80	98	85	299
Cl 1985	115	161	199	179	271	123	32	17	51	123
SO4 1985	48	72	77	91	152	134	74	75	16	159
ANC 1985	59	-8	15	68	-25	-55	-37	5	18	14
SBC* 1985	96	62	87	144	112	75	44	79	28	162
F-factor	0.37	0.24	0.34	0.54	0.43	0.29	0.17	0.31	0.11	0.60
SO4*	36	55	57	73	124	121	71	73	11	146
critical load condition										
required	-59	8	-15	-68	25	55	37	-5	-18	-14
change										
F-factor	0.37	0.24	0.34	0.54	0.43	0.29	0.17	0.31	0.11	0.60
Δ SO4*	-94	11	-23	-147	44	78	45	-7	-20	-35
Δ SO4*	130	45	79	219	80	44	26	80	31	181
critical conc. SO4*										
critical load SO4*	125	97	161	351	127	52	25	49	57	98
meq/m ² /yr										
Cl deposition 1985	110	349	406	286	428	146	31	10	93	66

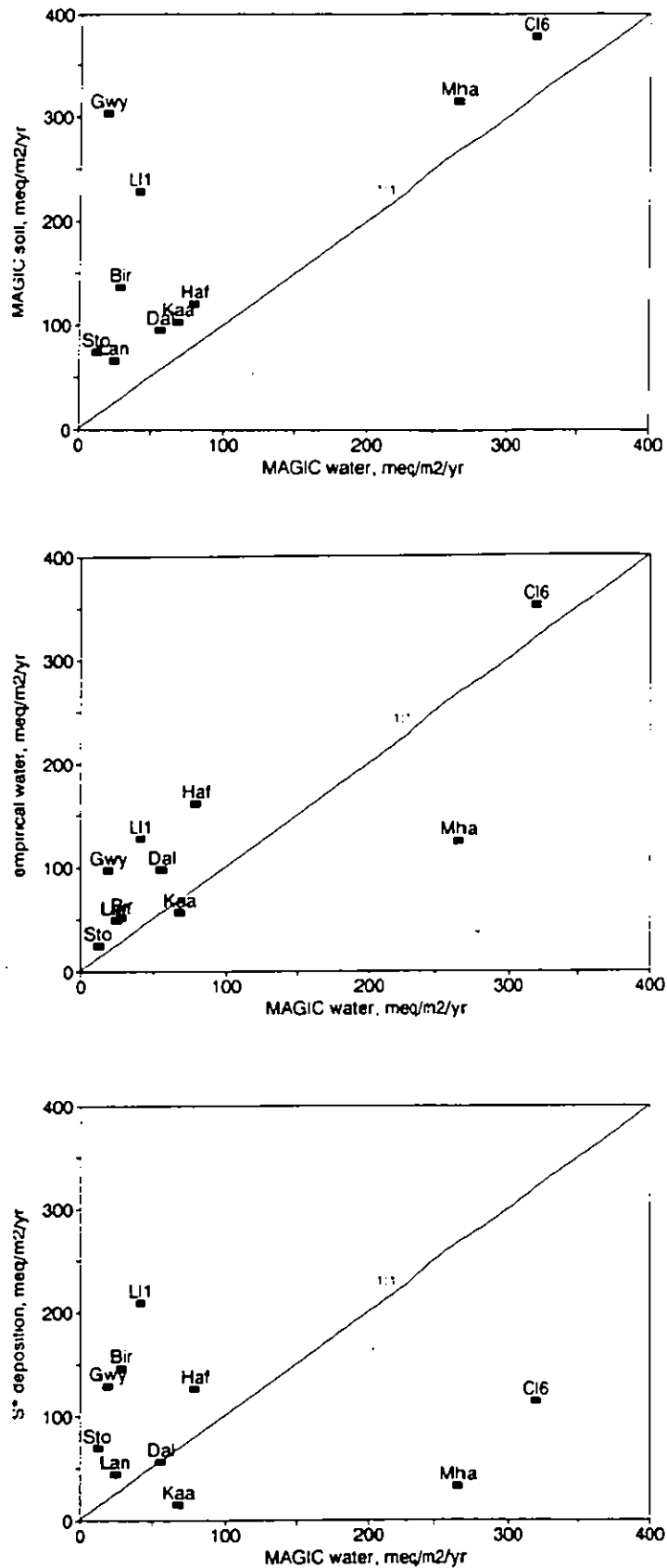


Figure 4. Critical loads for soils and waters at 10 ENCORE catchments calculated by MAGIC and by the empirical static method of Henriksen et al. (1992). Upper panel: critical loads for soils as compared to critical load for waters, both calculated by MAGIC. At all catchments soils are less sensitive (higher critical loads) than waters given the criteria used. Middle panel: critical loads for waters calculated by the empirical method and by MAGIC. The dynamic method gives somewhat lower critical loads at most sites. Lower panel: sulphur deposition and critical loads for waters. At catchments above the 1:1 line deposition exceeds the critical load.

buffering acidic input for the 50 year period used to determine the MAGIC critical load and since the empirical calculation assumes equilibrium conditions, the critical load is lower. The only Norwegian site as yet unaffected by acidic deposition is Kaarvatn where again the MAGIC critical load is higher than the empirical critical load.

At all other sites, the empirical critical load is approximately twice the MAGIC critical load (Figure 4). This discrepancy is entirely expected and consistent with the problems of considering static and dynamic calculation techniques. The MAGIC model incorporates soil recovery in response to decreased sulphate input and this causes a slower recovery and so over a 50 year period a lower load is required.

The purpose of determining critical loads is to set goals for future deposition rate of acidifying compounds such that the environment is protected. Critical loads are determined separately for forests, soils, and surface waters and will differ between these three categories for a given area as well from site-to-site depending upon the inherent sensitivity of the natural environment. The critical load for soils is effectively defined with respect to both waters and forests. In practice, then, at a given site the critical load for forests may be greater or lower than the critical load for water. Because the goal is to protect the whole environment the critical load thus becomes the lesser of these critical loads. In other words if the waters are inherently more sensitive than the forests, the critical load for waters will be lower than that for forests and for the environment as a whole the critical load thus becomes the critical load for waters.

For forests only the soil down through the rooting zone is of interest (for coniferous forests commonly 0-50 cm). Here the critical load for forests may be lower than the critical load for waters because runoff derives from the entire soil column including the commonly more alkaline deeper soil water. Comparison of critical loads calculated using MAGIC shows that for soil to be consistently higher than that for water. It must be remembered, however, that the critical load required to protect the top 50 cm of the soil column would be lower than that tolerated by the whole soil depth, assuming soils acidify from the top down. It is feasible that the critical loads for a thin upper soil layer could be lower than water critical loads at some sites.

Afforestation scenarios

The combined effect of catchment afforestation in the presence of high sulphate deposition loading has been shown to have an extreme acidifying effect on both soils and surface water. This is borne out by the model reconstructions at the Hafren and LII sites in Wales and supports earlier MAGIC applications to forested sites in Scotland (Cosby et al 1990, Jenkins et al 1990b).

Future response at these sites depends on both the assumed sulphate deposition scenario and the forest management policy. At both sites, the effect of the combined worst/best case sulphate deposition and cut/replant strategies interact such that the business as usual and replanting following forest harvesting scenarios produce a further pronounced decrease in streamwater alkalinity and soil base saturation (Figure 5). On the other hand, the best case sulphate deposition and cut with no replanting scenarios produce a marked recovery in stream

alkalinity and a stabilisation of soil base saturation over the 50-year forecast period (Figure 5).

