Institute of
Hydrology

1991/007

[redacted]

Natural Environment Research Council

REGIONAL MODELLING OF ACIDIFICATION AND PREDICTING REVERSIBILITY

by

A. JENKINS and P. G WHITEHEAD

Final Report
On Contract EV4V.0033 UK(H)
January 1991

TABLE OF CONTENTS

PREFACE

This report has been produced in fulfillment of Contract EV4V.0033 UK (H), a contract between the CEC and the UK Natural Environment Research Council (NERC). The work has been undertaken at the Institute of Hydrology, a component institute of NERC.

EXECUTIVE SUMMARY

Within the framework of this completed research programme a number of major conclusions have been reached:

(i) The acidity of lakes and streams across a wide area of the UK has increased substantially in the last 30 years. This increase in acidity, and so increased aluminium concentrations, has in many cases caused the impoverishment and/or loss of fish populations.

(ii) A decrease in sulphur deposition of at least 30% will be needed to arrest the declining water quality in most impacted systems. Furthermore, to achieve any substantial improvement in acid status, a decrease of at least 60% is necessary.

(iii) Land use, and in particular forestry practices, plays a considerable role in the determination of surface water acidity.

In addition, a number of modelling techniques have been developed:

(iv) The incorporation of a monte-carlo technique for evaluation of surface water changes across whole regions.

(v) Fuzzy optimisation techniques have improved our understanding of model sensitivity and enabled the assessment of uncertainty within model application.

(vi) Incorporation of hydrological routing has enabled preliminary analysis of short-term changes in stream chemistry

(vii) The resulting modelling 'package' represents a powerful research and analysis tool which will be essential to existing parallel research programmes assessing critical loads across Europe.

1. SUMMARY OF RESEARCH

1.1 Objectives

The objectives of the research were to apply mathematical models of catchment acidification processes to several key catchments, extend the modelling to a regional scale, link models to an air pollution model and investigate the effects of different emmission strategies on stream water quality.

1.2 Modelling Long Term Trends in Acidification

The MAGIC model (Model of Acidification of Groundwaters in Catchments) has been applied to a range of catchments in Scotland and Wales.

Section 2 of this report describes the application of MAGIC to the Llyn Brianne catchments in South-West Wales and to the Plynlimon Catchments in mid-Wales. In both areas MAGIC is shown to provide an excellent description of long term catchment acidification processes. For both grassland and forested catchments the model reproduces observed chemistry and can be used to assess the impacts of land use change such as afforestation. It is shown that afforestation increases the sulphate loading into a catchment by up to 80% and this has a major detrimental effect, increasing water acidity and increasing aluminium levels.

The MAGIC model has also been applied to several catchments in Scotland including Loch Dee in South-West Scotland and the Allt a Mharcaidh in the Cairngorms. Section 2 of this report describes the model's applications in these two areas. The Loch Dee catchments show a similar response to catchments in Wales in that historical acidification has been significant. However, the Allt a Mharcaidh catchment appears to be undergoing a transition from a relatively unacidified system to an acidified catchment. The major factor that has prevented rapid acidification has been the ability of the soils in the Allt a Mharcaidh to adsorb sulphate deposited in the catchment. As this natural buffering capacity is utilised stream acidity will increase and so the Allt a Mharcaidh represents a site in a transition from a pristine, moorland towards an acidified moorland stream.

A crucial aspect affecting acidification in the UK and elsewhere in Europe is the degree and type of afforestation. A conceptual model of the combined effects of afforestation and acidic deposition has been applied to two forested sites in central Scotland. Refinements are made to the model inputs specifically to include: increased dry deposition to the forests (in excess of the dry deposition expected for moorland sites) as the forest canopy develops; uptake of ions by the growing forests; and increased evapotranspiration (and thus decreased water yield) as the forests mature. The model is calibrated using a fuzzy optimisation technique (see section 2.6) which incorporates uncertainty in target variables (stream base cation concentrations and soil exchangeable bases) and uncertainty in selecting values for fixed and adjustable parameters which describe the physiochemical characteristics of the catchments. Simulated present day stream and soil chemistry closely match observed values at both sites. The calibrated models indicate that while the patterns of acidification in the two catchments are broadly similar, some differences do exist between the sites in the responses of the soils to acidic deposition and afforestation. It is concluded that the calibrated models provide a tool for; a) comparison of the relative effects of deposition and afforestation on soil and surface water acidification; and b) assessment of the likely effects of reductions in future deposition combined with future forestry management practices.

The model is further used to perform a series of simulation experiments to assess the relative effects of afforestation and acidic deposition on soil and surface water chemistry. The experiments compare and contrast: a) the simulated historical effects of increased acidic deposition and forest growth, both individually and in combination; and b) the simulated future effects of various levels of reduction of deposition in combination with the forestry strategies of harvesting with and without replanting. Results indicate that historical acidification of surface waters in areas receiving high levels of acidic deposition has been exacerbated by afforestation practices. Afforestation in the absence of acidic deposition, however, has had a lesser effect on surface water acidification even though the nutrient demands of forest growth have caused significant soil acidification. Comparisons of future forest management strategies in conjunction with likely deposition reductions indicate that, in sensitive areas replanting of a felled forest without treatment of the soil by addition of base cations, should not be undertaken even if significant deposition reductions are realised.

1.3 Comparisons with Paleoecological Evidence

MAGIC has been applied to a range of catchments in Scotland subject to different pollution inputs and land uses. The calibration technique developed (see section 2.6) allows sensitivity bands to be constructed around the 'mean' MAGIC output as illustrated in section 3 of the report. In this way, simulated historical trends in pH are compared with data from palaeolimnological reconstructions undertaken at the same sites. Both techniques produce similar historical acidification trends and closely match observed present day pH. Since the two methods of reconstruction represent very different modelling strategies the similarity of the output increases our confidence in both approaches and the independence of the two approaches makes this a good validation of the MAGIC model.

1.4 Linking Short-term and Long-term Response Model

A hybrid deterministic statistical approach has been developed for modelling extremes of water quality in catchments subjected to long-term acidification. The approach is based on the MAGIC model describing long-term variations in mean chemistry. Superimposed on these mean projections are distributions providing information on the extremes of water quality. The distributions are fitted to catchment data using maximum likelihood techniques. The approach is general and can be applied to the prediction of other water quality variables where samples can be regarded as belonging to a parametric probability distribution. A simple implementation of the approach using chemical data and a calibrated deterministic model for the Allt a Mharcaidh is used as an illustrative method in section 4.

An alternative approach to linking short-term behaviour has also been developed using mixing concepts, whereby the flow is assumed to be a mix of water from two distinct sources. Acidic water from the upper soil horizons and well buffered water from deeper 'groundwater' sources are used to represent the two endmembers and a chemical hydrograph separation technique is used to estimate the mean proportions of mix. The MAGIC model is calibrated in its two layer mode to these two endmember chemistries. The model produces a good fit to observed present day stream, soil and baseflow chemistry. Future predictions of changes in endmember chemistry are made so as to enable future episodic response to be modelled.

1.5 Regional Modelling

In order to assess the impact of acidification across a country or region it is necessary to employ a Monte Carlo strategy coupled to the MAGIC model. In this approach key parameters are identified and their variability across a region assessed. For example, soil base saturation levels will range from low levels on thin granitic systems to high levels on calcareous soils. Similarly, hydrological and chemical inputs will vary across a region. These regional variations are incorporated into the Monte Carlo approach and distributions of water quality across a region are simulated.

The regional simulations for South-West Scotland and Wales are presented in section 5 of the report and for both areas the observed distributions match the simulated distributions. The Monte Carlo approach provides a particularly useful technique for simulating regional behaviour.

1.6 Ecosystems Modelling and Reversibility

An approach to modelling the impact of acidification on the ecology of two Welsh streams is given in Section 6. Output from MAGIC is used to drive empirical models for predicting brown trout density, survival and invertebrate assemblages. The modelling shows that trout survival markedly decreased between 1844 and 1984 with the most severe decrease occurring in a stream draining a conifer afforested catchment. Here, the high aluminium concentration caused the virtual elimination of trout in the system. Forecasts shows that at least a 50% decrease in sulphate deposition is needed to retard the further decline in trout population.

The regional application of MAGIC to Wales is also assessed with respect to the biological models and detailed in Section 6.2. Some sites in Wales shows increased pH and alkalinity following a 30% decrease in deposition from 1984, however, even under this improvement in water quality, further biological impoverishment occurs on the regional scale due to continued mobilisation of aluminium.

In section 2 of this report examples are given of the effects of deposition reductions on stream water quality. At sites in Scotland and Wales and in the regional studies,reversibility is shown to be feasible although there is evidence that a significant and sustained reverse will only be achieved by major reductions in deposition levels of the order of 60%. For catchments with particularly thin soils and low buffering capacity a smaller reduction will produce a short term recovery but the continuing loss of soil base cations will eventually lead to increased stream water acidification. Particular problems are envisaged for forested sites.

At the afforested Scottish sites the modelling results indicate that, combined with deposition reduction of the order of 70%, a second generation forest planted on a recently felled site would not cause significantly greater acidification in the stream. Soil acidification, on the other hand, would continue to occur. To enable a significant recovery in these areas, which constitute a significant proportion of acid vulnerable sites in the UK, forests should not be replanted without considering the application of soil dressings such as limestone. Better still, second generation planting should not be carried out. In terms of critical load calculation, this work shows how land use change can affect the susceptibility of a site. Felling the forest in conjunction with a decrease in atmospheric deposition significantly improves stream acidity and this must be considered when critical loads are calculated for these sites.

1.7 Conclusions

The modelling studies have been particularly successful with applications to a wider range of moorland and forested catchments in Scotland and Wales. Comparisons with paleoecological evidence supports the modelling conclusions, that acidification of catchments, soils and streamwater has occurred on a major scale with particularly severe impacts on thin soils with granitic bedrock and in forested catchments. In addition, the techniques developed for regional analysis have proved to give excellent results for Wales and the Galloway Region of South West Scotland. Reversibility has been assessed on a site specific and regional basis and the major conclusion is that reversibility will be achieved at many sites given at least a 60% reduction in deposition. Higher reductions will be required for forested catchments or catchments which have to been subjected to very high levels of acid deposition. Similarly, fisheries and stream invertebrate populations have been affected by acidification and major improvements in stream chemistry are required before reversibility can occur.

The models and modelling techniques which have been developed, calibrated and applied over a wide variety of regions and across a large sulphur deposition gradient within the UK, are particularly useful for determining critical loads for both soil and aquatic ecosystems. The models (defined as level II analysis under the UNECE Critical Loads Mapping Procedure) add an extra dimension to the simplified empirical techniques of critical load determination in that they enable: (i) the time aspect of critical loads to be determined for a particular ecosystem; for example, the critical load to achieve a critical level of stream ANC = 0 within 50 years will be greater than for achieving the same critical level within 10 years; (ii) the effect of changing land use, in particular afforestation or deforestation can be incorporated into the critical load analysis; and (iii) target load scenarios can be assessed.

2. SITE SPECIFIC APPLICATIONS

2.1 Llyn Brianne - Wales

Journal of Hydrology, 101 (1988) 191–212
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

[3]

STREAM ACIDIFICATION TRENDS IN THE WELSH UPLANDS — A MODELLING STUDY OF THE LLYN BRIANNE CATCHMENTS

P.G. WHITEHEAD[1], S. BIRD[2], M. HORNUNG[3], J. COSBY[4], C. NEAL[1] and P. PARICOS[1]

[1] *Institute of Hydrology, Maclean Building, Crowmarsh Gifford, Wallingford, Oxon OX10 8BB (U.K.)*
[2] *Welsh Water, Tremains House, Coychurch Road, Bridgend, Wales (U.K.)*
[3] *Institute of Terrestrial Ecology, Bangor Station, Peurhos Road, Bangor, Wales (U.K.)*
[4] *Department of Environmental Sciences, University of Virginia, Charlottesville, VA (U.S.A.)*

(Received July 27, 1987; revised and accepted November 10, 1987)

ABSTRACT

Whitehead, P.G., Bird, S., Hornung, M., Cosby, J., Neal, C. and Paricos, P., 1988. Stream Acidification trends in the Welsh Uplands — A modelling study of the Llyn Brianne catchments. J. Hydrol., 101: 191–212.

Historical reconstructions and predictions of streamwater acidification are presented for moorland and afforested catchments in the Welsh Uplands at Llyn Brianne. The model MAGIC (Model of Acidification of Groundwater in Catchments) is calibrated using data from a moorland catchment and validated by application to a forested catchment. While atmospheric deposition is shown to be the primary cause of stream acidification, conifer afforestation can enhance stream acidity. The historical trends determined by the model indicate that acidification has been present since the turn of the century and will continue unless either deposition levels are reduced significantly or other land management actions such as liming are undertaken on a major scale.

INTRODUCTION

Catchment studies investigating the acidic behaviour of upland streams are expensive, time consuming and difficult to establish due to the complexity of hydrological, chemical and biological interactions. Nevertheless many catchment studies have been and are being established to evaluate short-term and long-term fluctuations in stream water chemistry. For example as part of the joint Scandinavian–British Surface Water Acidification Programme (Mason and Seip, 1985) major studies are being established in the U.K. and Scandinavia. Other studies have recently been established in the U.K. such as the Welsh Water Department of Environment Llyn Brianne Study (Stoner et al., 1984), the Solway River Purification Board Loch Dee Study (Burns et al., 1982), the Freshwater Fisheries Laboratory Loch Ard Study (Harriman and Morrison, 1981) and the Generating Board (CEGB) Loch Fleet Study (Howells, 1986). These studies follow mounting concern over the loss of fisheries in Scotland and Wales and the possible detrimental effects of stream acidity on

0022-1694/88/$03.50

water resources. Several researchers involved in these studies (Harriman and Morrison, 1981; Stoner, 1985) have reported elevated acidity and aluminium levels in upland streams draining afforested (conifer) catchments in the U.K. Moreover in many of the studies fish populations have deteriorated and restocking programmes have been unsuccessful.

It is with these problems in mind that the Institute of Hydrology has established and supported catchment studies in Scotland and Wales. In Wales, the Institute of Hydrology is involved in two principal study areas, namely Plynlimon (see Hornung, 1986; Neal et al., 1986; Whitehead et al., 1988) and Llyn Brianne (Stoner et al., 1984). As part of the Llyn Brianne study the Institute of Hydrology is responsible for developing hydrochemical models which can be used to assess both short-term acid pulses and long-term trends in catchment acidity. In this paper the MAGIC model has been applied to moorland and forested catchments at Llyn Brianne to investigate long-term trends in acidification and to test the model validity.

THE LLYN BRIANNE CATCHMENT STUDY

Recent work by the Welsh Water (Stoner et al., 1984; Stoner and Gee, 1985) has suggested that acidity and aluminium levels in many of the streams of the Upper Towy catchment, in which the Llyn Brianne river regulation reservoir is situated, are episodically very high. Moreover many streams cannot support fish and have depleted populations of aquatic plants and animals. Problems appear to be most acute in afforested catchments, particularly those where streamwaters are characterised by total hardnesses of less than $8\,\mathrm{mg\,l^{-1}}$ (as $CaCO_3$). Furthermore, the problem appears to be widespread in the extensive area of upland Wales underlain by chemically inert Ordivician and Silurian rocks which are characterised by acid, often peaty, soils and streamwater of very low hardness. Acid rainfall appears to be a contributory cause of streamwater acidity, despite the fact that the area lies to the west of the urban/industrial areas of Great Britain. Recent surveys have suggested that the rainfall is on average as acid as many sites in Scotland and Northern Europe (Donald et al., 1986).

Because of general concern about acid streamwaters and acid rainfall, a major multidisciplinary research programme was commissioned in 1984 by the Department of the Environment and the Welsh office, the project being coordinated by the Welsh Water. The project has as its primary aim an assessment of the effects of different types of land use (particularly afforestation) and land management practice on stream acidity. Fourteen catchments were selected for intensive study in the Llyn Brianne area; five acting as controls; eight are used to assess the impact of a variety of land management treatments; and one to assess the effects of artificial acidification experiments

Fig. 1. Maps showing Llyn Brianne area geology, land use, annual rainfall and monitoring sites.

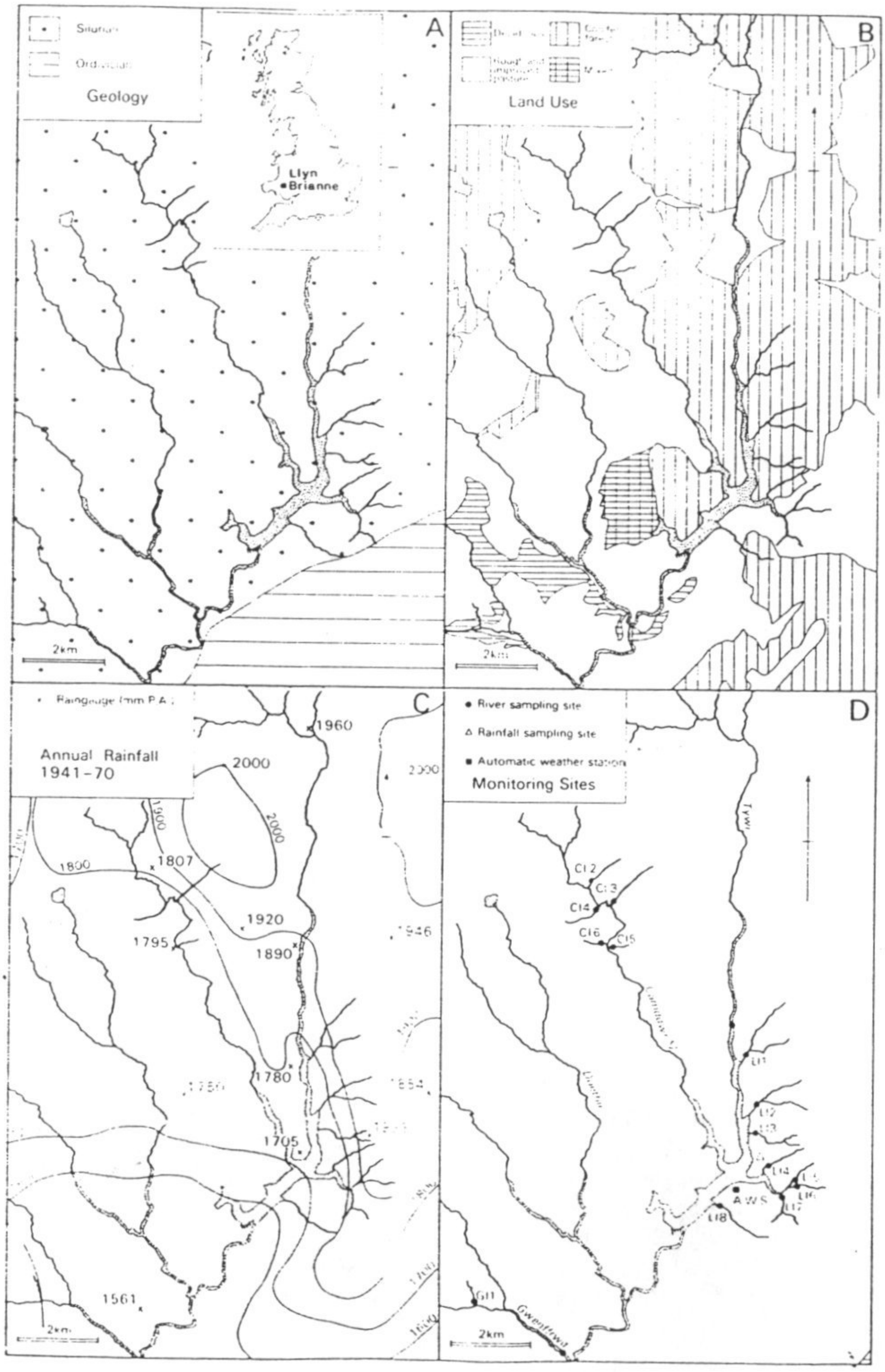

A
Silurian
Ordovician
Geology
Llyn Brianne
2km
B
Conifer forest
Rough and improved pasture
Land Use
2km
C
Raingauge (mm P.A.)
Annual Rainfall 1941-70
1960
2000
2000
2000
1900
1800
1807
1920
1795
1890
1946
1780
1750
1854
1705
1561
2km
D
River sampling site
Rainfall sampling site
Automatic weather station
Monitoring Sites
Tywi
C12
C13
C14
C16
C15
L11
L12
L13
L14
L16
L17
L18
A.W.S.
G11
Gwenffrwd
2km

TABLE 1

The study catchments: basic information

Site	Land use/treatment	Area (km²)	Year of treatment
LI1	Close canopy conifer forest control	2.53	-
LI2	Bankside clearance and liming of close canopy forest	1.05	1986
LI3	Bankside clearance of close canopy forest	0.64	1983
LI4	Bomb liming of close canopy forest	0.33	1987
LI6	Unacidified moorland control	0.68	-
LI7	Moorland used for artificial acidification studies	0.68	1985, 1986
LI8	Juvenile open canopy forest	0.66	-
GI1	Acid oak woodland	0.18*	-
CI2	Strip liming of acidified moorland	0.59	1987
CI3	Land improvement of acidified moorland	0.84	1986
CI4	Ploughing without planting of moorland	0.49	1986
CI5	Surface liming of acidified moorland	0.34	1987
CI6	Acidified moorland control	0.72	-
UC4	Ploughing and planting of moorland	2.60*	1987

* Estimated.

(Table 1 and Fig. 1). The present study concentrates upon conditions prevailing in just three of the fourteen catchments (LI1, CI5, and LI6) and looks at the possibility of modelling the long-term trends in acidification at Llyn Brianne.

CATCHMENT DESCRIPTIONS

LI1 is the largest catchment being studied (2.53 km²) and CI5 is one of the smallest (0.34 km²). LI6, although fairly small (0.68 km²), exhibits the highest drainage density (2.74 km km^{-2}) and channel slope (194 m km^{-1}), and hence exhibits a distinctly more rapid hydrological response.

All three catchments are underlain by Lower Silurian shales, mudstones, greywackes and grits, with the shales and mudstones being dominant (Fig. 1). The drift materials present are only locally derived and lie mainly on the interfluves and upper slopes in thin layers (< 1 m), although some of the lower slopes and valley bottoms have thicker masses of up to 5 m in depth, particularly in LI6 where the drift appears especially base rich (Hornung, 1986).

Available soil information indicates that LI1 is dominated by brown podzolic soils (34%), ferric stagnopodzols (19%), cambic stagnohumic gleys (12%), humic gleys (19%), and raw peat soils (12%) at an average depth of 0.75 m. CI5 is dominated by brown podzolics (21%), ferric stagnopodzols (23%), and cambic stagnohumic gleys (25%), all of a similar depth. LI6 is dominated by brown podzolic soils (ca. 40%), stagnopodzols (ca. 50%), peat (ca. 5%), and a valley bottom complex located on thick drift (ca. 5%), again at a similar depth.

The chemistry of the main soils in each catchment is summarised in Table 2.

All the soils are acid, with low percentage base saturations and exchange complexes dominated by aluminium. The subsoil, Bs and C horizons show little variation in chemistry. The main differences occur in the surface horizon and reflect the accumulation of varying amounts of organic matter and the development, in some of the soils, of an eluviated E horizon. The differences in the surface horizons reflect the accumulation of humus and, in the stagnopodzols, the development of a very acid, peaty horizon. The E horizons tend to have higher levels of exchangeable aluminium than the underlying Bs and C horizons. More importantly, the iron pan stagnopodzols under 25 year old Sitka Spruce are remarkably acid throughout their profile, especially in catchment LI1. More detailed soil information is available elsewhere (Hornung, 1986).

The vegetation cover of LI6 and CI5 is dominated by grass moorland, principally *Festuca* spp., *Agrostis* spp., *Nardus* spp., and *Molinia caerulea*. However, LI1 has been totally afforested largely with Sitka Spruce (*Picea Sitchensis*), planting having commenced in 1958 (Fig. 1).

PRESENT DAY RAINFALL AND STREAM QUANTITY AND QUALITY

Rainfall quantity and quality

The mean annual rainfall at CI5 has been estimated at 1800 mm, while at LI1 and LI6 the corresponding figure is at least 1900 mm (Fig. 1). However, catchment rainfall amounts can vary considerably with both altitude and aspect (Hornung, 1986).

TABLE 3

Bulk precipitation chemistry at sites C7 and L3 for 1984

	C7				L3			
	n	mean	wt m	sd	*n*	mean	wt m	sd
pH	34	4.7	4.2	0.6	33	4.9	4.1	0.9
NH_4	35	31	31	37	34	40	39	48
NO_3	35	44	44	71	34	38	37	49
Cl	35	177	142	241	34	144	113	183
SO_4	35	76	71	56	34	86	77	65
Na	34	147	114	198	32	109	90	108
K	34	8	8	6	32	7	7	8
Mg	34	36	28	48	32	30	25	30
Ca	33	21	17	22	32	30	28	36
H^+	34	63	59	143	33	44	50	73

All units in $\mu eq\, l^{-1}$ except pH. *n* is the number of samples. wt.m is the volume weighted mean; and sd is standard deviation

Two bulk precipitation sampling sites are monitored in the area. The first (C7) is located in the Camddwr catchment near CI5 (Fig. 1), while the second (L3), is located between LI1 and LI6. Table 3 summarises the composition of bulk precipitation at both sites for 1984. At C7 pH ranged from 3.1 to 6.9, with a volume-weighted mean of 4.19. Corresponding levels at L3 ranged from 3.4 to 7.1 and averaged 4.12. Acidity levels can thus be considered high and extremely high acid events do occur from time to time. Indeed, 25% of all those samples analysed, exhibited a pH of 4.4 or less.

SO_4 concentrations also exhibited a large range at both sites, with rainfall-weighted means of 71 μeq l^{-1} and 77 μeq l^{-1} at C7 and L3 respectively. Moreover, 25% of all those samples taken exceeded 83 μeq l^{-1} (C7) and 117 μeq l^{-1} (L3). The higher levels at L3 probably reflect its forest location which encourages enhanced occult and dry deposition of airborne contaminants.

In addition the high Na and Cl concentrations at both rainfall sites confirm the importance of marine salts. NO_3 and NH_4 levels however are low and thus appear relatively unimportant.

Streamwater quantity and quality

On average, runoff coefficients in all three catchments exceed 0.75. However, preliminary examination of the available flow records suggest that the coefficient is likely to be considerably higher in LI6; partly due to its reduced evapotranspirational losses compared to forested LI1, and partly due to its higher relief, steeper slopes, increased drainage density and compact shape. In addition, despite the enhanced evapotranspirational losses caused by the forest land use (Law, 1956; Calder, 1985), LI1 also appears to exhibit enhanced storm runoff volumes relative to CI5. This can probably be attributed to the presence of drainage ditches and macropore flow in the shallow soils which drain the forest floor (Neal et al., 1986). Further investigations into the catchment hydrology are continuing (Hornung, 1986).

The streamwater quality of each catchment is summarised in Table 4. LI1, compared to CI5 and LI6, is significantly more acid, with pH averaging 4.87. In addition, 25% of all spot samples taken in LI1 registered a pH of 4.6 or less. Such levels are comparable to the mean of the bulk precipitation samples, suggesting that LI1 has a limited buffering capability. SO_4 concentrations are also highest at LI1, averaging 154 μeq l^{-1}, with 25% of all samples exhibiting concentrations of 170 μeq l^{-1} or more. Hence, on average, concentrations are more than double those found in the bulk precipitation and presumably reflect the effects of large evapotranspirational losses (typically 30%) and an enhanced sulphate scavenging capacity associated with the forest land use.

NO_3 concentrations are low at LI1, averaging 11 μeq l^{-1}, some 25–30% of that found in the bulk precipitation. Clearly these low levels reflect the uptake of

TABLE 4

A comparison of streamwater chemistry for 1984/85

		C15	L11	L16
pH	mean	5.2	4.87	6.9
	std. dev.	0.34	0.44	0.30
	max	6.0	7.0	7.9
	min	4.6	4.3	6.2
	no. samples	103	101	97
H^+	mean	8	18	0.15
	std. dev.	5	11.6	0.11
	max	25	50	0.63
	min	1	0.1	0.01
	no. samples	103	101	97
SO_4	mean	102	154	103
	std. dev.	19	30	26.2
	max	150	260	198
	min	60	98	23
	no. samples	100	95	93
NO_3	mean	15	11	10
	std. dev.	12	5	6.5
	max	86	29	50
	min	7	7	7
	no. samples	103	102	98
NH_4	mean	1.5	1.5	1.6
	std. dev.	0.41	0.4	1.07
	max	5.0	5.0	11.4
	min	1.4	1.4	1.4
	no. samples	104	102	98
Na	mean	149	204	138
	std. dev.	31	52	29
	max	283	434	267
	min	90	4	36
	no. samples	94	99	95
Cl	mean	165	247	155
	std. dev.	42	61	24
	max	226	367	197
	min	85	113	85
	no. samples	104	102	98
Mg	mean	56	60	146
	std. dev.	14	15	77
	max	91	102	420
	min	33	24	44
	no. samples	95	99	96
Ca	mean	44	59	146
	st. dev.	11	20	81
	max	71	129	456
	min	20	13	23
	no. samples	95	100	96

TABLE 4 (continued)

		CI5	LI1	LI6
K	mean	6.6	5	11
	std. dev.	3.9	3.9	8.8
	max	21	26	43
	min	0.5	1	3
	no samples	93	95	94
Al	mean	18	42	7
	std. dev.	13	22	6
	max	70	94	53
	min	0.6	3	0.6
	no. samples	96	100	96

* All units $\mu eq\,l^{-1}$ except pH. Al assumed to be trivalent.

available nitrates by the mature conifer vegetation cover. NH_4 concentrations are similarly low.

The marine salts are present at much higher concentrations in LI1. Na averaging 204 $\mu eq\,l^{-1}$ and Cl, 247 $\mu eq\,l^{-1}$. These levels are more than double those found in the bulk precipitation, reflecting the strong sea salt influence, effective scavenging capability and larger evapotranspirational losses, of the forested catchment.

On the other hand, Ca and Mg concentrations are low, averaging 59 and 60 $\mu eq\,l^{-1}$, respectively. Such levels further support the suggestion of a very limited buffering capability in LI1 linked to its base poor rocks and soils. The low alkalinity levels also confirm the above.

Aluminium concentrations are very high at LI1 averaging 42 $\mu eq\,l^{-1}$, with a peak of 94 $\mu eq\,l^{-1}$ being recorded. These levels represent a major increase over those found at other sites and as will be seen later, clearly reflect the enhanced dissolution of aluminium silicates in the forest soils. The aluminium concentrations also exhibit a clear negative correlation with pH ($r = -0.70$), while pH and Ca concentrations are positively correlated ($r = 0.75$). These correlations further highlight the importance of a limited buffering capability during individual acid storm events.

In CI5, despite its nonforested land use, pH levels are only slightly higher, averaging 5.2, with 25% of all samples exhibiting a pH of 5.0 or less. SO_4 concentrations average 102 $\mu eq\,l^{-1}$, only 66% of the sulphate concentrations at LI1, but still 30% greater than bulk precipitation chemistry. Presumably the reduction in evapotranspiration and scavenging in the moorland catchment has contributed significantly to the above. NO_3 and NH_4 levels however, are similar to those found at LI1.

Na and Cl both exhibit quite high concentrations averaging 149 and 168 $\mu eq\,l^{-1}$, respectively. However, again these are much lower than those found in LI1, reflecting its reduced evapotranspirational losses and scavenging capacity. More surprisingly, base cation concentrations averaging 44 and 56 μeq l^{-1} for Ca and Mg, respectively, are even lower than in LI1. Hence, the buffering capacity in this acid moorland catchment is also very limited, although it is not exposed to the *extremes* of acidity found in LI1.

Not surprisingly dissolved aluminium levels are moderately high, averaging 18 μeq l^{-1} with extremes reaching 60 μeq l^{-1}. Hence slightly less acid waters when combined with such a limited buffering capacity are still likely to result in considerable biological stress during acid events. Moreover pH and aluminium concentrations ($r = -0.76$) and pH and Ca ($r = 0.51$) are correlated as at LI1.

LI6 however, displays very different stream quality. First, pH averages 6.9 and never falls below 6.2. As a result, none of the problems associated with high aluminium concentrations are apparent. Moreover, SO_4 levels although similar to those found at CI5 (averaging 103 μeq l^{-1}) cause few water quality problems. Clearly the key factor in this catchment is the high level of base cations available to buffer any acidity. For example, concentrations of Ca and Mg both average 146 μeq l^{-1}.

In summary, while the bulk precipitation quality in the area is dominated by marine salts and terrestrially derived anions, moderately acidic events do still occur. Moreover, the area receives large volumes of mildly acid precipitation. In addition within the study area, conifer afforested catchments, such as LI1, clearly exhibit the most acid streamwaters and highest aluminium concentrations, due to their limited buffering capacity. Conditions within the acid moorland catchments such as CI5 are also by no means satisfactory, despite their reduced scavenging capacity and evapotranspirational losses, since they too only possess a limited buffering capacity. Only the unacidified moorland site LI6 exhibits totally satisfactory stream conditions, principally as a product of the enhanced buffering capability derived from its soils and drift deposits.

CONCEPTUAL BASIS OF THE MODEL

The most serious effects of acidic deposition on catchment surface water quality are thought to be decreased pH and alkalinity and increased base cation and aluminium concentrations. In keeping with an aggregated approach to modelling whole catchments, a relatively small number of important soil processes — processes that could be treated by reference to average soil properties — could produce these responses. In two papers, Reuss (1980, 1983) proposed a simple system of reactions describing the equilibrium between dissolved and adsorbed ions in the soil and soil water system. Reuss and Johnson (1985) expanded this system of equations to include the effects of carbonic acid resulting from elevated CO_2 partial pressure in soils and demonstrated that large changes in surface water chemistry would be expected as either CO_2 or sulphate concentrations varied in the soil water. MAGIC has its roots in the Reuss–Johnson conceptual system, but has been expanded from their simple two-component (Ca–Al) system to include other important cations and anions in catchment soil and surface waters. MAGIC has been described in detail elsewhere (Cosby et al., 1984, 1985a, b, c, 1986). A further brief description is presented here to address questions such as gibbsite equilibria controls and the role of CO_2 in determining acidity.

Atmospheric deposition, mineral weathering and exchange processes in the soil and soil water are assumed to be responsible for the observed surface water chemistry in a catchment. Alkalinity is generated in the soil water by the formation of bicarbonate from dissolved CO_2 and water:

$$CO_2 + H_2O = H^+ + HCO_3^- \tag{1}$$

Bicarbonate ion concentrations in soil water are calculated using the familiar relationships between the partial pressure of CO_2 (P_{CO_2}, atm) and hydrogen ion activity in the soil water:

$$[HCO_3^-] = K_c \frac{P_{CO_2}}{[H^+]} \tag{2}$$

where the combined constant K_c is known for a given temperature.

The free hydrogen ion produced, eqn. (1), reacts with an aluminium mineral (e.g. gibbsite) in the soil:

$$3H^+ + Al(OH)_{3(s)} = Al^{3+} + 3H_2O \tag{3}$$

The MAGIC model assumes a cubic equilibrium relationship between Al and H^+. The equilibrium expression for this reaction is:

$$K_{Al} = \frac{[Al]}{[H^+]^3} \tag{4}$$

where the brackets indicate aqueous activities. Classically this relationship describes $Al(OH)_3$ solubility controls. However, as in most previous modelling studies where a cubic relationship is still used, it represents potentially a variety of chemical reactions. As such the equilibria constant does not have to have the value for the solubility product for gibbsite. Several aqueous complexation reactions of Al^{3+} are included in the model (Cosby et al., 1985). These reactions are temperature dependent and appropriate corrections for temperature and ionic strength are made in the model.

Generally, the cation exchange sites on the soil matrix have higher affinity for the trivalent aluminium cation than for di- or monovalent base cations. An exchange of cations between the dissolved and adsorbed phase results:

$$Al^{3+} + 3BCX_{(s)} = AlX_{3(s)} + 3BC^+ \tag{5}$$

where X is used to denote an adsorbed phase and BC^+ represents a base cation. The net result of these reactions is the production of alkalinity [e.g. $Ca(HCO_3)_2$]. As CO_2 partial pressure or the availability of base cations on the soil exchange sites increases, the equilibrium reactions proceed further to the right-hand side of eqn. (5) in each case resulting in higher alkalinity.

When the solution is removed from contact with the soil matrix and is exposed to the atmosphere (i.e. when soil water enters the stream channel), the CO_2 partial pressure of the solution declines. The pH of the solution increases as CO_2 is lost to the atmosphere. Because the solution is no longer in contact with the soil matrix, cation exchange reactions no longer occur. The alkalinity and base cation concentrations are thus unchanged.

If the exchangeable base cations on the soils become depleted, less aluminium is exchanged from the soil water, eqn. (3), and the Al^{3+} concentration in the water entering the stream is higher. As the streamwater loses CO_2 and the pH begins to rise, the solubility of aluminium species in the stream is exceeded and a solid phase of aluminium precipitates. These aluminium precipitation reactions retard the increase of streamwater pH as the CO_2 degasses, resulting in lower streamwater pH for the case where exchangeable cations are less available.

Less adsorption of aluminium by the soils also decreases the soil and surface water alkalinity. Consider an abbreviated definition of the alkalinity of soil and surface waters:

$$ALK = (HCO_3^-) - (H^+) - 3\,(Al^{3+}) \qquad (6)$$

where the parentheses indicate molar concentrations. It is apparent that as the ability of the catchment soils to exchange Al^{3+} declines and aluminium and hydrogen ion concentrations increase, the alkalinity of the solution must decline, even though the source of HCO_3^- is not affected.

The process of acidification is controlled in part by the rate at which the exchangeable base cations on the soil are depleted. This in turn is affected by the rate of re-supply through weathering of base cations from primary minerals and the rate of loss through leaching of base cations from the soil. Leaching of base cations is affected mainly by the concentration of strong acid anions (i.e. SO_4^{2-}, NO_3^-, Cl^-, and F^-) and base cations in the solution moving through the soil. As anions increase in concentration, there must be an equivalent increase in cation concentration to maintain a charge balance.

The model calculates the concentrations of four strong acid anions in both soil and streamwater (SO_4^{2-}, Cl^-, NO_3^- and F^-). Sulphate has an adsorbed phase in soil and the relationship between adsorbed sulphate (E_s, meq kg^{-1}) and the concentration of dissolved sulphate (SO_4^{2-}, meq m^{-3}) in soil water is assumed to follow a Langmuir isotherm:

$$E_s = E_{mx} \frac{(SO_4^{2-})}{C + (SO_4^{2-})} \qquad (7)$$

where E_{mx} = maximum adsorption capacity of the soils (meq kg^{-1}), and C = half saturation concentration (meq m^{-3}).

If anions derived from atmospheric deposition are accompanied by H^+, as is the case for acid deposition, the excess H^+ will initially displace base cations from the soil exchange sites. As the base saturation declines, aluminium and hydrogen ion become increasingly important in maintaining the ionic charge balance in solution. The water delivered to the stream becomes more acidic as the acidic deposition persists.

The model assumes that only Al^{3+} and four base cations are involved in cation exchange between soil and soil solution. The exchange reactions are modelled assuming an equilibrium-like expression:

$$S_{AlBC} = \frac{[BC^{2+}]^3 E_{Al}^2}{[Al^{3+}]^2 E_{BC}^3} \tag{8}$$

or:

$$S_{AlBC} = \frac{[BC^{+}]^3 E_{Al}}{[Al^{3+}] E_{BC}^3}$$

For divalent or monovalent base cations respectively, where the brackets indicate aqueous activities, S_{AlBC} is a selectivity coefficient (Reuss, 1983) and the E_{xx}s indicate exchangeable fractions of the appropriate ions on the soil complex. If the amount of Ca^{2+} on the soil of a catchment were given by X meq kg^{-1}, then:

$$E_{Ca} = \frac{X}{CEC} \tag{9}$$

where CEC is the cation exchange capacity of the soil (meq kg^{-1}).

The base saturation (BS) of the soil is then the sum of the exchangeable fractions of base cations:

$$BS = E_{Ca} + E_{Mg} + E_{Na} + E_{K} = 1 - E_{Al} \tag{10}$$

If the aluminium-base cation exchange equations in the model, eqn. (8), are combined with the aluminium solubility equation, eqn. (4), the resultant equations are the Gaines-Thomas expressions for hydrogen ion-base cation exchanges.

The parameters describing the cation exchange process in the model are the selectivity coefficients, S_{AlBC} (one coefficient for each base cation, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and the soil cation exchange capacity, CEC.

The MAGIC model is thus composed of: (1) a set of equilibrium equations which quantitatively describe the equilibrium soil processes and the chemical changes that occur as soil water enters the stream channel; (2) a set of mass balance equations which quantitatively describe the catchment input–output relationships for base cations and strong acid anions in precipitation and streamwater; and (3) a set of definitions which relate the variables in the equilibrium equations to the variables in the mass balance equations.

Details of the equations and the model structure have been given by Cosby et al. (1985a).

SIMULATION RESULTS FOR CI5

MAGIC had been applied to CI5 assuming a sulphate deposition pattern as shown in Fig. 2; significant increases in sulphate loadings have occurred since 1900 with a peak in 1970 and thereafter levels have fallen by approximately 25%.

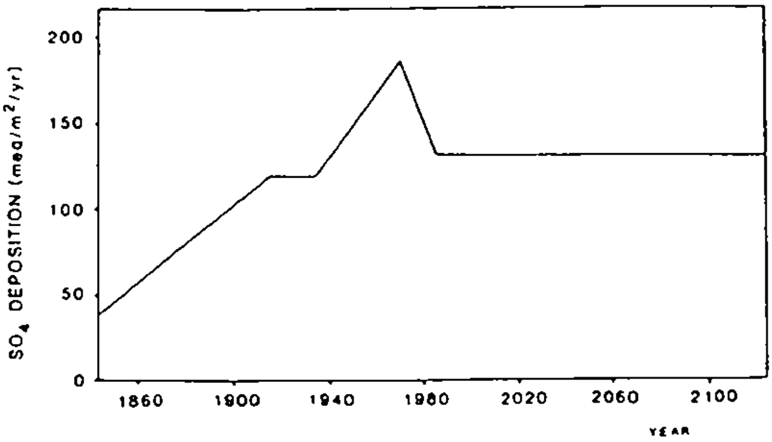


Fig. 2. Sulphate deposition pattern assumed for MAGIC.