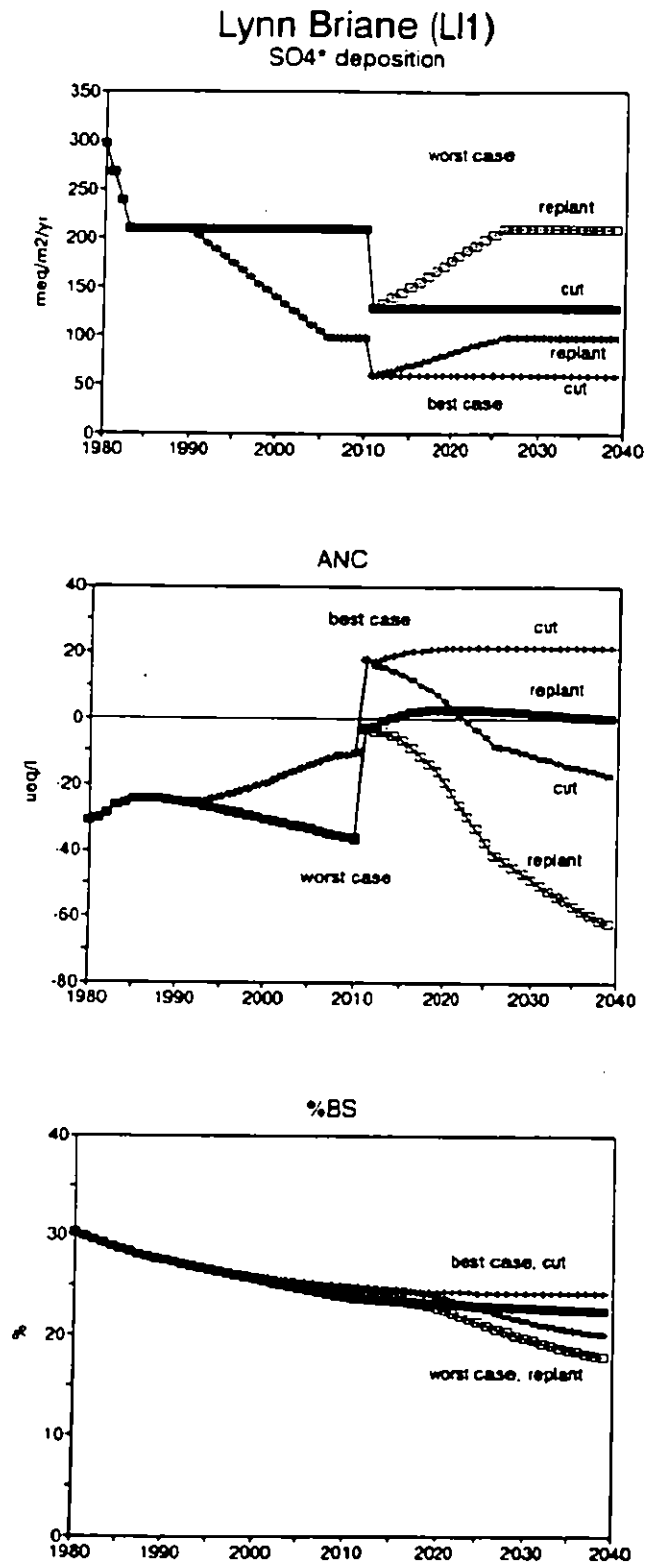


Figure 5. Prediction of future changes in streamwater ANC and soil base saturation at catchment LI1 (Llyn Brianne) under 4 scenarios of combined acid deposition and forest management. Acidification of waters and soils is most extreme under the scenario of constant sulphur deposition (worst case) and replanting after forest harvest (replant).

Future sulphate deposition reduction strategies must be formulated with land management strategies in mind. In the calculation and assessment of critical loads for forested sites, therefore, it is important to consider future forest management. At LI1 the empirical critical load is significantly higher than the MAGIC critical load assuming that all forest area in each catchment is felled at age 50 years and immediately replanted over the same area. This gives a 'steady-state' forestry option for critical load calculation using MAGIC. No such future land use considerations can be incorporated in the empirical model. If the extreme alternative land use strategy is adopted, that is, to cut the forest at age 50 years and not replant then the derived critical load is much higher.

Modelling N saturation

Because the deposition of both sulphur and nitrogen compounds contribute to acidification, the critical load must be specified in terms of sulphur and nitrogen deposition. The relative effects of sulphur and nitrogen deposition depend on several factors including (1) the type of receptor ecosystem in question (forest, soil or surface water), (2) the sensitivity of the ecosystem to acidification, and (3) in the case of forest and soil the land-use history.

In general the effects of sulphur and nitrogen deposition are additive but not necessarily linear; the critical load for sulphur is thus lower if the ecosystem also receives acid inputs from nitrogen. The response of ecosystems to acidic inputs as either sulphur and nitrogen is dynamic over time. Damage increases with time in ecosystems receiving constant acid deposition; recovery following reductions in deposition may not proceed at the same rate as acidification.

The ability of catchments to retain incoming nitrogen is a further factor influencing the critical load. Indications of incipient nitrogen saturation in Norway, such as the increase in nitrate concentrations in lakes in southernmost Norway over the period 1974 to 1986 (Henriksen et al. 1988), suggest that nitrate may play a larger role in the future. MAGIC provides a tool for the evaluation of the relative roles of sulphur deposition, nitrogen deposition, and nitrogen retention by the catchment. We illustrate these relationships at the Birkenes catchment.

The critical load for sulphur at Birkenes using MAGIC, the fish criterion of ANC = 0, and target year 50 years in the future (year 2038) is 39 meq/m²/yr (Figure 6), under the assumptions that nitrate deposition remains constant and that the % nitrogen retained by the catchment also remains constant. If, however, the % nitrate retained decreases from present-day levels of 90% to only 50% in the future, then the catchment will tolerate less sulphur; the critical load is now only about 30 meq/m²/yr. And with 0% retention of nitrate, critical load for sulphur will be about 0, if nitrate deposition is at present-day levels (Figure 6). Thus all 3 factors must be specified to before critical loads for either S or N (or both) can be quantified.

In order for a 'true' nitrogen critical load to be determined for surface waters and soils, however, a more detailed consideration of the terrestrial N cycle than is currently incorporated in MAGIC requires development. Such a model will need to include specific representation of the processes which determine the build up of N saturation in response to N deposition levels. These are essentially mineralisation of organic nitrogen, nitrification,

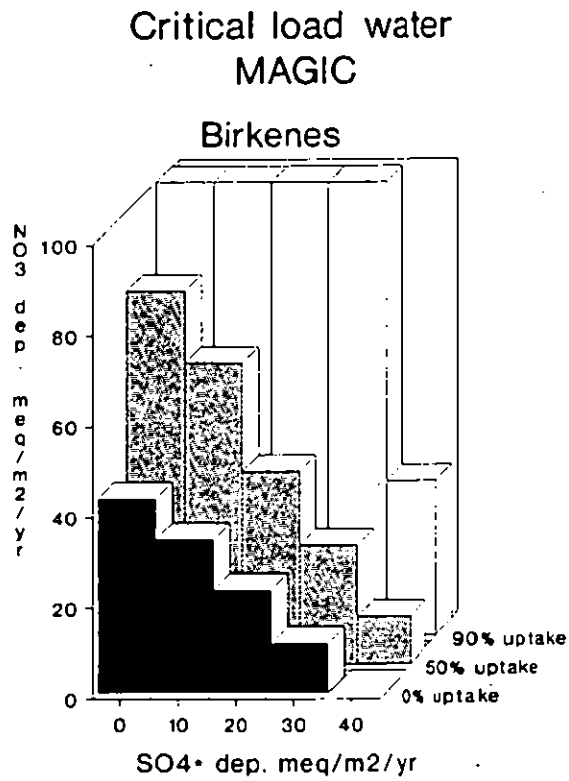


Figure 6. Critical load for water at Birkenes calculated by MAGIC. Shown are critical load for sulphur alone (x-axis), nitrate alone (y-axis) under 3 different scenarios of nitrogen retention in the catchment. Present-day SO_4^{\bullet} deposition is $146 \text{ meq/m}^2/\text{yr}$; NO_3 deposition is $96 \text{ meq/m}^2/\text{yr}$; nitrogen retention is 90%.

immobilisation and plant uptake. When this is achieved the linking of the two models could enable an assessment of total acidity critical loads as well as the implications of sulphur deposition damaging vegetation and thereby changing the nitrogen uptake characteristics leading to enhanced nitrate leaching.

4. MODEL EVALUATION AT MANIPULATED CATCHMENTS

Of prime importance to any discussion relating to limitation of anthropogenic pollutant emissions is the question of the expected improvement that potentially expensive reduction strategies will have on the environment. In terms of acid deposition, the key questions are; what degree of recovery in acidified surface waters and soils can be expected in heavily impacted areas, and how long will the recovery take. To assess different deposition scenarios, and scenarios for other factors which affect acidification response such as land use, it is necessary to construct and apply mathematical models of ecosystem response to pollutant input. In order that we can have confidence in the results of model predictions, however, it is necessary to validate the model against observed data. Clearly, for acidification, a problem which has built up over long time periods of the order of decades, such independent data is unavailable for validation and in any case since deposition reduction strategies have only recently started to take effect there is little, if any, direct evidence of ecosystem recovery or reversibility. Acidification models, therefore, have mainly been validated against data from sites where the acidification process is well advanced or against independent diatom evidence (Jenkins et al. 1990a).

To redress this problem a unique opportunity exists to validate long-term hydrochemical models against data from large scale ecosystem manipulation studies. Studies have been undertaken to decrease acid input to systems, to increase acid input to systems, to add lime to systems for acidity regulation and to plant forests on catchments. This latter category are not set up as manipulation experiments per se but are conventional commercial land management procedure for many upland areas throughout Europe. These manipulations, especially the acidification/deacidification, are necessarily intensive treatments. That is, in order to observe a response over a very short timescale (years) acid doses need to be high and acid input reductions need to be extreme. Such experiments provide a rigorous test for model structures which must be capable of capturing the observed responses if they are to be used more generally for scenario assessment.

Here we evaluate MAGIC by means of data from whole-catchment manipulations at 4 ENCORE sites: deacidification or reversibility (Risalsheia, Norway), acidification (Sogndal, Norway), terrestrial lime application (Storgama/Tjonnstrand, Norway) and afforestation (L18 Llyn Brianne, UK).

4.1. RISDALSHEIA -- experimental acid exclusion

Risalsheia, southernmost Norway, is the site of a large-scale manipulation experiment in which acid deposition is excluded from an entire headwater catchment. Incoming acid precipitation is intercepted by a 1200-m² transparent roof, cleaned by filtering and ion-exchange, natural levels of sea-salts re-added, and sprinkled beneath the roof. The experiment is part of the RAIN project (Reversing Acidification In Norway) and began in 1983 with treatment beginning June 1984. A total of 9 years of treatment data are available (Wright et

al. 1993).

Risdalsheia is located only 20 km from the south coast near Grimstad. The site is at 200 m above sea-level and is characterised by thin and patchy soils, granitic bedrock with glacial overburden of similar mineralogy, sparse and unproductive forests dominated by pine and birch, and abundant wetlands and lakes. The area receives high loading of acid deposition and surface waters in the region are acidic and most lost their native fish populations prior to the 1960's.

The RAIN experiment involves 3 catchments: KIM (850 m²) is covered by roof and receives clean rain; EGIL (400 m²) is covered by roof and receives recycled ambient rain; ROLF (220 m²) has no roof and receives ambient rain. Comparison of EGIL with ROLF allow assessment of a roof effect, while comparison of KIM with EGIL allows assessment of the effect of changing acid deposition.

Application of MAGIC to the catchments at Risdalsheia followed the same procedure as that for Sogndal. The model was first calibrated to the entire 8-years of data from the untreated control catchment (ROLF), and then run with only few changes in parameter values on the manipulated catchments KIM (roof, clean rain) and EGIL (roof, acid rain). Details are given by Cosby et al. (in review).

For the KIM catchment, the decline in excess sulphate and nitrate from acid exclusion is readily apparent in the time series of treatment and control data (Figure 7). The base cation concentrations also decline under the roof (Figure 7) but not as steeply as the acid anions. The differential response of acidic anions and base cations results in an increase in ANC under the treatment roof. While there is some indication that aluminium concentrations are declining in KIM, the pH is not changing appreciably probably due to organic acid buffering. In general, the KIM catchment shows a pronounced de-acidification response to acid exclusion.

The model closely simulates these treatment responses. The trends in the de-acidification responses are well matched, and while the model does not reproduce exactly the year-to-year variation, it does remarkably well in the overall trend. This smoothing of the treatment response is expected from an aggregated model like MAGIC.

The residuals emphasise the differences between simulation and observation. The absolute changes are much larger than these differences. For example, the changes over 8-years in concentrations of excess sulphate and base cations are about 50 µeq/L. ANC increases by about 25 µeq/L. The residual errors for these variables were less than 6 µeq/L. The model matched both trends well. The residuals indicate primarily the inability of the model to match the year-to-year noise around a well-represented trend.