An optimisation was applied initially to provide best estimates of the key parameters in the model. These include E_{mx} the maximum sulphate adsorption rate, nitrate and ammonia uptake rates, weathering rates, selectivity coefficients and the partial pressure of CO_2. From the optimisation runs the parameters shown in Table 5 were obtained.

E_{mx} is particularly low suggesting that the soils at Llyn Brianne have a relatively low capacity to adsorb sulphate, compared with catchments in the U.K. (Jenkins et al., 1987). Nitrate and ammonia uptake rates are high and reflect nutrient uptake by the vegetation. Weathering rates are low and this, coupled with the low base saturation levels, indicates the limited ability of the

TABLE 5

Optimal parameters for MAGIC applied to C15

E_{mx}	0.01 meq kg^{-1}
Nitrate uptake rate	68.9 meq m^{-2} yr^{-1}
Ammonia uptake rate	99.1 meq m^{-2} yr^{-1}
Weathering rates:	
Ca	25.0 meq m^{-2} yr^{-1}
Mg	15.0 meq m^{-2} yr^{-1}
Na	10.0 meq m^{-2} yr^{-1}
K	1.0 meq m^{-2} yr^{-1}
Selectivity coefficients:	
Log10 K Al/Ca	1.94
Log10 K Al/Mg	1.67
Log10 K Al/Na	−2.10
Log10 K Al/K	−5.33
pCO_2 in the soil	0.02 atm
Dry/occult deposition factor	1.2

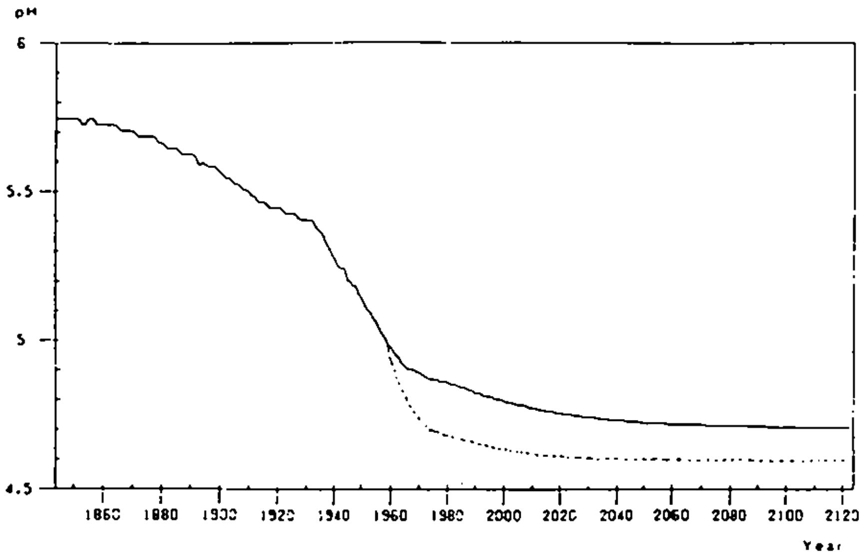


Fig. 3. Simulated pH in CI5 from 1844 to 2124 for moorland and forest conditions. Forest effects from 1958 shown as a dotted line

soils to buffer incoming acidity. The dry/occult deposition factor reflects the relatively low scavenging rate of moorland compared to forest catchments. In the moorland situation only 20% sulphate additional to that deposited by wet deposition, enters the catchment via deposition of dry particles, aerosols and

TABLE 6

Simulated runoff chemistry for CI5

	Without forest growth		With forest growth from 1958	
	(1984/85)	(2124)	(1984/85)	(2124)
Ca	43.7	36.8	54.1	44.8
Mg	55.3	43.0	71.6	56.0
Na	149.4	141.2	202.4	194.8
K	8.0	7.7	10.4	9.7
NH_4	1.6	1.6	2.3	2.3
SO_4	96.8	98.4	147.1	146.2
Cl	168.3	168.3	235.7	235.7
NO_3	15.3	15.4	21.5	21.5
Alkalinity	19.0	9.0	− 64.8	− 98.2
Al	19.2	41.9	53.7	85.0
pH	4.8	4.7	4.7	4.6
Soil base sat. (%)	9.6%	8.0%	9.0%	7.0%

All units $\mu eq\,l^{-1}$ except pH.

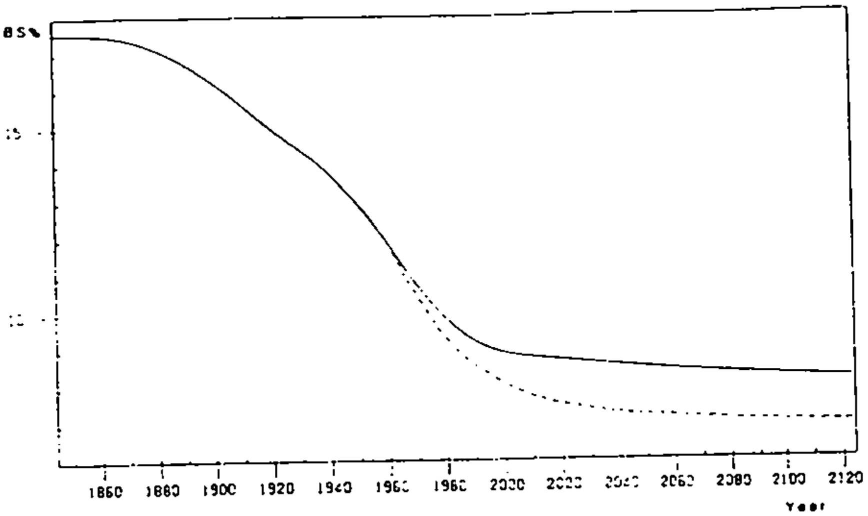


Fig. 4. Simulated base saturation in CI5 from 1844 to 2124 for moorland and forest conditions Forest effects from 1958 shown as a dotted line.

droplets of mist, fog and cloud (occult deposition). In the forest catchment this "additional" deposition can increase to 60% or more.

Table 6 shows that the model-simulated chemistry matches closely the observed values for CI5 (see Table 4) and Figs. 3, 4 and 5 show the historical reconstruction of pH, base saturation and aluminium trends for the catchment.

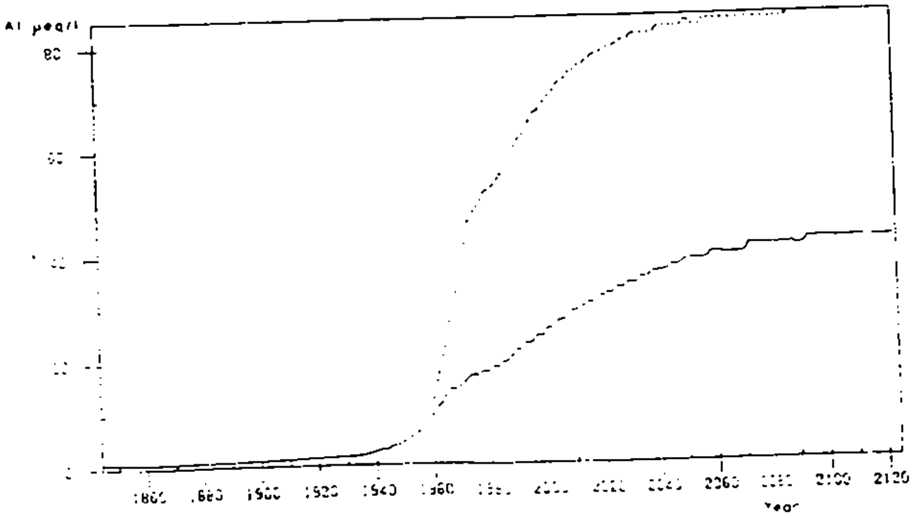


Fig. 5. Simulated aluminium concentrations in CI5 from 1844 to 2124 for moorland and forest conditions Forest effects from 1958 shown as a dotted line.

The significant decrease in the period 1940–1960 is very similar to the South West Scotland trends reported by Batterbee et al. (1985) and Cosby et al. (1986). Recent research by Batterbee and co-workers indicates that similar trends are observed in lakes in Wales (Battarbee, 1988). Figures 4 and 5 suggest that base saturation levels and aluminium concentrations have changed significantly over the same period with base saturation falling to very low levels and aluminium concentrations increasing to 19 μeq l^{-1}. The future predictions, assuming constant future deposition of sulphate at 1984 levels, as illustrated in Fig. 3, suggest a further slight deterioration in catchment pH, although, as shown in Table 6, aluminium levels will continue to rise significantly (Fig. 5). These future changes are accompanied by the continuing reduction in base saturation levels shown in Fig. 4.

Effects of afforestation on CI5

The effects of afforestation can be illustrated using the model. Table 6 and Figs. 3, 4 and 5 show the chemistry of the runoff and base saturation over time assuming a forest is grown on CI5 from 1958. This is achieved in the model by increasing the dry/occult deposition factor and by increasing evapotranspiration. These enhance the sulphate input to the system to 80% compared to 20% for the moorland situation. Sea salts are also increased by 40% during the transition from moorland to forest. The transition is presumed to occur linearly over a fifteen year period from 1958 to 1973 when canopy closure is assumed to occur. The effects of uptake of cations by trees during the early stages of growth are not included in this simulation; also excluded are the effects of hydrological changes caused by increased drainage immediately prior to afforestation. As discussed by Whitehead et al. (1986b) the latter can have significant effect on stream quality as the proportion of surface runoff to baseflow is increased by the additional drainage. However for the purposes of the current modelling exercise these two effects are ignored. Despite these omissions the simulated chemistry shown in Table 6 compares well with observed chemistry of the forest catchment LI1 shown in Table 4. The chemistry of the forest catchment differs markedly from that of the moorland catchment and the fact that the model can reproduce the principal changes in the anions and cations is very encouraging. It suggests that the MAGIC model does indeed capture the main components controlling stream acidification and can therefore be used for management purposes. The simulated long-term responses of the moorland catchment with and without the forest are illustrated in Figs. 3, 4 and 5. The effect of the forest is to reduce pH and base saturation slightly but to increase aluminium levels rapidly. Ormerod et al. (1987) have shown that fish are particularly sensitive to aluminium levels and the simulation results suggest that aluminium levels will rise to 85 μeq l^{-1} in the long term. The model results illustrate that acidification problems in the uplands will be with us for many years unless direct management action is taken and that afforestation does enhance the acidification levels.

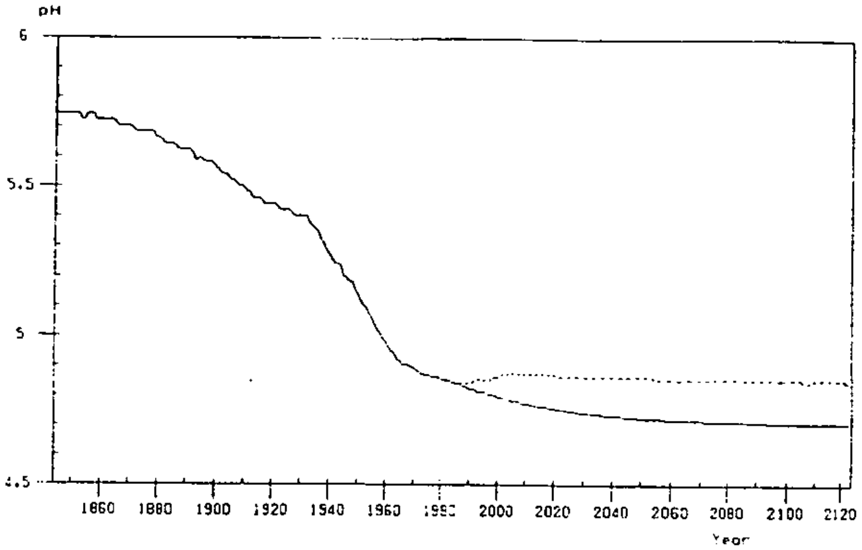


Fig. 6. Simulated pH in CI5 from 1844 to 2124 for moorland conditions assuming constant deposition from 1984 (continuous line) and deposition reduced by 50% since 1984 (dotted line).

Effects of reduced future deposition on CI5

The effects of reducing deposition in the future are illustrated in Fig. 6 which shows the pH in CI5 assuming a 50% reduction in deposition from 1984 levels phased in over a 20 year period. The effect on pH is not particularly striking; a slight recovery in pH or the continuation of current pH levels is shown in Fig. 6. This poor recovery is not surprising given that base saturations and weathering rates are low. In the afforested catchment simulation the long-term recovery in pH is similarly quite small. However aluminium levels are significantly changed as illustrated in Fig. 7 but even these changes will be of no benefit from a fisheries viewpoint (Ormerod et al., 1987).

SIMULATION OF CATCHMENTS LI1 AND LI6

The afforested catchment LI1 and the "unacidified" moorland catchment LI6 have been simulated using the same procedure as for CI5. In the case of LI1 the forest effect is simulated from 1958 with canopy closure occurring after 15 years. The dry/occult deposition factor increases linearly from 1.2 in 1958 to 1.7 for sulphate over this forest growth period. Sea salts are presumed to increase from 1.0 to 1.6 over the same period. In the case of LI6 the moorland catchment is highly buffered and this effect is simulated by increasing the weathering rates of both Ca and Mg to 170 μeq m^{-2}yr^{-1}.

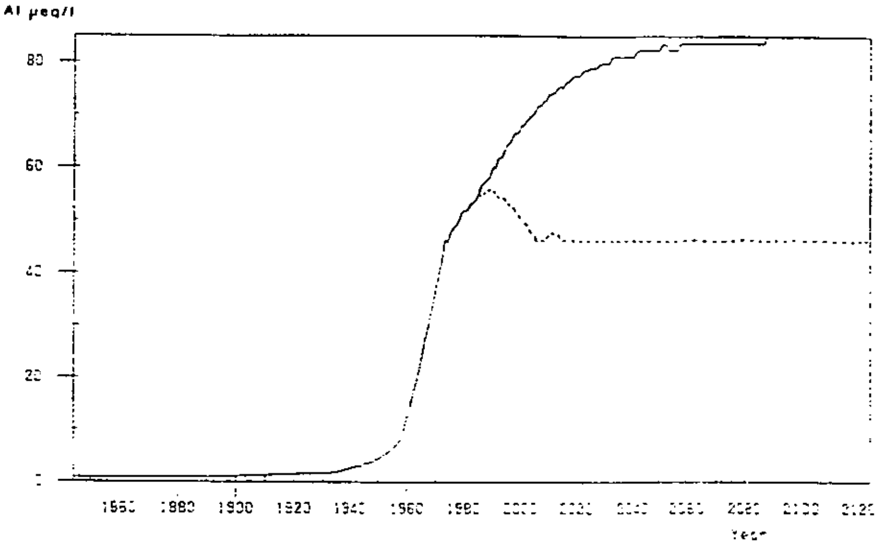


Fig. 7. Simulated aluminium in CI5 from 1844 to 2124 assuming forest growth from 1958 and with constant and reduced deposition levels. Effects of 50% reduction in deposition shown as a dotted line.

TABLE 7

LI1 and LI6 simulated chemistry

	LI1		LI6	
	(1984)	(2124)	(1984)	(2124)
Ca	62.9	46.5	146.9	144.2
Mg	60.9	41.4	145.3	141.1
Na	205.9	191.0	138.9	133.8
K	5.2	0.0	10.4	11.5
NH_4	0.0	0.0	2.1	2.1
SO_4	152.4	150.7	109.2	109.3
Cl	249.9	249.9	156.2	156.2
NO_3	14.0	14.0	12.8	12.8
Alkalinity	− 83.3	− 139.6	165.1	153.9
Al	70.8	124.7	1.6	1.5
pH	4.6	4.5	6.4	6.4
Soil base sat. (%)	6.2	3.8	13.4	12.4

All units except μeq l^{-1} except pH.

With these three major changes the simulated current and future chemistry obtained from the model is illustrated in Table 7. The simulated 1984 chemistry for both LI1 and LI6 compare well with the observed chemistry (Table 4). The contrast between the catchments is enormous with LI1 exhibiting very acid

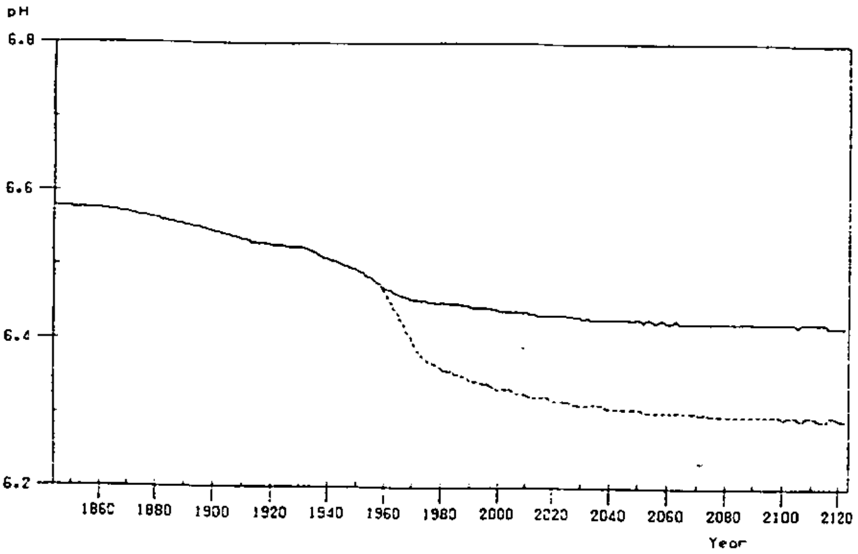


Fig. 8. Simulated pH in LI6 from 1844 to 2124 for moorland and forest conditions. Forest effects from 1958 shown as a dotted line.

conditions, low alkalinities and high aluminium levels and with LI6 showing highly buffered waters rich in cations, high alkalinities and very little aluminium. The long-term simulations for LI6 show that even growing a forest on the catchment would only reduce pH from 6.4 to 6.3, as illustrated in Fig. 8. Thus the internal sources of alkalinity in the catchment, probably generated by calcite intrusions, will buffer incoming acidity in the long term.

In the case of the forest catchment these highly acid conditions are unlikely to be affected even by 50% reduction in deposition.

CONCLUSIONS

The current research has illustrated the ability of the MAGIC model to reproduce catchment chemistry in both moorland and forest streams at Llyn Brianne. The model reconstructs historical trends in acidification; compares well with the trends in acidification derived from paleoecological analysis and provides some measure of confidence in using the model to predict future trends.

The poorly buffered upland catchments in Wales at Llyn Brianne are significantly affected by acid deposition, and are likely to be affected for some time even if deposition is reduced. Any short-term improvement will probably be effected by liming and land management.

Afforestation in the poorly buffered Welsh Uplands regions causes a major increase in acidification following the increased scavenging of sea-salts and anthropogenic sources of acidity.

Small variations in catchment hydrology, soils and geochemistry can have significant effects on the long-term behaviour of stream chemistry. It is essential therefore to collect detailed data on hydrology, geology and soils prior to modelling studies.

ACKNOWLEDGEMENTS

The authors are particularly grateful to the Department of the Environment and Welsh Water for funding the research and for providing data from the Llyn Brianne catchments. The views expressed in the paper are those of the authors and are not necessarily those of the Department of the Environment or the Welsh Water Authority. The authors would like to thank the numerous Welsh Water and UWIST field staff involved in the sample collection and laboratory analysis.

REFERENCES

Battarbee, R.W., 1988. Acidification in the United Kingdom, 1800–1986. Dep. Geogr. Rep., University College, London University.

Battarbee, R.W., Flower, R.J., Stevenson, B.C. and Rippey, B., 1985. Lake acidification in Galloway: A palaeoecological test of competing hypotheses. Nature, 314 (6009): 350–352.

Burns, J.C., Coy, J.S., Tervet, D.J., Harriman, R., Morrison, B.R.S. and Quine, C.P., 1982. The Loch Dee project: a study of the ecological effects of acid precipitation and forest management on an upland catchment in southwest Scotland. 1. Preliminary investigations. Fish. Manage., 15: 145–167.

Calder, I., 1985. Influence of woodlands on water quality. Woodland, Weather and Water. Proc. Inst. Biol., Symp. Edinburgh, pp. 13–22.

Christophersen, N., Seip, H.M. and Wright, R.F., 1982. A model for stream-water chemistry at birkenes, a small forested catchment in southernmost Norway. Water Resour. Res., 18: 977–986.

Christophersen, N., Rustad, S. and Seip, H.M., 1984. Modelling streamwater chemistry with snowmelt. Phil. Trans. R. Soc., London, Ser. B, 305: 427–439.

Cosby, B.J., Wright, R.F., Hornberger, G.M. and Galloway, J.N., 1984. Model of acidification of groundwater in catchments. Proj. Completion Rep., EPA/NCSU Acid Precipitation Program, Proj. No. E2-14.

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. Water 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. Water Resour. Res., 21: 1591–1601.

Cosby, B.J., Hornberger, G.M., Galloway, J.N. and Wright, R.F., 1985c. Fresh water acidification from atmospheric deposition of sulphuric acid: a quantitative model. Environ. Sci. Technol., 19: 1145–1149.

Cosby, B.J., Whitehead, P.G. and Neale, R., 1986. A preliminary model of long-term changes in stream acidity in southwestern Scotland. J. Hydrol., 84: 381–401.

Donald, A., Underwood, J. and Stoner, J., 1986. Results of a survey into deposition quality in Wales during 1984. Welsh Water Auth. Sci. Serv. Rep.

Fritz, S., Stevenson, A.C., Patrick, S.T., Appleby, P., Oldfield, F., Rippey, B., Darley, J. and Batterbee, R.W., 1986. Palaeoecological evaluation of the recent acidification of Welsh Lakes: 1. Llyn Hir, Dyfed. Palaeoecol. Res. Unit, Dep. Geogr., Univ. College London, Working Pap. 16, Rep. for the Dep. Environ.

Grip, H., Jansson, P.E., Honssonm, H. and Nilsson, S.I., 1986. Application of the birkenes model to two forested catchments on the Swedish west coast. Ecol. Bull. (in press).

Harriman, R. and Morrison, B., 1981. Forestry, fisheries and acid rain in Scotland. Scott. For., 36: 89-95.

Hornung, M., 1986. Llyn Brianne Project: catchment characteristics subgroup — First progress report. Welsh Water Auth., p. 75.

Howells, G. (Editor), 1986. The Loch Fleet Project: A report of the pre-intervention phase (1) 1984-1986, CEGB, Leatherhead, p. 110.

Jenkins, A., Whitcombe, A. and Whitehead, P.G., 1987. Hydrochemical behaviour of the Allt a Mharcaidh catchment. Surf. Water Acidification Proj. Conf., Bergen, R. Soc.

Kamari, J., Posch, M. and Kauppi, L., 1984. Development of a model analysing surface water acidification on a regional scale: application to individual basins in southern Finland. Proc. Nord. Hydrol. Workshop, Hydrol. Programme Rep. No. 10.

Law, F., 1956. The effect of afforestation upon the yield of water catchment areas. J. Br. Waterworks Assoc., 11: 489-494.

Mason, B.J. and Seip, H.M., 1985. The current state of knowledge on the acidification of surface waters and guide lines for future research. Ambio, 14: 49-51.

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. J. Geol. Soc. London, 143: 635-648.

Neal, C., Christophersen, N., Neale, R., Smith, C., Whitehead, P. and Reynolds, B., 1986. Chloride in precipitation and streamwater for the upland catchments of the River Severn in mid Wales: Some consequences for hydrochemical models describing the effects of acid deposition. Hydrol. Processes (in press).

Ormerod, S.J., Boole, P., McCahon, C.P., Weatherly, N.S., Pascoe, D. and Edwards, R.W., 1987. Short-term experimental acidification of a Welsh stream: comparing the biological effects of hydrogen ions and aluminium. Freshwater Biol., 17: 341-356.

Reuss, J.O., 1980. Simulations of soil nutrient losses resulting from rainfall acidity. Ecol. Model., 11: 15-38.

Reuss, J.O., 1983. Implications of the Ca-Al exchange system for the effect of acid precipitation on soils. J. Environ. Qual., 12: 591-595.

Reuss, J.O. and Johnson, D.W., 1985. Effect of soil processes on the acidification of water by acid deposition. J. Environ. Qual., 14: 26-31.

Seip, H.M. and Rustad, S., 1983. Variations in surface water pH with changes in sulphur deposition. Water, Air and Soil Pollut., 21: 217-223.

Seip, H.M., Seip, R., Dillon, P.J. and De Grosbois, E., 1986. Model of sulphate concentration in a small stream in the Harp Lake catchment, Ontario. Can. J. Fish. Aquat. Sci. (in press).

Stoner, J. and Gee, A., 1985. The effects of forestry on water quality and fish in Welsh rivers and lakes. J. Inst. Water. Eng. Sci., 39: 27-45.

Stoner, J., Gee, A. and Wade, K., 1984. The effects of acidification on the ecology of streams in the upper Tywi catchment in West Wales. Environ. Pollut., Ser. A. 35: 125-157.

Whitehead, P.G., Neal, C., Seden-Perriton, S., Christophersen, N. and Langan, S., 1986a. A time series approach to modelling stream acidity. J. Hydrol., 85: 281-304.

Whitehead, P.G., Neal, C. and Neale, R., 1986b. Modelling the effects of hydrological changes on stream acidity. J. Hydrol., 84: 353-364.

Whitehead, P.G., Reynolds, B., Hornung, M., Neal, C., Cosby, J. and Paricos, P., 1988. Modelling long stream acidification trends in Upland Wales at Plynlimon. Hydrol. Processes (in press).

Wright, R.F., Cosby, B.J., Hornburger, G. and Galloway, J.N., 1987. Interpretation of paleoecological reconstructions using the *MAGIC* model of soil and water acidification. Water, Air, Soil Pollut., J. (in press).

2.2 Plynlimon - Wales

HYDROLOGICAL PROCESSES, VOL. 2, 357–368 (1988)

MODELLING LONG TERM STREAM ACIDIFICATION TRENDS IN UPLAND WALES AT PLYNLIMON

P. G. WHITEHEAD
Institute of Hydrology, Wallingford, Oxon OX10 8BB, U.K.
B. REYNOLDS AND M. HORNUNG
Institute of Terrestrial Ecology, Bangor Research Station, Penrhos Road, Bangor, Wales
C. NEAL
Institute of Hydrology, Wallingford, Oxon OX10 8BB, U.K.
J. COSBY
Department of Environmental Science, University of Virginia, Charlottesville, U.S.A.
AND
P. PARICOS
Institute of Hydrology, Wallingford, Oxon OX10 8BB, U.K.

ABSTRACT

Historical reconstructions and predictions of streamwater acidification are presented for moorland and afforested catchments in the Welsh Uplands at Plynlimon. MAGIC (Model of Acidification of Groundwater In Catchments) is validated by application to an afforested catchment. MAGIC is used to illustrate that atmospheric deposition is primarily responsible for stream acidification but that conifer afforestation can enhance stream acidity. The historical trends determined by the model illustrate that long-term acidification has been present since the turn of the century and will continue unless either deposition levels are reduced significantly or liming is undertaken on a major scale.

KEY WORDS Acidification Modelling Wales Afforestation

INTRODUCTION

Stream acidification can be considered as a problem involving two timescales. On the one hand there are significant short-term pulses or flushes of acidity which, in small upland catchments occur on an hourly timescale and reflect hydrological changes (e.g. storm events) in the catchment (Whitehead *et al.*, 1986a). These acid pulses may be very severe causing considerable damage to fisheries (Stoner *et al.*, 1984). The short lived acid events are superimposed upon the effects of longer term acidification processes. Upland catchments in Western Britain have been subjected to high levels of acid deposition for many years, since the start of the industrial revolution in the nineteenth century. The buffering ability of the soils and rocks can, however, delay any resulting catchment acidification for many decades. The magnitude of the short-term pulses are highly dependent on how far the long-term process of acidification has progressed within a catchment. In any acidification study it is important to evaluate the current status of catchment acidity and the historical trends and processes that have occurred.

It is with these problems in mind that the Institute of Hydrology (IH) and Institute of Terrestrial Ecology (ITE) have established catchment studies in Scotland and Wales. In Wales there are two principal study areas, namely Plynlimon (see Hornung *et al.*, 1986; Neal *et al.*, 1985) and Llyn Brianne (Stoner *et al.*, 1984). In both studies IH is responsible for developing hydrochemical models which can be

0885-6087/88/040357-12$06.00

Received 8 September 1987
Revised 20 January 1988

used to assess both short-term acid pulses and long-term trends in catchment acidity. In Scotland catchments in the Galloway Region of southwest Scotland at Loch Dee are being investigated (Burns *et al.*, 1982; Cosby *et al.*, 1986) and a new catchment study has been established in the Cairngorms at the Allt a Mharcaidh under the auspices of the Royal Society Surface Water Acidification Project (Mason and Seip, 1985; Jenkins *et al.*, 1987).

In this paper the long-term acidification processes at Plynlimon are considered and the model MAGIC applied to a small grassland catchment. The effects on the grassland catchment of growing a forest are also investigated using the model and MAGIC is validated by reference to forest stream chemistry.

THE PLYNLIMON EXPERIMENTAL CATCHMENT

The Plynlimon experimental catchments comprising the headwaters of the Rivers Wye and Severn are located in the eastern slopes of the Plynlimon massif, approximately 24 km from the west coast of Wales, at altitudes which range between 300 m and 750 m above sea level. The area is underlain by base-poor Lower Palaeozoic mudstones, shales, and grits upon which a mosaic of acid upland soils (stagnopodzols, gleys, brown podzolic soils, rankers, and peats) have developed. Underlying the soils in some parts of the catchment are drift deposits of boulder clay and colluvium derived from the bedrock. Land-use in the upper Wye consists of sheep grazing on acid seminatural *Nardus-Agrostis-Festuca* grassland and areas improved by the application of lime and compound fertilizer (Hornung *et al.*, 1986). The average grazing density is 1·1 ewe ha^{-1}. The majority of the upper Severn catchment is covered by plantation conifer forest consisting mainly of Sitka spruce (*Picea sitchensis*) and Norway spruce (*Picea abies*) planted in three phases between 1937 and 1964. The forest has been extensively drained by ploughing and ditching; these ditches cut through the various soil horizons and, in some cases, penetrate to bedrock. The catchments are described in greater detail by Newson (1976).

Data from two first-order catchments are presented in this paper. The seminatural grassland catchment, C2, is located in the Cyff catchment of the Upper Wye (Figure 1). The forest site, F2, is situated in the Hore catchment of the Upper Severn, and was planted with Sitka spruce in 1949. Both catchments are of similar size (2–4 ha) and contain a similar range and distribution of soils; they differ only in land-use and vegetation.

The rainfall and runoff chemistry for the unimproved grassland catchment, C2, and the forest stream, F2, is shown in Table 1.

The forest catchment runoff is significantly more acidic with an average pH of 4·7 compared to that of the grassland site C2, with pH 5·3. The region is subject to high rainfall (3030 mm per year) and rainfall chemistry is dominated by marine salts (Na, K, Mg, and Cl), however sulphate levels are high and well in excess of marine levels, indicating that anthroprogenic sources of sulphate are significant, (Reynolds *et al.*, 1984).

Soils are thin (depth *c.* 0·75 m) and base poor with a base saturation of 7·5 per cent and cation exchange capacity of 48·3 $\mu eq\ kg^{-1}$.

CONCEPTUAL BASIS OF MAGIC

The most serious effects of acidic deposition on catchment-surface water quality are thought to be decreased pH and alkalinity and increased base cation and aluminium concentrations. In keeping with an aggregated approach to modelling whole catchments, a relatively small number of important soil processes—processes that could be treated by reference to average soil properties—could produce these responses. In two papers, Reuss (1980, 1983) proposed a simple system of reactions describing the equilibrium between dissolved and adsorbed ions in the soil–soil water system. Reuss and Johnson (1985) expanded this system of equations to include the effects of carbonic acid resulting from elevated CO_2 partial pressure in soils and demonstrated that large changes in surface water chemistry would be expected as either CO_2 or sulphate concentrations varied in the soil water. MAGIC has its roots in the

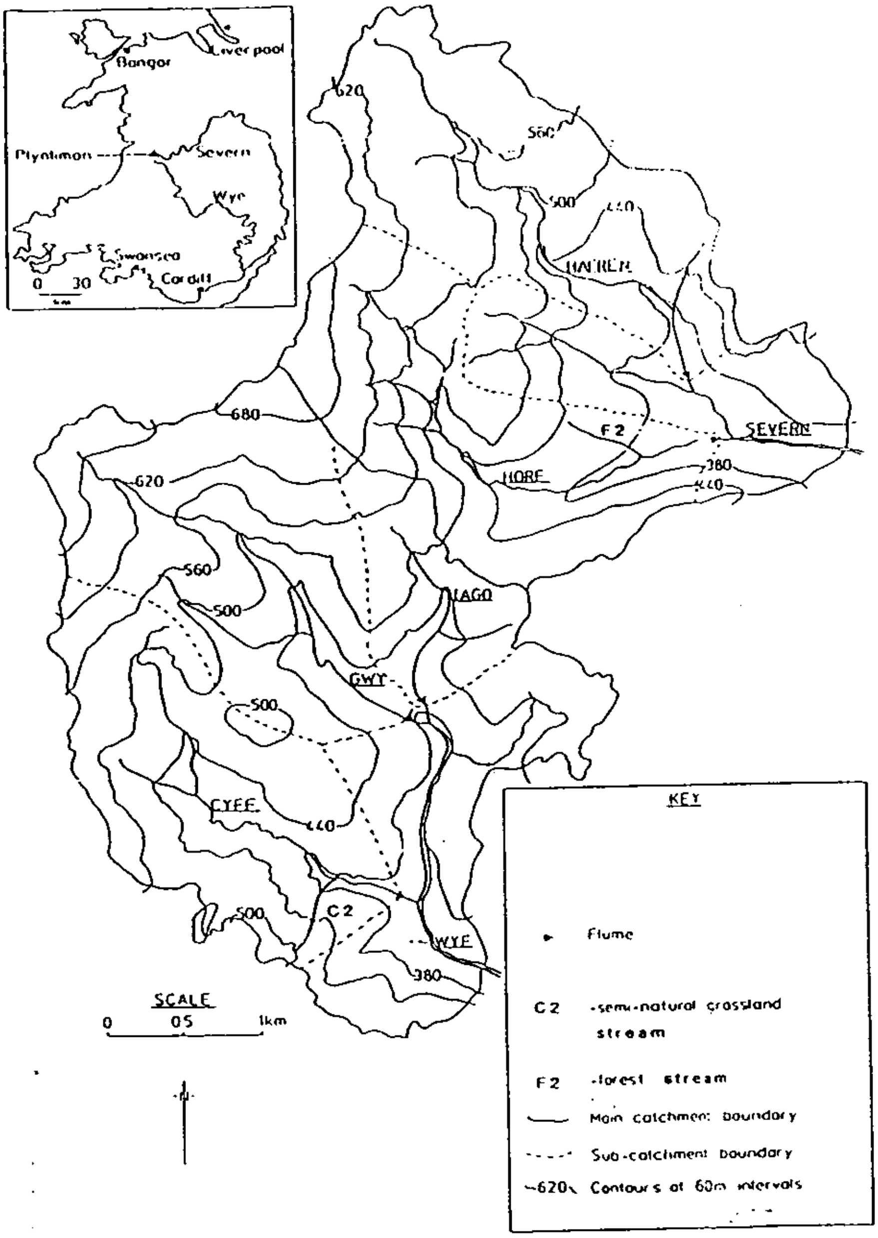


Figure 1. Location of the study sites

Reuss–Johnson conceptual system, but has been expanded from their simple two-component (CA–Al) system to include other important cations and anions in catchment soil and surface waters.

Atmospheric deposition, mineral weathering, and exchange processes in the soil and soil water are assumed to be responsible for the observed surface water chemistry in a catchment. Alkalinity is generated in the soil water by the formation of bicarbonate from dissolved CO_2 and water:

$$CO_2 + H_2O = H^+ + HCO_3^- \tag{1}$$

Table 1. Rainfall and runoff chemistry

		Rainfall	C2	F2
Ca	μeq l^{-1}	13·0	54·9	37·9
Mg	μeq l^{-1}	19·7	57·6	70·7
Na	μeq l^{-1}	79·6	134·9	205·3
K	μeq l^{-1}	2·3	2·6	4·6
NH_4	μeq l^{-1}	15·7	0·0	0·0
SO_4	μeq l^{-1}	62·5	99·9	123·7
Cl	μeq l^{-1}	98·7	141·1	222·6
NO_3	μeq l^{-1}	16·4	5·0	21·4
Alkalinity	μeq l^{-1}	—	20·8	−25·5
pH	μeq l^{-1}	4·2	5·3	4·7
Al	mg l^{-1}	—	0·0	0·42
% base saturation		—	7·5	6·0
Years of Record		1980–81	1980–81	1984–85

Bicarbonate ion concentrations in soil water are calculated using the familiar relationships between the partial pressure of CO_2 (P_{CO_2}, atm) and hydrogen ion activity in the soil water:

$$[HCO_3^-] = K_C \frac{P_{CO_2}}{[H^+]} \qquad (2)$$

where the combined constant K_C is known for a given temperature (Stumm and Morgan, 1970).

The free hydrogen ion produced (Equation 1) reacts with an aluminium mineral (e.g. gibbsite) in the soil:

$$3H^+ + Al(OH)_3(s) = Al^{3+} + 3H_2O \qquad (3)$$

The MAGIC model assumes a cubic equilibrium relationship between Al and H. The equilibrium expression for this reaction is:

$$K = \frac{[Al^{3+}]}{[H^+]^3} \qquad (4)$$

where the accolades indicate aqueous activities. Classically this is considered as relationship to $Al(OH)_3$ solubility controls. However here, as in most previous modelling studies, while a cubic relationship is still used it represents potentially a variety of chemical reactions. As such the equilibria constant does not have to have the value for the solubility product for gibbsite. Several aqueous complexation reactions of Al^{3+} are included in the model (Cosby *et al.*, 1985a). These reactions are temperature dependent and appropriate corrections for temperature and ionic strength are made in the model.

Generally, the cation exchange sites on the soil matrix have higher affinity for the trivalent aluminium cation than for di- or monovalent base cations. An exchange of cations between the dissolved and adsorbed phase results:

$$Al^3 + 3BCX(s) = AlX_3(s) + 3BC^+ \qquad (5)$$

where X is used to denote an adsorbed phase and BC^+ represents a base cation. The net result of these reactions is the production of alkalinity (e.g. $Ca(HCO_3)_2$). As CO_2 partial pressure or the availability of base cations on the soil exchange sites increases, the equilibrium reactions proceed further to the right hand side in each case resulting in higher alkalinity.

When the solution is removed from the contact with the soil matrix and is exposed to the atmosphere (i.e. soil water enters the stream channel), the CO_2 partial pressure of the solution declines. The pH of the solution increases as CO_2 is lost to the atmosphere. Because the solution is no longer in contact with the soil matrix, cation exchange reactions no longer occur. The alkalinity and base cation concentrations are thus unchanged.

If the exchangeable base cations on the soils become depleted, less aluminium is exchanged from the soil water (Equation 3) and the Al^{3+} concentration in the water entering the stream is higher. As the streamwater loses CO_2 and the pH begins to rise, the solubility of aluminium species in the stream is exceeded and a solid phase of aluminium precipitates. These aluminium precipitation reactions retard the increase of streamwater pH as the CO_2 degasses, resulting in lower streamwater pH for the case where exchangeable cations are less available.

Less adsorption of aluminium by the solid also decreases the soil and surface water alkalinity. Consider an abbreviated definition of the alkalinity of soil and surface waters:

$$\mathrm{ALK} = (\mathrm{HCO_3^-}) - (\mathrm{H^+}) - 3(\mathrm{Al^{3+}}) \tag{6}$$

where the brackets indicate molar concentrations. It is apparent that as the ability of the catchment soils to exchange Al^{3+} declines and aluminium and hydrogen ion concentrations increase, the alkalinity of the solution must decline, even though the source of HCO_3^- is not affected.

The process of acidification is controlled in part by the rate at which the exchangeable base cations on the soil are depleted. This in turn is affected by the rate of re-supply through weathering of base cations from primary minerals and the rate of loss through leaching of base cations from the soil. Leaching of base cations is affected mainly by the concentration of strong acid anions (i.e. SO_4^{2-}, NO_3^-, Cl^-, and F^-) and base cations in the solution moving through the soil. As anions increase in concentration, there must be an equivalent increase in cation concentration to maintain a charge balance.

The model calculates the concentrations of four strong acid anions in both soil and streamwater (SO_4^{2-}, Cl^-, NO_3^-, and F^-). Sulphate has an adsorbed phase in soil and the relationship between adsorbed phase (E_x, meq kg^{-1}) and the concentration of dissolved sulphate (SO_4^{2-}, meq m^{-3}) in soil water is assumed to follow a Langmuir isotherm (Singh, 1984).

$$E_x = E_{mx} \frac{(\mathrm{SO_4^{2-}}}{C + (\mathrm{SO_4^{2-}})} \tag{7}$$

E_{mx} = maximum adsorption capacity of the soils (meq kg^{-1})
C = half saturation concentration (meq m^{-3})

If anions derived from atmospheric deposition are accompanied by H^+, as is the case for acid deposition, the excess H^+ will initially displace base cations from the soil exchange sites. As the base saturation declines, aluminium and hydrogen ion become increasingly important in maintaining the ionic charge balance in solution. The water delivered to the stream becomes more acidic as the acidic deposition persists.

The model assumes that only Al^{3+} and four base cations are involved in cation exchange between soil and soil solution. The exchange reactions are modelled assuming an equilibrium-like expression (Gaines and Thomas, 1953):

$$S_{Al\,BC} = \frac{[\mathrm{BC^{2+}}]^3 E_{Al}^2}{[\mathrm{Al^{3+}}]^2 E_{BC}^3} \quad \text{or} \quad S_{Al\,BC} = \frac{[\mathrm{BC^{+}}]^3 E_{Al}}{[\mathrm{Al^{3+}}] E_{BC}^3} \tag{8}$$

For divalent or monovalent base cations respectively, where the brackets indicate aqueous activities, $S_{Al\,BC}$ is a selectivity coefficient (Reuss, 1983) and the E_{xx}'s indicate exchangeable fractions of the appropriate ions on the soil complex. If the amount of Ca^{2+} on the soil of a catchment were given by X meq kg^{-1}, then

$$E_{Ca} = \frac{X}{CEC} \tag{9}$$

where CEC is the cation exchange capacity of the soil (meq kg^{-1}).

The base saturation (BS) of the soil is then sum of the exchangeable fractions of base cations:

$$BS = E_{Ca} + E_{Mg} + E_{Na} + E_{K} = 1 - E_{Al} \tag{10}$$

If the aluminium–base cation exchange equations in the model (Equation 8) are combined with the aluminium solubility equation (Equation 4), the results are equations that are Gaines–Thomas expressions for hydrogen ion – base cation exchanges.

The parameters describing the cation exchange process in the model are the selectivity coefficients, $S_{Al\,BC}$ (one coefficient for each base cation, Ca^2, Mg^2, Na^+, K^+) and the soil cation exchange capacity, CEC.

The MAGIC model is composed of:

1. A set of equilibrium equations which quantitatively describe the equilibrium soil processes and the chemical changes that occur as soil water enters the stream channel
2. A set of mass balance equations which quantitatively describe the catchment input–output relationships for base cations and strong acid anions in precipitation and streamwater
3. A set of definitions which relate the variables in the equilibrium equations to the variables in the mass balance equations.

Details of the equations and the model structure have been given by Cosby *et al.* (1985a).

SIMULATION RESULTS

MAGIC had been applied to the grassland catchment, C2, using the pattern of emissions shown in Figure 2 to drive the model. The assumed deposition shows the significant increases in sulphate loadings since 1900 with a peak reached in 1970. Since 1970 levels have fallen by approximately 25 per cent.

A Rosenbrock optimization was applied initially to provide best estimates of the key parameters in the model. These include E_{mx} the maximum sulphate adsorption rate, nitrate and ammonia uptake rates, weathering rates, selectivity coefficients, and the partial pressure of CO_2. From the optimization runs the parameters shown in Table II were obtained. This is the first research at Plynlimon in which such parameters have been estimated and laboratory analysis is currently being undertaken to evaluate the selectivity coefficients for comparison with model estimates.

These optimal parameter values indicate

(a) The high rates of uptake of ammonia and nitrate, presumably by the vegetation
(b) The high rates of weathering of Ca, Mg, Na
(c) The significant additional loadings of sulphate via the occult and dry deposition factor
(d) The relatively high storage of sulphate on the soils. Here the E_{mx} represents the maximum uptake capacity and at 3·38 meq kg^- is fairly high compared to other catchment studies (see Whitehead *et al.*, 1987).

A typical simulation of pH in the catchment (see Figure 3) shows relatively high background pH with a decreasing trend which accelerates in the period 1940–1970 to give a rapid fall in pH. Note, however, a slight recovery in pH in the early 1980s which represents response to the falling deposition levels. Table III shows the simulated catchment chemistry which compares extremely well with the observed chemistry for C2 shown in Table I. The trends in pH decline match closely with the trends in algal changes

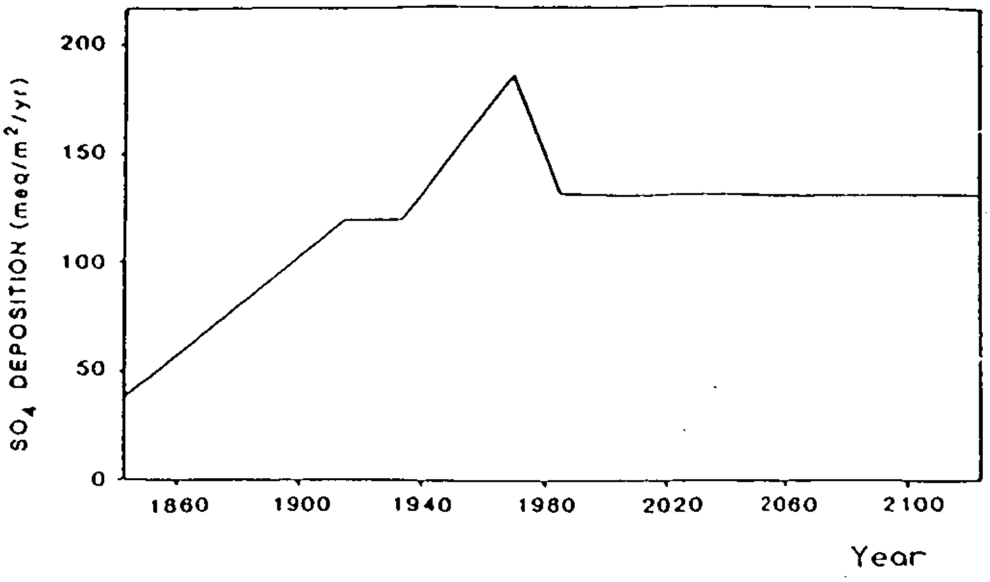


Figure 2. Sulphate deposition pattern 1844–2124 assuming constant deposition since 1984

Table II. Optimal parameter values

E_{mx}	=	3·38	meq kg^{-1}
Nitrate uptake rate	=	73·4	meq m^{-2} $year^{-1}$
Ammonia uptake rate	=	99·7	meq m^{-2} $year^{-1}$
Weathering rates Ca	=	116·9	meq m^{-2} $year^{-1}$
Mg	=	88·2	meq m^{-2} $year^{-1}$
Na	=	66·4	meq m^{-2} $year^{-1}$
Selectivity Coefficients			
Log_{10} K Al Ca	=	2·70	
Log_{10} K Al Mg	=	3·27	
Log_{10} K Al Na	=	−0·65	
Log_{10} K Al K	=	−4·70	
p CO_2 atm	=	0·0328	
Occult and Dry deposition factor	=	1·3	

determined by Fritz *et al.* (1986), Batterbee *et al.* (1985) in Wales and Galloway respectively. The long term decline is a result of progressive lowering of base saturation (see Figure 4) caused by the weathering of cations by incoming acidity. In Plynlimon the base saturation is initially high at 18 per cent but by 1984 has been reduced to 4·2 per cent, a very low level for soils.

An important aspect of acidification is the release of aluminium into the soil and stream water. Fish are particularly sensitive to elevated aluminium levels and it is important water quality parameter with regard to other stream fauna such as invertebrates. Figure 5 shows the simulated total aluminium levels for the grassland catchment, historical levels are very low but by 1980 are just beginning to rise.

EFFECTS OF AFFORESTATION

The effects of afforestation on acidification trends can be highly significant. Firstly hydrological flowpaths change following increased drainage, then enhanced evapotranspiration concentrates solutes, and finally

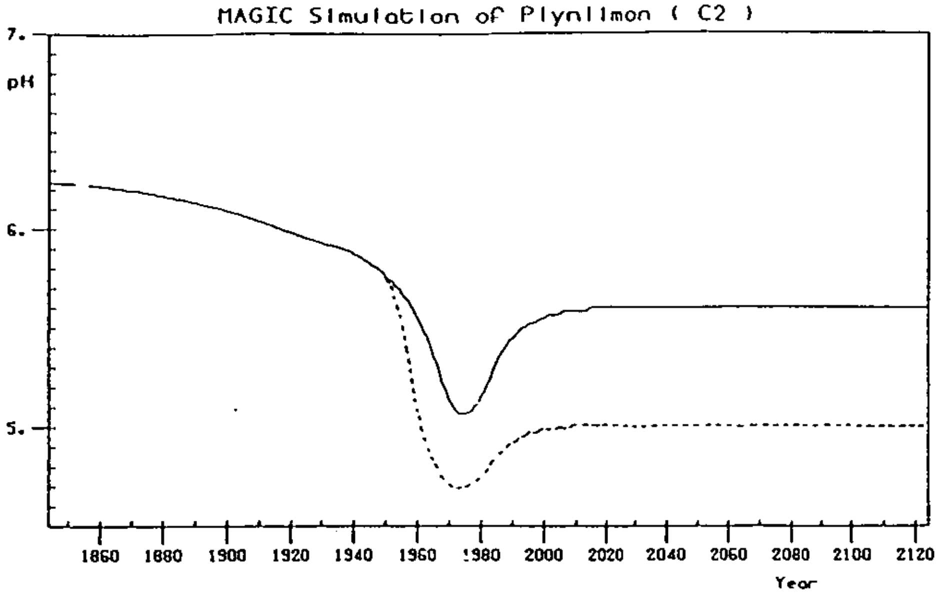


Figure 3. Simulated pH trends in moorland (——) and forest (---) catchments

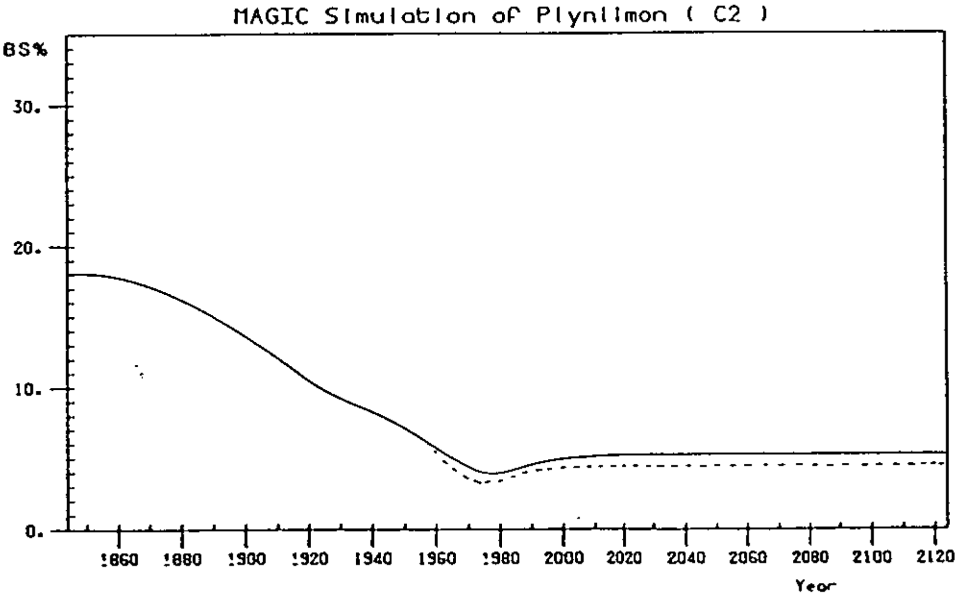


Figure 4. Simulated Base Saturation % trends in moorland (——) and forest (---) catchments

once canopy closure is complete a major additional influx of sulphate and marine salts is achieved via occult and dry deposition. The effects of hydrological changes have been investigated by Whitehead *et al.* (1986b). In the current study the effects of altering the evapotranspiration rate and dry and occult deposition following afforestation are considered. The MAGIC model can be used to simulate these effects by allowing the concentration of the incoming marine salts (Na, K, Mg, and Cl) to increase by a factor of 60 per cent and allowing incoming sulphate concentration to increase by 80 per cent.

These increases are phased in over a ten year period from 1949 to 1959 the approximate dates of afforestation and canopy closure at Plynlimon. The effects of this are shown in Table III which presents

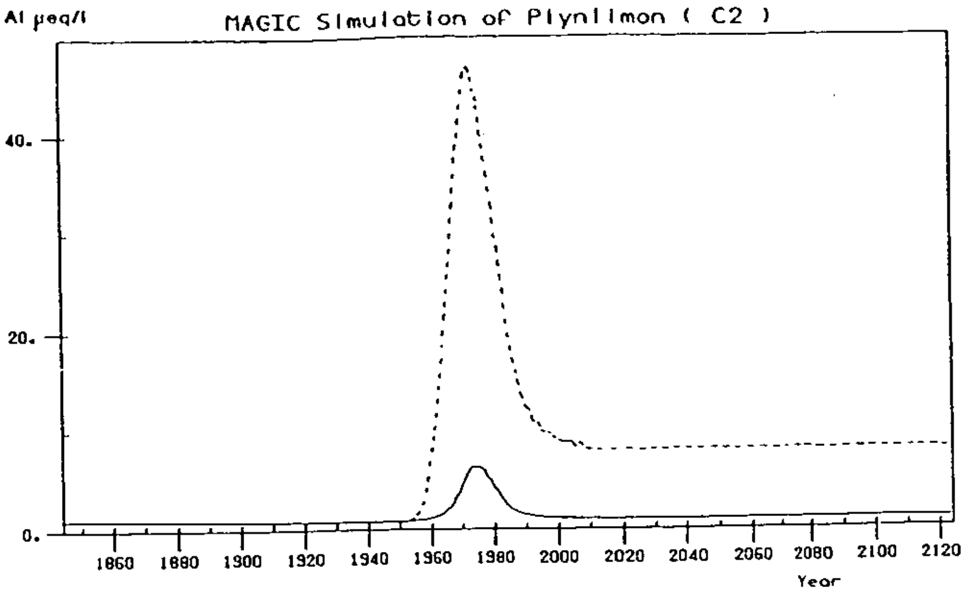


Figure 5. Simulated aluminium in moorland (——) and forest (---) catchments

Table III. Simulated stream chemistry

		Grassland stream	Forest stream
pH		5·3	4·8
Ca	μeq l^{-1}	54·9	61·0
Mg	μeq l^{-1}	57·5	73·9
Na	μeq l^{-1}	134·9	201·1
K	μeq l^{-1}	3·4	4·7
NH_4	μeq l^{-1}	0·1	0·1
SO_4	μeq l^{-1}	99·9	135·5
Cl	μeq l^{-1}	140·6	224·9
NO_3	μeq l^{-1}	5·0	7·0
Alkalinity	μeq l^{-1}	5·2	−26·8
Al (assuming Al^{3+})	μeq l^{-1}	2·4	20·5
% Base saturation)		4·2	3·9

simulation chemistry. The results are close to the observed chemistry from the forest catchment at Plynlimon (see Table I) and this has been achieved without recalibrating the model and therefore provides a validation of the model. That the model can reproduce the forest chemistry by simply increasing the occult/dry deposition factors is particularly interesting since it suggests that these processes are dominant and other effects such as uptake of cations by the growing trees may be of less importance to the final equilibrium chemistry.

Afforestation has a significant effect on acidification trends as shown in Figures 3, 4, and 5 for pH, base saturation, and total aluminium (Al^{3+}). In the case of pH a very significant decline is simulated with final equilibrium levels at 4·8 per cent. Base saturation falls to 3·9 per cent and aluminium concentrations increase dramatically to equilibrium levels of 20 μeq l^{-1}.

EFFECTS OF REDUCED DEPOSITION

One possible management option to control acidification is to reduce sulphate emissions from power stations and thereby reduce deposition of sulphate on remote catchments. Unfortunately, because of the complex nature of physical and chemical processes operating, the relationship between emission and deposition is non-linear (Derwent and Nodop, 1986). Nevertheless it is possible to simulate the effects of reduced deposition using MAGIC. With the future deposition reduced by 50 per cent over the next 20 years and thereafter remaining constant, there is a marked effect on simulated catchment chemistry, as illustrated in Figures 6 and 7, which show the pH and aluminium (Al^{3+}) changes over time for the

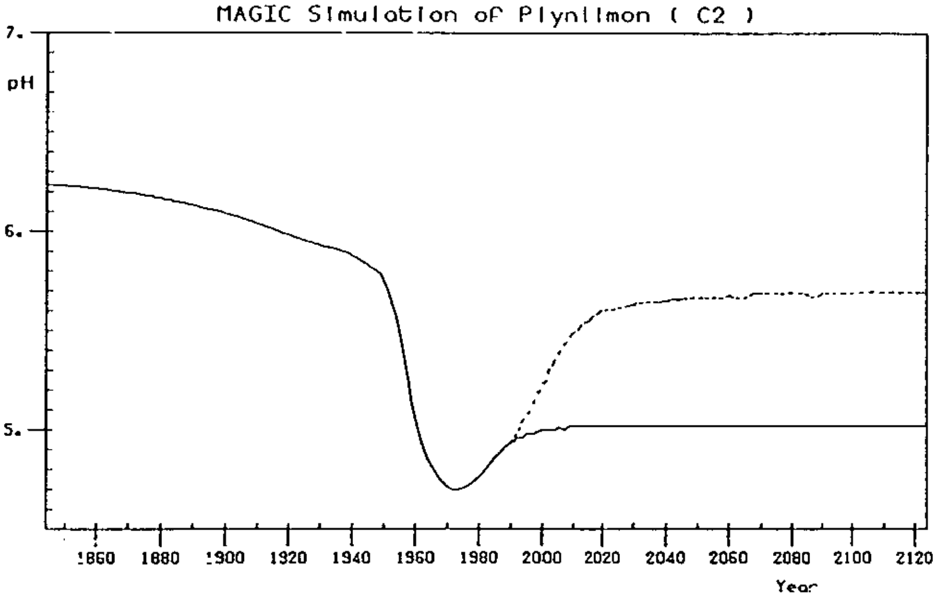


Figure 6. Simulated pH in forest catchment assuming constant (——) and reduced (---) future deposition

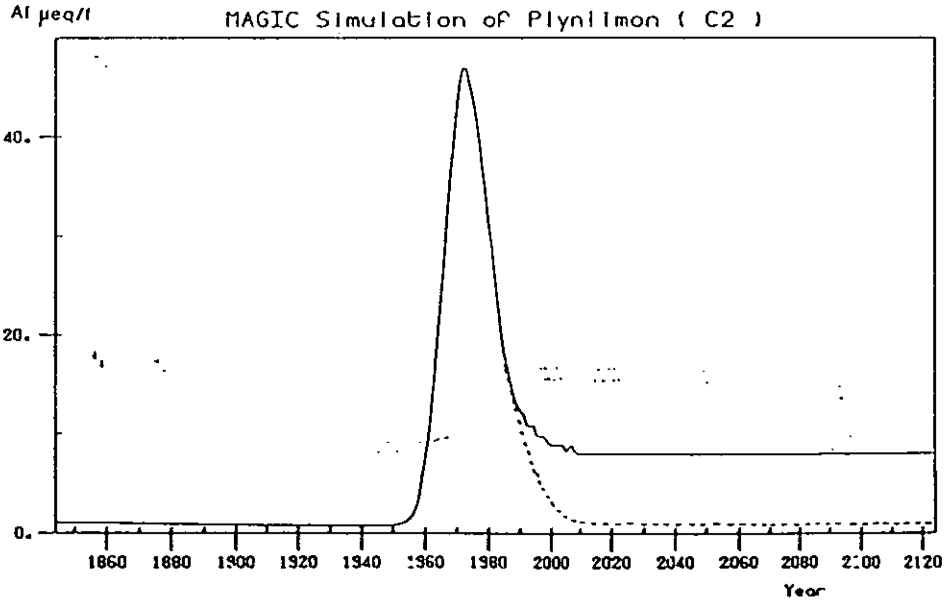


Figure 7. Simulated aluminium in forest catchment assuming constant (——) and reduced (---) future deposition levels

afforested catchment. Aluminium levels fall significantly and pH recovers to reasonable levels. These results indicate that a 50 per cent reduction in deposition may have an effect if it could be achieved. Atmospheric modelling studies are required, however, to convert this reduction in deposition to a reduction in emission.

CONCLUSIONS

The current research has illustrated the ability of the MAGIC model to reproduce catchment chemistry in both grassland and forest streams at Plynlimon. Of particular interest is the ability of the model to reconstruct historical trends in acidification derived from palaeological analysis (Batterbee *et al.*, 1985; Wright *et al.*, 1987) and provide some measure of confidence in using the model to predict future trends. The upland catchments in Wales are significantly affected by acidic deposition and will continue to be unless deposition is reduced or liming is undertaken on a large scale. Also the effects of afforestation are severe causing a major increase in scavenging of sea-salts and anthropogenic sources of acidity. Finally from a process point of view the MAGIC model appears to be the most appropriate model to date for simulating long-term chemical changes in catchment acidification. The validity of the model has been demonstrated by application to the forest catchment and this has been an important aspect of the modelling study.

REFERENCES

Batterbee, R. W., Flower, R. J., Stevenson, A. C. and Rippey, B. 1985. 'Lake acidification in Galloway: a palaeoecological test of competing hypotheses', *Nature*, **314** (6009): 350–352.

Burns, J. C., Coy, J. S., Tervet, D. J., Harriman, R., Morrison, B. R. S. and Quine, C. P. 1982. 'The Loch Dee project: a study of the ecological effects of acid precipitation and forest management on an upland catchment in southwest Scotland. 1. Preliminary investigations', *Fish. Manage.*, 15, 145–167.

Cosby, B. J., Wright, R. F., Hornberger, G. M. and Galloway, J. N. 1984. 'Model of acidification of groundwater in catchments', *Project Completion Rep., EPA/NCSU Acid Precipitation Program*, Project number E2–14.

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', *Water 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', *Water Resour. Res.*, 21, 1591–1601.

Cosby, B. J., Whitehead, P. G. and Neale, R. 1986. 'A preliminary model of long-term changes in stream acidity in southwestern Scotland', *J. Hydrol.*, 84, 381–401.

Derwent, R. G. and Nodop, K. 1986. 'Long range transport and deposition of acidic nitrogen species in North West Europe', *Nature*, 324, 356–358.

Fritz, S., Stevenson, A. C., Patrick, S. T., Appelby, P., Oldfield, F., Rippey, B., Darley, J. and Batterbee, R. W. 1986. 'Palaoelogical evaluation of the recent acidification of the Welsh Lakes: I.Lynn Hir, Dyfed', Palaoelogy research unit, Dept. Geography, Univ. College London. *Working Paper no. 16, Report for the Dept. Environment.*

Gaines, G. L. and Thomas, H. C. 1953. 'Adsorption studies on clay minerals: II. A formulation of the thermodynamics of exchange adsorption', *J. Chem. Phys.*, 21, 714–718.

Hornung, M., Stevens, P. A. and Reynolds, B. 1986. 'The impact of pasture improvement on the soil solution chemistry on some Stagnopodzols in Mid-Wales', *Soil Use & Management*, 2, 18–26.

Jenkins, A., Whitcombe, A. and Whitehead, P. G. 1987. 'Hydrochemical behaviour of the Allt a Mharcaidh catchment', *SWAP conference proceedings*, Bergen.

Mason, B. J. and Seip, H. M. 1985. 'The current state of knowledge on the acidification of surface waters and guide lines for future research', *Ambio*, 14, 49–51.

Neal, C., Reynolds, B., Stevens, P. A. and Hornung, M. 1985. 'Factors influencing stream water chemistry in the Welsh Uplands; examples from Plynlimon', *Welsh Soils Discussion Group* (in press).

Newson, M. D. 1976. 'The physiography, dposits and vegetation of the Plynlimon catchments', *Institute of Hydrology report No. 30.*

Reynolds, B., Hornung, M. and Stevens, P. A. 1984. 'Factors influencing bulk precipitation chemistry at an upland site in Mid-Wales', *Int. J. Environ. Studies*, 22, 196–205.

Reuss, J. O. 1980. 'Simulations of soil nutrient losses resulting from rainfall acidity', *Ecol. Model.*, 11, 15–38.

Reuss, J. O. 1983. 'Implications of the Ca–Al exchange system for the effect of acid precipitation on soils', *J. Environ. Qual.*, 12, 591–595.

Reuss, J. O. and Johnson, D. W. 1985. 'Effect of soil processes on the acidification of water by acid deposition", *J. Environ. Qual.* 14, 26–31.

Seip, H. M. and Rustad, S. 1983. 'Variations in surface water pH with changes in sulphur deposition', *Water, Air and Soil Poll.*, 21, 217–223.

Singh, B. R. 1984. 'Sulphate sorption by acid forest soils: 1. Sulphate adsorption isotherms and comparison of different adsorption equations in describing sulphate adsorption', *Soil Sci.*, 138, 189–197.

Stoner, J. H., Gee, A. S. and Wade, K. R. 1984. 'The effects of the acidification on the ecology of streams in the upper Tywi catchment in West Wales', *Environ. Pollut.*, 35, 125–157.

Stumm, W. and Morgan, J. J. 1970. *Aquatic chemistry*. Wiley Interscience, New York, N.Y.

Whitehead, P. G., Neal, C., Seden-Perriton, S., Christophersen, N. and Langan, S. 1986a. 'A time series approach to modelling stream acidity', *J. Hydrol., (Amst.)*, 85, 281–304.

Whitehead, P. G., Neal, C. and Neale, R. 1986b. 'Modelling the effects of hydrological changes on stream acidity', *J. Hydrol., (Amst.)*, 84, 353–364.

Whitehead, P. G., Bird, S., Hornung, M., Cosby, J., Neal, C. and Paricos, P. 1987. 'A modelling study of the Lynn Brianne catchments', *J. of Hydrology* (In press).

Wright, R. F., Cosby, B. J., Hornburger, G. and Galloway, J. N. 1986. 'Interpretation of palaeoecological reconstructions using the MAGIC model of soil and water acidification', *Water, air, soil pollution. Proceedings of Muskoka Meeting on Acidic Precipitation*, 30, 367–381.

2.3 Loch Dee - Scotland

Transactions of the Royal Society of Edinburgh: Earth Sciences, **78**, 385–392, 1987

Modelling the effect of acid deposition in upland Scotland

P. G. Whitehead and C. Neal

ABSTRACT: As part of the joint British–Scandinavian Surface Waters Acidification Programme, the Institute of Hydrology is establishing catchment studies in Scotland. Data from these catchment studies are being used to develop a range of models for investigating short-term and long-term changes in catchment acidity. Information on the modelling techniques available at the Institute of Hydrology is presented together with applications of the models to catchments in Scotland.

KEY WORDS: acidification, afforestation, catchments, models.

Catchment studies investigating the acidic behaviour of upland streams are expensive, time-consuming and difficult to establish due to the complexity of hydrological, chemical and biological interactions. Nevertheless, many catchment studies have been and are being established to evaluate short-term and long-term fluctuations in stream water chemistry. For example as part of the joint Scandinavian–British Surface Water Acidification Programme (Mason & Seip 1985) major studies are being established in the United Kingdom and Scandinavia. Other organisations such as the Welsh Water Authority (Llyn Brianne Study; Stoner *et al.* 1984) the Solway River Purification Board (Loch Dee study; Burns *et al.* 1982) and the Freshwater Fisheries Laboratory (Harriman & Morrison 1981) have also established catchment studies following mounting concern over the loss of fisheries in Scotland and Wales and the possible detrimental effects of stream acidity on water resources. Several researchers involved in these studies (Harriman & Morrison 1981; Gee & Stoner 1984) have reported elevated acidity and aluminium levels in upland streams draining afforested (conifer) catchments in the United Kingdom. Moreover, in many of these areas and particularly in forested catchments fisheries have deteriorated and restocking programmes have been unsuccessful.

It is with these problems in mind that the Institute of Hydrology has established a catchment study in Wales at Plynlimon (see Neal *et al.* 1986). The Institute of Hydrology is also establishing a catchment study in the Cairngorm region of Scotland in collaboration with The Department of Agriculture and Fisheries for Scotland, the Macaulay Institute of Soil Science and Imperial College, Department of Civil Engineering. The Institute of Hydrology is responsible for providing stream-gauging, rainfall stations, a weather station, snow surveys, sampling and continuous water quality monitoring. The Institute of Hydrology is also responsible for the subsequent data management, analysis and interpretation. The Department of Agriculture and Fisheries for Scotland is responsible for all chemical and biological analysis, with the exception of snowmelt chemistry, which will be undertaken by The Institute of Hydrology. The Macaulay Institute is responsible for soil-surveys and soil-water chemistry and Imperial College are establishing plot studies.

The hydrological and chemical data collected from the catchment studies form the basis of a comprehensive modelling research programme by The Institute of Hydrology. Recently there has been considerable use of mathematical models to describe the dominant interactions and processes operating in catchments and to simulate catchment behaviour. Steady state models have been used prescriptively to demonstrate the long term consequences of changes in the industrial emissions of SO_x (Cosby *et al.* 1985a; Kamari *et al.* 1984). Correspondingly, dynamic models have been successfully applied descriptively to several catchments (Christophersen *et al.* 1982, 1984). For example, Christophersen *et al.* 1982 have developed a simple conceptual model that reproduces major trends in chemical and hydrological behaviour in Norwegian catchments. This model has been successfully extended (Seip *et al.* 1985) and applied descriptively to the Harp Lake catchment in Canada. The model has also been applied to two forested catchments in Sweden (Grip *et al.* 1985).

A wide range of mathematical modelling techniques are available at The Institute of Hydrology for analysing catchment data. These include CAPTAIN (Computer Aided Package for Time Series Analysis and the Identification of Noisy Systems; Venn & Day 1977; Whitehead *et al.* 1986a, b), MIV (Multivariable time series model; Young & Whitehead 1977), the BIRKENES model (Christopherson *et al.* 1982), MAGIC (Cosby *et al.* 1985a), EKF (Extended Kalman Filter; Beck & Young 1976) TOPMODEL (Beven *et al.* 1984) and IHDM (Institute of Hydrology Distributed Model; Morris 1980). In this paper three of these techniques are described and applied to investigate short-term catchment responses or events and long-term acidity of soil and stream waters.

1. Time series or 'event' type models and their application to Loch Dee

Time series models are suitable where the overall input-output behaviour is of prime importance and where internal mechanisms are particularly complex. It is assumed that a law of large systems applies (Young 1978) whereby the combination of all the complex non-linear and distributed elements gives rise to an aggregated system behaviour that is relatively simple in dynamic terms.

Loch Dee has a remote setting in the Galloway Hills in SW Scotland. The catchment is made up of three sub-basins:

Dargall Lane to the W, White Laggan Burn with its tributary the Black Laggan towards the S, and Green Burn entering from the SE. The outflow at the NE end of the loch is the source of the River Dee. Catchment altitudes range from 225 m on the loch shore to 716 m on Lamachan at the head of the Dargall Lane. Nearly two-thirds of the catchment lies above 305 m. Geologically the area comprises two distinct rock types: Ordovician greywackes/shales and granites of Old Red Sandstone age (Burns *et al.* 1982).

In Loch Dee an extensive record of hydrological water quality data has been collected over a five year period (Burns *et al.* 1982). Analysis has been restricted initially to a time series model relating flow to hydrogen ion concentration for the White Laggan sub-catchment. The White Laggan is subject to episodic acidification, primarily attributed to atmospheric inputs. The model fitted is an autoregressive moving average type of the form

$$x_t = -\delta_1 x_{t-1} + \omega_0 u_t$$

where x_t is the hydrogen ion concentration ($\mu\text{eq}\,l^{-1}$) and u_t is the flow ($\text{m}^3\,\text{sec}^{-1}$) in the stream at time t. The parameters δ_1 and ω_0 were estimated using a time series algorithm applied to 200 hourly observations of pH and flow. The parameters were estimated to be

$$\delta_1 = -0{\cdot}680 \text{ (standard error } 0{\cdot}012)$$

$$\omega_0 = 0{\cdot}659 \text{ (standard error } 0{\cdot}022)$$

and Figure 1 shows the simulated hydrogen concentration against the observed concentration. A remarkably good fit to the data is obtained with 93% of the variance explained and suggests that H^+ ion and flow are closely related. However a true test of the model would be to use an additional data set; Langan (1986) has applied the approach to all three subcatchments of Loch Dee and found that equally good models have been obtained for a wide range of storm events. In the case of the White Laggan a mean response time (T) of 2·6 hours is obtained, reflecting the fast response time between output flow and hydrogen ion concentrations. Further applications of the time series techniques to data from Welsh and Norwegian catchments are given by Whitehead *et al.* (1986a).

2. Applications of the 'Birkenes' models

A second class of models has been applied to data from the Loch Dee study. These include the 'Birkenes' model developed by Christophersen *et al.* (1982, 1984). The model comprises a simple two-reservoir hydrological model operating on a daily timestep upon which has been superimposed the important chemical processes that control the acidification of catchments. Inputs to the model are precipitation, mean daily temperature, mean daily soil temperature and sulphate deposition rates. Figure 2 shows the principal hydrological and chemical processes operating. The model outputs daily concentrations of hydrogen ion, aluminium, sulphate, calcium + magnesium (M^{2+}) and bicarbonate in the stream along with predicted flow.

The 'Birkenes' model has also been used to assess the sensitivity of stream acidity to hydrological parameters and changes in baseflow. Flow movement between the soil and groundwater compartments is restricted by a "percolation" equation as follows;

$$A_{SIG} = P - (B - B_{min})/B_{max} \quad \text{for } B > B_{min}$$

and

$$A_{SIG} = 1{\cdot}33P - 0{\cdot}33P(B/B_{min})^3 \quad \text{for } B < B_{min},$$

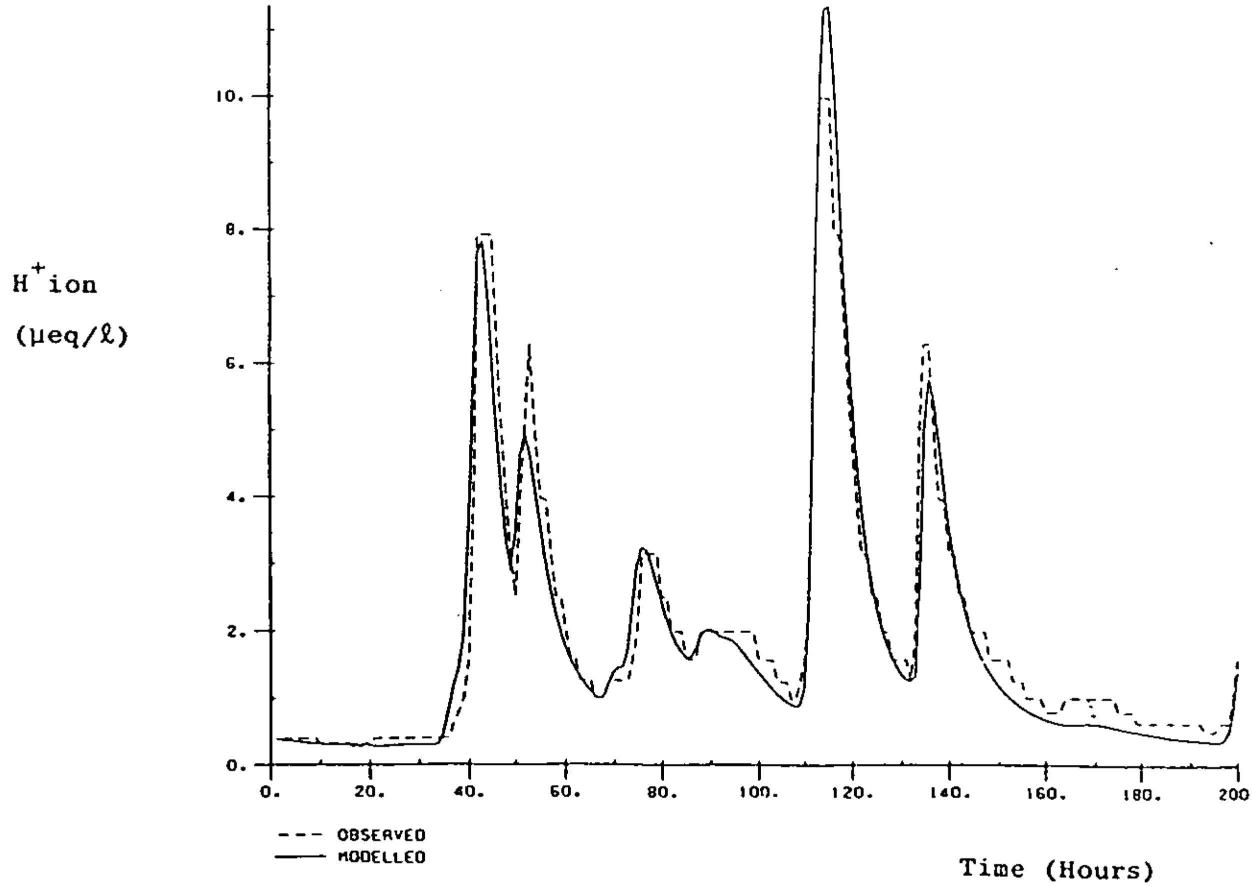
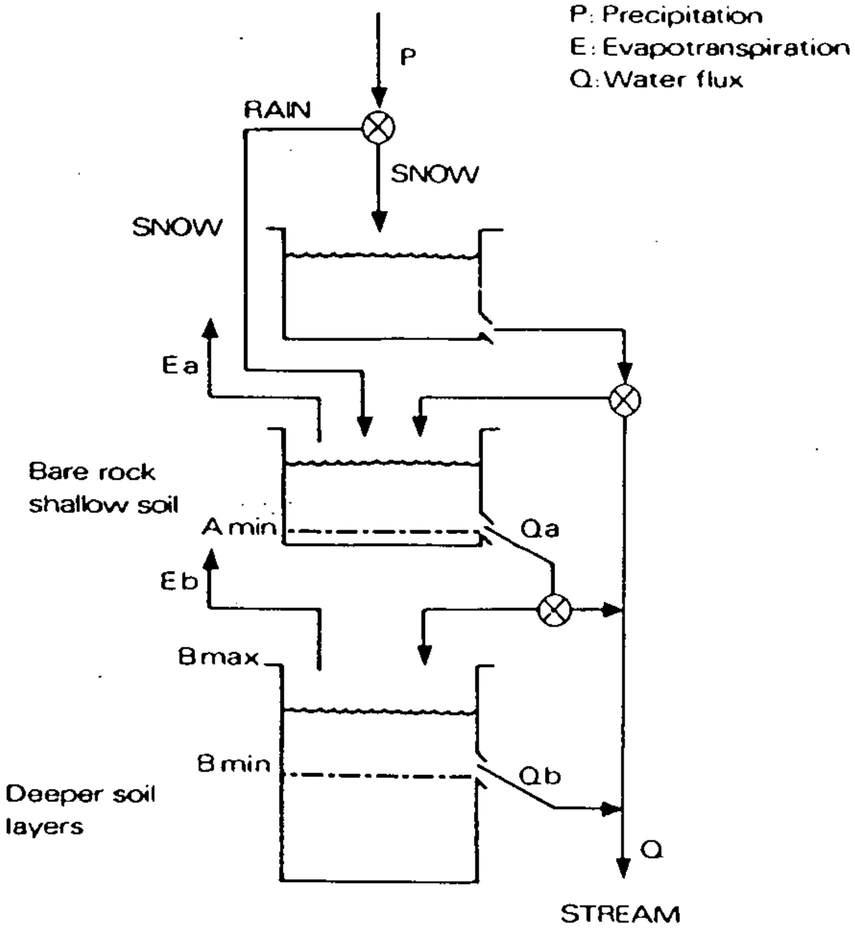


Figure 1 Simulated and observed H⁺ ion in the White Laggan, Loch Dee, Scotland, based on the flow model.

where B refers to the groundwater compartment water level and B_{min} and B_{max} refer to minimum and maximum water levels, respectively (see Fig. 2). The parameter, P, can be considered as a percolation parameter so that increasing P increases the fraction of flow, A, routed to the lower SIG reservoir. This leads to an increase in the baseflow contribution to the stream. The model also includes a piston flow component to describe the hydraulic movement of water out of the groundwater compartment.

The change in stream water concentrations for H^+ ion and Al^{3+} in response to varying baseflow is highly non-linear. This is illustrated in Figures 3 and 4, which show H^+ and Al^{3+} maximum and mean values for a range of baseflow conditions; all concentration values fall as the baseflow increases, the rate of decrease varying from one variable to another. In general increases in baseflow result in significant reductions in H ion and Al concentrations. Studies by Seip and Rustad (1983) show a similar non-linear behaviour when upper and lower soil horizon waters are mixed. Further results are given by Whitehead *et al.* (1986b) and confirm the sensitivity of the model to parameter, and hence baseflow, changes.



Processes operating

	Shallow soil reservoir	Deeper soil reservoir
H_2O	precipitation, evapotranspiration, infiltration to lower reservoir, discharge to stream	infiltration, evapotranspiration, discharge to stream, piston flow
SO_4^{2-}	wet + dry deposition, adsorption/desorption, mineralisation	adsorption/desorption, reduction
$Ca^{2+} + Mg^{2+}$	ion exchange	release by weathering, adsorption/desorption
H^+	ion exchange and equilibrium with gibbsite	consumption by weathering, adsorption/desorption, equilibrium with gibbsite
Al^{3+}	equilibrium with gibbsite	equilibrium with gibbsite, adsorption/desorption
HCO_3^-		equilibrium with a seasonal varying CO_2 pressure

Figure 2 Hydrological model used for Harp Lake catchment and main processes operating.

3. Application of MAGIC to Loch Dee

MAGIC (Model of Acidification of Groundwater In Catchments; Cosby *et al.* 1985a, b, 1986) is explicitly designed to perform long term simulations of changes in soilwater and streamwater chemistry in response to changes in acidic deposition. The processes on which the model is based are: anion retention by catchment soils (e.g. sulphate adsorption); adsorption and exchange of base cations and aluminium by soils; alkalinity generation by dissociation of carbonic acid (at high CO_2 partial pressures in the soil) with subsequent exchange of hydrogen ions for base cations; weathering of minerals in the soil to provide a source of base cations; control of Al^{3+} concentrations by an assumed equilibrium with a solid phase of Al(OH). A sequence of atmospheric deposition and mineral weathering is assumed for MAGIC. Current deposition levels of base cations, sulphate, nitrate and chloride are needed, along with some estimate of how these levels have varied historically. Historical deposition variations may be scaled to emissions records or may be taken from other modelling studies of atmospheric transport into a region. Weathering estimates for base cations are extremely difficult to obtain. Nonetheless, it is the weathering process that controls the long-term response and recovery of catchments to acidic deposition and some estimate is required. The MAGIC program has been applied to the Dargall Lane sub-catchment in Loch Dee and a detailed description of the application is given by Cosby *et al.* (1986).

Several chemical, biological and hydrological processes control stream water chemistry. These processes are often interactive and not easily identifiable from field observation. Modelling allows separation of the different factors and the establishment of their relative importance quantitatively. Here the factors considered are afforestation, dry and occult deposition, variations in acidic oxide loading and deforestation.