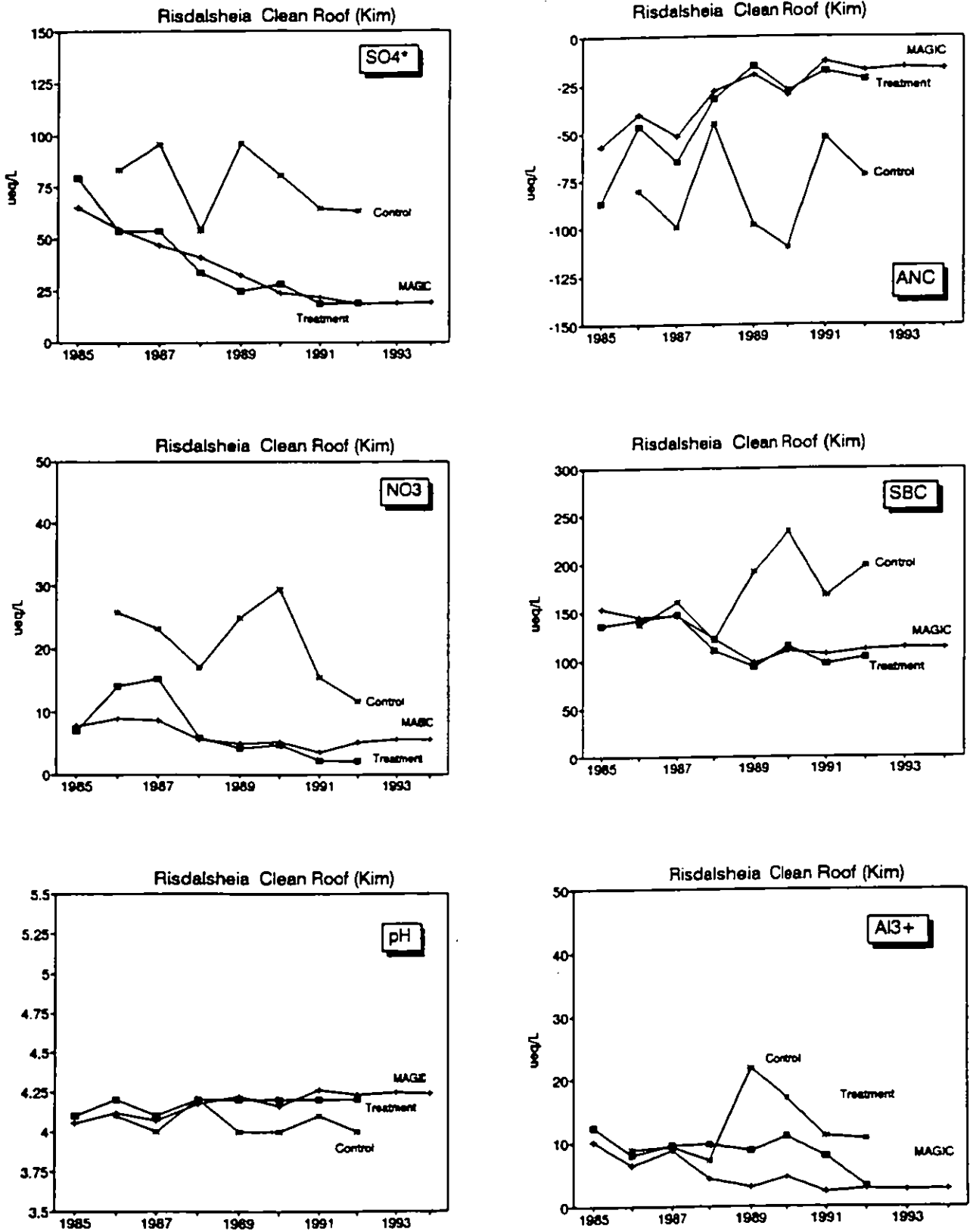


Figure 7. Time series of simulated and observed volume-weighted annual average concentrations of selected variables in runoff at KIM catchment (roof, clean rain) at Risdalsheia, Norway. The observed values of the control catchment (ROLF) are also shown.

4.2. SOGNDAL -- experimental acid addition

Sogndal, west-central Norway, is the site of a large-scale manipulation experiment in which acid is added to 2 entire headwater catchments. Acid is sprayed onto the snowpack in late winter and added in 5 portions of 11 mm water by means of commercial irrigation sprinkling system in the summer. The acid is added at pH 3.2. Total acid added is 100 meq/m²/yr. The experiment is part of the RAIN project (Reversing Acidification In Norway) and began in 1983 with treatment beginning November 1983. A total of 9 years of treatment data are available (Wright et al. 1994).

The Sogndal site is at 900 m above sea-level and is characterised by thin and patchy soils, gneissic bedrock with glacial overburden of similar mineralogy, alpine vegetation dominated by heather and blueberry, and abundant wetlands and lakes. The area is nearly pristine and receives very low loadings of acid deposition. Surface waters in the region support brown trout.

The RAIN experiment at Sogndal involves 4 catchments: SOG2 (7220 m²) receives 100 meq/m²/yr sulphuric acid; SOG4 (1940 m²) receives 100 meq/m²/yr of 1:1 mixture of sulphuric and nitric acids; SOG1 (93000 m²) and SOG3 (38000 m²) receive ambient rain.

The RAIN experiment provides a unique opportunity for evaluation of MAGIC model, in that the change in acid deposition is large, rapid and carefully measured. The resulting changes in runoff chemistry can be thus compared to changes predicted by MAGIC.

MAGIC was first calibrated to the 8-year volume-weighted mean concentrations in the control stream. This procedure calls for a 140-year simulation of soil and water chemistry from 1844 to 1984 (the last pre-treatment year). The deposition used to drive the model for this long-term simulation begins with estimated background levels of deposition and increased to the observed 8-year mean wet deposition at the site. Additional inputs of sea salt and an additional dry input of sulphate, nitrate, hydrogen ion and ammonium were added to the measured wet deposition by assuming input-output mass balance for chloride and sulphate over the 8-year period in the control catchment.

Organic acids are represented in MAGIC by a triprotic acid analogue. The total concentration of organic acid is based on a charge density and the observed DOC in streamwater. The charge density is a calibrated parameter selected such that the simulated and observed concentrations of organic anions in discharge agree.

A 1-box version of MAGIC was used with the soil variable being geometric means of all samples taken at the site. Uptake of nitrate and ammonia were adjusted such that the 1984 simulated outputs matched the observed. Weathering rates and initial (historical) base saturation of the soils were then adjusted until the simulated streamwater concentrations of base cations matched the observed and the present-day soil base saturation for each of the 4 cations also matched.

These simulations were performed using the inputs and parameters for the control catchment applied unaltered to the treatment catchment with three exceptions: a) deposition levels were

reduced or increased to match observed at the manipulated catchment; b) the nitrogen uptake dynamics were modified to match those observed in the manipulated catchments; and c) the amount of organic acid was adjusted using observed data on anion charge deficit in the manipulated catchments.

Adjustment of nitrogen dynamics is necessary because there is no process-basis for nitrogen retention in MAGIC that will allow the uptake rate to vary as a function of external or internal conditions. Adjustment of organic acid dynamics is necessary because there is no process basis for organic dynamics in MAGIC other than changes in speciation of the fixed amount of organic acid specified for the simulations. The catchments had different anion deficits. Some of the difference might have resulted from the treatments; some may simply be the result of heterogeneity in these small catchments. The different anion deficits that were observed among the catchments were incorporated by calibrating the organic acid charge density at each catchment.

For SOG2 catchment (sulphuric acid addition) the increase in non-marine sulphate due to acid addition is readily apparent and well simulated by MAGIC (Figure 8). This increase is accompanied by a modest increase in concentrations of base cations, but mainly a decrease in acid neutralising capacity (ANC). The acid addition results in long-term chronic acidification of streamwater (Wright et al. 1994).

As the catchment acidifies, concentrations of inorganic aluminium in runoff rise sharply (Figure 8). The observed decline in pH is not as pronounced as the simulated response, perhaps because of buffering by natural organic acids.

Overall MAGIC simulates these responses very closely. The trends are well matched and while the model does not reproduce the year-to-year variations, it does remarkably well with the overall trends. This smoothing of the response is expected from an aggregated model such as MAGIC.

4.3. TJØNNSTROND - whole-catchment liming

Tjønnstrond is the site of a whole-catchment liming experiment carried out in June 1983, with subsequent monitoring of runoff chemistry and the restocked fish population. The catchment is adjacent to the ENCORE catchment at Storgama, Norway, which has been a calibrated research site since 1974 and included in the Norwegian national environmental monitoring program since 1980 (SFT 1993). The site is located at about 600 meters above sea-level in sparse and unproductive forests and moorlands. Brown trout populations in lakes in the regions were lost in the 1950's. The region receives moderate amounts (for Norway) of acid (non-marine sulphate deposition 69 meq/m²/yr.). Prior to treatment the streams at both Tjønnstrond and Storgama were highly acidified with pH about 4.5.

The Tjønnstrond catchment consists of two small ponds of 3.0 and 1.5 ha in area which drain a terrestrial catchment of 25 ha. The ponds are shallow (mean depth 1 m) and have short water retention time (about 2 months). Traditional lake liming at this site was thus impractical, and the site was chosen for an experimental terrestrial liming, as part of the Norwegian Liming Project.