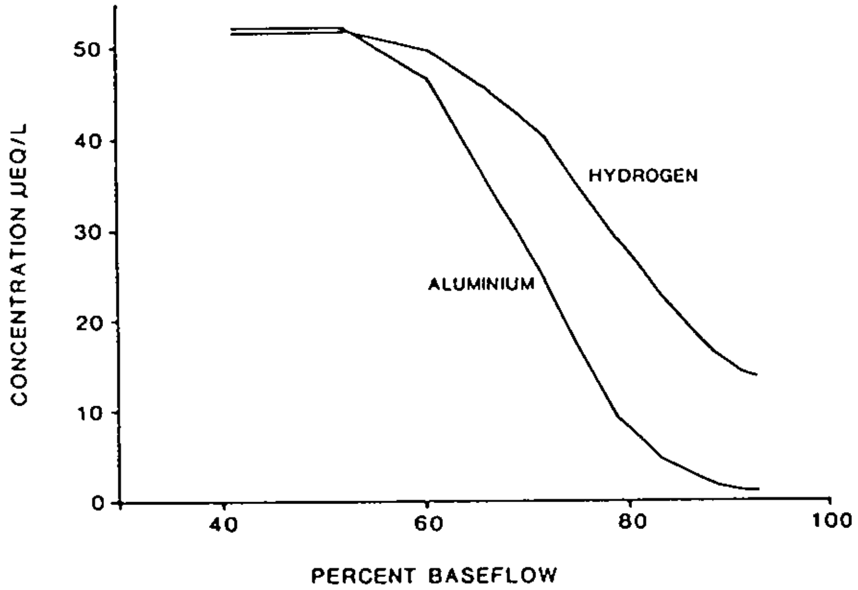


Figure 3 Maximum H^+ and Al^{3+} concentrations in the stream, showing variation over a range of baseflow conditions (Three Year Simulation 1977–1980).

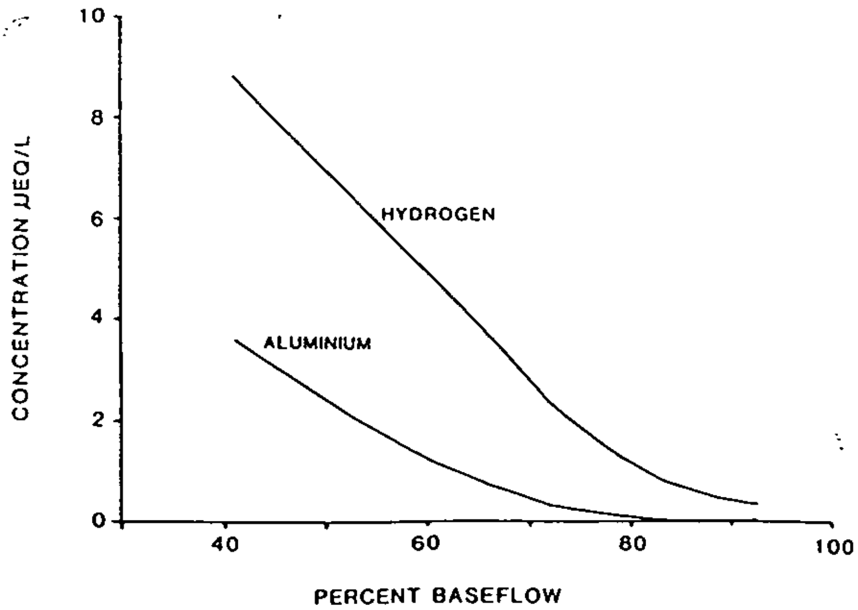


Figure 4 Mean H^+ and Al^{3+} concentration in the stream, showing variation over a range of baseflow conditions (Three Year Simulation 1977–1980).

4. Long-term acidification trends for Dargall Lane

Figure 5 shows a simulation of long-term acidity for the Dargall Lane catchment. The sulphate deposition history is shown in Figure 5a and this drives the MAGIC model. The historical simulation of pH shown in Figure 5b is similar to the values obtained from the diatom records of lochs in the region in that a significant decrease in pH from 1900 onwards is inferred (Battarbee *et al.* 1985; Flower & Battarbee 1983). The steeper decline from 1950 to 1970 follows from the increased emission levels during this period. The model can also be used to predict future stream water acidity given different future deposition levels. For Dargall Lane, stream acidity trends are investigated assuming two scenarios for future deposition. Firstly, assuming deposition rates are maintained in the future at 1984 levels, the model indicates that annual average stream pH is likely to continue to decline below presently measured values. Secondly, assuming deposition rates are reduced by 50% from 1984 levels (between 1985 and 2000) the results indicate that current stream water acidity will be maintained (Fig. 5b). Further details of the application of this model are given elsewhere (Cosby *et al.* 1986). Note an increase in stream water pH about 1980; this follows a significant drop in sulphur emissions during the 1970s. Note also that an earlier decline in streamwater acidity is predicted if there had been no reductions in emissions since 1970.

5. Afforestation

Afforested systems are more complex to model than grassland systems because the introduction of the forest perturbs a grassland ecosystem which in itself is difficult to

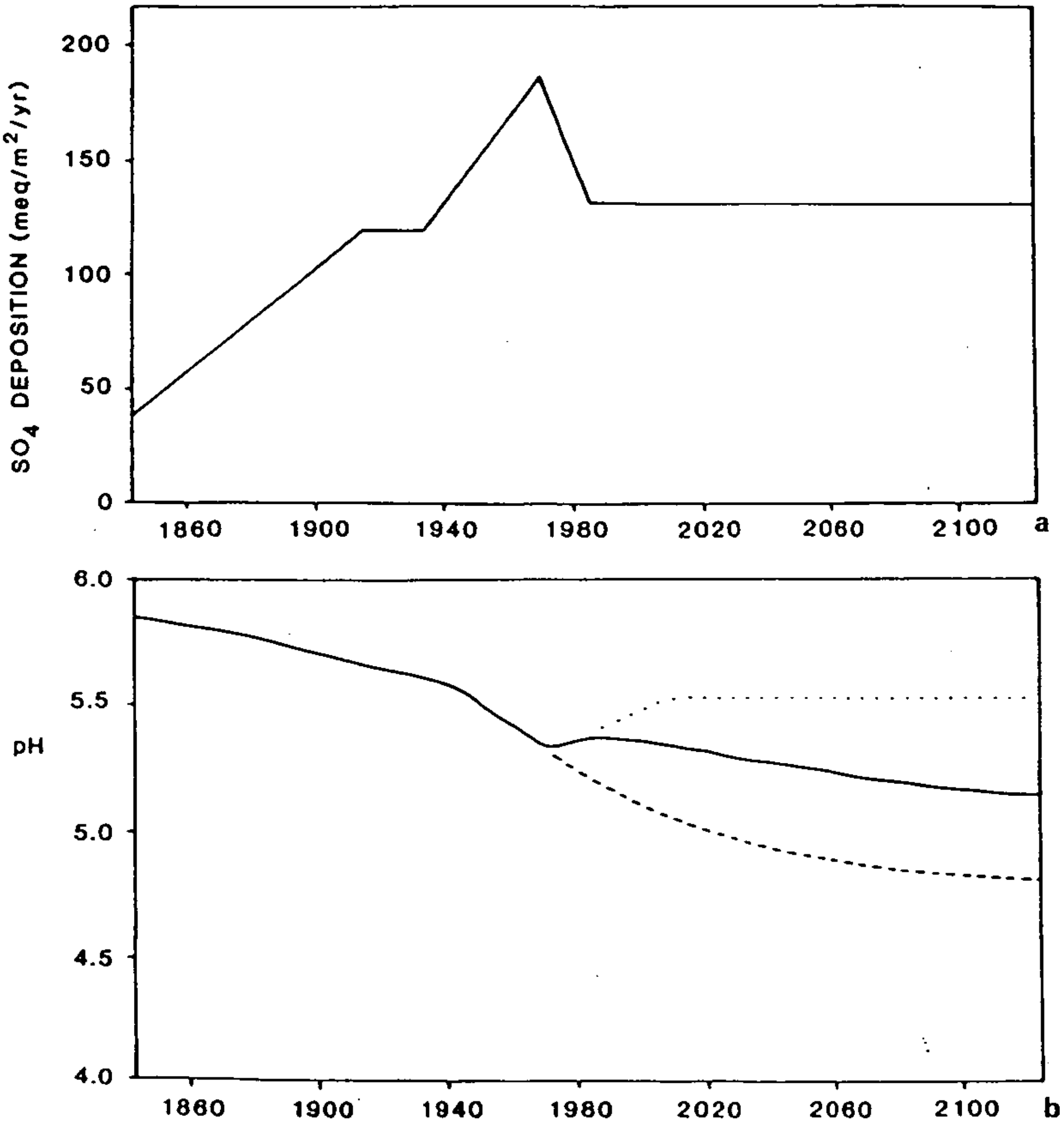


Figure 5 (a) Sulphate deposition history used as input for the MAGIC reconstruction of pH in the Dargall Lane moorland catchment; (b) Simulation of the pH of streamwater in the Dargall Lane moorland catchment assuming three sulphate deposition scenarios:—historical levels to 1984 and constant 1984 levels thereafter (see Fig. 5(a)); · · · · · historical levels to 1984 and 1984 levels reduced by 50% by the year 2000, and constant thereafter; - - - - historical levels to 1970 and constant 1970 levels thereafter.

model. The effects of the forest root system, leaf litter layer and drainage ditches will change the hydrological pathways, this will control the nature and extent of the chemical reactions in the soil and bedrock. Further, the additional filtering effect of the tree on the atmosphere will enhance occult/particle deposition, and evapotranspiration will increase the concentration of dissolved components entering the stream. The magnitude of these different effects varies considerably; for example, evapotranspiration from forests in the British uplands is typically of the order of 30% of the precipitation which is almost twice the figure for grassland. This will have the consequence that the total anion concentrations within the stream and soil waters increase by 14% following afforestation. The forest will also increase anion and cation loading due to the enhanced filtering effect of the trees on air and occult sources. The filtering effects will apply both to marine and pollutant aerosol components. Altering the hydrological pathways can also have a major effect on stream water quality, since the forest tends to increase surface runoff thereby flushing/displacing highly acidic water from the surface layers, the soil zone acts as a proton and aluminium source, while the bedrock, if silicate or carbonate bearing, provides proton consumption by weathering reactions. To illustrate the effects of afforestation simply in terms of increased concentrations from both enhanced dry deposition and evapotranspiration, the MAGIC model has been applied to the Dargall Lane catchment assuming that a forest is developed over the next forty years. It should also be noted that, here, no allowance has been made for the effects of cation and anion uptake by the trees during their development; the incorporation of base cations into the biomass would result in an enhanced acidification effect during this period.

Of critical importance is the relative and absolute contribution of marine and pollutant inputs from dry and occult deposition. Figure 6 shows the effects of increasing evapotranspiration from 16% to 30% over the forest growth period with varying levels of marine, pollutant, and marine plus pollutant inputs. Increasing either marine or pollutant components leads to enhanced stream water acidity, the greatest effects being observed when both components are present; the effect of simply increasing evapotranspiration from 16% to 30% is similar, but the changes are much smaller. The important features of these results are that the enhanced acidic oxide inputs from increased scavenging by the trees result in a marked reduction in pH levels and that there is an additive effect when both processes are combined. These reductions are much greater than the effect of evapotranspiration.

6. Atmospheric acidic oxide inputs

An important factor in determining stream acidity in the upland United Kingdom is the level of acidic oxide deposition; rates of deposition (non marine wet deposition and dry deposition) can vary from 0·5 to over $6\,\mathrm{g\,S\,m^{-2}\,yr^{-1}}$ and from 0·1 to over $0{\cdot}5\,\mathrm{g\,N\,m^{-2}\,y^{-1}}$. Figure 7 shows the effects of such variations for both moorland and forested catchments; the highest level corresponds to areas with high atmospheric acidic oxide rates (three times the historic and 1984 deposition levels observed in the Southern Uplands of Scotland). With increasing atmospheric acidic oxide pollution, the decline in stream pH is accelerated, the changes occur much earlier, and the final pH of the stream water is lower.

7. Deforestation

While afforestation increases stream acidity, as shown both by the model predictions and field evidence, deforestation will result in a reduction in stream water acidity. Figure 8 shows the effects of deforestation from the present time for a range of acidic input loadings. The result shows that while there is a short-term improvement in stream acidity, the long-term acidification trend is maintained. It is interesting to note that the recovery following deforestation at the

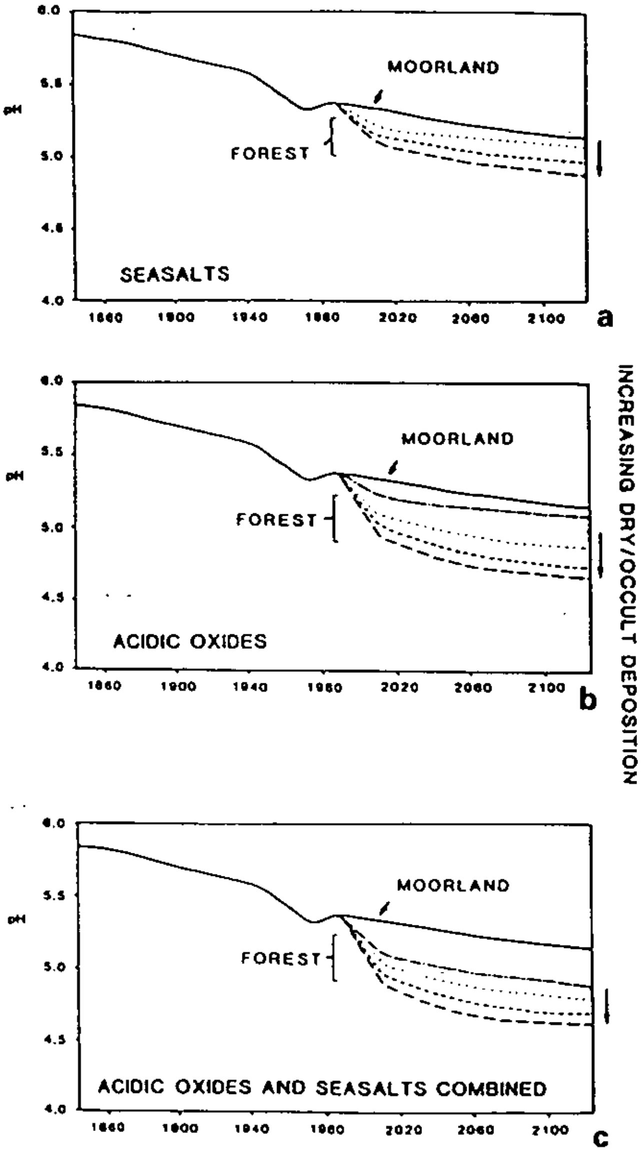


Figure 6 (a) Simulation of the pH of the streamwater from the Dargall Lane catchment, comparing: the moorland catchment response assuming Figure 5(a) deposition rates (——), the effect of 14% additional evaporation following afforestation (. . . .), the effect of 14% additional afforestation in 1985 (- - -), and the effect of 14% additional evaporation plus 30% additional input of natural sea salts following afforestation in 1985 (— — —). (b) Simulation of the pH of streamwater from the Dargall Lane catchment, comparing the moorland response (——) to the forested catchment response, assuming increased evaporation (- · - · -) with different levels of pollutant scavenging (. . . . 20% additional sulphate; - - - 40% additional sulphate; ——— 60% additional sulphate). (c) Simulation of the pH of streamwater from the Dargall Lane catchment, showing the moorland response (——) and the combined effects on the forested catchment of increased evapotranspiration, increased scavenging of natural sea salts, and various levels of increased scavenging of pollutant inputs (- · - · - zero additional pollutant scavenging; . . . . 20% pollutant scavenging; - - - 40% pollutant scavenging; — — — 60% pollutant scavenging).

intermediate deposition levels is greater than that at the higher levels. This is because base saturation has not been completely depleted, and the reduced deposition following deforestation can be buffered by the available cations. Under the higher deposition levels, base saturation is reduced to very low levels, making recovery much less significant. Note that afforestation following tree harvesting will negate the improvement in stream water acidity.

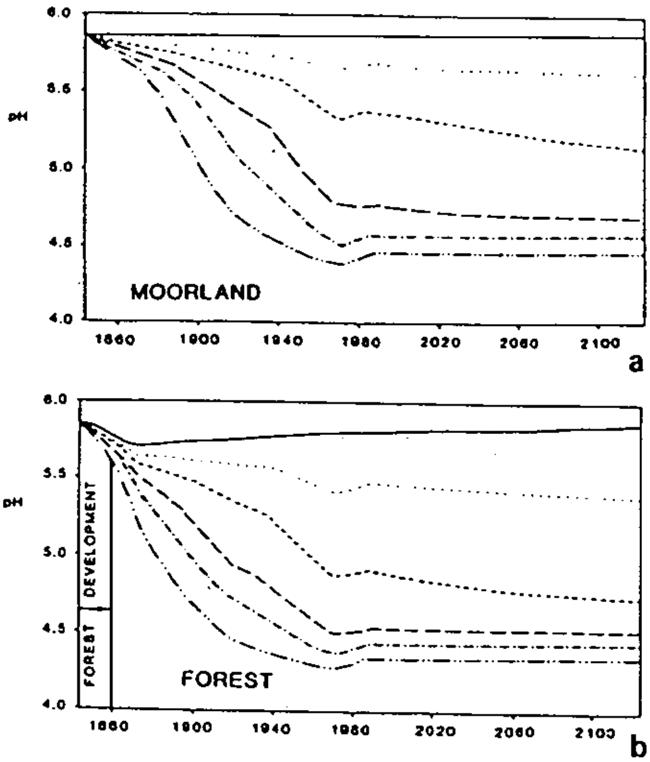


Figure 7 (a) Simulation of the pH of streamwater from the Dargall Lane moorland catchment, assuming sulphate deposition patterns (shown in Fig. 5(a)) modified by various factors to reproduce a range of loading conditions (i.e. from pristine to heavy pollution) ——background rates (pristine conditions); ...... 0·5 × Figure 5(a) deposition concentrations (low pollution); - - - - - - 1 × Figure 5(a) deposition concentrations (intermediate pollution); —— 1·5 × Figure 5(a) deposition concentrations (intermediate pollution); –·–·–2 × Figure 5(a) deposition concentrations (heavy pollution); –··–··3 × Figure 5(a) deposition concentrations (heavy pollution). (b) Simulation of the pH of streamwater from the 'forested' Dargall Lane catchment, assuming afforestation from 1844 onwards and sulphate deposition patterns (see Fig. 5(a)) multiplied by various factors to reproduce a range of loading conditions from pristine to heavy pollution; see caption to Figure 7(a) for key.

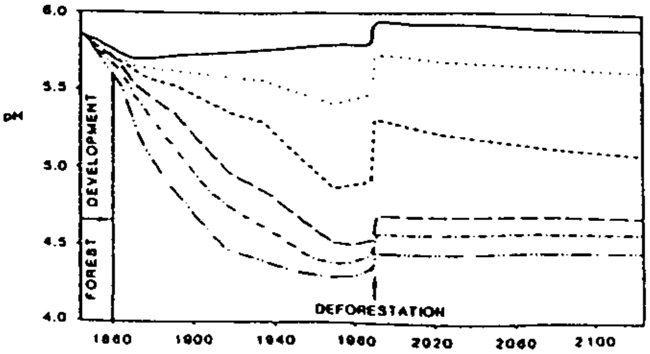


Figure 8 Simulation of the pH of streamwater for the Dargall Lane catchment, assuming afforestation from 1844 and deforestation in 1990; see caption to Figure 7(a) for key.

8. Implications

The modelling enables assessment of the relative effects of atmospheric acidic oxide pollution and conifer afforestation, as well as highlighting some of the topics that need further consideration. For example, the long-term trends in stream water acidification for the grassland catchment suggest that for at least part of the upland United Kingdom, acidic oxide pollutant inputs are the dominant source of increased stream water acidity. The model predictions are similar to observations of stream acidity found in southern Scandinavia and add weight to the conclusion that such pollutant inputs are also a major source of stream acidification in those countries as well. How important this acidification process is on a regional basis in the upland United Kingdom cannot be gauged immediately, because many unresolved factors remain, as mentioned above. However, much of the British uplands has soils which are susceptible to acidic inputs; it is therefore reasonable to assume the results of this present modelling exercise are widely applicable. If the above results are representative of sensitive upland areas, then reductions in present acidic emissions of the order of 50% are required to prevent further increase in stream acidity of moorlands; afforested catchments require greater reductions. The study points to the need for further regional analysis of soil and stream water chemistry, as well as a better understanding of hydrogeochemical processes operating within catchments. Further, the study provides an example of the need to establish the extent of scavenging of aerosols onto plant surfaces, and more generally on the benefits of multidisciplinary catchment studies. Finally, the detrimental effect on stream water quality caused by conifer afforestation in uplands subject to acidic deposition is irrefutable. While there is uncertainty regarding the nature and the extent of the hydrogeochemical processes operative, there is a need to change existing forestry practices which are of immediate pragmatic concern.

9. Conclusions

The model techniques applied at the Institute of Hydrology have proved to be particularly useful, yielding information on the catchment responses, processes and possible future behaviour. On the hydrological side, time series techniques, lumped and distributed hydrological models are available. In the case of chemical processes, time series techniques can be applied, but the principal models available at the Institute of Hydrology are the BIRKENES and MAGIC models. Modifications such as the introduction of sea salt will be necessary in the case of the BIRKENES model before application to the Loch Dee and Plynlimon catchments is possible. Also, it may be necessary to reassess the dominant equilibria used in the model; for example, is aluminium controlled by Al(OH), Al(OH)SO or by Al(OH)$_{1-x}$ Si$_x$O$_2$. We hope to develop a modified and combined BIRKENES and MAGIC chemistry and couple this with the distributed models to provide an additional tool with which to investigate catchment behaviour.

10. Acknowledgements

The authors are particularly grateful to the Solway River Purification Board for providing data from the Loch Dee Study and to the British-Scandinavian SWAP committee and the Commission of the European Communities for providing research funding. Figures 1, 3 and 4 are

reproduced from Whitehead *et al.* (1986a, b) by kind permission of Elsevier Science Publishers.

11. References

Battarbee, R. W., Flower, R. J., Stevenson, A. C. & Rippey, B. 1985. Lake acidification in Galloway: A palaeoecological test of competing hypotheses. NATURE, LONDON **314**, 350–352.

Beck, M. B. & Young, P. C. 1976. Systematic Identification of DO-BOD model structure. PROC AM SOC CIV ENG **102**, 909–927.

Beven, K. J., Kirby, M. J., Schofield, N. & Tagg, A. F. 1984. Testing a physically based flood forecasting model (TOPMODEL) for three UK Catchments. J HYDROL **69**, 119–143.

Box, G. E. P. & Jenkins, G. M. 1970. *Time series analysis forecasting and control.* San Francisco: Holden Day.

Burns, J. C., Coy, J. S., Tervet, D. J., Harriman, R., Morrison B. R. S. & Quine, C. P. 1982. The Loch Dee Project: a study of the ecological effects of acid precipitation and forest management on an upland catchment in southwest Scotland. 1. preliminary investigations. FISH MANAGE **15**, 145–167.

Christophersen, N., Seip, H. M. & Wright, R. F. 1982. A model for streamwater chemistry at Birkenes, a small forested catchment in southernmost Norway. WATER RESOUR RES **18**, 977–966.

Christophersen, N., Rustad, S. & Seip, H. M. 1984. Modelling streamwater chemistry with snowmelt. PHILOS TRANS R SOC LONDON **305**, 427–439.

Cosby, B. J., Wright, R. F., Hornberger, G. M. & 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., Wright, R. F., Hornberger, G. M. & 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.

Cosby, B. J., Whitehead, P. G. & Neale, R. 1986. Modelling long term changes in stream acidity in South-West Scotland. J HYDROL (AMST) **84**, 381–401.

Flower, R. J. & Battarbee, R. W. 1983. Diatom Evidence for Recent Acidification of Two Scottish Lochs. NATURE, LONDON **305**, 130–133.

Gee, A. S. & Stoner, J. H. 1984. *The effects of seasonal and episodic variations in water quality on the ecology of upland waters in Wales.* Institute of Water Pollution Control/Institute of Water Engineering and Science joint meeting on Acid Rain.

Grip, H., Jansson, P. E., Jonsson, H. & Nilsson, S. I. 1985. Application of the "Birkenes" model to two forested catchments on the Swedish west coast. ECOL BULL (in press).

Harriman, R. & Morrison, B. R. S. 1981. Forestry, fisheries and acid rain in Scotland. SCOTT FOR **36**, 89–95.

Kamari, J., Posch, M. & Kauppi, L. 1984. *Development of a model analysing surface water acidification on a regional scale: application to individual basins in southern Finland.* Proceedings of the Nordic H.P. Workshop. (NHP REP 19) Uppsala.

Langan, S. 1986. *Atmospheric Deposition, Afforestation and Water Quality at Loch Dee, S.W. Scotland.* Ph.D. Thesis, University of St. Andrews.

Mason, B. J. & Seip, H. M. 1985. The current state of knowledge on acidification of surface waters and guidelines for future research. AMBIO **14**, 45–51.

Morris, E. M. 1980. *Forecasting flood flows in the Plynlimon catchments using a deterministic, distributed mathematical model.* Proceedings of the Oxford Symposium, April 1980, 247–255. (INT ASSOC HYDROL SCI PUBL-AISH PUBL **239**).

Neal, C. 1986. Hydrochemical balances in the Forested Afon Hafren and Afon Hore catchments; Plynlimon, North Wales. *Proceedings of Muskoka conference.*, WATER AIR SOIL POLLUT (in press).

Neal, C., Whitehead, P., Neale, R. & Cosby, J. 1986. Modelling the Effects of Acidic Deposition and Conifer Afforestation on Stream Acidity in the British uplands. J HYDROL **86**, 15–26.

Seip, H. M., Seip, R., Dillon, P. J. & De Grosbois, E. 1985. Model of sulphate concentration in a small stream in the Harp Lake catchment, Ontario. CAN J FISH AQUATIC SCI (in press).

Seip, H. M. & Rustad, S. 1983. Variations in surface water pH with changes in sulphur deposition. WATER, AIR AND SOIL POLLUT **21**, 217–223.

Stoner, J. H., Gee, A. S. & Wade, K. R. 1984. The effects of acidification on the ecology of streams in the Upper Tywi catchment in West Wales. ENVIRON POLLUT—LONDON **A35**, 125–157.

Venn, M. W. & Day, B. 1977. *Computer aided procedure for time series analysis and identification of noisy processes (CAPTAIN)—user manual* (REP 39). Wallingford: Institute of Hydrology.

Whitehead, P. G., Neal, C., Seden-Perriton, S., Christophersen, N. & Langan, S. 1986a. A time series approach to modelling stream acidity. J HYDROL (AMST) **85**, 281–304.

Whitehead, P. G., Neal, C. & Neale, R. 1986b. Modelling the Effects of Hydrological Changes on Stream Acidity J HYDROL (AMST) **84**, 353–364.

Young, P. C. 1978. A general theory of modelling for badly defined systems. *In* Vansteenkiste, G. C. (ed.) *Modelling and simulation of land, air and water resource systems.* New York: Elsevier, North Holland.

Young, P. C. & Whitehead, P. G. 1977. A recursive approach to time-series analysis for multivariable systems. INT J CONTROL **25**, 457–482.

P. G. WHITEHEAD and C. NEAL, Institute of Hydrology, Wallingford, Oxfordshire OX10 8BB, U.K.

MS received 8 October 1986. Accepted for publication 13 July 1987.

2.4 Allt a Mharcaidh - Scotland

A MODELING STUDY OF LONG-TERM ACIDIFICATION IN AN UPLAND SCOTTISH CATCHMENT

ALAN JENKINS*, R. C. FERRIER**, T. A. B. WALKER**,
and P. G. WHITEHEAD*

(Received December 26, 1987; revised June 30, 1988)

Abstract. A modeling study of the Allt a Mharcaidh catchment in the Cairngorm region of Scotland has been undertaken to investigate long term trends in acidification and model sensitivity to soil physical and chemical characteristics. The MAGIC model (Model of Acidification of Groundwater In Catchments) is used to demonstrate that the sulphate adsorption ability of the soil and quality and quantity of rainfall inputs have significant effects on model output. Optimal weathering rates and predicted present day ion concentrations in streamwater compare well with measured and observed values. The analysis shows that the catchment has become progressively acidified since pre-industrial times but major changes in stream acidity have yet to occur.

1. Introduction

The case for development and implementation of process-based models describing the response of surface waters to acidic deposition has been widely and eloquently stated in recent literature (e.g., Cosby *et al.*, 1985a; Neal *et al.*, 1986). For the purpose of such deterministic modelling exercises, acidification of surface water may be considered to be essentially a problem over two very different time scales. Short term fluctuations in surface water acidity caused by the flushing of near surface waters or snowmelt are generally driven by the hydrological processes operating in the catchment. The timescale of these events is of the order of hours, or at most days, and the level of acidity will be largely controlled by the ability of the catchment to buffer incoming acidity within the catchment hydrological response time. Models addressing this dynamic response have been developed, for example, by Christopherson *et al.* (1984) and Schnoor *et al.* (1984). On the other hand, the Model of Acidification of Groundwater in Catchments (MAGIC), developed by Cosby *et al.* (1985a, b) addresses the changes in buffering capacity that occur over long periods (i.e., decades) where short term hydrological response is assumed to be negligible and yearly averages of deposition levels provide the principal driving force to the model.

The MAGIC model is a relatively simple yet process-orientated model whereby long-term dynamic equations based on input-output mass balances for all major ions in atmospheric deposition are linked with equilibrium equations that describe soil processes. It has been applied to a variety of catchments in the U.S., Scandinavia (Wriht *et al.*, 1985), Scotland (Cosby *et al.*, 1986a) and Wales (Whitehead *et al.*, 1988) and has proved a useful tool for assessing future acidification levels in response to

[*] Institute of Hydrology, Wallingford, Oxon, OX10 8BB, U.K.
[**] Macaulay Land Use Research Institute, Aberdeen, U.K.

Water, Air, and Soil Pollution **40** (1988) 275–291.

various deposition scenarios. The results of these simulations show that the model adequately reproduces present day observed stream chemistry but its performance has not been assessed against measured values of soil chemical parameters and estimates of weathering rates. Indeed, all previous applications of MAGIC have been undertaken in catchments with only one dominant soil type or, in areas of more than one soil type, have assumed some 'mean' characteristics for the whole catchment.

This study sets out to attempt a more rigorous application of the MAGIC model against a comprehensive soil data set from the Allt a Mharcaidh catchment in the Cairngorm Mountains of Scotland. We examine the validity of using a 'mean' catchment soil approach and assess the sensitivity of the model to two soil types. The analysis is also employed to identify the most important processes affecting stream water acidity within this area and the parameters which most influence model behaviour. Catchment response is assessed given that this area is not presently acidified but is thought to be at risk from future acidification problems.

2. Methods and Materials

2.1. STUDY SITE

The Allt a Mharcaidh catchment lies on the western flank of the Cairngorm Mountains draining an area of approximately 10 km^2 into the River Feshie which is a tributary of the River Spey. Altitude ranges from 225 m at the catchment outflow to 1111 m at the highest point. The catchment is underlain by intrusive biotite-granite of Lower Old Red Sandstone age associated with the late stages of the Caledonian Orogeny. Thick deposits of boulder clay, derived from local rock, cover much of the valley floor overlain by a covering of peat. Vegetation is mainly a mixture of heather and fescue grassland although a sparse stand of natural, native pinewood covers an area of c. 1 km^2 near the outflow on the lower slopes. Soils are essentially of three main types, as shown in Figure 1, being c. 60% alpine and peaty podsols of the Countesswells Association and c. 40% blanket peat. Table I shows the chemical and physical characteristics of both the organic (peat) and mineral (podsols) soils, together with a 'mean' catchment soil with characteristics ratioed areally from two main soil types.

This work was conducted as a part of the Surface Water Acidification Programme which was initiated in 1985 as a collaborative project of research into the causes and effects of acidification of surface waters (Mason and Seip, 1985). Within this program catchments were selected for detailed study to represent heavily acidified, pristine and transitional areas. The Allt a Mharcaidh was selected as one transitional site, that is, a catchment which is not acidified, does not receive a particularly high loading of anthropogenic pollutants but due to its physical characteristics is thought to be at risk as regards future acidification problems.

2.2. METHODOLOGY

The area receives approximately 1000 mm of precipitation per annum, although this is extremely variable from year to year and up to 30% of this may fall as snow. Precipitation

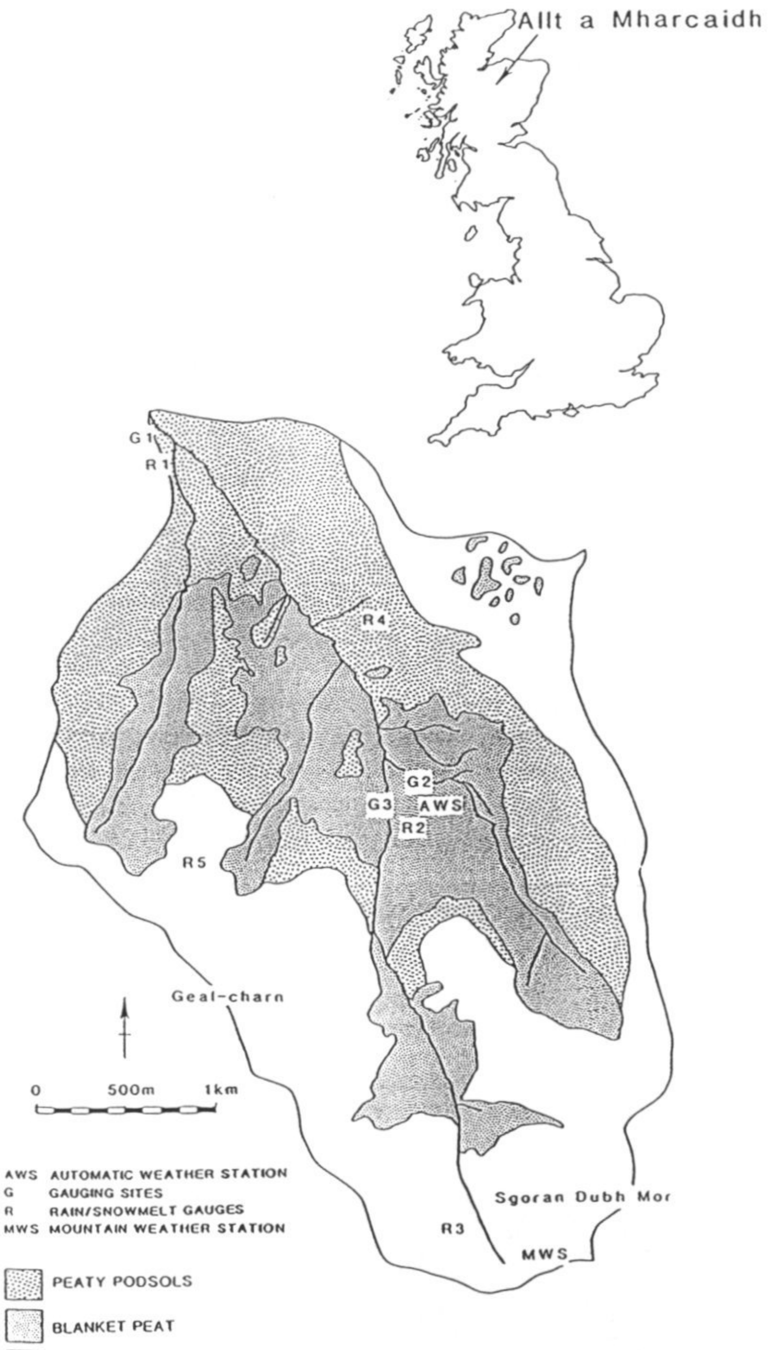


Fig. 1. Distribution of soil types and location of rain samplers (R1–5) and gauging stations (G1–3).

TABLE I

Chemical and physical characteristics of the organic, mineral and 'mean' catchment soils

	Organic soil	Mineral soil	Mean soil
Soil depth (m)	0.55	0.95	0.83
Porosity (fraction)	0.65	0.45	0.51
Bulk density (kg m^{-3})	140	1260	924
CEC (μeq g^{-1})	1200	100	430
Total organic's (μmol L^{-1})	150	100	115
PK1 org	4.25	4.25	4.25
PK2 org	10.15	10.15	10.15
% base saturation	9.07	2.58	3.3
Exchangeable Ca %	3.91	0.74	1.0
Exchangeable Mg %	3.95	0.49	0.7
Exchangeable Na %	0.56	0.63	0.61
Exchangeable K %	0.64	0.77	0.73
SO_4 half saturation coefficient[a] (meq m^{-3})	100	156	156

[a] Estimated, not measured – see Section 3.2.

was sampled weekly from five bulk collectors since January 1986. The network of collectors was designed to account for variations in altitude and exposure within the catchment. Stream samples have been collected bi-weekly from the catchment outflow, G1 (Figure 1), since July 1985. Subsequent water chemistries were determined using the following methodology; pH by remote KCl electrode, anions (Cl, NO_3, SO_4) by ion chromatography, Ca and Mg by atomic absorption spectrophotometry, Na and K by flame emission spectrophotometry and NH_4 by colorimetric techniques. Volume weighted mean chemistry of inputs and outputs is given in Tables II and III, respectively. Mean pH was calculated by conversion to H^+ concentrations.

Soil samples were taken from four profiles from each of the three dominant soil types (Figure 1). Cation exchange capacity and exchangeable bases were measured at pH 7 using a barium acetate exchange procedure. Total organic concentrations in soil waters

TABLE II

pH and volume weighted mean ion concentrations (μeq L^{-1}) in bulk precipitation for 1986

pH	4.63
Ca	10.3
Mg	21.5
Na	84.0
K	7.5
NH_4	7.3
SO_4	52.0
Cl	96.5
NO_3	5.4

TABLE III

Predicted and observed (in brackets) soil and stream chemistry (μeq L^{-1}) for 1986

Soil	Org. soil	Min. soil	Mean soil
% BS	6.7 (9.1)	1.9 (2.6)	2.1 (3.3)
Exchangeable Ca %	3.5 (3.9)	1.0 (0.7)	0.5 (1.0)
Exchangeable Mg %	2.6 (3.9)	0.5 (0.5)	1.0 (0.7)
Exchangeable Na %	0.5 (0.6)	0.5 (0.6)	0.6 (0.7)
Exchangeable K %	0 (0.6)	0.0 (0.8)	0.1 (0.9)
pH	4.6	4.7	4.7
Stream			
pH	5.1	5.2	5.2 (5.7)
Ca	38.8	38.3	38.0 (37.1)
Mg	32.3	31.3	31.0 (39.9)
Na	118.3	117	117.2 (116.1)
K	11.7	9.8	9.7 (8.4)
NH_4	2.0	2.0	2.0
SO_4	59.9	50.1	50.2 (50.1)
Cl	111.0	111	111.0 (111.0)
NO_3	2.3	2.1	2.0 (2.1)
Total Al	5.5	3.7	3.8
Alkalinity	30.5	36	35.7 (33)

were determined by UV-persulphate digestion and dissociation constants (PK1 and PK2) were obtained from Perdue (1985).

2.3. MAGIC MODEL

The MAGIC model assumes a catchment to be represented by essentially three homogeneous compartments representing the biomass (soil), soil solution and stream/ground water. Five chemical processes are taken to govern the response of surface water quality to acidic deposition from the atmosphere. These are: (i) anion retention by soils; (ii) cation exchange by soils; (iii) solubility and mobilization of Al; (iv) weathering of minerals as a source of base cations; (v) dissociation of carbonic acid (resulting from elevated partial pressure of CO_2 in soils). Alkalinity is generated by formation of bicarbonates when CO_2, under high partial pressure in the soil, dissolves with the soil water;

$$CO_2 + H_2O = H^+ + HCO_3^- . \tag{1}$$

Soil Al chemistry is assumed to be controlled by the equilibrium of a solid phase of aluminium hydroxide with free H^+ ions;

$$3H^+ + Al(OH)_3(s) = Al^{3+} + 3H_2O . \tag{2}$$

The Al released may complex with F, SO_4 or OH but generally exchanges with base cations as the trivalent Al ions are retained by the soil matrix in preference to monoor di-valent base cations;

$$Al^{3+} + 3BCX(s) = AlX_3(s) + 3BC^+ , \qquad (3)$$

where X represents an adsorbed phase and BC^+ represents a base cation. Cation exchange equilibria are evaluated using Gaines–Thomas expressions.

Dynamic simulation of stream and soil water chemistry is achieved by coupling the equilibria concepts (Equations (1) to (3)) with dynamic mass budgets for each base cation and strong acid anion in the soil model. Sulphate has an adsorbed phase in the soil and the relationship between adsorbed phase (E_s, meq kg^{-1}) and concentration of dissolved sulphate (SO^{2-}_4, meq m^{-3}) in soil water is assumed to be described by a Langmuir isotherm (Singh, 1984) of the form;

$$E_s = E_{mx} \frac{(SO_4^{2-})}{C + (SO_4^{2-})} ,$$

where E_{mx} is the maximum adsorption capacity of the soil (meq kg^{-1}) and C is the half saturation concentration (meq m^{-3}).

Acid anions are linked to base cation by assuming a charge balance for soil water and so the movement of strong acid anions through the soil is accompanied by leaching of base cations from the soil.

The mathematical representations of these processes and detailed model structures are discussed by Cosby *et al.* (1985a, b, 1986b).

2.4. APPLICATION TO ALLT A MHARCAIDH

The MAGIC model has been applied using the pattern of deposition shown in Figure 2 (Warren Spring Laboratory, 1983) to produce historical recontructions of streamwater

Fig. 2. Sulphate deposition pattern 1845–2125 assuming constant deposition since 1985.

and soil chemistry. An automatic calibration procedure was utilized to provide optimal values for the parameters governing the chemical reactions. A Rosenbrock technique formed the basis of this optimization procedure and this was applied in two stages. Initially an anion optimization was carried out on E_{mx} and nitrate and ammonia uptake rates, thereby obtaining a best fit for the concentration of anions in the streamwater. In the second stage the optimal values for the anion parameters are incorporated and the weathering rates of base cations, selectivity coefficients controlling base cation exchange and partial pressure of soil CO_2 are optimized to produce a best fit to present day observed streamwater concentrations and base saturations in catchment soils. The optimization procedure was applied assuming the catchment to consist of entirely organic soil, mineral soil, or of a 'mean'catchment soil.

Optimized weathering rates, selectivity coefficients, pCO_2 and E_{mx} are given in Table IV. Comparison of the three catchment soil types shows consistent weathering rates although selectivity coefficients vary considerably between soils reflecting differences in soil base saturations. The most significant difference between, the optimized solutions, however, lies in the anion budget and in particular the E_{mx}. The optimized E_{mx}'s for the organic and mineral soils are zero and nine, respectively, whereas the optimal E_{mx} for the mean soil is 14.1. The fact that this lies outside the range of the organic and mineral soil values may reflect an instability in the model or optimization procedure but is more likely a reflection of the physical characteristics incorporated in the application of the Langmuir isotherm.

TABLE IV

Optimized values for selectivity coefficient (S) weathering rates (W), pCO_2 and E_{mx} in the organic, mineral and mean catchment soils; observed weathering rates in brackets

	Organic	Mineral	Mean
W CA (meq m^{-2} yr^{-1})	24.7 (0.8)	22.7 (7.0)	23.3
W Mg (meq m^{-2} yr^{-1})	5.7 (0.9)	4.5 (8.0)	4.6
W Na (meq m^{-2} yr^{-1})	20.6 (3.5)	17.9 (30.8)	17.1
W K (meq m^{-2} yr^{-1})	2.7 (2.9)	1.0 (26.1)	0.8
S CA	−0.33	1.94	2.7
S Mg	−0.17	2.57	1.49
S Na	−0.23	0.25	−0.21
S K	0.39	2.22	−0.32
pCO_2 (atm)	2.0	2.0	2.0
E_{mx} (meq kg^{-1})	0	9	14.4

3. Results

3.1. CATCHMENT RESPONSE

Present day stream chemistry has been reproduced by the model (Table II) regardless of the soil type used. pH is predicted to be 0.5 units lower than observed but this is directly attributable to the inclusion of organic matter in both soils and streamwater. Further model runs excluding the organic components reproduce observed stream pH without affecting any other parameters. Clearly further work is necessary on this aspect of the MAGIC model as organic matter simply acts as a further source of H^+ and no account is taken of cation complexation and chelation. Table III also shows that predicted base saturation for 1986 is well reproduced with the exception of K. This is due to the low optimal value for K weathering rate.

Figure 3 shows the reconstructed and forescast response of pH, alkalinity, Al and sulphate in the stream and the percentage base saturation in the soil for the three model runs. Results are shown as mean annual concentrations and assume model fixed parameters (e.g., rainfall quality and quantity, evaporation, etc.) are constant through time. All of the curves converge around 1986 but show very different patterns prior to that time. The organic soil shows the most variable response as a result of the very low E_{mx} and consequently a very rapid response to changing acidic input. Both the mineral soil and the mean soil respond much more smoothly to changes in input due to their ability to adsorb sulphate. Following 1986 further changes in stream chemistry occur but these tend towards an equilibrium value because of the constant level of inputs. The organic soil is the least acidic due to the high base saturation maintaining a supply of base cations and the absence of adsorbed sulphate. This is also seen in the equilibrium values reached for sulphate, alkalinity and total Al.

3.2. SULPHATE ADSORPTION CHARACTERISTICS

The levels of soluble and adsorbed sulphate were measured in the three major soil types in the Allt a Mharcaidh (n.b. the alpine and peaty podsols are lumped together for the model application). Figure 4 shows the accumulation of high levels of adsorbed sulphate in the lower mineral horizons, particularly those containing sesquioxides. The high level of soluble sulphate in the organic horizons is due to mineralized S associated with the organic matter. The levels of sulphate in these soils vindicate the choice of a relatively high value for C (half saturation coefficient) for each of the soils and this represents a measured soil water sulphate concentration from the lower mineral horizon.

Studies were undertaken to assess whether the mineral soils were capable of adsorbing further inputs of sulphate. The adsorption isotherms for the peaty podsol are shown in Figure 5 and indicate that the mineral horizons can adsorb sulphate from solutions at similar concentrations to those found in the field. Furthermore, if a Langmuir isotherm is used to describe the adsorption characteristics of these soils it is likely, from these data, that E_{mx} will be a high value. Peat has a limited ability to exchange sulphate on any available positively charged sites on the organic matter but has no real capacity for adsorption as in the mineral soils.

3.3. ASSESSMENT OF WEATHERING RATES

Rate of loss of base cations in the catchment scale has been calculated by Mellor and Wilson (1987) by comparing the chemical composition of individual soil horizons with that of the parent material (Table IV). Their data show that in absolute terms K and

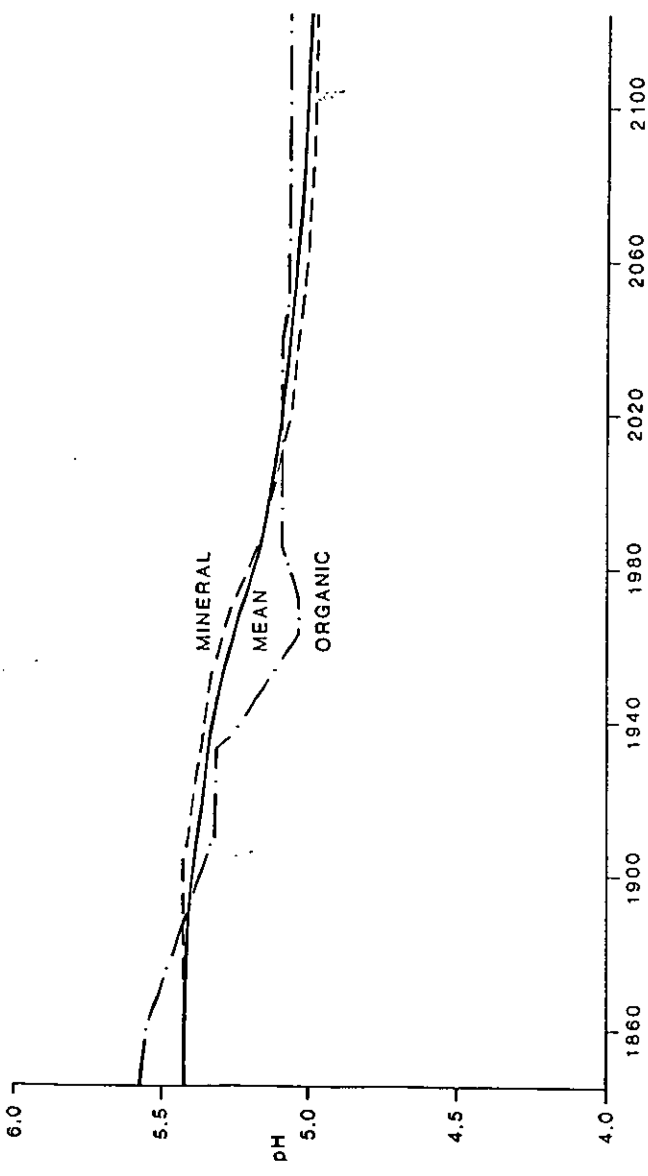

pH
6.0
5.5
5.0
4.5
4.0
1860
1900
1940
1980
2020
2060
2100
MINERAL
MEAN
ORGANIC

Fig. 3a.

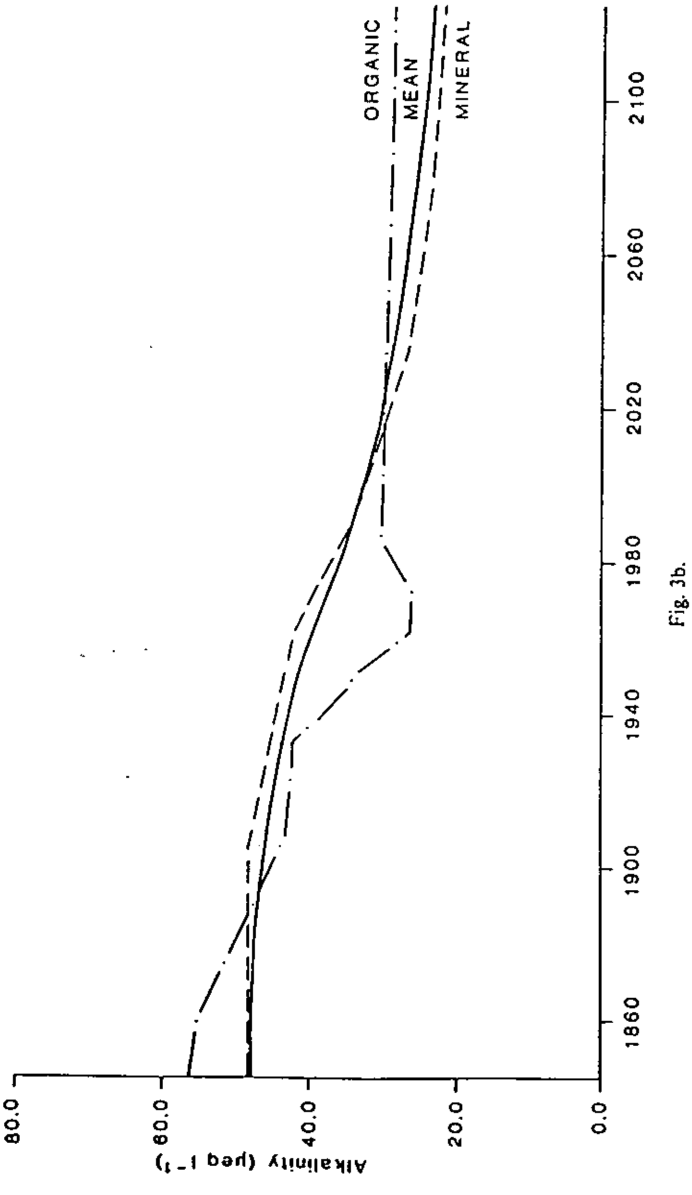

ORGANIC
MEAN
MINERAL
Alkalinity (μeq l-1)
80.0
60.0
40.0
20.0
0.0
1860
1900
1940
1980
2020
2060
2100

Fig. 3b.

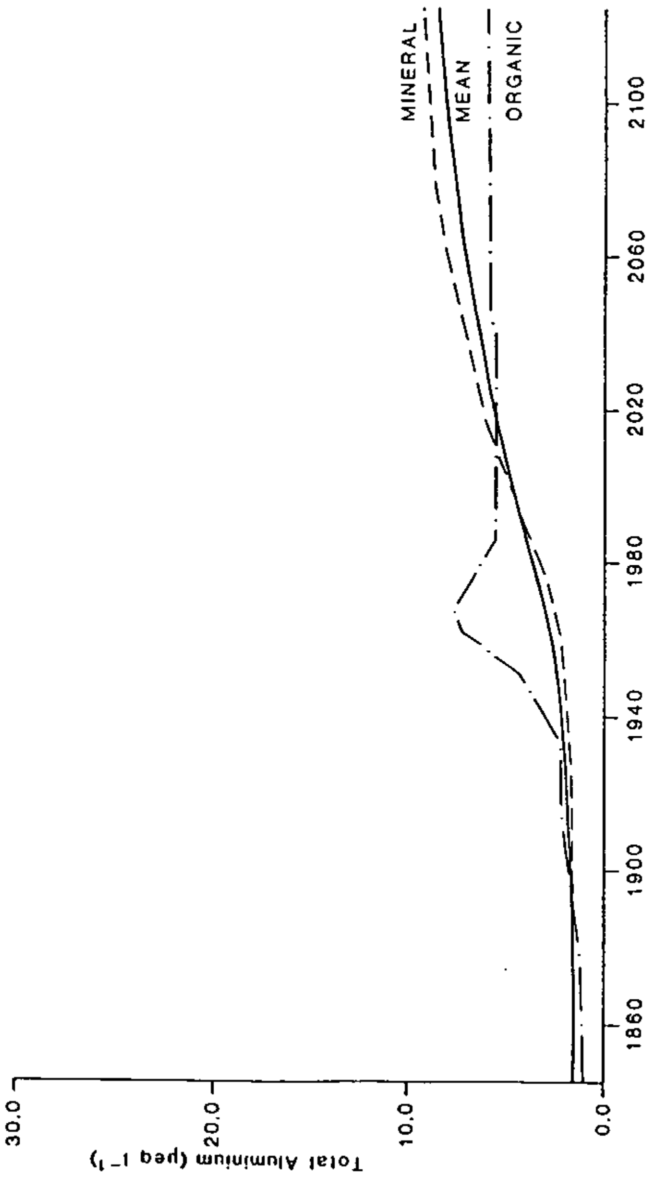

Total Aluminium (µeq l⁻¹)
0.0
10.0
20.0
30.0
1860
1900
1940
1980
2020
2060
2100
MINERAL
MEAN
ORGANIC

Fig. 3c.

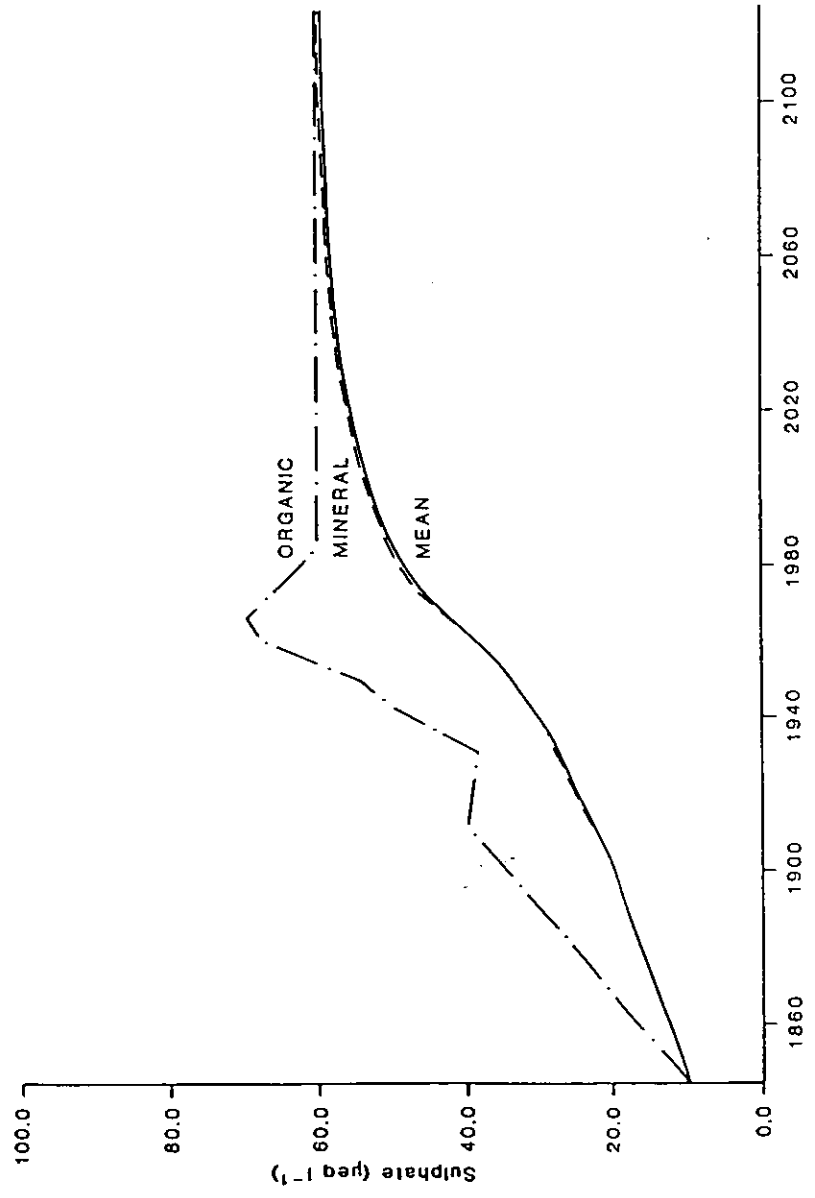

Sulphate (µeq l⁻¹)
100.0
80.0
60.0
40.0
20.0
0.0
1860
1900
1940
1980
2020
2060
2100
ORGANIC
MINERAL
MEAN

Fig. 3d.

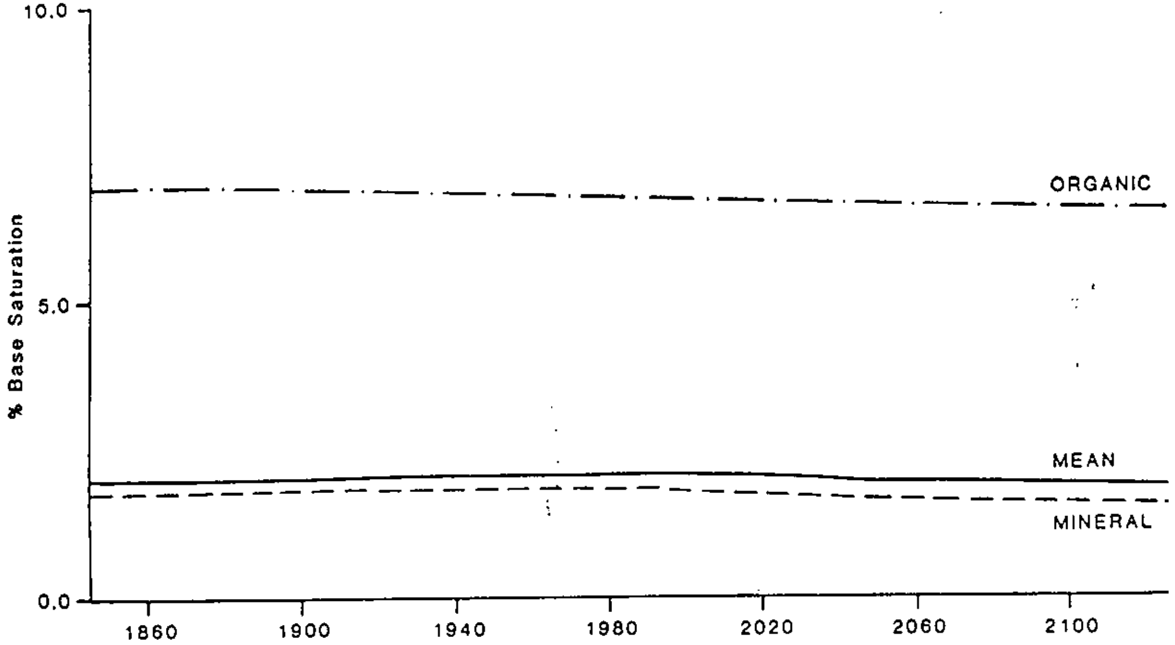


Fig. 3e.

Fig. 3. Reconstructed and forecast changes in stream pH (a), alkalinity (b), Al (c), sulphate (d), and soil base saturation (e) for the three soil types.

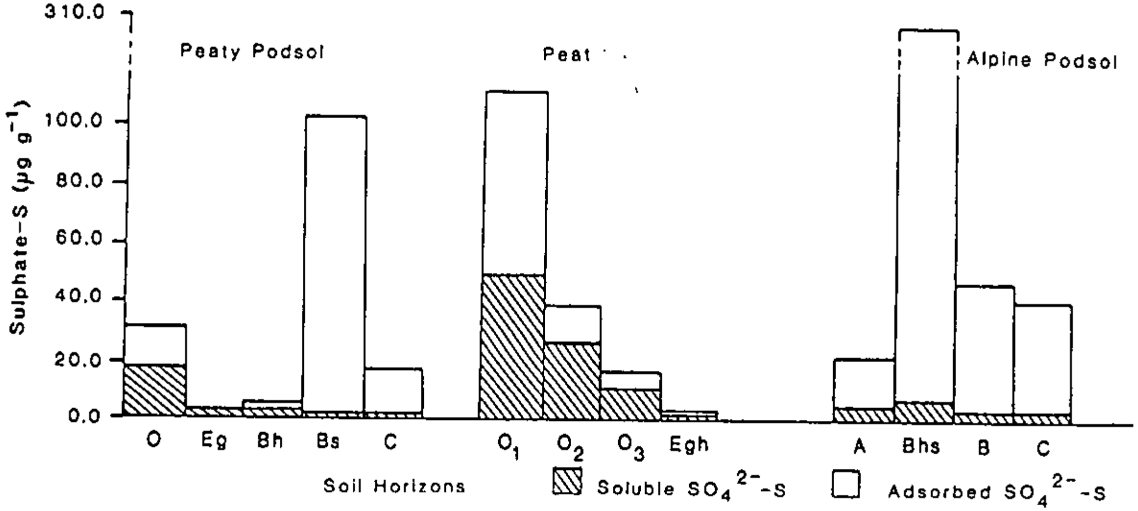


Fig. 4. Levels of soluble and adsorbed sulphate in Allt a Mharcaidh soils.

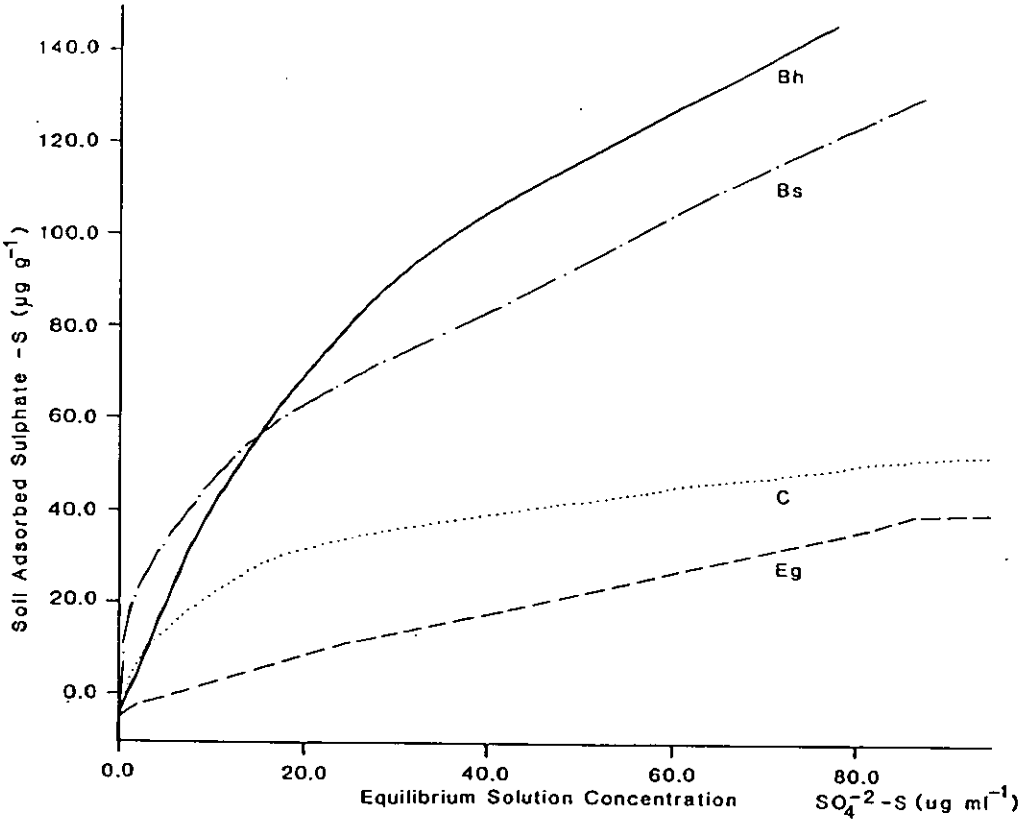


Fig. 5. Sulphate adsorption isotherms of the four horizons of the peaty podsol profile.

Na exhibit greater rates of loss than Ca and Mg. If the results are recalculated in terms of element loss as a percentage of the original total in the parent material Ca and Mg are lost more rapidly than Na and K. From the model optimisations for the three types of soil, however, Ca and Na consistently show the highest weathering rates. It should be remembered though that the figures of Mellor and Wilson represent a total elemental loss rate from the catchment and as such are not direct estimates of weathering because changing inputs and biomass uptake will directly affect cation exchange processes in the soil.

4. Discussion

MAGIC is capable of reproducing present day stream and soil chemistry and the chemical and physical characteristics of the soil determine the pattern of change both historically and in the future. The different model responses for the soil types represent the range of stream chemistry which might be expected in using a 'mean' soil type for the catchment, assuming all other model parameters can be correctly specified. From this point of view the effect of the different soil types on water quality implies that key soil parameters and model variables are determining catchment response to incoming acidity. This analysis has highlighted the importance of sulphate dynamics within the soil as a major determinant of stream chemistry. It is essential that further work in the field and laboratory be undertaken to improve the specification of the Langmuir parameters, in particular the half saturation values required to run the model give values far greater than any sulphate concentrations found in the field. Nevertheless, the soils in the Allt a Mharcaidh catchment have a high sulphate adsorption capacity which is surprising and contrary to the findings of Wright *et al.* (1985) who applied MAGIC to four lakes in the U.S.A., Norway, Sweden, and Scotland. They concluded that at all four sites where young, post-glacial podsolic soils dominated, the choice of parameter values for sulphate adsorbtion was not of critical importance because such soils typically have little ability to adsorb sulphate. Clearly, in the case of the Allt a Mharcaidh, where similar soils exist, this does not appear to be the case.

One of the major difficulties encountered in the application of the model was accurately specifying the quantity and quality of inputs, both of which are highly variable from year to year, and are difficult to measure (Ferrier *et al.*, 1988). Clearly both the mean annual rainfall quantity and quality directly affect the chemical budgets and so also partly determine the sulphate adsorption characteristics. In terms of rainfall quality, a discrepancy in inputs will affect both weathering rates and selectivity coefficients because model calculations are dependent upon an input-output balance. Increasing inputs will lower optimized weathering rates and vice versa, and a change in the relative concentrations of ions in precipitation will affect the magnitude of the selectivity coefficients.

Future work must concentrate on assessing the sensitivity of the model to changes in deposition parameters and work on a multi-box approach to model the two catchment soils simultaneously by incorporating some flow routing structures is currently in progress.

In terms of the Surface Water Acidification Programme the choice of the Allt a Mharcaidh catchment as a transitional site is vindicated in that serious stream acidification has not yet taken place and the model predictions suggest that a drop in streamwater pH will occur even if deposition levels are maintained at present values.

Acknowledgments

This research is supported by the Royal Society as part of the Surface Water Acidification Programme. The authors wish to thank R. Harriman, B. Smith, J. D. Miller, and H. Anderson for soil and water chemistry and the journal's editor and referees for comments on an earlier version of this paper.

References

Christophersen, N., Rustad, S., and Seip, H. M.: 1984, *Philos. Trans. R. Soc. London, Ser. B* **305**, 427.

Cosby, B. J., Wright, R. F., Hornberger, G. M., and Galloway, J. N.: 1985a, *Water Resour. Res.* **21**, 1591.

Cosby, B. J., Hornberger, G. M., Galloway, J. N., and Wright R. F.: 1985b, *Water Resour. Res.* **21**, 51.

Cosby, B. J., Whitehead, P. G., and Neale, R.: 1986a, *J. Hydrol.* **84**, 381.

Cosby, B. J., Hornberger, G. M., Wright R. F., and Galloway, J. N.: 1986b, *Water Resour. Res.* **22**, 1283.

Ferrier, R. C., Jenkins, A., Miller J. D., and Walker, T. A. B.: 1988, (in prep.).

Mason, B. J. and Seip, H. M.: 1985, *Ambio* **14**, 49.

Mellor, A. and Wilson, M. J.: 1987, 'Processes and Products of Mineral Weathering in Soils of the SWAP Catchments in Scotland and Norway', *SWAP Mid-Term Conference Proceedings*, Bergen.

Neal, C., Whitehead, P. G., Neale, R. and Cosby, J.: 1986, *J. Hydrol.* **86**, 15.

Perdue, E. M.: 1985, 'Acidic Functional Groups of Humic Substances', in G. R. Aiken, D. M. McNight, R. L. Wershaw and P. MacCarthy (eds.), *Humic Substances in Soil, Sediment and Water*, J. Wiley & Sons, New York.

Schnoor, J. L., Palmer, W. D., Jr., and Glass, G. E.: 1984 'Modeling Impacts of Acid Precipitation for Northeastern Minnesota', in J. L. Schnoor (ed.), *Modeling of Total Acid Precipitation Impacts*, Butterworth, Boston, pp 155-173.

Singh, B. R.: 1984, *Soil Sci.* **138**, 189.

Warren Spring Laboratory Report: 1983, *Acid deposition in the U.K.*, Warren Spring Laboratory, Stevenage, U.K.

Whitehead, P. G., Bird, S., Hornung, M., Cosby, J., Neal, C., and Paricos, P.: 1988, *J. Hydrol.* (in press).

Wright, R. F., Cosby, B. J., Hornberger, G. M., and Galloway, J. N.: 1985, 'Interpretation of Palaeolimnological Recontructions Using the Magic Model of Soil and Water Acidification', *Proceedings of the Muskoka Conference*, September 1985.

2.5 Loch Chon and Kelty Water - Scotland

Journal of Hydrology, 120 (1990) 143–162
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

[3]

MODELLING STREAM ACIDIFICATION IN AFFORESTED CATCHMENTS: LONG-TERM RECONSTRUCTIONS AT TWO SITES IN CENTRAL SCOTLAND

B.J. COSBY[1], A. JENKINS[2], R.C. FERRIER[3], J.D. MILLER[3] and T.A.B. WALKER[3]

[1]*School of Forestry and Environmental Studies, Duke University, Durham, NC 27706 (U.S.A.)*
[2]*Institute of Hydrology, Wallingford, OX10 8BB (U.K.)*
[3]*Macaulay Land Use Research Institute, Craigiebuckler, Aberdeen (U.K.)*

(Received December 30, 1989; accepted after revision February 28, 1990)

ABSTRACT

Cosby, B.J., Jenkins, A., Ferrier, R.C., Miller, J.D. 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.

A conceptual model of the combined effects of afforestation and acidic deposition is applied to two forested sites in central Scotland. Refinements are made to the model inputs specifically to include: increased dry deposition to the forests (in excess of the dry deposition expected for moorland sites) as the forest canopy develops; uptake of ions by the growing forests; and increased evapotranspiration (and thus decreased water yield) as the forests mature. The model is calibrated using a fuzzy optimisation technique which incorporates uncertainty in target variables (stream base cation concentrations and soil exchangeable bases) and uncertainty in selecting values for fixed and adjustable parameters which describe the physico-chemical characteristics of the catchments. Simulated present-day stream and soil chemistry closely match observed values at both sites. The calibrated models indicate that while the patterns of acidification in the two catchments are broadly similar, some differences do exist between the sites in the responses of the soils to acidic deposition and afforestation. It is concluded that the calibrated models provide a tool for: (a) comparison of the relative effects of deposition and afforestation on soil and surface water acidification; (b) assessment of the likely effects of reductions in future deposition combined with future forestry management practices.

INTRODUCTION

Lakes and streams in large areas of eastern North America and Northern Europe have become increasingly acidified during the past several decades (e.g. Likens et al., 1979; Wright, 1983; Haines, 1986). The principal cause of this acidification has been attributed to atmospheric deposition of sulphur (Likens, 1976; Wright and Henriksen, 1979; Overrein et al., 1980; Haines, 1986), although land use changes on the acidic soils which may dominate sensitive regions have also been held partly or wholly responsible (Krug and Frink, 1983; Rosenquist, 1980). In the U.K. a determined land management strategy of conifer afforestation, implemented since the 1940s, has also been held responsible for surface water acidification as a result of proton fluxes connected with plant uptake and mineralisation of organic matter (Nilsson, 1985). Indeed, many studies have reported that compared with moorland sites, conifer afforestation enhances the acidity of drainage waters (Harriman and Morrison, 1982; Nilsson et al., 1982; Stoner et al., 1984).

Three mechanisms may increase the acidity of water draining forested catchments: (1) increased water losses through evapotranspiration thereby concentrating dissolved pollutants entering the stream; (2) uptake of base cations by the growing forest; (3) the increased ability of the forest canopy to scavenge acidic material from the atmosphere (Law, 1956; Calder and Newson, 1979; Miller, 1984; Grennfelt and Hultberg, 1986). Increased scavenging includes contributions from both wet and dry deposition (Fowler, 1984). All of these factors are interactive and, solely on the basis of catchment input–output budgets, it is difficult to discriminate among the effects of the deposition, leaching, interception and vegetation uptake processes.

A modelling approach to examine the relative importance of deposition and afforestation on surface water acidification has therefore been adopted. The model used is Model of Acidification of Groundwater in Catchments (MAGIC), an intermediate-complexity process-oriented model for soil and water acidification. To enable the model to be used in a predictive mode for assessing the relative acidifying effects of forest growth and atmospheric acidic deposition, it is first necessary to calibrate the model to forested sites. The model was applied to two catchments, Chon and Kelty, in the Loch Ard Forest area of central Scotland. These catchments have been subjected to similar deposition and land management histories and have similar (but not identical) bedrock geology. Tree species and soil types on the catchments are, however, different. The waters draining both of these catchments are acidified to differing degrees. The historical development of acidification at the two sites, as simulated by the model, is used to interpret the relative effects of deposition and afforestation on present-day streamwater chemistry.

Previous applications of MAGIC to assess forest effects identified canopy scavenging and increased dry deposition as important factors causing reductions in the pH of surface water (Neal et al., 1986; Whitehead et al., 1988a,b). Those studies, however, were preliminary applications of the model to afforested sites; they only included increased forest filtering and a simple representation of increased evapotranspiration effects and made no attempt to include uptake of ions from the soil by the vegetation. Here a revised and more thorough application uses a refined version of the model with time-varying inputs reflecting the dynamic effects of afforestation and forest growth. It incorporates cation and anion uptake by the vegetation, pre-afforestation dry deposition inputs, enhanced deposition input (both wet and dry) through canopy filtering processes and a continuously variable water yield factor as evapotranspiration increases in response to forest growth.

The structure, calibration procedure and output of the refined model are presented in this paper for the Chon and Kelty catchments. In a companion paper (Jenkins et al., pp. 163–181), the model calibrated for the Chon catchment is used to perform a series of simulation experiments to assess the relative effects of afforestation and acidic deposition on soil and surface water chemistry. Those experiments compare and contrast: (a) the simulated historical effects of increased acidic deposition and forest growth both individually and in combination: (b) the simulated future effects of various levels of deposition reduction in combination with the forestry strategies of harvesting with and without replanting.

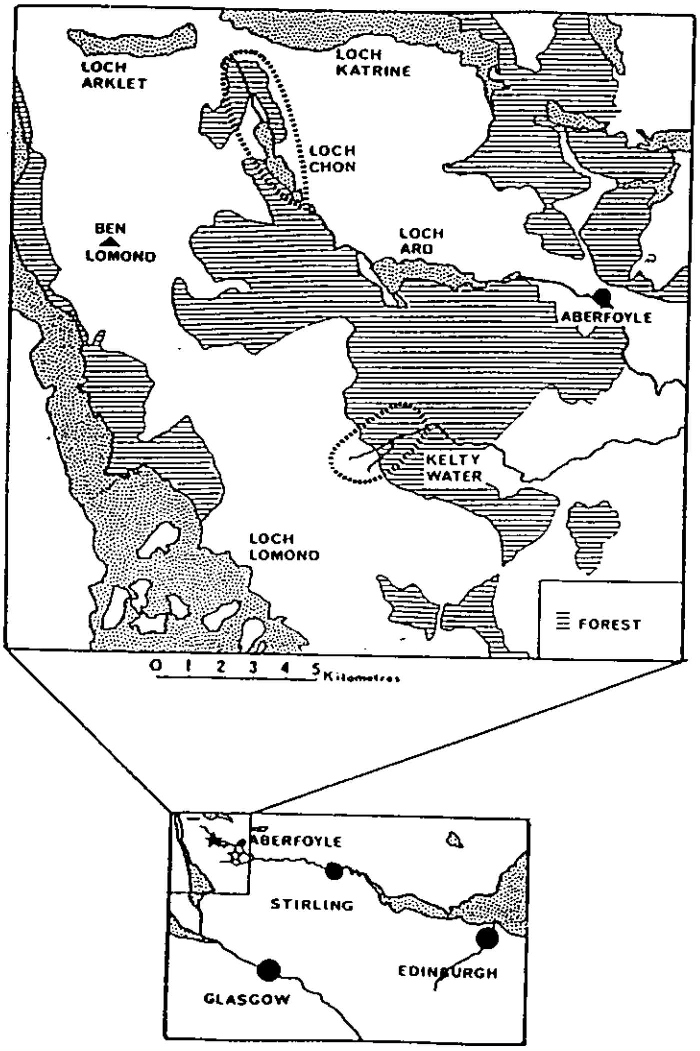


Fig. 1. The Loch Ard study area.

STUDY AREA

As part of the Surface Water Acidification Programme (Mason and Seip, 1985) integrated monitoring of hydrology, chemistry and biology is being undertaken in two forested catchments, Loch Chon (1.87 km^2) and Kelty Water (1.32 km^2), in the Queen Elizabeth Forest Park, Loch Ard (Fig. 1). This area is ~40 km north of Glasgow and is subject to high levels of anthropogenic deposition (ca. 20 kg ha^{-1} year^{-1} sulphate). Rainfall volume in the area varies from 1.8 to 2.4 m year^{-1}. The entire area, including that of the two catchments, has undergone extensive conifer afforestation with planting initiated in 1950. The catchment of Kelty Water was planted with Sitka spruce (*Picea sitkensis*) while the catchment of Loch Chon was planted with Norway Spruce (*Picea abies*). The geology of both catchments is mainly Dalradian metamorphic–igneous rocks comprised of fine grained slates, phyllites and mica-schists (Anderson, 1947). This is overlain by glacial till deposits derived from local rocks. Sampling at Loch Chon and Kelty Water was initiated in the autumn of 1986 (Miller et al., 1990). We use data for calendar year 1987 in this study.

Field sampling strategies and laboratory analyses of the precipitation and streamwater samples are described by Jenkins et al. (1988) and Miller et al. (1990). Bulk deposition and precipitation volumes were collected bi-weekly at both sites in open, nipher-shielded, funnel gauges situated 6 m above the ground in open areas of the forests. The volume weighted mean bulk precipitation chemistries in 1987 are similar for both catchments (Table 1). Streamwater was also collected bi-weekly at both sites using flow-proportional samplers. Despite similar bedrock characteristics and deposition inputs to the two catchments, the volume weighted mean streamwater chemistries for both sites

TABLE 1

Volume weighted mean bulk precipitation concentrations at Chon and Kelty for 1987. Mean annual precipitation volume was 2.3 m at both sites

	Chon	Kelty
Ca^{2+}	19.1	16.8
Mg^{2+}	19.4	26.9
Na^{+}	112.4	135.5
K^{+}	7.5	5.5
NH_4^{+}	16.3	25.0
SO_4^{2-}	56.2	60.4
Cl^{-}	130.5	148.3
NO_3^{-}	11.4	11.0
H^{+}	22.4	31.0
pH	4.6	4.5

Concentrations are given in μeq l^{-1}.

TABLE 2

Volume weighted annual stream concentrations observed and simulated at Chon and Kelty for 1987

	Chon		Kelty	
	Obs.	Sim.	Obs.	Sim.
Ca^{2+}	43.3	45.4	19.0	20.1
Mg^{2+}	48.3	46.0	36.9	35.5
Na^+	181.3	184.1	200.9	199.9
K^+	7.1	8.2	7.8	8.1
NH_4^+	7.2	6.9	13.2	12.9
SO_4^{2-}	93.3	102.8	100.0	106.1
Cl^-	224.5	217.7	216.5	214.7
NO_3^-	3.0	2.9	10.2	10.1
Al^{3+}	24.4	20.0	48.8	48.2
H^+	24.5	24.4	95.5	95.2
pH	4.6	4.6	4.0	4.0
Organic anion	15.3[1]	14.2	95.4[1]	95.2
Sum base cations	280.0	283.7	264.6	263.6
Sum acid anions	320.8	323.4	326.7	330.9
Calc. alkalinity	− 33.6	− 32.8	− 48.9	− 54.4

[1] Observed organic anion concentrations calculated as difference between the sum of concentrations of positively and negatively charged ions.
Concentrations are given in $\mu eq\, l^{-1}$.
Sum base cations = sum of calcium + magnesium + sodium + potassium concentrations; sum acid anions = sum of chloride + sulphate + nitrate concentrations; calculated alkalinity = sum base cations plus ammonium minus sum acid anions.

are different in some respects (Table 2). Kelty Water has higher concentrations of aluminium, sulphate, nitrate, and organic ions, and lower pH and calcium concentrations than Loch Chon. Kelty Water is no longer capable of sustaining a viable fish population but Loch Chon maintains a reduced fish population.

Physical and chemical parameters of the soil in the two catchments were determined by a detailed sampling and analysis strategy at the outset of the project (Hudson and Hipkin, 1986; Henderson and Campbell, 1986). The soils in both catchments belong to the Strichen association and consist of peaty gleys at Kelty and humus iron podsols at Chon. Soil parameters were measured for individual horizons from a number of soil pits within the catchments. Individual horizon values were weighted using the depth of each horizon to give a vertically aggregated value for each soil type. These vertically aggregated values were then weighted by percentage area of each soil type within the catchment to give weighted mean values of the soil physical and chemical characteristics for use in the model (Table 3).

TABLE 3

Observed soil characteristics at Chon and Kelty. Weighted mean values for the aggregated soils in each catchment (see text)

	Chon	Kelty
Depth (m)	1.0	1.0
Cation exchange capacity (meq kg^{-1})	204	410
Sulphate adsorption maximum capacity (meq kg^{-1})	7.0	3.5
Sulphate adsorption half saturation (meq m^{-3})	1200	1200
Bulk density (kg m^{-3})	964	844
Base saturation (%)	3.0	3.5
Exchangeable Ca^{2+} (%)	1.2	1.9
Exchangeable Mg^{2+} (%)	0.6	0.7
Exchangeable Na^{+} (%)	0.5	0.6
Exchangeable K^{+} (%)	0.7	0.3

MODELLING TECHNIQUES

The MAGIC *model*

The MAGIC model is a lumped parameter, long-term simulation model of soil and surface water quality (Cosby et al., 1985a,b). It consists of the following: (1) a soil–soil solution chemical equilibria section in which the concentrations of major ions are assumed to be governed by simultaneous reactions involving

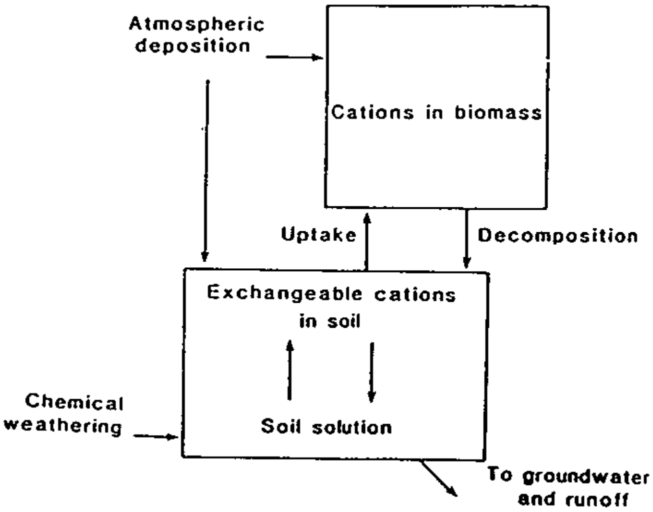


Fig. 2. Schematic representation of the MAGIC model.

sulphate adsorption, cation exchange, dissolution and precipitation of aluminium, speciation of organic acids, and dissolution and speciation of carbonic acid; (2) a mass balance section in which the flux of major ions to and from the soil is assumed to be controlled by atmospheric inputs, chemical weathering inputs, net uptake in biomass and losses to runoff (Fig. 2). At the heart of 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 as a result of changes in atmospheric deposition and biological uptake/release, the chemical equilibria between soil and soil solution shift to give changes in surface water chemistry.