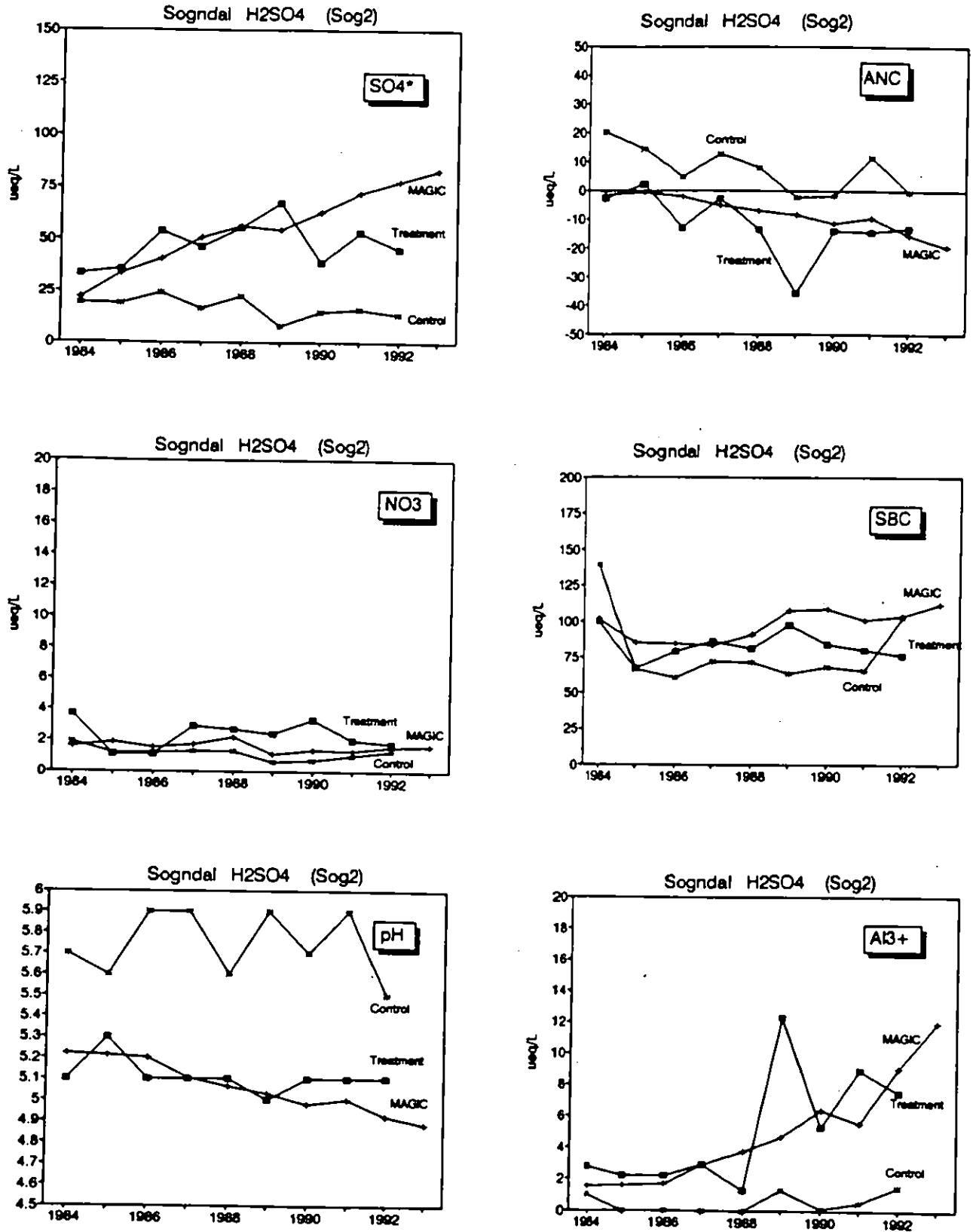


Figure 8. Time series of simulated and observed volume-weighted annual average concentrations of selected variables in runoff at SOG2 catchment (sulphuric acid addition) at Sogndal, Norway. The observed values of the control catchment (SOG1) are also shown.

In June 1983 73 metric tons of powdered limestone were spread by helicopter to the terrestrial area. No limestone was added to the ponds themselves. The dose of 3 ton/ha corresponds to 934 kg Ca/ha. The liming and hydrochemical response are described by Traaen (1990). Subsequent stocking of brown trout was also successful.

MAGIC has previously been calibrated to Storgama and used to estimate critical loads for the catchment (Wright et al. 1990). That calibration was based on soils data from Storgama collected in 1983. In 1992 the soils of both Tjønnsstrond and Storgama were re-sampled by the Norwegian Forest Research Institute (NISK, T.Frogner pers. comm.). We use these to recalibrate MAGIC, and to evaluate the usefulness of MAGIC in simulating the changes in soil and water chemistry as a result of the terrestrial liming.

MAGIC was first calibrated using the 3-year mean input-output data from Storgama for the period 1981-83. This procedure calls for a 140-year reconstruction of soil and water chemistry from 1842-1982 with changes driven by estimated long-term changes in acid deposition. A 2-box version of MAGIC was used, with the upper box corresponding to the organic A horizon (15 cm thickness) and the lower box corresponding to the aggregated B and C horizons (total 17 cm thickness). No flow routing was used; all water was assumed to move from through the upper soil and lower soil boxes. In the model the limestone was added to the upper soil box and fully dissolved during the year 1983. The carbonate added with the Ca was simulated in MAGIC by increasing the CO₂ partial pressure in soil air. Nitrate retention was decreased in the model for the first 2 years after liming.

The model was then run for a 9-year post-liming period from 1983 to 1992. Observed precipitation and runoff volume and deposition chemistry data from the 9 year period 1983-92 were used to drive the model.

Liming caused large and immediate changes in surface water chemistry at Tjønnsstrond. pH increased from 4.5 to 7.0, Ca increased from 40 to 200 µeq/l, ANC increased from -30 to +70 µeq/l, and reactive-Al decreased from about 200 to 100 µg/l (Traaen 1990). During the subsequent 9 years the chemical composition of runoff has decreased gradually back towards the acidic pre-treatment situation. The chemistry in 1992, however, is still of adequate quality to permit fish survival.

The Ca flux data and the 1992 soils data indicate that of the 4670 meq/m² Ca added, about 3500 meq/m² is in the soil on as exchangeable Ca, 690 meq/m² has been lost in runoff and the remainder of 500 meq/m² unaccounted for. The fraction on the soils is obtained by comparing the 1992 exchangeable Ca on the soils at Storgama with that on the soils at Tjønnsstrond. Because of large spatial variations in soil chemistry within each catchment, however, these estimates are uncertain.

MAGIC is able to simulate these major changes in soil and surface water chemistry. The changes in Ca, ANC, pH, Al and NO₃ observed in the first year following liming as well as the subsequent 9-year gradual re-acidification are all reproduced by MAGIC (Figure 9). Neither the measured data nor the MAGIC simulations indicate significant changes in any other major ion as a result of liming.

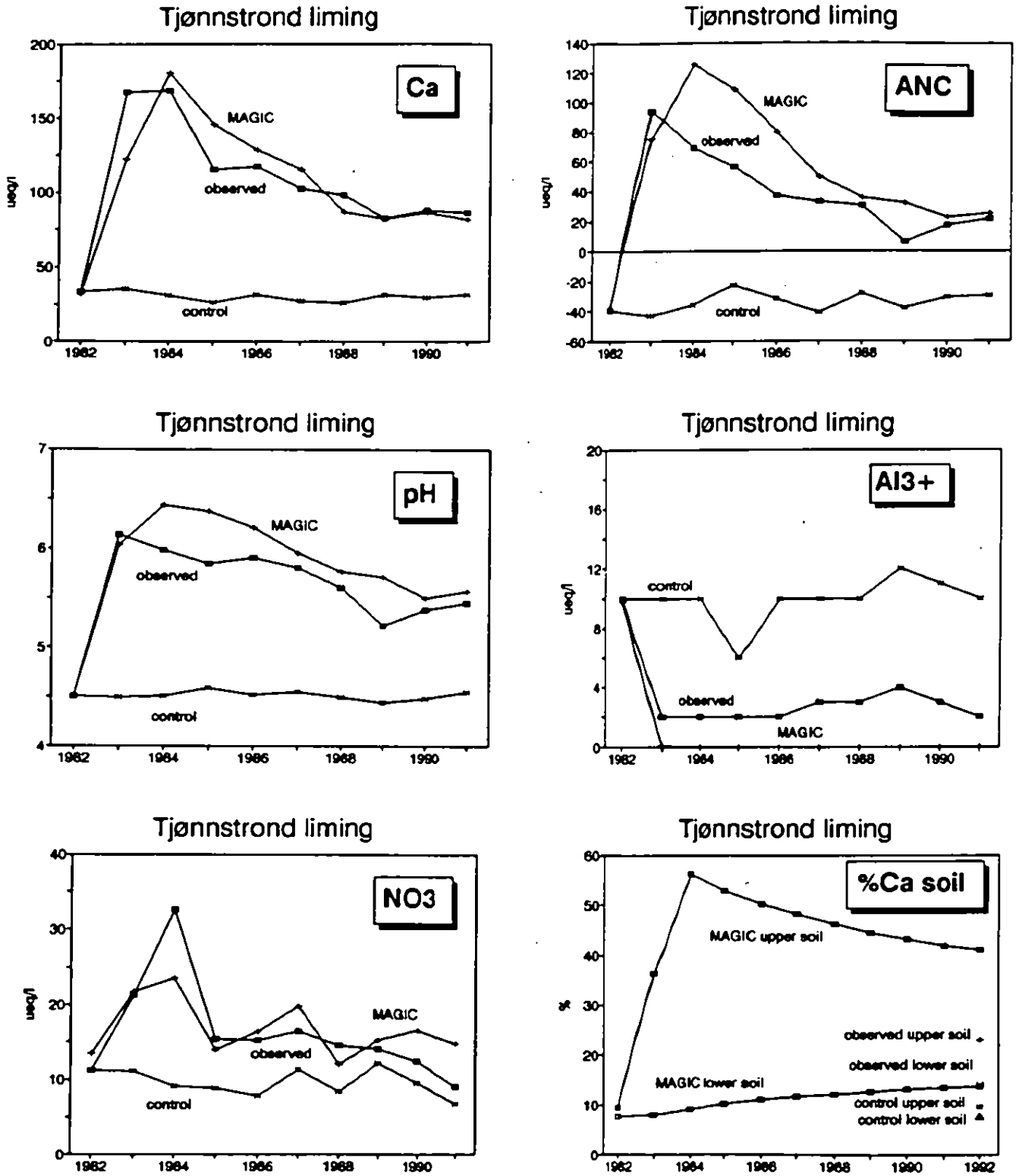


Figure 9. Measured and predicted annual volume-weighted concentrations of Ca, ANC (acid neutralising capacity), pH, inorganic Al, and NO₃ and Ca saturation in upper and lower soil at Tjønnsstrond (limed) and Storgama (untreated control). Tjønnsstrond was limed in June 1983. Observed data are from Traaen (1990) and Traaen (pers. comm.).

Cation exchange is a key process in MAGIC. Conceptually the model is set up to account for the changes caused by the liming as follows. The limestone added at Tjønnsstrond was assumed to dissolve completely within the first year with the Ca in the limestone assumed to participate fully in ion-exchange reactions with the uppermost 15 cm of soil. This would effectively raise the Ca saturation of the surface soil from about 10% to about 57% (Figure 9). During the following years the upper soil gives off Ca to soil solution. This Ca-rich solution then moves down through the lower soil where a portion of the Ca is removed from solution by ion-exchange with the more-acid soil. The net effect is to move Ca from the upper to lower soil, as well as result in elevated Ca concentrations in runoff. These are indeed the effects observed in the Tjønnsstrond liming.

That none of the other base cations (Na, K, Mg, NH_4) exhibits large changes after liming is due to the fact that although the high Ca concentrations in soil solution should displace these cations from the soil, the relative fraction of Ca on the soil has increased greatly at the expense of the acid cations, primarily Al. These offset each other such that no large changes in concentrations in other base cations are predicted by MAGIC, and indeed no changes are observed in the data.

4.4. LI8 (LLYN BRIANNE) -- Afforestation

LI8 is a recently afforested catchment at Llyn Brianne in the Cambrian Mountains of mid-Wales, UK. Monitoring of the stream commenced in the early 1980's as part of the Llyn Brianne Acid Waters Study within which scheme this site was utilised to assess the impact of afforestation on streamwater chemistry. This programme was completed in 1990 and only monthly chemical sampling is currently undertaken by the UK National Rivers Authority, Welsh Region.

MAGIC has been previously applied to this site to assess the effect of upland afforestation (Waters and Jenkins 1992). This application utilises a complete recalibration of the model based on the observed time series of water and rainfall chemistry for the period 1982 - 1992.

Forest was planted over the entire catchment area in two phases. During 1971 most of the lower catchment slopes were planted and in 1977 the upper slopes were completed. Trees were planted at 2m spacing. by 1992, canopy closure was complete on the lower slopes but not on the upper slopes. Consequently, ground flora remains on the upper slopes and provides an important source for acid neutralisation. Chemical monitoring began in 1982 by which time the forest was well established on the lower slopes (11 years old) and only 5 years old on the upper slopes. Canopy closure occurred at about 15 years age (1986) on the lower slopes and is still incomplete on the upper slopes.

The model was calibrated to observed stream chemistry data for 1989 using observed rain chemistry data for the same year. Soils physical and chemical data was collected in 1987 (Reynolds et al. 1988, Reynolds and Norris 1990) and characteristics for the three dominant soil types, valley bottom peats, ferric stagnopodsols and brown podsolics, were lumped to produce a single soil layer in the model. Forest uptake, deposition enhancement and runoff changes for the growing forest were assumed to be linear interpolations from time of planting to canopy closure (Cosby et al. 1991). The calibration, therefore, necessarily incorporates

some of the early forestry impact at the site. Addition of fertilisers during site preparation and planting phases is only implicitly included since the impact of these soil dressings on soil and water chemistry will be incorporated in the observations over the entire period.

Measured wet deposition used for the calibration was supplemented with sea-salts and SO_4 from dry deposition and from scavenging or filtering by the forest canopy. On the basis of Cl conservativity the extra deposition required to match the output flux for 1989 was calculated. This was partitioned between dry deposition and canopy filtering using the same dry deposition factor (c. 1.35) as was required at the moorland site nearby (CI5). The remaining input was ascribed to canopy filtering and this was assumed to increase linearly from the time of planting to canopy closure 20 years later (approximately present day). The calibrated model was then run using measured deposition from 1986 - 1990 using identical dry deposition factors for all ions and the assumed linear increase in canopy filtering. No attempt was made to calibrate the input fluxes for each year on the basis of output flux of any ion and so this application represents a true test (blind validation) of the assumptions used in previous applications (Cosby et al. 1991) relating to canopy filtering.