Sulphate adsorption is treated in the model by a Langmuir isotherm. A detailed investigation of the sulphate subsection of the model is given by Cosby et al. (1986a). Aluminium dissolution and precipitation is assumed to be controlled by equilibrium with a solid phase of $Al(OH)_3$. Speciation of aluminium and inorganic carbon is computed from known equilibrium equations. Cation exchange is treated using equilibrium (Gaines-Thomas) exchange equations. Weathering rates are assumed to be constant with time in the model. Organic acids are modelled as diprotic acids using equilibrium expressions for dissociation based on the pK values of the acid. Given a description of the historical deposition and afforestation effects at a site, the model equations are solved numerically to give long-term reconstructions of surface water chemistry.

Application to Chon and Kelty

Until afforestation in 1950 both sites were under moorland vegetation and a water yield of 90% was assumed. This figure is consistent with other model applications to moorland sites in Scotland (Jenkins and Cosby, 1989). Following planting in 1950 a 15-year growth period is assumed before canopy closure, during which time evapotranspiration increases linearly with age of the forest. At the point of canopy closure, evapotranspiration was assumed to be at its maximum and a water yield of 75% was chosen. The net result of this sequence on annual streamflow volumes is shown in Fig. 3(d).

Historical loadings to the catchments for use in the simulations were derived in two stages. First, the historical loadings in the absence of growing forests and in the absence of anthropogenic acidic deposition were estimated for both sites for both wet and dry deposition. Second, the moorland wet and dry loadings were modified subsequent to 1950 to reflect the effects of afforestation.

Current (1987) mean annual precipitation input is 2.3 m at both sites; the mean composition of the bulk rainfall is shown in Table 1. These measurements are made in forest clearings with bulk collectors and are taken to be approximately equal to the wet deposition loading in the absence of enhanced scavenging by the forest canopy. These wet loadings can be partitioned into natural (sea salt) and anthropogenic components. Wet loadings for sulphate, nitrate and ammonium in excess of sea salt contributions (anthropogenic

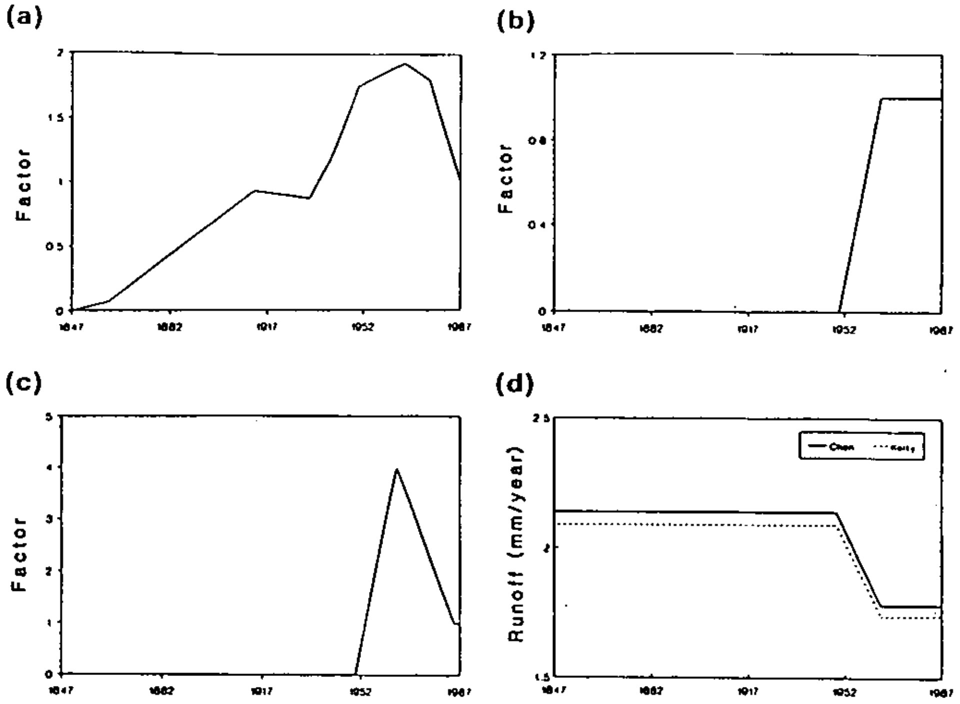


Fig. 3. Variable inputs used in the model simulations at both sites: (a) wet deposition; (b) dry deposition; (c) vegetation uptake; and (d) dry deposition due to canopy filtering processes. Wet and dry deposition and uptake are scaled to present-day values.

components) were assumed to have increased following the sequence of sulphur emissions described by the Warren Spring Laboratory (1983, 1987) up to 1973, with a modification based on sulphur emission data from 1973 to 1987 (Warren Spring Laboratory, unpublished data, 1988). The resulting trajectory for wet loading of anthropogenic components in the absence of a forest canopy is shown in Fig. 3(a). The historical wet loadings of sea salt in the absence of a forest canopy are assumed to be constant.

Particulate or occult (dry) deposition loadings for both sea salt and anthropogenic components were simulated by multiplying the wet loadings by 'deposition factors' to obtain total (wet plus dry) loadings; the deposition factors for sea salt are based on occult sea salt deposition calculations for two nearby moorland sites in the region (Jenkins and Cosby, 1989). These factors were derived by calculating the additional sea salt necessary to give a conservative mass balance for chloride, given the measured wet atmospheric deposition and stream export for those moorland sites. The sea-salt deposition factors used in the simulations prior to afforestation in 1950 were 1.10 for Chon and 1.01 for Kelty. A deposition factor of 1.24 for anthropogenic components was used for both sites prior to 1950 to represent dry deposition of particulate and gaseous sulphur to moorland sites. This factor was derived by calculating the additional sulphate necessary to give a conservative mass balance for sulphate, given the measured wet atmospheric deposition and stream export for nearby moorland sites (Jenkins and Cosby, 1989; the soils at the sites had low sulphate adsorption capacities as do the soils at Chon and Kelty). Because the deposition factors are multipliers for wet deposition, the effective dry deposition of anthropogenic components increases along the same trajectory as the wet deposition until 1950 (Fig. 3a); the effective dry deposition of sea salt components remains constant.

The deposition factors for sea salt and anthropogenic components were increased after 1950, to represent the increases in both wet and dry loadings resulting from the increased scavenging by the forest canopies in Chon and Kelty. For the 15-year tree growth period between planting and canopy closure, the forest filtering effect is assumed to produce a linear increase in total deposition. The assumed pattern of increase in the deposition factors due to forest effects is shown in Fig. 3(b). Deposition factors for sea salt components increased to 1.3 for Chon and 1.1 for Kelty. The magnitudes of the increases were calculated to give simulated streamwater chloride concentrations equal to observed chloride concentrations in 1987 with forests present at both sites. Throughfall and stemflow measurements from the two sites indicate that the different tree species in each catchment have different characteristics of pollutant scavenging and canopy leaching, especially with respect to sulphate. Kelty shows consistently higher sulphate concentrations in throughfall and stemflow. The deposition factor for anthropogenic components at Kelty was increased to 1.35 after afforestation while that for Chon was maintained at 1.24. The final deposition factors for the anthropogenic components resulted in good agreement between simulated and observed sulphate for the two sites (Table 2).

The estimation of net nutrient uptake by vegetation is problematic given the difficulties of assessing processes such as crown leaching and below-ground turnover (Miller, 1984). A general pattern of net uptake, may, however, be estimated. Miller (1981) showed that, in even-aged forests, the greatest demand for soil nutrients occurs early in the life of the crop, during crown development and the rapid build-up of foliar biomass. The demand for soil nutrients reaches a maximum well before the time of maximum stem growth. As the forest matures, nutrients progressively accumulate on the forest floor as organic litter, at a rate broadly proportional to that of tree growth rate (Miller and Miller, 1976). The nutritional requirement of maturing trees may be much larger than that of younger trees but a larger component is met through recycling of nutrients in litter (Miller, 1981). Older trees recycle a greater proportion of their annual uptake through the litter, and there is an increasing dependence upon nutrient cycling within the organic horizons (Khanna and Ulrich, 1984). The resultant decrease in rates of uptake from the soil, combined with efficient capture of atmospheric nutrients and rapid cycling in the litter, results in a decline in net nutrient demand from the soil as the forest matures. This relative pattern of net nutrient uptake from the soil (Fig. 3c) is used in simulations of forest growth. The simulated net uptakes of calcium, magnesium, sodium, potassium and sulphate in the simulations are scaled to the shape in Fig. 3(c) using maximum uptake rates estimated from biomass concentrations of the ions and biomass accumulation rates (Miller and Miller, 1976).

In Scottish forest soils over three-quarters of the nitrogen uptake by trees is in the form of ammonium (Williams et al., 1979) and therefore trees accumulate an excess of cations over anions balanced by a reverse flux of hydrogen from the roots to the soil. This nitrogen accumulation thus results in a net acidification of soils by forest growth (Brand et al., 1986) and, although rates of acidification vary with productivity of the stands, the pattern of acidification over time remains the same (Nilsson et al., 1982). In the simulations, uptake of nitrogen species (NO_3^- and NH_4^+) from the soils is modelled as a first order process. The first order rate constant for each catchment is selected such that simulated streamwater concentrations of nitrate and ammonium match observed concentrations.

Calibration of the model

The calibrations proceeded in a sequential manner. First, the concentrations of chloride and sulphate were calibrated by adjusting occult and dry deposition of sea salts and gaseous/particulate sulphur compounds under the assumptions outlined in the previous section. Base cation concentrations were then calibrated using an optimisation procedure based on the Rosenbrock (1960) algorithm (see below). Finally, the organic acid concentrations in the streams were calibrated to match the organic anionic charges observed.

The base cation calibration involved fitting the results of long-term model simulations to currently observed water and soil base cation data (surface water concentrations of calcium, magnesium, sodium, and potassium, and soil exchangeable fractions of calcium, magnesium, sodium and potassium). These 'target variables' thus comprise a vector of measured values all of which must be reproduced by the model if a calibration is to be successful. The use of multiple, simultaneous targets in an optimisation procedure provides robust constraints on model calibration (Cosby et al., 1986b).

Those physico-chemical soil and surface water characteristics measured in the field are considered fixed parameters in the model (Table 4). These measurements, are, however, subject to error and so ranges were chosen to represent this error and the spatial heterogeneity within the catchment. A range of uncertainty for each observed, weighted-mean soil parameter was defined using the maximum and minimum vertically-aggregated single-pit values for each parameter. These estimated uncertainties in the observed values (Table 4) were used in the calibration procedure. For those fixed parameters for which no direct measurements were available (i.e. CO_2 partial pressure and organic acid content), single values with no range of uncertainty were assumed.

Base cation weathering rates and base cation exchange selectivity coefficients for the soils are not directly measurable and were used as 'adjustable'

TABLE 4

The ranges and mean values of fixed parameters used in the optimisation procedure

	Chon		Kelty	
	Range	Mean	Range	Mean
Soil				
Depth (m)	0.9–1.1	1.02	0.9–1.1	1.00
Bulk density (kg m^{-3})	864–1064	962	744–944	842
Cation exchange capacity (meq kg^{-1})	154–254	202	360–460	410
Sulphate adsorption maximum capacity (meq kg^{-1})	5.0–9.0	7.0	2.0–5.0	3.4
Sulphate adsorption half saturation (meq m^{-3})	1100–1300	1211	1100–1300	1190
Al solubility coefficient ($\log_{10}$)	8.7–9.4	9.1	8.7–9.4	9.1
CO_2 partial pressure (atm)	–	0.033	–	0.033
Organic matter content (m mol. m^{-3})	–	60	–	150
Organic matter pK_1 ($\log_{10}$)	–	4.25	–	4.50
Water				
Runoff (m $year^{-1}$)	1.56–1.90	1.78	1.56–1.90	1.74
Al solubility coefficient ($\log_{10}$)	–	8.6	–	7.2
CO_2 partial pressure (atm)	–	0.0033	–	0.0033
Organic matter content (m mol. m^{-3})	–	20	–	300
Organic matter pK_1 ($\log_{10}$)	–	4.25	–	4.40

model parameters to be optimised in the calibration procedure. The calibrations were performed on simulations run from 1847 to 1987. After each historical simulation, the model variables in 1987 were compared with observations in 1987, the adjustable parameters were modified as necessary to improve the fit, the historical simulation was re-run and the procedure was repeated until no further improvement in the fit could be achieved.

Because the measurements of the fixed parameters and the target variables are subject to errors, a 'fuzzy' optimisation procedure was implemented for calibrating the models. The fuzzy optimisation procedure consisted of multiple calibrations of each model structure, using perturbations of the values of the fixed parameters and estimated uncertainties of the target variables. The sizes of the perturbations of the fixed parameters were based on known measurement errors or spatial variability of the parameters. The uncertainties in the target variables were estimated as the measurement errors of the variables (5 μeq l^{-1}

or 10%, whichever was the larger, for concentrations of surface water variables; 0.5% for soil base saturation variables).

Each of the multiple calibrations began with: (a) a random selection of perturbed values of the fixed parameters; (b) a random selection of the starting values of the adjustable parameters; (c) specification of uncertainty in the target variables. The adjustable parameters were then optimised using the Rosenbrock algorithm to achieve a minimum error fit to the target variables. The optimisation algorithm was stopped and the calibration considered complete when the simulated values of all target variables were within the pre-specified uncertainty limits for the observations. This procedure was undertaken ten times for each site. The final calibrated model for each site consists of the mean parameter and variable values of at least 8 successful calibrations.

Using the fuzzy optimisation based on multiple calibrations, uncertainty bands for the model simulations can be presented as maximum and minimum values for output variables in any year derived from the group of successful calibrations. These uncertainty bands encompass the range of variable values which were simulated, given the specified uncertainty in the fixed parameter values and measured target variables. When examining simulation results, the maximum and minimum values are both plotted through time. The 'true' model calibration is taken to fall between these lines. When comparing simulation results from two model structures, the overlap of the uncertainty bands provides a measure of the degree to which the structures behave similarly.

Organic anions in the model

Organic anions in MAGIC are simulated by specifying the total amount of a diprotic organic acid (in m mol. l^{-1} of carboxyl groups) and the two pK values (for dissociation of the carboxyl groups). Thus, a total organic acid content of 10 m mol. l^{-1} (as H_2A) would produce 10 μeq l^{-1} of organic charge when the first proton was totally dissociated (all acid as HA^-) and 20 μeq l^{-1} of organic charge when the second proton was also totally dissociated (all acid as A^{2-}). By selecting appropriate values for the total organic acid content and the pK values, the total organic charge ($[HA^-] + [A^{2-}]$) can be adjusted for any pH. The ratio of total organic charge to the total dissolved organic carbon concentration (DOC, on a weight per volume basis) is referred to as the effective charge density of the organic acid. In calibrating the model, therefore, either the total organic acid content or the effective charge density and DOC of the organic must be specified along with the pK values. These values are needed for both the soil and surface water compartments of the model.

As seen from the measured ionic concentrations in the streams of the two catchments (Table 2), organic anions comprise a significant proportion of the total ionic charge at each site. No direct measurement of the dissolved organic charge was available for either soil or stream water. The DOC was available for the streams (Chon = 6 mg l^{-1}; Kelty = 16 mg l^{-1}). These measurements were

TABLE 5

Percentage values of observed and simulated soil chemistry variables

	Chon		Kelty	
	Obs.	Sim.	Obs.	Sim.
Exchangeable Ca^{2+}	1.2	1.2	1.9	1.7
Exchangeable Mg^{2+}	0.6	0.6	0.7	0.9
Exchangeable Na^{+}	0.5	0.5	0.6	0.6
Exchangeable K^{+}	0.7	0.4	0.3	0.4
Base saturation	3.0	2.7	3.5	3.6

TABLE 6

Optimised weathering rates and soil exchange selectivity coefficients for the Chon and Kelty models

	Chon	Kelty
Weathering rates		
Calcium (meq m^{-2} $year^{-1}$)	53.3	0.6
Magnesium (meq m^{-2} $year^{-1}$)	58.3	16.8
Sodium (meq m^{-2} $year^{-1}$)	7.7	26.8
Potassium (meq m^{-2} $year^{-1}$)	10.2	14.1
Selectivity coefficients		
Calcium ($\log_{10}$)	1.16	−0.82
Magnesium ($\log_{10}$)	2.22	0.77
Sodium ($\log_{10}$)	0.28	0.07
Potassium ($\log_{10}$)	−3.42	−3.62

used, with the assumption of an effective charge density of ~ 10 for the organic acids, and that the organic acids in the soils were equivalent to those in the stream, to derive the total organic acid content for the soil water at the two sites given in Table 4. The pK values for the first dissociation in the two soils are also given in the table. The pK values for the second dissociation were set to 10.5 (thus effectively producing a monoprotic acid for the low pH of these soils). The models were calibrated to the observed base cation concentrations observed in the streams (as described above) with these values of parameters for the organic acids in the soils and stream.

Subsequent to the calibration of the soils, the parameters of the organic acids simulated in the stream were modified (calibrated) to give an effective organic charge concentration approximately equal to that calculated from the observations (Table 2). The calibrated stream organic acid parameters (Table 4) corresponded to an effective charge density of 3.3 for the 6 mg l^{-1} DOC measured at Chon, and 12.5 for the 16 mg l^{-1} DOC measured at Kelty.

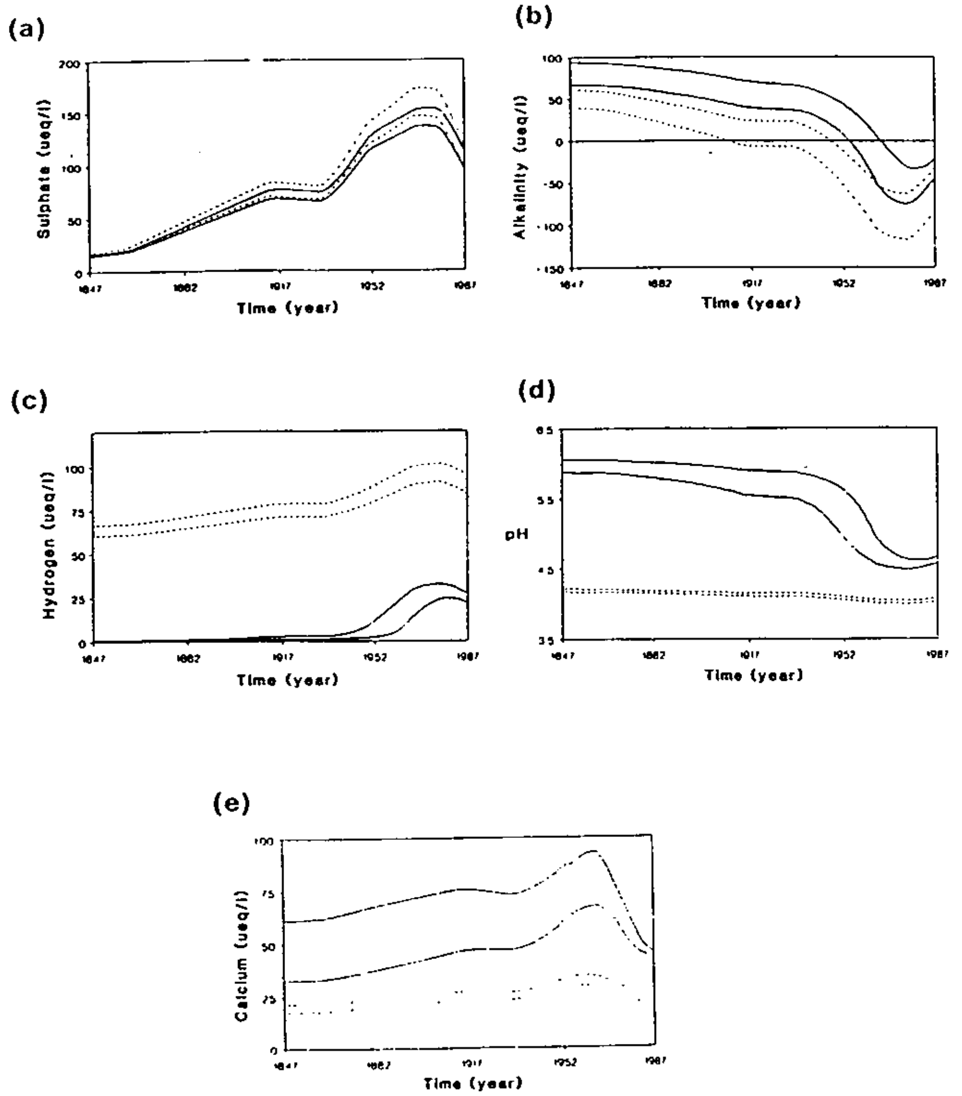


Fig. 4. Simulated values at Chon (——) and Kelty (- - -) of: (a) stream sulphate concentration; (b) alkalinity concentration; (c) hydrogen ion concentration; (d) pH; (e) calcium concentration. The two curves for each site represent the confidence limits of the simulation as derived from the fuzzy optimisation.

RESULTS

Simulated stream chemistry (Table 2) matches observed chemistry closely at both Chon and Kelty. The model also successfully simulates present-day soil chemistry (Table 5) as soil base exchange fractions at the two sites are well matched with measured data. The final values of the optimised parameters (weathering rates and soil exchange selectivity coefficients) resulting in these fits to the data are given in Table 6. Values of weathering of calcium and magnesium are higher at Chon and this accords well with field observation of a doleritic dyke within the catchment which affects the outflow concentrations of these ions.

Stream pH, hydrogen, alkalinity (expressed as sum of base cations plus ammonium minus sum of acid anions), calcium and sulphate hindcast reconstructions for the two sites from 1847 to 1987 are shown in Fig. 4. Chon shows a very low background hydrogen concentration with an increasing trend which accelerates in the period 1950–1960 to give a rapid increase in hydrogen concentration (Fig. 4). Kelty shows a similar accelerated increase during that period but has a very high background hydrogen concentration. This is because of the high levels of organics in the catchment, which are assumed to be at a constant level throughout the simulation. The period of rapidly increasing hydrogen corresponds to the planting and growth of the forest. At the time of canopy closure, 1965, both catchments are subject to the most severe acidifying processes; (a) total load of anthropogenic wet and dry deposition is at a high level as the assumed deposition curve peaks at this time; (b) input from canopy filtering is also at a maximum because canopy closure (and thus, maximum filtering by the trees) and maximum deposition coincide; (c) maximum cation uptake coincides with canopy closure; (d) the concentrating effect of increased evapotranspiration is also at a maximum. Around 1970 stream concentrations level off and by 1980 have started to decrease. This is in response to the falling deposition levels in recent years (Fig. 3a) and to the decrease in uptake of base cations as the forest matures.

The base saturation reconstruction (Fig. 5) indicates a progressive soil acidification through time as base cations are leached in response to the incoming acidity. High weathering rates at Chon produce a high initial base saturation although this falls steadily until 1950 and then accelerates downwards at the onset of afforestation. At Kelty, although the apparent

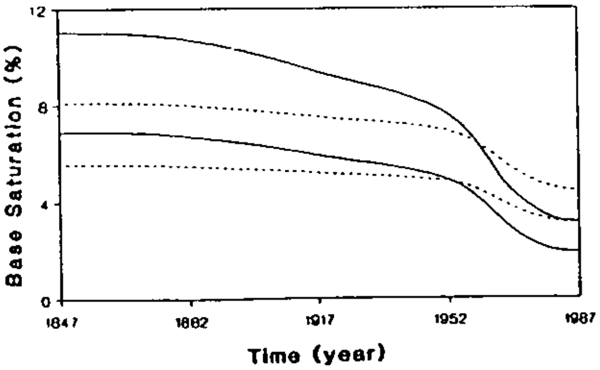


Fig. 5. Simulated soil percent base saturation at Chon (——) and Kelty (- - -). The two curves for each site represent the confidence limits of the simulation as derived from the fuzzy optimisation.

initial base saturation is not as high as at Chon, the model indicates that cation losses from the soil will result in slightly higher percent base saturation. No recovery of base saturation is seen at either site in response to decreased emissions since 1970, although the rate of decrease slows, and this accords well with the expected slower recovery of soils as they continue to desorb sulphate (Wright et al., 1988).

DISCUSSION

The application of the MAGIC model to these two sites demonstrates the effect of soil properties and forest growth on the historical acidification pattern in this area. It also demonstrates that the two sites, in relatively close proximity, show broadly similar responses but are quite different in detailed comparison. Clearly, the organics in the Kelty system have a major influence on historical pH, although sulphate is the dominant mobile anion affecting the historical decline in alkalinity at both sites. A discussion of the sulphate budget and dynamics as simulated by the model, therefore, can aid understanding of the acidification history of these two sites and offers an explanation for the observed differences between them.

Observed wet sulphate loading is similar at both sites (Table 1); under the deposition assumptions used, the total sulphate (wet plus dry) was historically similar until afforestation in 1950 (Fig. 6a). Thereafter, differences in the effects of tree species (altering dry deposition and interception) have enhanced the differences in total sulphate loading between the two sites (Fig. 6a). The decrease after 1970 at both sites is due to decreased emissions. The relative difference between the two diminishes because the dry deposition factors for the sites are applied as a constant proportion of wet deposition. Simulated stream sulphate concentrations closely follow the deposition curve (Fig. 6b), Kelty being consistently higher because of its higher input and the greater soil adsorption at Chon (Fig. 6c).

The cumulative loss of total exchangeable base cations at the two sites demonstrates that more base cations are lost from the exchange sites at Chon compared with Kelty and that the relative difference in loss rates intensifies as anthropogenic sulphate input increases over time (Fig. 7). At the period of forest planting and growth the two curves converge as loss from soil exchange sites is dominated by plant uptake which exceeds losses of base cations associated with mobile sulphate anions. At canopy closure, uptake rates decrease and the differences between the two sites become apparent again.

Forest growth at the two sites accelerates acidification of the surface water from the steady pre-afforestation decline caused by the gradual increase of anthropogenic deposition. The model clearly demonstrates that evapotranspiration and cation uptake cause a significant acidification of the soil on top of the effect of canopy interception. This can at times cause enhanced surface water acidification, the degree depending on the dynamics of the mobile-anion and the base cation status of the soil. At Kelty the increased soil acidification

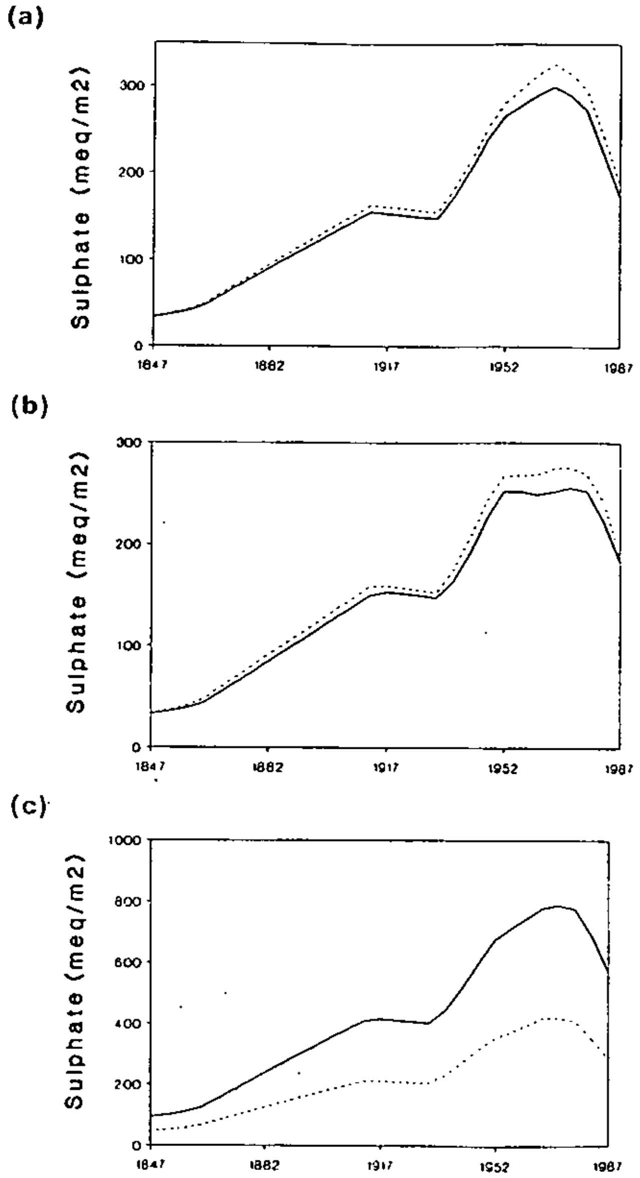


Fig. 6. Components of the sulphate budget at Chon (——) and Kelty (- - -): (a) total deposition loading; (b) total stream output; and (c) soil adsorbed sulphate.

appears to lead to water acidification because hydrogen is leached from the soil, whereas at Chon, the exchange of base cations affords some buffer to the stream acidity.

If uptake is an important process affecting the surface water and soil responses at these sites, the mechanisms and processes of uptake need adequate

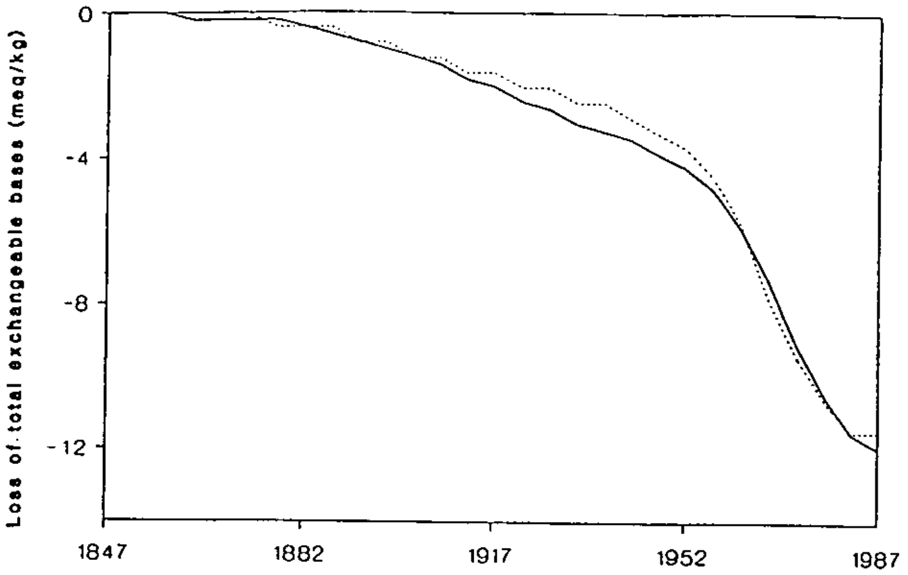


Fig. 7. Cumulative loss of total exchangeable base cations from the soils at Chon (——) and Kelty (- - -).

representation in the model. Uptake has been treated relatively simply, and no account is taken of organic matter build-up in the litter layer. It is, however, impossible to separate true vegetational uptake from immobilisation in the organic matter accumulation. Owing to the role of the latter in nutrient cycling during growth, it is assumed to be an inseparable component of vegetational uptake within the context of the model. Also, at no time in the lifespan of the forest did nutrient requirements exceed supply from the soil, i.e. no stand fertilisation was required for major elements and no trace element deficiencies developed. Finally, it is assumed that deposition levels of anthropogenic pollutants in this area of Scotland do not have a direct effect upon tree physiology, through direct physical damage, mineral nutrition, metal toxicity, or increased susceptibility to biological attack.

CONCLUSIONS

The use of a relatively simple model of soil/water chemistry with inputs reflecting the effects of forest growth can provide a conceptual basis for comparing the relative effects of afforestation and acid deposition on surface water acidification.

When applied to two forested sites in Scotland, the model successfully simulates present-day chemistry at both sites and can be used to examine current and historical differences in the responses to acidification between the sites.

These successful applications suggest that the coupled model can be used in speculative simulation experiments to assess the relative effects of land use changes and/or deposition reductions on soil and surface water acidification. The results of these experiments are presented in the companion paper by Jenkins et al. (pp. 163–181).

REFERENCES

Anderson, J.G.C., 1947. Geology of the Highland Border: Stonehaven to Arran. Philos. Trans. R. Soc. Edinburgh, LXI, No. 18.

Brand, D.G., Kehoe, P. and Connors, M., 1986. Coniferous afforestation leads to soil acidification in central Ontario. Can. J. For. Res., 16: 1389–1391.

Calder, I.C. and Newson, M.D., 1979. Land use and upland water resources in Britain — a strategic look. Water Resour. Bull., 15: 1628–1639.

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. Water 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. Water Resour. Res., 21: 1591–1601.

Cosby, B.J., Hornberger, G.M., Wright, R.F. and Galloway, J.N., 1986a. Modelling the effects of acid deposition: control of long-term sulfate dynamics by soil sulfate adsorption. Water Resour. Res., 22: 1283–1291.

Cosby, B.J., Hornberger, G.M., Wright, R.F., Rastetter, E.B. and Galloway, J.N., 1986b. Estimating catchment water quality response to acid deposition using mathematical models of soil ion exchange processes. Geoderma, 38: 77–95.

Fowler, D., 1984. Transfer to terrestrial surfaces. Phil. Trans. R. Soc., London, Ser. B., 305: 281–297.

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.

Haines, T.A., 1986. Fish population trends in response to surface water acidification. In: Acid Deposition, Long-term Trends, National Academy Press, Washington, DC, pp. 300–334.

Harriman, R. and Morrison, B., 1982. Forestry, fisheries and acid rain in Scotland. Scott. For., 36: 89–95.

Henderson, D.J. and Campbell, C.G.B., 1986. The north Loch Chon catchment area. Macaulay Land Use Research Institute (MLURI) Int. Rep., 40 pp.

Hudson, G. and Hipkin, J.A., 1986. Soil survey of the Kelty water catchment. Macaulay Land Use Research Institute (MLURI) Int. Rep., 32 pp.

Jenkins, A. and Cosby, B.J., 1989. Modelling surface water acidification using one and two soil layers and simple flow routing. In: J. Kamari, D.F. Brakke, A. Jenkins, S.A. Norton and R.F. Wright (Editors), Regional Acidification Models, Springer, New York, pp. 253–266.

Jenkins, A., Ferrier, R.C., Walker, T.A.B. and Whitehead, P.G., 1988. A modelling study of long-term acidification in an upland Scottish catchment. Water, Air, Soil Pollut., 40: 275–291.

Jenkins, A., Cosby, B.J., Ferrier, R.C., Walker, T.A.B. and Miller, J.D., 1990. Modelling stream acidification in afforested catchments: an assessment of the relative effects of acid deposition and afforestation. J. Hydrol., 120: 163–181.

Khanna, P.H. and Ulrich, B., 1984. Soil characteristics influencing nutrient supply in forest soils. In: G.D. Bowen and E.K.S. Nambiar (Editors), Nutrition of Plantation Forests. Academic Press, London, pp. 79–117.

Krug, E.C. and Frink, C.R., 1983. Acid rain on acid soil: a new perspective. Science, 221: 520–525.

Law, F., 1956. The effect of afforestation upon the yield of water catchment areas. J. Br. Waterworks Assoc., 35: 489–494.

Likens, G.E., 1976. Acid Precipitation. Environ. Sci. Technol., 10: 29A–44A.

Likens, G.E., Wright, R.F., Galloway, J.N. and Butler, T.J., 1979. Acid rain. Scientific American, 241: 43–51.

Mason, B.J. and Seip, H.M., 1985. The current state of knowledge on acidification of surface waters and guidelines for further research. Ambio, 14: 45–51.

Miller, H.G., 1981. Forest fertilisation: some guiding concepts. Forestry, 54: 157–167.

Miller, H.G., 1984. Dynamics of nutrient cycling in plantation ecosystems. In: G.D. Bowen and E.K.S. Nambiar (Editors), Nutrition of Plantation Forests. Academic Press, London, pp. 53–78.

Miller, H.G. and Miller, J.D., 1976. Effects of nitrogen supply on net primary production in Corsican Pine. J. Appl. Ecol., 13: 249–256.

Miller, J.D., Anderson, H.A. and Ferrier, R.C., 1990. Comparison of the hydrological budgets and detailed hydrological responses in two forested catchments. Forestry, in press.

Neal, C., Whitehead, P.G., Neale, R. and Cosby, B.J., 1986. Modelling the effects of acidic deposition and conifer afforestation on stream acidity in the British Uplands. J. Hydrol., 86: 15–26.

Nilsson, S.I., 1985. Why is Lake Gardsjon acid? An evaluation of processes contributing to soil and water acidification. Ecol. Bull. (Stockholm), 37: 311–318.

Nilsson, S.I., Miller, H.G. and Miller, J.D., 1982. Forest growth as a possible cause of soil and water acidification: an examination of the concepts. Oikos, 39: 40–49.

Overrein, L.N., Seip, H.M. and Tollan, A. (Editors), 1980. Acid Precipitation, Effects on Forest and Fish. SNSF Project Final Report, Sur Nederdors Pa Skog og Fisk, Oslo, Norway.

Rosenbrock, H.H., 1960. An automatic method for finding the greatest or least value of a function. Comput. J., 3: 175–184.

Rosenquist, I.T., 1980. Influence of forest vegetation and agriculture on the acidity of fresh water. In: J.R. Tsasslin and E.N. Ziegler (Editors), Advances in Environmental Science and Engineering, Vol. 3. Gordon and Breach, pp. 56–79.

Stoner, J.H., Gee, A.S. and Wade, K.R., 1984. The effects of acidification on the ecology of streams in the Upper Tywi catchment in west Wales. Environ. Pollut., Series A, 35: 125–157.

Warren Spring Laboratory, 1983. Acid deposition in the United Kingdom. Warren Spring Laboratory, Stevenage, 72 pp.

Warren Spring Laboratory, 1987. Acid deposition in the United Kingdom 1981-1985. Warren Spring Laboratory, Stevenage, 104 pp.

Whitehead, P.G., Bird, S., Hornung, M., Cosby, R.J., Neal, C. and Paricos, P. 1988a. Stream acidification trends in the Welsh Uplands — a modelling study of the Llyn Brianne catchments. J. Hydrol., 101: 191–212.

Whitehead, P.G., Reynolds, B., Hornung, M., Neal, C., Cosby, B.J. and Paricos, P., 1988b. Modelling long term stream acidification trends in upland Wales at Plynlimon. Hydrol. Process., 2: 357–368.

Williams, B.L., Cooper, J.M. and Pyatt, D.G., 1979. Effects of afforestation with *Pinus contorta* on nutrient content, acidity and exchangeable cations in peat. Forestry, 51: 29–35.

Wright, R.F., 1983. Predicting Acidification of North American Lakes. Rep. 0-81036, Norwegian Institute for Water Research, Oslo, 165 pp.

Wright, R.F. and Henriksen, A., 1979. Sulphur: Acidification of freshwaters. In: International Symposium on Sulphur Emissions and the Environment. Soc. Chem. Ind., London, pp. 277–301.

Wright, R.F., Lotse, E. and Semb, A., 1988. Reversibility of acidification shown by whole-catchment experiments. Nature, 334: 670–675.

Journal of Hydrology, 00 (1990) 000–000 HYDROL 1662
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

[3]

MODELLING STREAM ACIDIFICATION IN AFFORESTED CATCHMENTS: AN ASSESSMENT OF THE RELATIVE EFFECTS OF ACID DEPOSITION AND AFFORESTATION

A. JENKINS,[1] B.J. COSBY,[2] R.C. FERRIER,[3] T.A.B. WALKER[3] and J.D. MILLER[3]
[1]*Institute of Hydrology, Wallingford, Oxon (U.K.)*
[2]*School of Forestry and Environmental Studies, Duke University, Durham, NC 27706 (U.S.A.)*
[3]*Macaulay Land Use Research Institute, Craigiebuckler, Aberdeen (U.K.)*

(Received December 30, 1989; accepted for publication February 28, 1990)

ABSTRACT

Jenkins, A., Cosby, B.J., Ferrier, R.C., Walker, T.A.B. and Miller, J.D. 1990. Modelling stream acidification in afforested catchments: an assessment of the relative effects of acid deposition and afforestation. J. Hydrol., 00: 000–000.

A model of the combined long-term effects of acidic deposition and forest growth has been developed and calibrated for an upland site in Scotland. The model is used to perform a series of simulation experiments to assess the relative effects of afforestation and acidic deposition on soil and surface water chemistry. The experiments compare and contrast: (a) the simulated historical effects of increased acidic deposition and forest growth, both individually and in combination; (b) the simulated future effects of various levels of reduction of deposition in combination with the forestry strategies of harvesting with and without replanting. Results indicate that historical acidification of surface waters in areas receiving high levels of acidic deposition has been exacerbated by afforestation practices. Afforestation in the absence of acidic deposition, however, has had a lesser effect on surface water acidification even though the nutrient demands of forest growth have caused significant soil acidification. Comparisons of future forest management strategies in conjunction with likely deposition reductions indicate that, in sensitive areas, replanting of a felled forest without treatment of the soil by addition of base cations, should not be undertaken even if significant deposition reductions are realised.

INTRODUCTION

In large areas of eastern North America and Europe a recent trend toward increased acidification has been observed in lakes and streams (e.g. Likens et al., 1979; Wright, 1983; Haines, 1986). This has occurred in surface waters draining both moorland and afforested catchments although paired catchment studies have concluded that runoff from forested catchments is more acidic than from moorland catchments (Harriman and Morrison, 1982; Stoner et al., 1984). Many studies of soils in forested areas have demonstrated that enhanced soil acidification has occurred and that the effect of coniferous trees themselves is stronger than that resulting from atmospheric deposition (Troedsson, 1980). On the other hand, in moorland areas, no clear evidence exists as to whether acidic precipitation has enhanced the podsolisation process (Linzon and Temple, 1980); yet many studies in moorland areas demonstrate increased surface water acidity in response to acidic deposition (Battarbee, 1988).

Empirical evidence from catchment monitoring experiments is difficult to interpret because of the synergistic nature of afforestation and of acid deposition in causing acidification. Recent modelling studies have indicated that forests promote acidification by a combination of increased deposition, increased evapotranspiration and increased uptake of base cations to support tree growth (Neal et al., 1986; Whitehead et al., 1988a, b; Cosby et al., this volume, pp. 00–00). These findings lend support to the results of the paired catchment studies. Whether the trees themselves, in the absence of acidic deposition, would decrease surface water alkalinity to the same extent remains uncertain.

Considerable debate has arisen in the U.K. as to whether afforestation in the uplands should continue without due recourse to the sensitivity of drainage waters to acidification (Department of Environment, 1989). Nisbet (1989) and Bancroft (1988), argue that evidence for the acidifying effect of forests from paired catchment studies is not conclusive because of physical and chemical differences between the study catchments and suggest that only long-term studies can provide acceptable data. Historical data from upland areas, however, are insufficient to show changes following afforestation and the gathering of suitable data will require considerable time (Department of Environment, 1989).

This contribution to the debate uses the MAGIC model for long-term soil and water chemistry reconstructions. The model has previously been applied successfully to afforested catchments in central Scotland and performs well in capturing the major processes thought to be operating. These applications are fully described in a companion paper (Cosby et al., this volume, pp. 00–00). Here the calibrated model for one of the sites is subjected to a series of hypothetical land use and deposition scenarios to assess the relative contribution of forests and acid deposition to soil and water acidification. The model is also run in predictive mode to explore the recovery of soils and surface water in response to planting/harvesting and to decreased atmospheric emission strategies.

MODELLING PROCEDURE

The MAGIC model is a lumped parameter, long-term simulation model of soil and surface water quality (Cosby et al., 1985a, b, c). The application of a modified version of MAGIC to two forested catchments in the Loch Ard area of central Scotland describes in detail the calibration and parameterisation of the model to these sites (Cosby et al., this volume, pp. 00–00). The modified model incorporates cation and anion uptake by the growing forest, pre-afforestation dry deposition inputs, enhanced deposition input through canopy filtering processes and a continuously variable water yield as evapotranspiration changes in response to the water demand of the forest. For this study the calibrated model for the Loch Chon site is chosen to manipulated input and land use scenarios.

The Chon site was afforested in 1950. The area currently receives an acidic deposition loading of ~20 kg ha^{-1} year^{-1} sulphate. Surface water is acidic but relatively high concentrations of calcium and magnesium, possibly owing to the existence of a doleritic dyke within the catchment area, facilitate the maintainance of a fish population. Cosby et al. (this volume, pp. 00–00) suggest that both soils and surface water have undergone severe acidification since pre-industrial times and that the rate of acidification increased markedly following the period of afforestation. In the simulation experiments which follow, the values for all fixed parameters (hydrological and soil physical parameters) and chemical variables (weathering rates and initial base saturations) were taken from the previously calibrated model (Cosby et al., this volume, pp. 00–00).

Relative effects of historical acid deposition and afforestation

Three simulation scenarious were implemented to assess the relative effects of afforestation and acid deposition on historical changes in soil and surface water chemistry. The base line scenario consists of (a) the model as calibrated by Cosby et al. (this volume, pp. 00–00) with both acid deposition and afforestation present. By modifying wet and dry deposition, runoff yield and vegetation uptake sequences, two further hindcast simulations are undertaken here. These describe the historical build-up of soil and water acidification through time for an area with identical chemical and physical characteristics of the Chon site but with (b) acid deposition with no forest growth and (c) no acid deposition with forest growth.

(a) Acid deposition with afforestation

This represents the historical and prevailing deposition and land use scenario at the site. Present-day observed amounts of deposition area increased by dry deposition of sea salts and dry deposition of sulphate (Cosby et al., this volume, pp. 00–00). Deposition of all ions is assumed to be constant throughout the hindcast period except for sulphate, nitrate and ammonium which increase as a result of anthropogenic sources. The trajectory for those ions which increase follows that described by the Warren Spring Laboratory (1983, 1987) for anthropogenic emmissions with a modification based on sulphate deposition data from 1973 (Warren Spring Laboratory, unpublished data). Background sulphate concentration is assumed to be equal to sea-salt concentration. Background concentrations of nitrate and ammonium are assumed to be zero. (1) (2)

Prior to afforestation in 1950 the Chon catchment was under moorland vegetation and so a runoff yield factor of 90% was assumed which is consistent with previous model calibrations to moorland sites in Scotland (Jenkins and Cosby, 1989). After afforestation the trees are assumed to decrease runoff yield, through increased evapotranspiration, at a linear rate until the canopy closed in 1965 when a yield of 75% is assumed. The increased ability of the growth forest to scavenge atmospheric pollutants is achieved by incorporating an explicit, time-varying dry deposition factor. This increased deposition is assumed to begin when the forest is planted and increases linearly until a maximum is reached at canopy closure; thereafter, this maximum level of enhanced input continues for the life of the forest. Uptake of base cations and sulphate ions from the soil in response to the nutritional requirements of the growing forest are pre-specified in the model (Cosby et al., this volume, pp. 00–00).

(b) Acid deposition with no forest growth

Deposition of base cations, ammonium, and acid anions follow the same assumptions as (a). There is no forest growth and so the runoff yield factor remains constant at 90%. Dry deposition is constant at the level calculated for moorland conditions (see Cosby et al., this volume, pp. 00–00) and there is no increased deposition from canopy scavenging. Vegetation uptake is not included except for the first order functions for nitrate and ammonium.

(c) No acid deposition with forest growth

There is no change in atmospheric deposition of any ion throughout the hindcast simulation. That is, the deposition of anthropogenically derived sulphate, nitrate and ammonium remain at the background levels, while deposition of base cations and chloride are assumed to be at present-day observed concentrations adjusted to account for sea-salt contributions. Sulphate is assigned the relevant sea-salt fraction whilst nitrate and ammonium are assumed to be zero to maintain consistency with (a) and (b) where background concentrations of these ions in rainfall are assumed to be zero. The forest uptake and runoff yield sequence described in (a) is followed and increased scavenging by the forest canopy is assumed to be in ratio only to sea-salt concentrations.

Relative effects of future deposition reductions and forestry strategies

Fifty-year forecast simulations were carried out to investigate the future course of acidification for the three historical situations under consideration: (a) the current 'true' situation of afforestation with acid deposition; (b) the simulated situation of acid deposition with no afforestation; (c) the simulated situation of afforestation with no acid deposition. The forecasts examine a combination of future emission scenarios and forest management options (Fig. 1a).

Three future deposition strategies were simulated; (1) constant deposition at 1987 levels until the year 2037; (2) a linear decrease to 50% of 1987 levels by the year 2000 with deposition held constant at the reduced level thereafter until the year 2037; (3) a linear decrease to background sea-salt levels (i.e. no acid

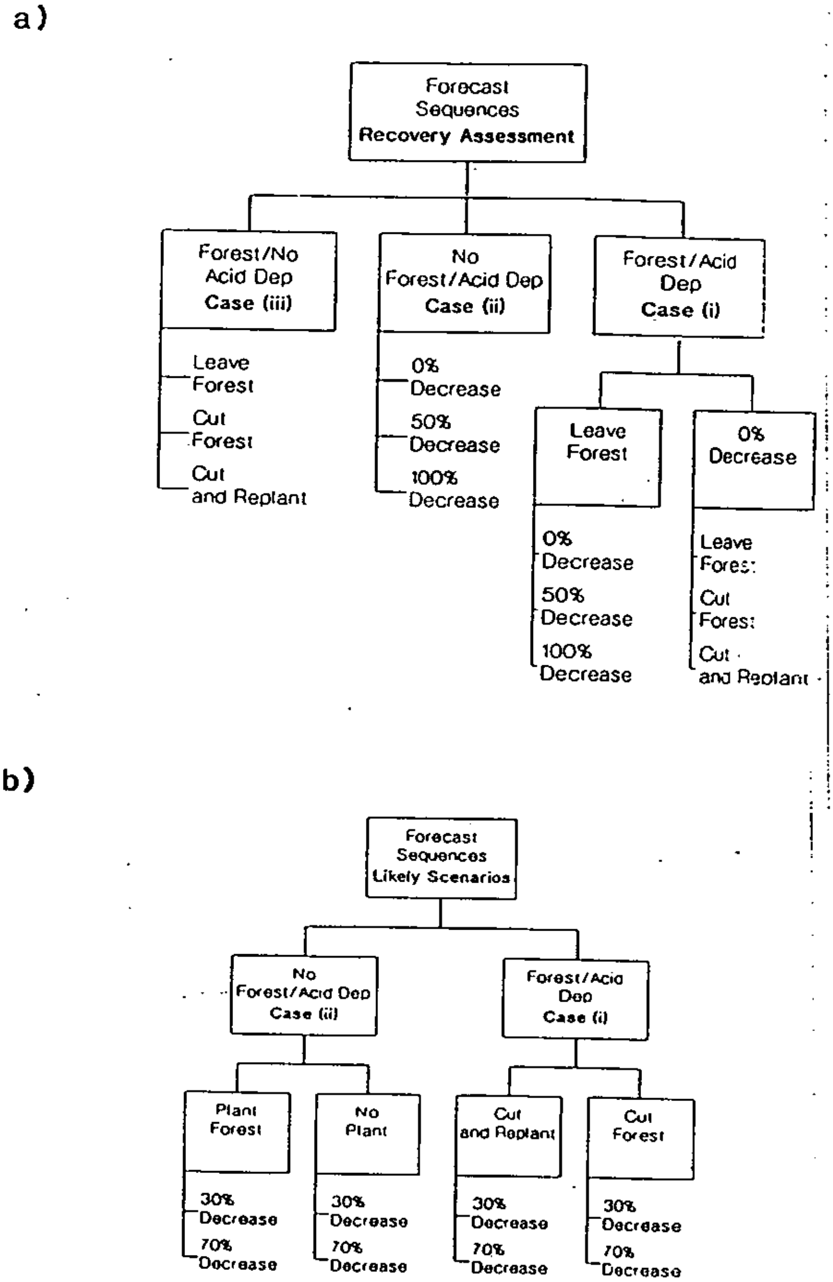


Fig. 1. The combination of land use and deposition reduction scenarios adopted to assess: (a) the degree of reversibility and (b) the implications of currently proposed emissions reduction and land management strategies on stream water and soil acidification.

deposition) by the year 2000 with deposition held constant at background level thereafter until the year 2037. For the deposition reduction scenarios, only the anthropogenically derived components of current deposition were reduced (sulphate, nitrate and ammonium).

Three future forest management options were also simulated: (1) leave the existing forest in place for the 50-year simulation; (2) harvest the forest assuming clear felling in 1990, leaving the site as moorland after the harvest; (3) harvest the forest assuming clear felling in 1990, followed by replanting the forest in 1992. For the cases of clear felling, the simulated runoff yield canopy enhanced dry deposition, and uptake all revert to the pre-afforestation values described above for the historical simulations. For the case of re-planting in 1992, these model inputs follow the same temporal patterns described above for the historical afforestation (see also Cosby et al., this volume, pp. 00–00).

These future land management and deposition scenarios represent extreme options in some cases (i.e. leaving a 50-year-old forest in place for a further 50 years, or complete reduction of anthropogenic deposition) and in reality are unlikely to be employed. However, these assumptions were made to examine the maximum degree of reversibility, or further deterioration, which may be expected in the future.

Most probable forestry and emissions reduction strategies

Further 50-year forecast simulations were used to examine the response of the hypothetical systems to deposition and land management scenarios considered most likley in the light of currently proposed reduction strategies and forestry options (Fig. 1b). Land management practices most pertinent to upland forestry in the U.K. currently consist of planting or not planting a moorland site (future land use for historical situation (b), above), and felling a forested site and planting or not planting a second generation crop on the same site (future land use for historical situation (a), above). The most probable deposition reduction strategies are the accepted U.K. policy to reduce emmissions by 30% and the recently proposed reduction to 705 of present-day levels by 2003.

RESULTS AND DISCUSSION

The effects of the various combinations of historical/future forestry practices and deposition on stream chemistry were examined by considering two important chemical characteristics of surface waters: hydrogen ion concentration (H^+, $\mu eq\, l^{-1}$) and alkalinity concentration (ALK, $\mu eq\, l^{-1}$, defined here as the sum of base cation concentrations plus ammonium concentration minus the sum of acid anion concentrations). These stream variables are measures of the acid neutralising capacity or acidity of stream waters. The effects on soils were examined by considering two soil chemical characteristics: the soil base saturation (BS, %) and the total exchangeable bases in the in chloride and sodium scavenged by the canopy and passed through the soil

soil (TEB, eq m^{-2}, defined here as the product of base saturation times cation exchange capacity times bulk density of the soil times depth of the soil). These soil variables are measures of the buffering capacity of soils.

Relative effects of historical acid deposition and afforestation

For the case of afforestation with no acid deposition (Case c) stream chemistry remains constant (Fig. 2) until it is perturbed by afforestation. The

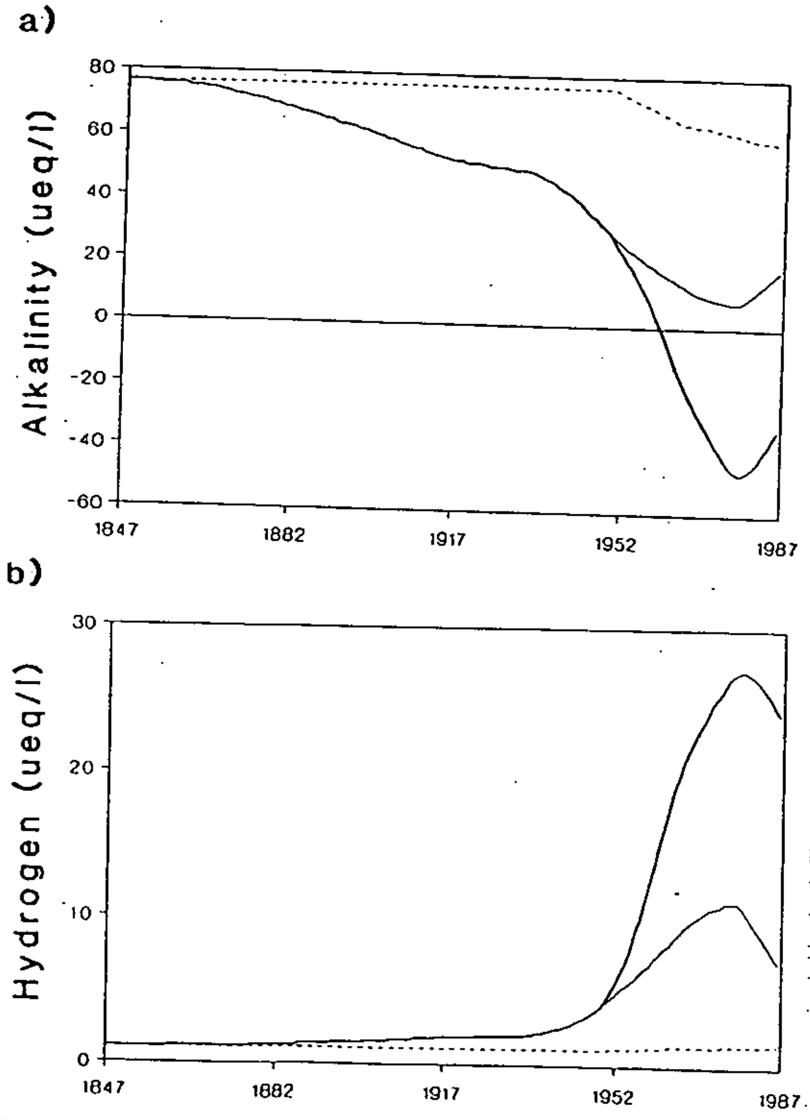


Fig. 2. (a) Simulated streamwater alkalinity and (b) hydrogen ion concentration for the three historical scenarios. Forest with acid deposition i.e. past and prevailing situation (——), no forest with acid deposition (——) and forest with no acid deposition (– – –).

growth of the forest is associated with a decrease in alkalinity form a pre-afforestation value of 76.5 μeq l^{-1} to 59.5 μeq l^{-1} at the end of the simulation. This decrease in alkalinity is accompanied by only a slight increase in hydrogen ion concentration from 1.1 to 1.6 μeq l^{-1}. The net effect of afforestation on the stream water is a loss of alkalinity, but no significant increase in mineral acidity. The effect of forest growth on the soils, however, is more pronounced. Soil base saturation responds to the varying nutritional requirement of the growing trees for base cations. This requirement is assumed to be at a maximum at the time of canopy closure whereafter it falls slowly to a constant level 20 years after canopy closure (see Cosby et al., this volume, pp. 00–00). In response to this uptake sequence, the rate of decline of percent base saturation is initially large, then decreases and begins to level off by 1980 (Fig. 3).

The interaction between increased dry deposition of sea salts and uptake by the forest explains these observed changes in soil and stream water chemistry. Both the sum of acid anions (SAA, sum of nitrate plus chloride plus sulfate concentrations) and the sum of base cations (SBC, sum of calcium plus magnesium plus sodium plus potassium concentrations) in the stream increase after the forest is planted (Fig. 4). This effect occurs largely through increases to the stream. The base cations other than sodium tend to decrease in concentration as uptake requirements of the growing forest exceed increases in input and the base saturation of the soil declines. The net effect is a slower increase in SBC than SAA and a subsequent decline in alkalinity. The model supports the hypothesis that in the absence of acidic deposition afforestation will not lead to increases in mineral acidity of the stream but will tend to lower

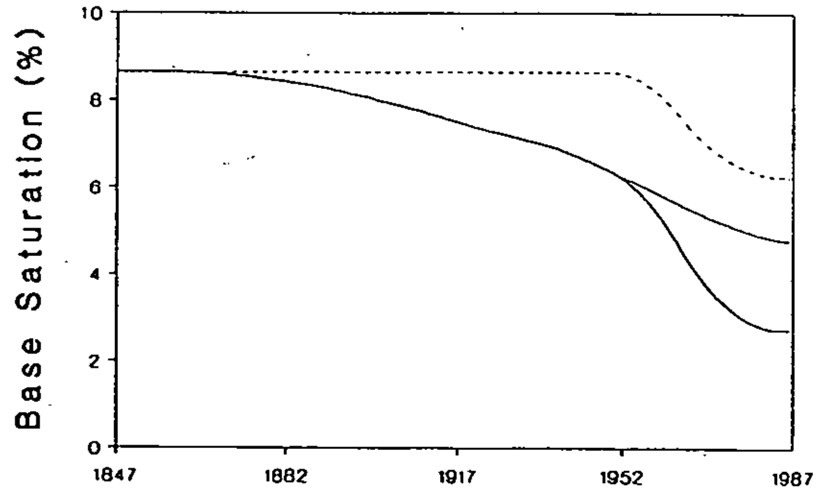


Fig. 3. Simulated soil percent base saturation for the three historical scenarios. Forest with acid deposition, i.e. past and prevailing situation (——), no forest with acid deposition (——) and forest with no acid deposition (– – –).

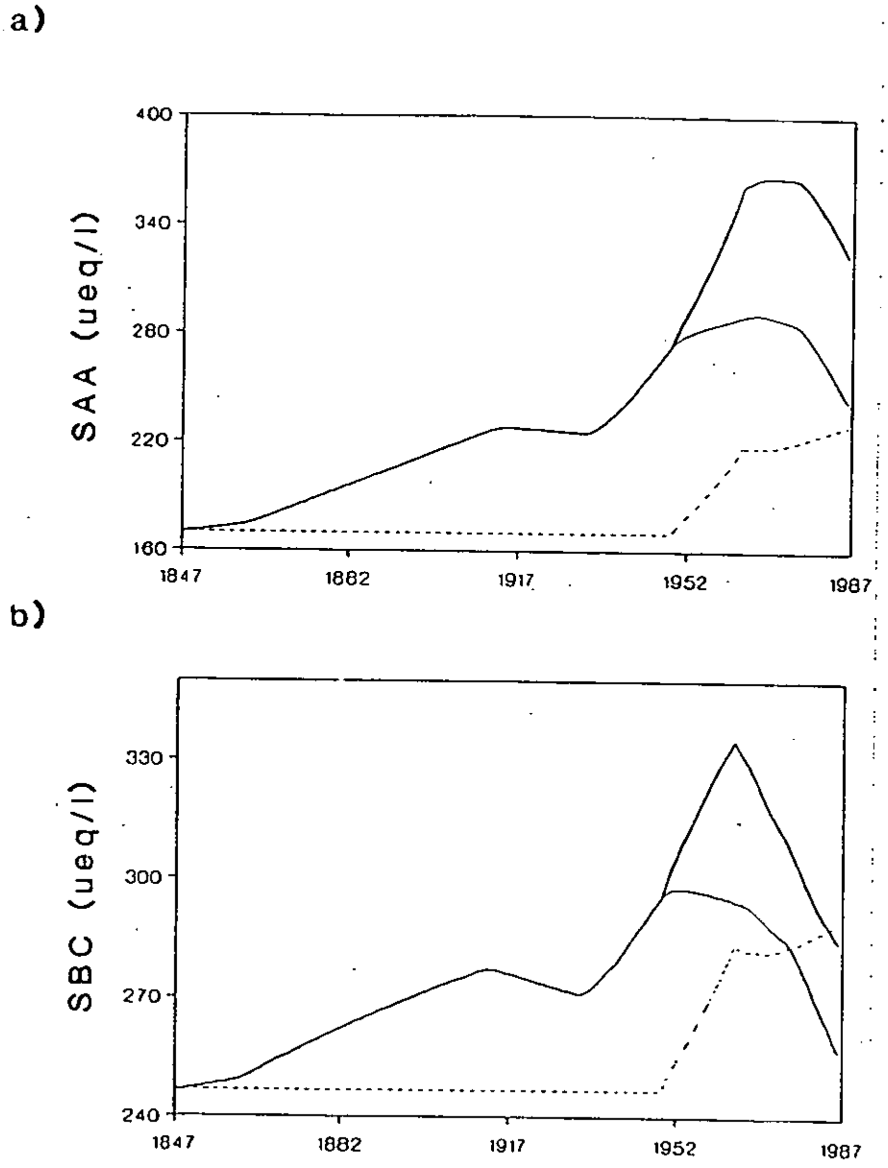


Fig. 4. (a) Simulation stream water sum of acid anion concentrations. (SAA) and (b) sum of base cation concentrations (SBC) for the three historical scenarios. Forest with acid deposition i.e. past and prevailing situation (——), no forest with acid deposition (——) and forest with no acid deposition (– – –).

the stream alkalinity and the base status of the soil. Such declines in soil base status under afforestation have been documented by Hallbacken and Tamm (1986) and Falkengren-Grerup (1987).

The moorland site under acid deposition (Case b) shows a progressive streamwater acidification as sulphate emissions increase (Fig. 2). Alkalinity drops from 76.5 to 18.6 μeq l^{-1} and hydrogen increases from 1.1 to 7.2 μeq l^{-1} (Table 1). These changes in stream water chemistry are greater than those produced by afforestation in the absence of acid deposition. Some recovery in alkalinity is simulated, however, after 1976 as sulphur emissions have decreased. Soil percent base saturation declines gradually to 4.8% at present from a background value of 8.7% (Fig. 3, Table 1), as base cations are leached in response to increased input of mobile sulphate ions. This decrease represents a loss of ~50% of the total exchangeable bases held on the soil (Table 1). As for the stream variables, the simulated changes in soil variables produced by acid deposition are greater than those produced by afforestation alone (acid deposition results in almost twice the loss of soil base cations, Table 1). This pattern of acidification is characteristic of previous model applications to moorland sites in Scotland and compares well with palaeoecological reconstructions at those sites (Jenkins et al., 1990).

Growing a forest on a site receiving acid deposition (Case a) produces the most severe acidification response in both soils and stream water (Figs. 2 and 3). The net result is not simply the sum of the two previously discussed situations. The combined system perturbations produce enhanced ionic input, and the model responds by producing very different chemical dynamics. Stream water alkalinity decreases from 76.5 to −32.5 μeq l^{-1} and hydrogen increases from 1.1 to 24.2 μeq l^{-1} (Table 1). Soil base saturation is depleted from a background level of 8.7–2.7% at the present day, a loss of ~60% of total exchangeable cations held on the soil (Table 1). Stream and soil acidification intensifies as the increased sulphate input from canopy filtering far exceeds the forest uptake requirement. At the same time, occult inputs of base cations are

TABLE I

Simulated background (1847) and present-day (1987) stream hydrogen ion (H) and alkalinity (ALK) concentrations, soil percent base saturation (BS) and total exchangeable base cations (TEB). The magnitude of the change from 1847 to 1987 is shown in parentheses

Hindcast scenario	1847				1987			
	ALK	H	BS	TEB	ALK	H	BS	TEB
Forest/ no acid deposition	76.5	1.1	8.7	17.3	59.5 (−17)	1.6 (+0.5)	6.3 (−2.4)	12.5 (−4.8)
No forest/ acid deposition	76.5	1.1	8.7	17.3	18.6 (−57.9)	7.2 (+6.1)	4.8 (−3.9)	9.5 (−7.8)
Forest/ acid deposition	76.5	1.1	8.7	17.3	−32.5 (−109)	24.2 (+23.1)	2.7 (−6.0)	5.4 (−11.9)

ALK, H = μeq l^{-1}, BS = %, TEB = eq m^{-2}.

far lower than uptake requirement and so the soil must contribute an increasing amount of base cations to support tree growth, thereby enhancing soil acidification. This is reflected in the sharp decrease in percent base saturation following planting (Fig. 3). This simulation corresponds to the currently observed conditions at the site.

Relative effects of future deposition reductions and forestry strategies

For the situation of historical afforestation with no acid deposition (Case c), recovery was assessed for three future forestry strategies: leave the forest, cut the forest, and cut and replant the forest. Fifty-year forecasts with the forest left in place indicate that there will be essentially no recovery in hydrogen ion or alkalinity concentrations of the stream, and that total exchangeable bases in the soil will continue to decline (Table 2). If the forest is felled and not replanted, significant recovery is simulated for stream alkalinity and total exchangeable bases over the 50-year forecast period (Table 2), although hydrogen ion concentration changes little. Replanting a forest on a clear felled site, however, produces a further deterioration in all variables over the 50-year future simulation (Table 2), largely as a result of the uptake requirements of the second forest exceeding input loadings. It must be noted, however, that the simulated changes in all of the forecast scenarios are small (in the absence of acid deposition) and even under the replant scenario the stream retains a high positive alkalinity and low hydrogen ion concentration.

For the situation of a moorland site subjected to historical acid deposition (Case b) recovery was assessed under three deposition reduction scenarios: 0%, 50% and 100% reduction. The major effect of the 50-year simulations with no reduction of acid deposition is a further loss of soil base cations (Table 2). In general, little improvement in stream chemistry is found for this scenario. A significant recovery in streamwater chemistry is achieved by a 50% reduction in deposition although recovery of the soil base status is markedly slow (Table 2). Total reduction of emissions produces the largest simulated changes in both stream and soil variables (Table 2). Comparing simulated historical changes (Table 1) with forecast changes for the 50-year simulation (Table 2), indicates that the stream has recovered 67% of its lost alkalinity, lost 89% of the increased hydrogen concentration and yet the soils recovered only 24% of their lost exchangeable bases for this extreme deposition reduction.

For the situation of historical afforestation with historical acid deposition (Case a), recovery was assessed for six future scenarios representing extreme combinations of the various forestry and deposition reduction strategies (Fig. 1a). Effects of three deposition reductions (0%, 50% and 100% reduction) were assessed for the forestry strategy of leaving the forest in place. Because the major interaction of forest and deposition is the increased scavenging of pollutants, leaving the forest in place while assessing deposition reductions should produce the greatest effect of those reductions. Effects of three forestry strategies (leave the forest, cut the forest, and cut and replant the forest) were assessed for no decrease in deposition.

If the forest is left in place for the 50-year forecast and no deposition reductions are implemented, a slight recovery of alkalinity and hydrogen ion is achieved with no appreciable change in soil exchangeable base cations (Table 2). On the other hand, if the forest is felled and no deposition reductions are implemented, significant improvements in alkalinity, hydrogen ion and total exchangeable bases are achieved (Table 2). Replanting on the same site with no deposition reduction causes a further serious increase in both soil and water acidity (Table 2).

If the forest is left in place and deposition reductions are implemented,

TABLE II

Simulated future (2037) stream hydrogen ion (H) and alkalinity (ALK) concentration, soil percent base saturation (BS) and total exchangeable base cations (TEB). The magnitude of the change from 1987 to 2037 is shown in parentheses. 1987 values in Table 1

Hindcast scenario	Deposition reduction (%)	Forestry option	2037			
			ALK	H	BS	TEB
Forest/ no acid deposition	0	Leave forest	58.5 (−1.0)	1.6 (0.0)	6.0 (−0.3)	11.9 (−0.6)
	0	Cut forest	66.9 (+7.4)	1.3 (−0.3)	6.7 (+0.4)	13.4 (+0.9)
	0	Replant forest	44.2 (−15.3)	2.4 (+0.8)	4.4 (−1.9)	8.6 (−3.9)
No forest/ acid deposition	0	Moorland	21.7 (+3.1)	6.2 (−1.0)	4.5 (−1.8)	9.0 (−0.5)
	50	Moorland	41.1 (+22.5)	2.6 (−4.6)	5.1 (+0.3)	10.2 (+0.7)
	100	Moorland	58.8 (+40.2)	1.6 (−5.6)	5.7 (+0.9)	11.4 (+1.9)
Forest/ acid deposition	0	Leave forest	−19.2 (+13.3)	20.7 (−3.5)	2.7 (0.0)	5.4 (0.0)
	50	Leave forest	10.7 (+43.2)	9.5 (−14.7)	3.2 (+0.5)	6.3 (+0.9)
	100	Leave forest	35.4 (+67.9)	3.3 (−20.9)	3.7 (+1.0)	7.3 (+1.9)
	0	Cut forest	8.2 (+40.7)	11.2 (−13.0)	3.5 (+0.8)	6.9 (+1.5)
	0	Replant forest	−46.1 (−13.6)	27.2 (+4.1)	1.7 (−1.0)	3.4 (−2.0)

ALK, H = μeq l^{-1}, BS = %, TEB = eq m^{-2}.

improvements in both stream and soil variables are realised (Table 2). As might be expected, the improvements for 100% reduction are greater than for 50% reduction, but the recoveries are not all linear with deposition reduction. Stream alkalinity and hydrogen ion improve by approximately a factor of 2 for the doubling in reductions implemented, but the recovery of the soil base cations is much slower (Table 2).

The reafforestation scenarios make no attempt to account for soil treatment prior to replanting. Clearly, if soil fertilisation is undertaken the effect of the second generation forest growth on soil and water chemistry may be ameliorated. However, fertilisation of these systems generally consists of an application of nitrogen, phosphorus and potassium at establishment of the stand with additions as prescribed until canopy closure and depending on soil type and tree species (Miller and Miller, 1987). Addition of base cations in the form of lime is not a standard treatment and so the effect of the fertilisation is unlikely to influence the acid status of the soils and surface water.

Most probable forestry and emission reduction strategies

Given that much of northern England, Scotland and Wales currently receives (and historically have received) high levels of acidic deposition and that large areas of these uplands are under pressure from commercial forestry land management options, the most likely future scenarios have been simulated (Fig. 1b).

The time sequences of hydrogen ion, alkalinity and soil base saturation under the two probable deposition reduction strategies at a forested site that is clear cut and not replanted all show marked improvement (Fig. 5). The relative improvement in stream variables for the larger deposition reduction is roughly in proportion to the relative increase in deposition reduction (Table 3). The effects of the clear cutting are immediately apparent in the stream variables for both levels of deposition reduction (Fig. 5). These immediate effects are produced by the decreased scavenging of pollutants as the forest canopy is removed, and the increased runoff as the site reverts to a moorland.

Change in the soil base saturation are much slower, not showing an immediate response to clear cutting, but indicating slower long-term improvement for both deposition reductions if the forest is not replanted. Soil acidification has a much longer recovery period than does stream acidification.

The time sequence of hydrogen ion, alkalinity and soil base saturation under the two probable deposition reduction strategies at a forested site that is clear cut and then replanted differs markedly from the case where no replanting is undertaken (Fig. 5). The initial responses of the stream variables to the clear felling is similar, but the effects of the second forest growth produce much lower alkalinity and higher hydrogen ion concentrations (Fig. 5, Table 3). Even with a 70% reduction in deposition, replanting a forest following clear felling results in acidic stream conditions during the growth of the second forest. The acidic conditions persist even after the forest growth is complete (Fig. 5).

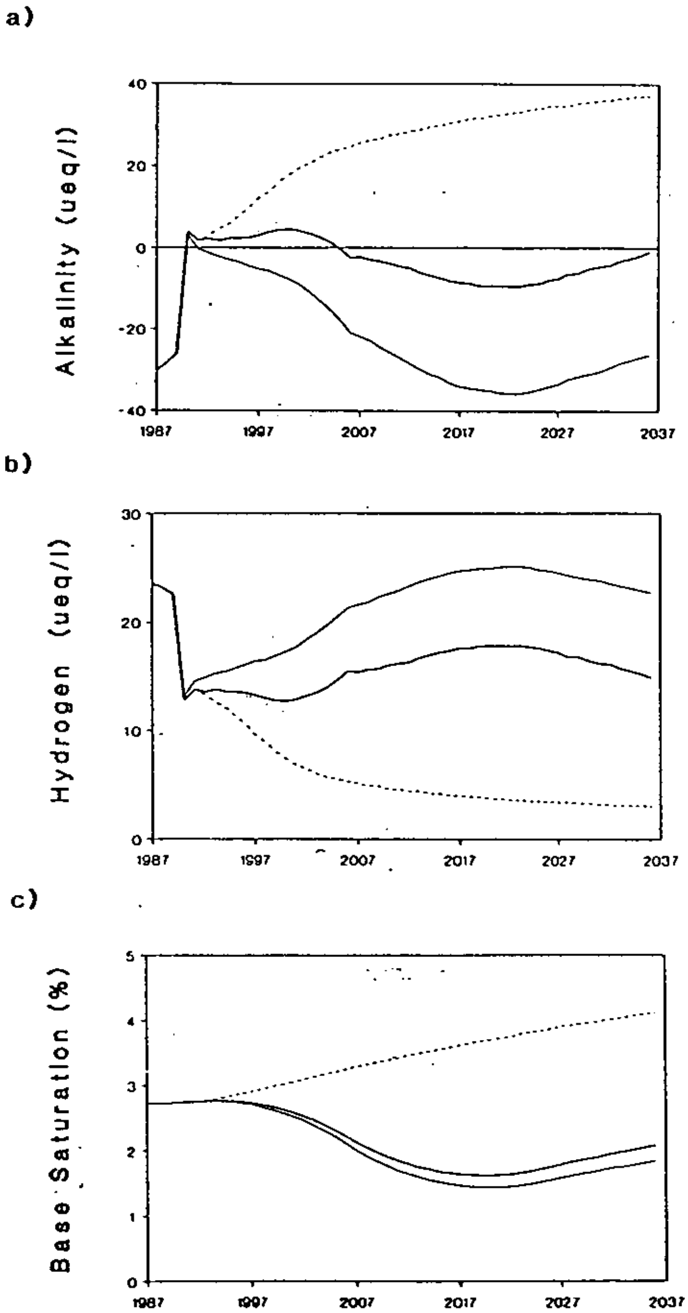


Fig. 5. (a) Simulated stream alkalinity (b), hydrogen ion concentration and (c) soil percent base saturation for a presently forested catchment under likely future land management and emission reduction scenarios. Replanting under 30% reduction (——), replanting under 70% reduction (——), felling under 30% reduction (·····) and felling under 70% reduction (– – –).

TABLE III

Simulated future (2037) variables for most probable future scenarios. Stream hydrogen ion (H) and alkalinity (ALK) concentration, soil percent base saturation (BS) and total exchangeable base cations (TEB). The magnitude of the change from 1987 to 2037 is shown in parentheses. 1987 values in Table 1

Hindcast scenario	Deposition reduction (%)	Forestry option	2037			
			ALK	H	BS	TEB
No forest acid deposition	30	Plant	− 7.2 (−25.8)	17.0 (+9.8)	2.8 (−2.0)	5.5 (−4.0)
	70	Plant	16.5 (−2.1)	8.0 (+0.8)	3.1 (−1.7)	6.2 (−3.3)
	30	No plant	34.0 (+15.4)	3.5 (−3.7)	4.9 (+0.1)	9.6 (+0.1)
	70	No plant	48.5 (+29.9)	2.1 (−5.1)	5.3 (+0.5)	10.6 (+1.1)
Forest/ acid deposition	30	Cut forst	21.6 (+54.1)	6.2 (−18.0)	3.7 (+1.0)	7.4 (+2.0)
	70	Cut forest	37.2 (+69.7)	3.0 (−21.2)	4.1 (+1.4)	8.2 (+2.8)
	30	Replant forest	−26.3 (+6.2)	22.7 (−1.5)	1.8 (−0.9)	3.6 (−1.8)
	70	Replant forest	−1.1 (+31.4)	14.9 (−9.3)	2.1 (−0.6)	4.1 (−1.3)

ALK, H = $\mu eq\,l^{-1}$, BS = %, TEB = $eq\,m^{-2}$.

As with the case of no replanting, there is little difference in the future soil base saturation between the two probable deposition reduction scenarios when a second forest is planted. Compared with the case of no replanting, however, large differences in base saturation occur. With replanting, the soils show further deterioration following replanting and recover only slowly following forest maturation in either deposition case. Regardless of the deposition reduction, the largest differences in the future soil base saturation depend on whether or not the decision to replant the forest is taken (Fig. 5, Table 3).

Moorland sites, as previously discussed, are subject to lower deposition loading than afforested areas and so decreases in deposition produce a rapid recovery in stream alkalinity if no forest is planted (Fig. 6, Table 3). Comparison of simulated historical changes (Table 1) with forecast changes for the 50-year simulation (Table 3), indicates that a 70% reduction in deposition recovers 71% of stream alkalinity, allows hydrogen to decrease by 91%, and

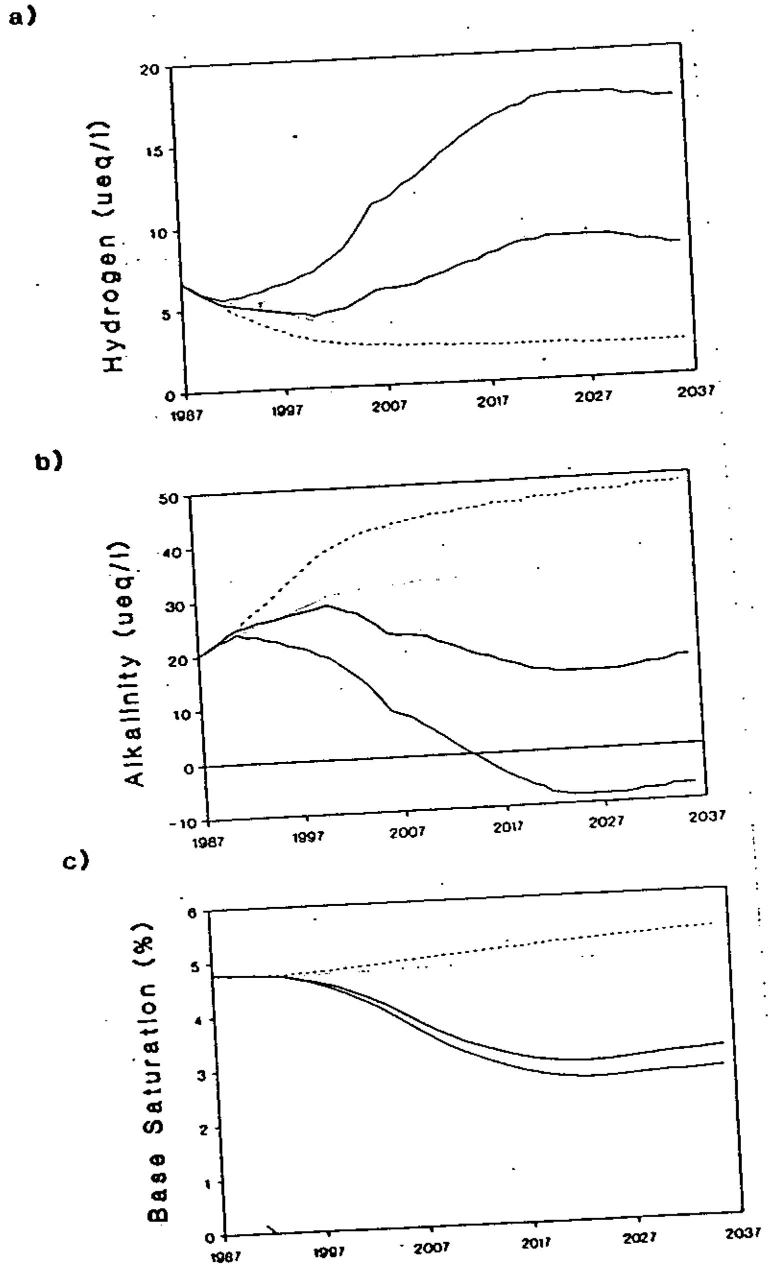


Fig. 6. (a) Simulated stream hydrogen ion concentration, (b) alkalinity and (c) soil percent base saturation for a presntly moorland catchment under likely future land management and emission reduction scenarios. Planting under 30% reduction (——), planting under 70% reduction (——), no planting under 30% reduction (· · · ·) and no planting under 70% reduction (– – –).

allows the soil to recover 23% of its lost base cations. Recoveries of this order would allow fish populations to return to many acidified moorland areas.