Uptake of ions by the growing forest are absolute fluxes specified as a function of forest age (Cosby et al. 1991) and evapotranspiration is assumed to increase from 10% prior to planting to 24% to match observed water fluxes in 1989.

From 1982 to 1992 a significant change in surface water chemistry is observed compared to the grazed moorland control catchment CI4 (Figure 10). Na and Cl concentrations show a consistent increase from 1982 - 92 indicating increased sea-salt inputs generally across the region. pH has decreased over the period from about 5.4 to 5.1. No other monitored site in the area shows a similar decrease in pH. That this is not reflected in the data collected at nearby control catchments (forest and moorland) indicates that the changes observed are not attributable to increased atmospheric deposition but to the growing forest.

The model simulates the observed changes in stream chemistry (Figure 10). The predicted gradual decline in pH closely matches the observed trend although the modelled decrease is smoother than observations. The observed increase in Na and Cl is equally well matched despite a large annual variability in sea-salt inputs to the site. Predicted and observed stream SO_4 concentrations are must be interpreted in the light of the lack of data with which to calibrate the SO_4 adsorption characteristics of the soil. Nevertheless, predicted concentrations are close to observed and the increase in concentration since 1986 is well matched by the model.

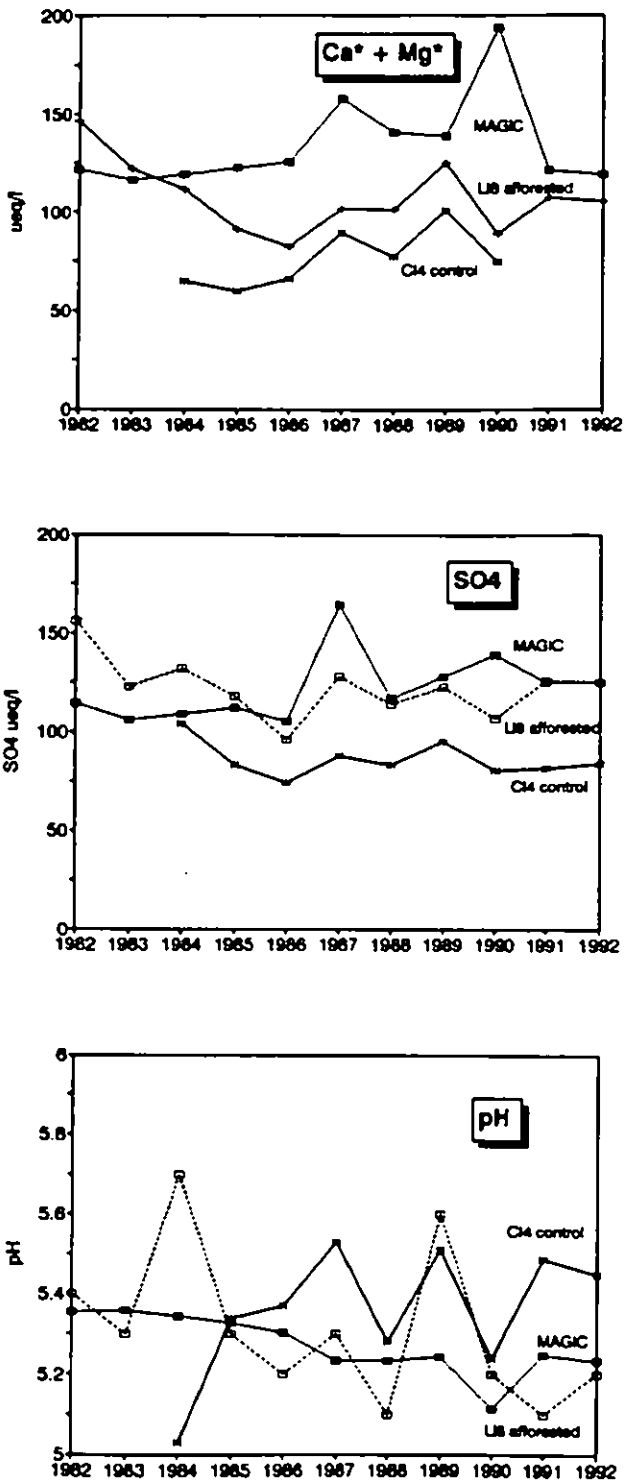


Figure 10. Measured and predicted annual volume-weighted concentrations of excess calcium and magnesium ($\text{Ca}^{2+} + \text{Mg}^{2+}$), SO_4 , and pH in streamwater at catchment LI8 (afforested) and CI4 (grazed moorland control) at Llyn Brianne, Wales, UK.

4.5. Discussion - manipulation experiments

The applications of MAGIC to the paired-watershed manipulation experiments at the Risdalsheia and Sogndal sites in Norway indicate that the MAGIC model is well suited for predicting acidification and de-acidification responses of catchments subjected to changing acidic deposition. The analyses indicate that there are some shortcomings in the model in simulating year-to-year variability and aluminium dynamics which probably arise from the aggregated structure of the model and from biases between treatment and control catchment data. In general, however, the model successfully reproduced significant and important responses at both sites.

MAGIC accounts for both the immediate and long-term trends in soil and runoff chemistry following liming at Tjønnsstrond. Several important parameters, however, must be determined first. Among these are the fraction of limestone assumed to dissolve, the partial pressure of CO₂ in soil air to simulate the bicarbonate generated by dissolution of the limestone, and the increase in mineralization of N following liming. These parameters are difficult to predict for terrestrial liming, as there have been only a few large-scale terrestrial liming experiments in which effects on surface waters are included. MAGIC offers a useful tool in accounting for the major changes in surface water chemistry following whole-catchment liming.

The MAGIC application at LI8 represents an important evaluation of the assumptions incorporated in the model regarding afforestation impacts on hydrochemistry. Most importantly it appears that the changes in interaction between the forest and acid deposition during the life of the forest is adequately represented within the model structure. Assumed change in hydrological response, as increased evapotranspiration, follow a similar shape to canopy closure and the 1992 values are in line with measured differences between mature forest and moorland catchments in other nearby areas (cf Plynlimon, Afon Hafren and Afon Gwy). Nutrient uptake is assumed to increase linearly to a peak at canopy closure and decrease thereafter at a rate which slows through time. These key sequences are extremely simplified but enable the model to simulate and predict afforestation impacts on soil and water chemistry.

Although MAGIC successfully simulated the major overall response at these 4 sites, this does not imply that the model is "validated" or "verified". Indeed models of environmental systems probably cannot be validated (Oreskes et al., 1994). In every model evaluation there are *a priori* expectations that the model will fail in some ways. Models are, after all, imperfect representations of complex systems and are usually built because we have imperfect knowledge of the systems. Therefore, the purpose of model evaluations is not to establish the realism of a model nor to reject the model as unrealistic. Rather, model evaluations such as we present here should strive to provide increased awareness of the weakest elements which hopefully will lead to improvements not only in the model structure but also in understanding of the system.

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6. REFERENCES

- Cosby, B.J., Homberger, G.M., Wright, R.F. and Galloway, J.N, 1985a. Modelling the effects of acid deposition: assessment of a lumped parameter model of soil water and streamwater chemistry. *Water Resour. Res.*, 21: 51-63.
- Cosby, B.J., Jenkins, A., Miller, J.D., Ferrier, R.C. and Walker, T.A.B, 1990. Modelling stream acidification in afforested catchments: long-term reconstructions at two sites in central Scotland. *J. Hydrol.*, 120: 143-162.
- Cosby, B.J., Wright, R.F. and Gjessing, E.T. In review. An acidification model (MAGIC) with organic acids evaluated using whole-catchment manipulations in Norway. *J. Hydrol.*
- Cosby, B.J., Wright, R.F., Homberger, 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. *Water Resour. Res.*, 21: 1591-1601.
- Ferrier, R.C., Jenkins, A., Walker, T.A.B., and Anderson, H.A. 1990. Assessment of wet deposition mechanisms in an upland Scottish catchment. *J. Hydrol.* 113: 285-296.
- Grennfelt, P. and Hultberg, H. 1986. Effects of nitrogen deposition on the acidification of terrestrial and aquatic ecosystems. *Water Air Soil Pollut.* 30: 945-963.
- Grieve, I.C. 1989. A laboratory test of the soil chemical submodels of two models of catchment acidification. *Hydrological Processes* 3: 339-346.
- Henriksen, A., Lien, L., Traaen, T.S., Sevelrud, I.S. and Brakke, D.F, 1988. Lake acidification in Norway -- present and predicted chemical status. *Ambio*, 17: 259-266.
- Henriksen, A., and Brakke, D.F. 1988. Sulfate deposition to surface waters. Estimates of critical loads for Norway and the Eastern United States. *Environ. Sci. Technol.* 22: 8-14.
- Henriksen, A., Kämäri, J., Posch, M., and Wilander, A. 1992. Critical loads of acidity: Nordic surface waters. *Ambio* 21: 356-363.
- Hornung, M., Roda, F., and Langan, S.J. (Eds.) 1990. A review of small catchment studies in western Europe producing hydrochemical budgets. *Air Pollution Research Report 28*, Commission of European Communities, Brussels.

- Jenkins, A. and Cosby, B. J., 1989. Modelling surface water acidification using one and two soil layers and simple flow routing. p. 253- 266, In: J. Kämäri, D. F. Brakke, A. Jenkins, S. A. Norton and R. F. Wright (Editors), *Regional Acidification Models*, Springer-Verlag, New York.
- Jenkins, A., Cosby, B.J., Ferrier, R.C. , Walker, T.A.B. and Miller, J.D, 1990b. Modelling stream acidification in afforested catchments: an assessment of the relative effects of acid deposition and afforestation. *J. Hydrol.*, 120: 163-181.
- Jenkins, A., Ferrier, R.C., Walker, T.A.B., and Whitehead, P.G. 1988. A modeling study of long term acidification in an upland Scottish catchment. *Water Air Soil Pollut.* 40: 275-291.
- Jenkins, A., Whitehead, P. G., Cosby, B. J. and Birks, H. J. B., 1990a. Modelling long term acidification: a comparison with diatom reconstructions and the implications for reversibility. *Phil. Trans. R. Soc. Lond. B* 327: 435-440.
- Neal, C., Robson, A., Reynolds, B., and Jenkins, A. 1992. Prediction of future short-term stream chemistry - a modeling approach. *J. Hydrol.* 130: 87-103.
- Neal, C., Smith, C.J., Walls, J., and Dunn, C.S. 1986. Major, minor and trace element mobility in the acidic upland forested catchment of the upper River Severn, mid-Wales. *Q.J. Geol. Soc.* 143: 635-648.
- Neal, C., Whitehead, P.G., and Jenkins, A. 1988. Reversal of acidification. *Nature* 334: 109-110.
- Nilsson, J. and Grennfelt, P.. 1988. Critical loads for Sulphur and Nitrogen. Miljørapport 1988: 15, Nordic Council of Ministers, Copenhagen, 418pp.
- Nolan, A., Lilly, A., and Robertson, J.S. 1985. Surface water acidification programme: the soils of the Allt a Mharcaidh catchment. Internal Report, Macauley Land Use Research Institute, Aberdeen, UK.
- Oreskes, N., Shrader-Frechette, K. and Belitz, K, 1994. Verification, validation, and confirmation of numerical models in the earth sciences. *Science*, 263: 641-646.
- Reuss, J.O. 1990. Critical loads for soils in Norway. Analysis of soils data from eight Norwegian catchments. *Naturens Tålegrenser, Fagrapport 11*, Norwegian Institute for Water Research, Oslo, 78pp.
- Reynolds, B., and Norris, D.A. 1990. Llyn Brianne Acid Waters Project: Summary of Catchment Characteristics. Institute of Terrestrial Ecology, Bangor, Wales, UK.
- Reynolds, B., Hornung, H.M., and Hughes, S. 1989. Chemistry of streams draining grassland and forest catchments at Plynlimon, mid-Wales. *Hydrological Sciences J.* 36: 667-685.

- Reynolds, B., Neal, B., Hornung, M., Hughes, S., and Stevens, P. A. 1988. Impact of afforestation on the soil solution chemistry of stagnopodsols in mid-Wales. *Water Air Soil Pollut.* 38: 55-70.
- Robson, A., Jenkins, A., and Neal, C. 1991. Towards predicting future episodic changes in stream chemistry. *J. Hydrol.* 125: 161-174.
- Sverdrup, H., de Vries, W. and Henriksen, A., 1990. Mapping Critical Loads. Report NORD 1990:98, Nordic Council of Ministers, Copenhagen, 124pp.
- Traaen, T.S. 1990. Monitoring Tjønnstrond catchment. Hydrochemical measurements. Annual report for 1989. Report 2432, Norwegian Institute for Water Research, Oslo, 15 pp. (in Norwegian).
- SFT. 1990. Monitoring of long-range transported polluted air and precipitation. Annual Report 1989, State Pollution Control Authority, Oslo.
- SFT. 1991. Monitoring of long-range transported polluted air and precipitation. Annual Report 1990, State Pollution Control Authority, Oslo.
- Waters, D. and Jenkins, A. 1992. Impacts of afforestation on water quality trends in two catchments in mid-Wales. *Environ. Pollut.* 77: 167-172.
- Whitehead, P.G., Reynolds, B., Hornung, M., Neal, C., Cosby B.J. and Paricos, P., 1988. Modelling long term stream acidification trends in upland Wales at Plynlimon. *Hydrol. Proc.*, 2: 357-368.
- Whitehead, P.G. 1992. Hydrochemical models of acidification in catchments. In: P. Young (Ed.), *Concise Encyclopedia of Environmental Systems*, Wiley, New York.
- Wright, R. F., Cosby, B. J., Flaten, M. B. and Reuss, J. O. 1990. Evaluation of an acidification model with data from manipulated catchments in Norway. *Nature* 343: 53-55.
- 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., Lotse E. and Semb, A, 1994. Experimental acidification of alpine catchments at Sogndal, Norway: results after 8 years. *Water Air Soil Pollut.* 72: 297-315.
- Wright, R.F., Stuanes, A.O., Reuss, J.O., and Flaten, M.B. 1990a. Critical Loads for Soils in Norway. Preliminary Assessment based on data from 9 calibrated catchments. *Naturens Tålegrenser, Fagrapport 11*, Norwegian Institute for Water Research, Oslo, 56 pp.

Wright, R.F., and Traaen, T.S. 1992. Dalelva, Finnmark, northernmost Norway: prediction of future acidification using the MAGIC model. Report 486/92, Statlig Program for forurensingsovervåking, State Pollution Control Authority, Oslo, 17pp.