On the other hand, planting a forest on these moorland areas, despite large reductions in deposition, will lead to rapid and severe acidification (Fig. 6, Table 3); this will be particularly severe in the soil, the base saturation of which has been steadily depleted through acidic deposition for many years prior to future afforestation (Figs. 3 and 6, Tables 1 and 3).

CONCLUSIONS

This simulation analysis demonstrates that, in areas receiving high levels of acidic deposition such as upland Scotland, afforestation exacerbates the acidification problem in both soils and surface waters. Afforestation per se does not greatly acidify surface waters in the absence of acidic deposition (although there is a small salt effect). Afforestation does, however, lead to a significant decrease in the base status of the soil, mainly because of the uptake requirements of the growing forest. This decrease in the base status of the soils can render the soils (and surface waters) more sensitive to acid deposition. Acid deposition, on the other hand, can directly cause acidification of surface waters, either in the presence or absence of afforestation because of the high input of acidic, mobile anions.

Clear-felling a forested site will cause a significant reversal in stream acidification; it will also allow the soils to begin recoverying. Deposition reductions produce a similar reversal of soil and surface water acidification. The interaction of forestry practices and deposition reductions are not strictly additive. In general, however, the greater emission reductions that can be achieved, the greater the degree of soil and surface water recovery. Replanting a forest on the same site will lead to further soil and stream acidification but, provided a reduction in acidic deposition can be simultaneously achieved, the stream will not deteriorate to a greater level than under the first generation forest. Because of the slower response of soils to decreased deposition, however, the second generation forest will cause an enhanced soil acidification effect. This analysis indicates that in sensitive areas replanting in the absence of soil amendments (addition of bases) should not be undertaken even in the light of large reductions in deposition levels.

It should also be noted that the site chosen for this analysis has relatively high calcium and magnesium input from weathering owing to the presence of a doleritic dyke within the catchment area. In areas where soils are of lower base status, the effects demonstrated here would be enhanced and so the absolute levels of acidity are not necessarily representative on a wider regional scale. The relative pattern of changes will, however, be similar across the region if the same assumptions regarding deposition and afforestation effects are applied.

REFERENCES

Bancroft, C., 1988. Forestry; The debate continues. Rural Wales Magazine, 18–20. ③

Battarbee, R.W., 1988. Lake acidification in the United Kingdom. Ensis Publishing, London, 68 pp.

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. Water 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. Water Resour. Res., 21: 1291–1601.

Cosby, B.J., Hornberger, G.M., Galloway, J.N. and Wright, R.F., 1985c. Time scales of catchment acidification: a quantitative model for estimating freshwater acidification. Environ. Sci. Technol., 19: 1144–1149.

Cosby, B.J., Jenkins, A., Miller, J.D., Ferrier, R.C. and Walker, T.A.B., 1990. Modelling stream acidification in forested catchments: long term reconstructions at two sites in central Scotland. J. Hydrol., 00–00.

Department of the Environment, 1989. Acidity in United Kingdom Fresh Waters. Second Report of the United Kingdom Acid Waters Review Group, HMSO, London.

Falkengren-Grerup, U., 1987. Long-term changes in pH of forest soils in southern Sweden. Environ. Pollut., 43: 79–90.

Haines, T.A., 1986. Fish population trends in response to surface water acidification. In: Acid Deposition, Long-term Trends. National Academy Press, Washington, DC, pp. 300–334. ④

Hallbacken, L. and Tamm, C.O., 1986. Changes in soil acidity from 1927 to 1982–1984 in a forest area of southwest Sweden. Scand. J. For. Res., 1: 219–232.

Harriman, R. and Morrison, B., 1982. Forestry, fisheries and acid rain in Scotland. Scott. For., 36: 89–95.

Jenkins, A. and Cosby, B.J., 1989. Modelling surface water acidification using one and two soil layers and simple flow routing. In: J. Kamari, D.F. Brakke, A. Jenkins, S.A. Norton and R.F. Wright (Editors), Regional Acidification Models: Geographic Extent and Time Development. Springer, New York, pp. 253–266.

Jenkins, A., Whitehead, P.G., Cosby, B.J. and Birks, H.J.B., 1990. Modelling long-term acidification: a comparison with diatom reconstructions and the implications for reversibility. Phil. Trans. R. Soc. (in press).

Likens, G.E., Wright, R.F., Galloway, J.N. and Butler, T.J., 1979. Acid rain. Scientific American, 241: 43–51.

Linzon, S.N. and Temple, P.J., 19890. Soil resampling and pH measurements after an 18-year period in Ontario. In: D. Drablos and A. Tollan (Editors), Ecological Impact of Acid Precipitation, SNSF Project, Oslo, Norway, p. 184.

Miller, H.G. and Miller, J.D., 1987. Nutritional requirements of Sitka spruce. Proc. R. Soc. Edinburgh, 93B: 75–83.

Neal, C., Whitehead, P.G., Neale, R. and Cosby, B.J., 1986. Modelling the effects of acidic deposition and conifer afforestation on stream acidity in the British uplands. J. Hydrol. 86: 15–26.

Nisbet, T.R., 1989. Forestry and surface water acidification: Is there a link? Timber Grower, Spring: 18–19.

Stoner, J.H., Gee, A.S. and Wade, K.R., 1984. The effects of acidification on the ecology of streams in the Upper Tywi catchment in west Wales. Environ. Pollut., Ser. A., 35: 125–157.

Troedsson, T., 1980. Ten years acidification of Swedish forest soils. In: D. Drablos and A. Tollan (Editors), Ecological Impact of Acid Precipitation, SNSF Project, Oslo, Norway, p. 184.

Warren Spring Laboratory, 1983. Acid deposition in the United Kingdom. Warren Spring Laboratory, Stevenage.

Warren Spring Laboratory, 1987. Acid deposition in the United Kingdom 1981–1985. Warren Spring Laboratory, Stevenage.

Whitehead, P.G., Bird, S., Hornung, M., Cosby, B.J., Neal, C. and Paricos, P., 1988a. Stream acidification trends in the Welsh uplands – a modelling study of the Llyn Brianne catchments. J. Hydrol., 101: 191–212.

(5) Whitehead, P.G., Reynolds, B., Hornung, M., Neal, C., Cosby, B.J. and Paricos, P., 1988b. Modelling long-term stream acidification trends in upland Wales at Plynlimon. Hydrol. Process.

Wright, R.F., 1983. Predicting Acidification of North American Lakes. Report 0-81036, Norwegian Institute for Water Research, Oslo, Norway, 165 pp.

2.6 Round Loch - Scotland

Chapter 19

Modelling Surface Water Acidification Using One and Two Soil Layers and Simple Flow Routing

Alan Jenkins[1] *and Bernard J. Cosby*[2]

Summary

The Model of Acidification of Groundwater In Catchments (MAGIC) was applied to two sites in Scotland to assess the influence of model structure on hindcast and forecast water quality variables. Three model structures were implemented for each site; a single soil layer model, a two soil layer model and a two layer model with simple flow routing. The structures were calibrated using a fuzzy optimization procedure that provided estimates of calibration uncertainty for all variables. All three structures at both sites were capable of reproducing observed surface water chemistry. The different model structures, however, produced significant differences in the simulation of soil and soil water variables. These differences were related to the difficulty of estimating base cation weathering and soil base cation exchange in the aggregated or distributed structures. The differences in simulation results among the model structures were small, however, compared to measurement errors. We conclude that, given currently available data, a one-layer model structure is sufficient for long term simulation of acid deposition effects on the sites studied.

Introduction

The Model of Acidification of Groundwater in Catchments (MAGIC) has been applied to individual sites in the U.S., U.K. and Scandinavia to assess the long-term acidification of surface waters (e.g. Cosby et al. 1985a; 1985b; 1986a; Jenkins et al. 1988; Wright et al. 1986). MAGIC has also been applied on a regional scale to reproduce the observed disributions of water quality variables of many catchments within a geographical region and to predict region-wide changes of water quality in response to acidic deposition (e.g.

---

[1] Inst. of Hydrology Wallingford, Oxon, UK OX10 8BB
[2] Dept. of Environm. Sci., Univ. of Virginia, Charlottesville, VA, USA 22903

Hornberger et al. 1986, this volume; Cosby et al. 1988, this volume). All of the regional applications and many of the individual site applications have used the MAGIC model in its simplest form, employing one soil layer. To implement the one-layer version, aggregated values of soil physical and chemical parameters must be employed which represent the average characteristics of spatially variable soils. The use of a single aggregated soil layer precludes inclusion of hydrological routing of water through the simulated soil profile. An implicit assumption in the implementation of a single layer model structure is that all water entering the soil percolates through the entire soil column.

In the uplands of the UK, soils within a catchment are often markedly horizonated, usually characterized by a relatively thin organic or peaty layer overlying a mineral horizon (podzolic soils). In addition to this marked vertical layering, the mostly glaciated valleys are often dominated by mineral soils on the steep side slopes with blanket peat covering the 'flat' valley bottoms. The distinctly different physical and chemical characteristics of peats and mineral soils in these catchments has implications for the use of models employing only one soil reservoir. The two layer nature of upland U.K. catchment soils also has implications for hydrological flow routing. Observations from a number of instrumented catchments in Scotland frequently show flow along the interface of the upper organic layer and lower mineral layer, (Howells 1986; Wheater et al. 1987). Consequently, some runoff does not contact the mineral layer.

The simplifications inherent in a one-layer model structure obviously limit the utility of the model for reproducing short-term, episodic responses of water quality. The question arises whether the simplifications will also affect simulated long-term, chronic changes in soil and surface water chemistry. To assess the effect of including a further soil layer and to examine the appropriateness of the one-layer structure we compare long-term simulations for two upland U.K. catchments using three modified model structures: an aggregated one-layer soil version; a vertically-distributed two-layer version without vertical flow routing; and a vertically-distributed two-layer version with simple vertical flow routing.

Methods

The Conceptual Model and Structural Modifications

The structure of the MAGIC model is described in detail by Cosby et al. (1985a,b,c) and briefly summarized by Cosby et al. (this volume). Here we calibrate three variations of the model structure for both the Round Loch of Glenhead in the Galloway region of southwest Scotland and the Allt a Mharcaidh in the Cairngorm Mountains of northeast Scotland. The model structures used for the single layer application are shown in Figure 1a. At Round Loch the catchment-to-lake area ratio is 8.6 which means that 12 % of the precipitation enters the lake directly. Allt a Mharcaidh is a stream site and direct precipitation to the stream surface is assumed negligible. For the one-layer structures, all water input to the soil surface was passed through the soil to the stream/lake. For the two-layer structures, two flow-routing schemes were devised such that: (i) 35 % of the water draining soil layer 1 passed directly to the stream/lake (Figure 19.1); and (ii) all water flowed through both horizons (apart from direct precipitation to the water body, Figure 19.1).

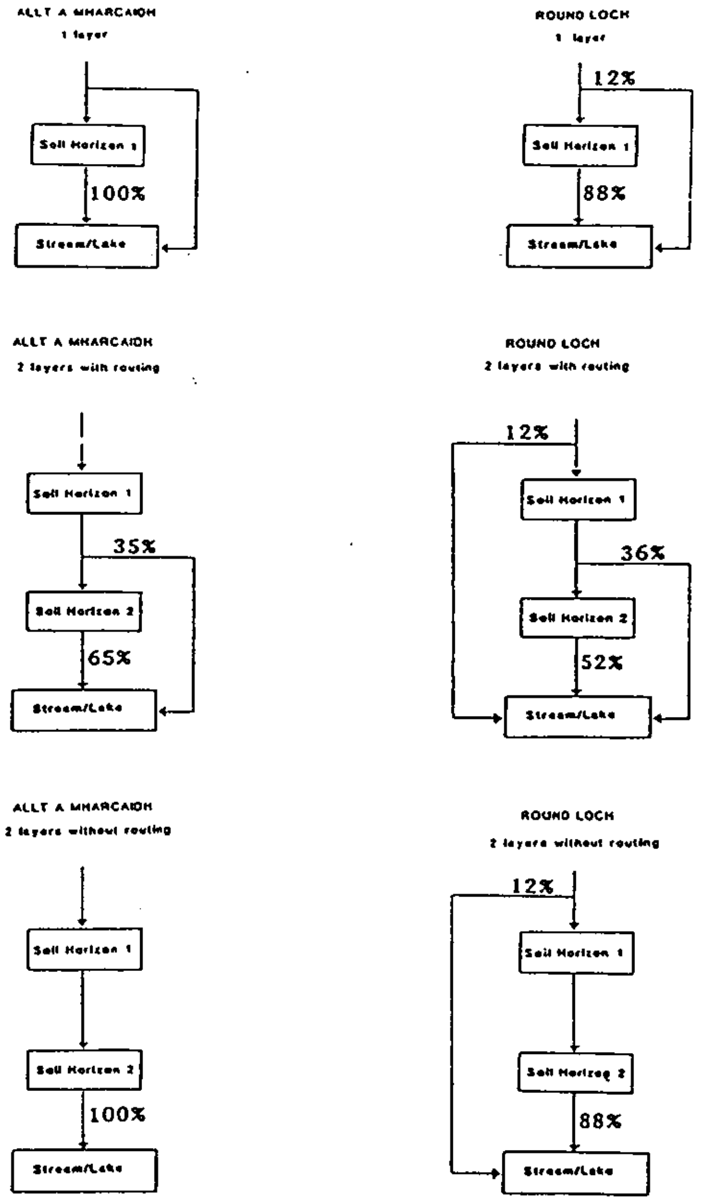


Figure 19.1. The model structures used at Allt a Mharcaidh and Round Loch; (top) one-layer, (middle) two-layer with flow routing and (bottom) two-layer without flow routing.

Model Application to Round Loch of Glenhead

Lake chemistry data for Round Loch of Glenhead were taken from Battarbee et al. (1988). The lake area comprises 12 % of the catchment although this was allowed to vary within the range 9 % - 15 % to account for possible year to year fluctuations in storage volumes.

Deposition data were taken from the adjacent Loch Dee deposition monitoring site (Warren Springs Laboratory 1983, 1987); Cl concentrations in precipitation were slightly modified to give an exact charge balance and an improved Na/Cl ratio. Precipitation volume was assumed equal to that at Loch Dee (2.57 $m\,yr^{-1}$). Occult input of sea salt was added to match the observed Cl concentration in the loch given the observed Cl input and an assumed catchment water yield of 90 %. This gave an effective dry and occult seasalt deposition equal to 1.032 times seasalt in wet deposition. Sulfate deposition was increased by a factor of 1.37 (representing dry deposition of gaseous/particulate S) to match simulated to observed loch SO_4 concentrations. We assumed that peat soils do not adsorb SO_4 and that the mineral soils have the relatively minor SO_4 adsorption characteristics shown in Table 19.1.

Soils of the Round Loch catchment consist of peats, peaty rankers and peaty gleys (Macaulay Land Use Research Institute, unpublished data). Data describing soil physical parameters and exchangeable bases were divided into peat and mineral components.

For the one-soil-layer application, the characteristics for the aggregated soil were derived from the characteristics of peat and mineral soils assuming that: a) peat soils comprised 0.4 m peat overlying 0.4 m mineral; b) mineral soils contain no peat in the profile; and c) the catchment area consisted of 2/3 peat soils and 1/3 mineral soils. The aggregated soil characteristics for the one-layer application was thus weighted with 1/3 peat characteristics and 2/3 mineral soil characteristics. When the two layer model was used, the upper layer was assumed to be pure peat (with appropriate characteristics) and the lower layer was assumed to be mineral soil (with appropriate characteristics). The 1/3 peat to 2/3 mineral partitioning derived above was used to set the relative depths of each layer (lower layer twice as thick as upper layer).

The ranges of lake and soil physical characteristics (fixed parameters) used for the model calibrations at Round Loch are given in Table 19.1. The average optimal values of the adjustable parameters (weathering and selectivity coefficients) resulting from the multiple calibrations are given in Table 19.2.

Model Application to Allt a Mharcaidh

Stream chemistry is sampled routinely twice a week and bulk precipitation weekly from six collectors widely distributed within the catchment. We use data from 1986 for this calibration of Allt a Mharcaidh (Jenkins et al. 1987; Harriman et al. 1987). Runoff measurements give a mean annual streamflow of 0.945 $m\,yr^{-1}$ from a precipitation input of 1.064 $m\,yr^{-1}$ (Institute of Hydrology,unpublished data). The water yield of the catchment is thus 87 %. As this is a stream site the water surface area of the catchment is very small and so an arbitrary value of 0.1 % was used. This was allowed to vary between 0.0 % and 0.2 % to account for year to year variation in catchment antecedent wetness.

Seasalt was added to measured bulk deposition to match the observed streamwater Cl concentrations given the water yield and the assumption of Cl steady state. This corresponds to an effective occult seasalt deposition equal to 1.153 times wet deposition. No dry deposition of S is included because sea salt adjusted SO_4 deposition combined

Table 19.1. The ranges of physical and chemical characteristics used for model optimization at Round Loch and Allt a Mharcaidh.

Variable	Allt a Mharcaidh		Round Loch	
	1-layer	2-layer	1-layer	2-layer
SOIL 1				
Depth (m)	0.73-0.93	0.26	0.7-0.9	0.27
Bulk density ($kg\,m^{-3}$)	824-1024	40-240	669-869	200-400
Cation Exchange capacity ($meq\,kg^{-1}$)	389-480	1150-1215	165-265	1046-1146
SO_4 adsorption capacity ($meq\,kg^{-1}$)	9.8-13.8	0.01-0.5	2.5-6.5	0.01-0.5
SO_4 adsorption half saturation ($meq\,m^{-3}$)	450-650	205-405	440-640	440-640
Al solubility coefficient ($\log_{10}$)	8.7-9.4	8.7-9.4	8.7-9.4	8.7-9.4
CO_2 partial pressure (atm)	0.033	0.033	0.033	0.033
Organic matter content ($mmol\,m^{-3}$)	100	100	100	100
SOIL 2				
Depth (m)	-	0.57	-	0.53
Bulk density ($kg\,m^{-3}$)	-	1020-1220	-	900-1100
Cation Exchange capacity ($meq\,kg^{-1}$)	-	106-206	-	51-151
SO_4 adsorption capacity ($meq\,kg^{-1}$)	-	13.2-15.2	-	5.75-7.75
SO_4 adsorption half saturation ($meq\,m^{-3}$)	-	572-772	-	440-640
Al solubility coefficient ($\log_{10}$)	-	8.7-9.4	-	8.7-9.4
CO_2 partial pressure (atm)	-	0.033	-	0.033
Organic matter content ($mmol\,m^{-3}$)	-	100	-	100
WATER				
Al solubility coefficient ($\log_{10}$)	8.6	8.6	8.6	8.6
Relative area (%)	0.0-0.2	0.0-0.2	9-15	9-15
Runoff ($m\,yr^{-1}$)	0.83-1.03	0.83-1.03	0.83-1.03	0.83-1.03
CO_2 partial pressure (atm)	0.0033	0.0033	0.0033	0.0033
Organic matter content ($mmol\,m^{-3}$)	0.0	0.0	0.0	0.0

Table 19.2. Optimized weathering rates and selectivity coefficients used in all model runs.

	Allt a Mharcaidh			Round Loch		
		Top	Bottom		Top	Bottom
	one-layer	two-layer		one-layer	two-layer	
Weathering Rates (meq $m^{-2}yr^{-1}$)						
Ca	13.8	1.0	16.6	20.0	2.6	17.4
Mg	1.9	0.2	2.8	0.6	0.0	0.0
Na	32.9	1.9	32.2	2.2	0.3	2.2
K	1.6	0.1	1.5	3.4	0.3	1.7
Selectivity Coefficients ($\log_{10}$)						
Ca	1.22	-1.57	2.93	-1.11	-2.06	0.02
Mg	1.12	-1.00	2.31	-0.54	-1.01	0.06
Na	-0.35	-0.80	-0.47	-0.30	-0.26	-0.41
K	-4.67	-6.07	-4.12	-4.40	-4.60	-4.74

with the observed water yield reproduce the observed stream SO_4 concentrations. This result is consistent with the remoteness of this site from sources of anthropogenic S and our previous assumption that soils in the region do not adsorb significant amounts of SO_4 (Table 19.1).

Soil parameters and percentage soil base saturation were derived from soil samples taken within the catchment (Macaulay Land Use Research Institute, unpublished data). The catchment consists of three main soil types, alpine podsols, peaty podsols and blanket peat. For this application the blanket peats were considered to be relatively unimportant and the alpine and peaty podsol characteristics were weighted by bulk density

and depth to give aggregated soil parameters for the one layer model. For the two layer models, no weighting was attempted and the data for the organic and mineral horizons of the peaty podsol were used for the upper and lower layers, respectively.

The ranges of stream and soil physical characteristics (fixed parameters) used for the model calibrations at Allt A Mharcaidh are given in Table 19.1. The average optimal values of the adjustable parameters (weathering and selectivity coefficients) resulting from the multiple calibrations are given in Table 19.2.

Calibration of the Modified Structures

The calibrations proceeded in a sequential manner. First, the concentrations of the stream Cl and SO_4 were calibrated by adjusting occult and dry deposition of sea salts and gaseous/particulate S compounds under the assumption that these ions are in approximate steady-state with respect to atmospheric inputs. Next, the NO_3 and NH_4 concentrations were calibrated by adjusting first-order uptake functions to match observed surface water concentrations. Finally, the base cation concentrations were calibrated using an optimization procedure based on the Rosenbrock (1960) algorithm.

The base-cation calibration involved fitting the results of long-term model simulations to currently observed water and soil base-cation data (the target variables). The target variables consisted of: surface water concentrations of Ca, Mg, Na, and K; and soil exchangeable fractions of Ca, Mg, Na and K (for both soil layers, if applicable). The target variables thus comprise a vector of measured values all of which must be reproduced by the model if a calibration is to be successful. The use of multiple, simultaneous targets in an optimization procedure provides robust constraints on model calibration (Cosby et al. 1986b).

Those physico-chemical soil and surface water characteristics measured in the field (see Table 19.1) were considered "fixed" parameters in the model and the measurements were directly used in the models during the calibration procedure. Base-cation weathering rates and base-cation exchange selectivity coefficients for the soils are not directly measurable and were used as "adjustable" model parameters to be optimized in the calibration procedure (see Table 19.2).

The calibrations were performed on simulations run from 1845 to 1985. The historical deposition sequence over this period was estimated by scaling currently observed deposition to a reconstruction of S emissions for the U.K. (Warren Spring Laboratory 1983, 1987). This scaling procedure has been described elsewhere for regions in North America (Cosby et al. 1985b). After each historical simulation, the model variables in 1985 were compared with observations in 1985; the adjustable parameters were modified as necessary to improve the fit; the historical simulation was re-run; the procedure was repeated until no further improvement in the fit was achieved.

Because the measurements of the fixed parameters and the target variables are subject to errors, we implemented a "fuzzy" optimization procedure for calibrating the models. The fuzzy optimization procedure consisted of multiple calibrations of each model structure using perturbations of the values of the fixed parameters and estimated uncertainties of the target variables. The sizes of the perturbations of the fixed parameters were based on known measurement errors or spatial variability of the parameters (Table 19.1). The uncertainties in the target variables were estimated as the measurment errors of the variables (5 μeq^{-1} for concentrations of surface water variables; 0.5 % for soil base saturation variables).

Each of the multiple calibrations began with: i) a random selection of perturbed values of the fixed parameters; ii) a random selection of the starting values of the adjustable parameters; and iii) specification of uncertainty in the target variables. The adjustable parameters were then optimized using the Rosenbrock algorithm to achieve a minimum error fit to the target variables.

The optimization algorithm was stopped and the calibration considered complete when the simulated values of all target variables were within the pre-specified uncertainty limits for the observations. This procedure was undertaken ten times for each structure at each site. The final calibrated model for each structure at each site consists of the mean parameter and variable values of at least 8 successful calibrations.

Using the fuzzy optimization based on multiple calibrations, uncertainty bands for the model simulations can be presented as maximum and minimum values for output variables in any year derived from the group of successful calibrations. These uncertainty bands encompass the range of variable values which were simulated given the specified uncertainty in the fixed parameter values and measured target variables. When examining simulation results, the maximum and minimum values are both plotted through time. The "true" model calibration is taken to fall between these lines. When comparing simulation results from two model structures, the overlap of the uncertainty bands provides a measure of the degree to which the structures behave similarly.

The calibrated models were used for 140 year hindcast reconstructions of lake and soil water chemistry and for 50 year forecasts under two different scenarios of future deposition: 1) constant deposition at 1985 levels until the year 2035; and 2) a 30% decrease in deposition by year 2000 with constant deposition at that level until year 2035. The effects of the structural modifications were assessed by comparing hindcasts and forecasts for the different structures.

Results and Discussion

Succesful calibrations were obtained for all three model structures at both sites. The simulated fits to observed chemistry were within 5 μeq l^{-1} for all surface water variables and within 0.5% for soil base saturation variables. A detailed examination of 'goodness of fit' of any single structure to the observed data is not included here because the intercomparison of model structures is the primary interest. Our evaluation of the intercomparisons focuses on differences in hindcast and forecast values of several variables that are important in the assessment of effects of acidic deposition (Ca, Mg and alkalinity concentrations in surface water and the base saturation of the soils).

The first comparison is of the effects of one-layer *vs* two-layer structures utilizing the simple flow routing implementation of the two-layer model (all water flows through both soil layers). This comparison is made for both catchments. The second comparison is of the effects of flow routing *vs* no flow routing utilizing the two-layer structures only. This comparison is performed only on the Allt a Mharcaidh (the presence of the loch at the Round Loch site serves to integrate and perhaps obscure the effects of two-layer interflow).

One-layer/Two-layer Comparison

Simulated Ca and Mg concentrations for the Allt a Mharcaidh catchment show distinctly different patterns for the one-layer vs the two-layer structure when examined over the period 1845 to 2035 (using the constant deposition scenario for the period 1986 to 2035; Figure 19.2). The differences are not as pronounced for the Round Loch catchment (Figure 19.2). We would expect that a more complex (two-layer) structure containing a greater number of parameters would be less constrained than a simpler (one-layer) structure when given the same data availability. This implies that simulations derived from the different structures would be expected to differ at times when observations are not available (e.g. the hindcast and forecast years 1845 and 2035 in Figure 19.2). The differences in hindcast and forecast values for the two structures applied to Allt a Mharcaidh (Figure 19.2) are thus to a certain extent expected. An objective choice of a "correct" structure for Allt a Mharcaidh cannot be made given the data used here. At the only times in the simulations when observations are available to constrain the model (1985), the two structures fit the observations equally well.

The differences that do exist in hindcast and forecast Ca and Mg concentrations between the two structures at Allt a Mharcaidh are only on the order 5 μeq l^{-1} which is approximately the magnitude of measurement error. These differences are thus not operationally important. Furthermore, the differences between the simulations based on the two structures diminish as the simulations approach the calibration year. Given

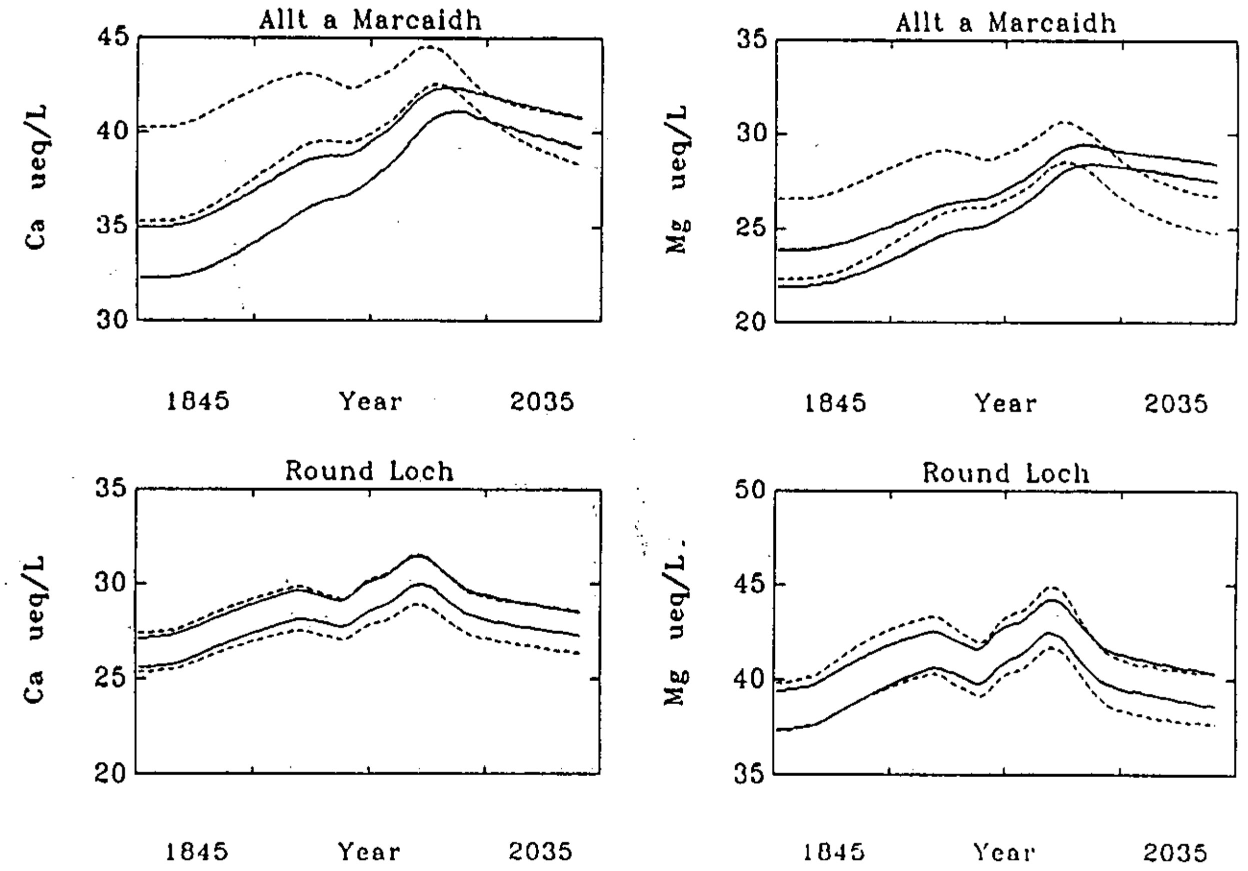


Figure 19.2. Simulated annual average Mg and Ca concentrations for Allt a Mharcaidh and Round Loch of Glenhead. Solid lines are maximum and minimum values for the one-layer structure; dashed lines are maximum and minimum values for the two-layer

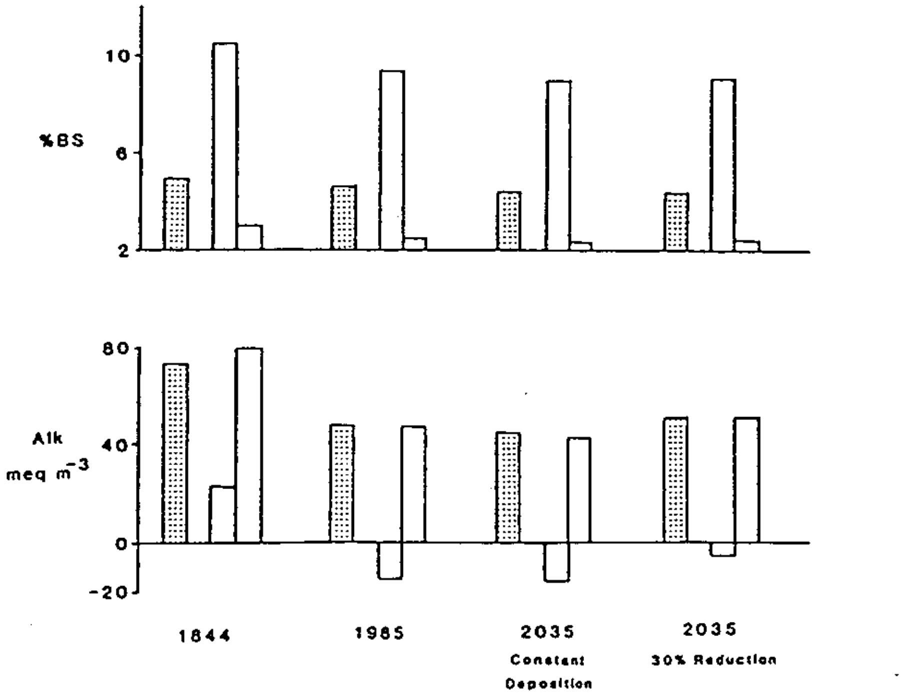


Figure 19.3. Simulated annual average soil water alkalinity and per cent base saturation for Allt a Mharcaidh for the hindcast year, calibration year and two forecast years. Shaded bars are for the one-layer structure; open bars are for the two-layer structure without flow routing.

the relative unimportance of the differences between structures for the Allt a Mharcaidh (and the lack of differences between structures for Round Loch), we conclude that the performance of both the one-layer and two-layer structures are similar for these two catchments. A one-layer structure is sufficient for long-term simulation of these systems given currently available data. Nevertheless, the differences in hindcast and forecast Ca and Mg concentrations at Allt a Mharcaidh point out a problem with identifiability of model structures. Improved confidence in the structures might be achieved by a more rigorous parameterization of the models using data from additional sources (such as calibration to paleo-ecological pH reconstructions).

A gradual acidification of soil and soil water is evident in both the one-layer and two-layer structures at Allt a Mharcaidh (Figure 19.3). This is seen as an historical decrease in soil water alkalinity and a decrease of soil base saturation between 1844 and 1985. For the constant deposition scenario there is a further small acidification response between 1985 and 2035 while the 30% deposition reduction scenario shows a slight increase in both variables (Figure 19.3). Simulated soil and soil water characteristics from the one-layer structure are not simply the means of the simulated characteristics for both soils in the two-layer structure.

The behavior of the soils in the two-layer structure highlights some important differences in their responses to acid deposition. The upper soil layer has a high base saturation

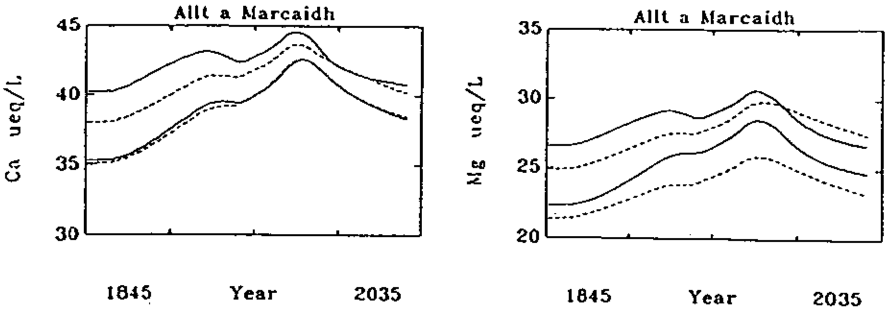


Figure 19.4. Simulated annual average Mg and Ca concentrations for Allt a Mharcaidh. Solid lines are maximum and minimum values for the two-layer structure without flow routing; dashed lines are maximum and minimum values for the two-layer structure with flow routing.

compared to the lower soil layer. Because of the low bulk density in the upper soil (Table 19.1), however, there are fewer exchange sites and fewer base cations held on the soil. Consequently, the upper layer responds quickly to changes in atmospheric deposition with base saturation falling from 10.5 % in 1845 to 8.9 % in 2035 (assuming constant present day deposition levels from 1985 to 2035) whereas the lower mineral layer changes from 2.9 % to 2.3 % under the same scenario. Soil base saturation in the one-layer structure, on the other hand, changes less rapidly than the upper soil of the two-layer structure (Figure 19.3) because of the aggregated nature of the soil characteristics in the one-layer structure.

With respect to soil water chemistry, the one-layer model demonstrates a drop in alkalinity of 28 μeq l^{-1} between 1845 and 2035 (constant deposition for 1985 to 2035). The upper layer of the two-box structure drops 38 μeq l^{-1} over the same period and the low layer drops by 36 μeq l^{-1}. These predicted relative changes in alkalinity are consistent with the expected behavior of organic and mineral soils and the absolute levels of alkalinity are important with respect to streamwater acidification. The predicted alkalinity of the organic top layer is negative in 1985 whereas the mineral lower layer retains a high alkalinity (Figure 19.3). Clearly, if we assume that during baseflow the dominant flow path is through the entire soil column the surface waters will be well buffered by base cations from the bottom soil layer and will not show rapid acidification. During storm events, however, if we assume that a high proportion of water will flow along surface and near surface preferential pathways thereby only contacting the organic top soil layer, the water will not be buffered by base cations from the soils and severe acid shocks will occur in the drainage waters. The one-layer structure is incapable of reproducing such episodic responses. It may be that short-term episodic data will prove the most useful for discriminating between one-layer and two-layer structures.

Routing/No-Routing Comparison

The differences between simulations (based on two layers) with *vs* without flow routing are again operationally small for simulated Ca and Mg concentrations in Allt a Mharcaidh (Figure 19.4). The differences are less than 5 μeq l^{-1}, the measurement error. This result suggests that annual average surface water data alone are not sufficient to constrain the

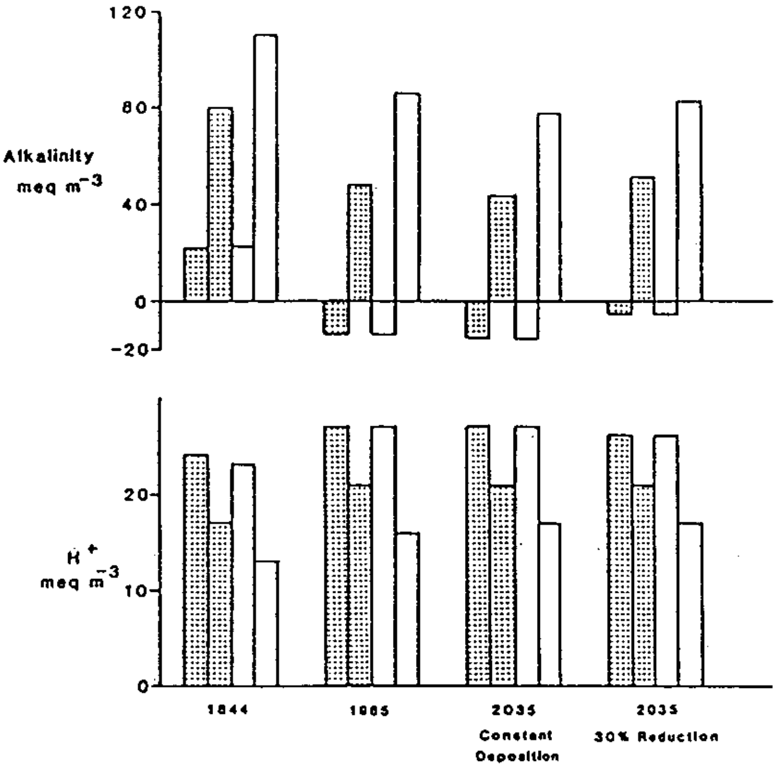


Figure 19.5. Simulated annual average soil water alkalinity and soil water hydrogen ion concentrations for Allt a Mharcaidh for the hindcast year, calibration year and two forecast years. Shaded bars are for the two-layer structure without flow routing; open bars are for the two-layer structure with flow routing.

calibration of a model if preferential flowpaths are important. Based on this interpretation, we can conclude that two-layer structures will be identifiable and necessary for long-term simulation of surface water chemistry only in those cases where the hydrological routing results in a significant proportion of annual through-flow bypassing a significant portion of the soil. In upland catchments the soils are generally thin and bypassing flows may be rare except during extreme events. Thus, a one-layer structure may be sufficient for long-term simulation of annual surface water concentrations in many cases.

If, however, the intent of the modelling exercise is to simulate changes in the soil or soil water characteristics, two-layer structures may be necessary even in the absence of flow routing. Clearly, the upper soil will exhibit the same characteristics for both structures because all water flows through the layer in each case (Figure 19.5). The effect of the flow routing is demonstrated by the higher alkalinity and lower hydrogen ion concentration in the lower soil layer for the structure with flow routing compared to the structure without flow routing (Figure 19.5). The flow routing allows 35 % of the water draining the upper layer (which is high in acidity) to bypass the lower layer. Hence, the exchangeable base cations and alkalinity generated by weathering in the lower layer are not as rapidly depleted.

Conclusions

We have compared the effects of inclusion of one or two soil layers and flow routing on the simulation of long-term acidification of surface waters for two upland U.K. catchments. The comparisons were based on MAGIC using modified structures for the soil compartments. Three model structures were implemented for the catchments; a single-soil-layer model, a two- soil-layer model and a two-layer model with simple flow routing. The structures were calibrated using a fuzzy optimization procedure that provided estimates of calibration uncertainty for all variables. All three structures at both sites were capable of reproducing observed, present-day surface water chemistry. Differences were evident among the various model structures, however, in the simulated soil variables. These differences were related to the difficulty of estimating base cation weathering and soil base cation exchange in the aggregated or distributed structures. The differences in simulation results among the model structures were small, however, compared to measurement errors. We conclude that, given currently available data, a one-layer model structure is sufficient for long-term simulation of acid deposition effects on the sites studied.

Acknowledgements

The authors would like to thank Bob Ferrier, Bruce Walker, John Miller, Basil Smith and Cyril Bown for soils data at the two sites. This work is supported in part by the Royal Society, London, under the Surface Water Acidification Programme.

References

Battarbee, R.W.: 1988, *Lake Acidification in the United Kingdom 1800-1986*. ENSIS Publishing, London

Cosby, B.J., G.M. Hornberger, J.N. Galloway, and R.F. Wright: 1985a, *Water Resour. Res.* 21, 51

Cosby, B.J., R.F. Wright, G.M. Hornberger, and J.N. Galloway: 1985b, *Water Resour. Res.* 21, 1591

Cosby, B.J., G.M. Hornberger, J.N. Galloway, and R.F. Wright: 1985c, *Environ. Sci. & Tech.* 19, 1144.

Cosby, B.J., P.G. Whitehead, and R. Neale: 1986a, *J. Hydrol.* 84, 381

Cosby, B.J., G.M. Hornberger, R.F. Wright, E.B. Rastetter, and J.N. Galloway: 1986b, *Geoderma* 38, 77

Cosby, B.J., G.M. Hornberger, and R.F. Wright: in press, 'A regional model of surface water acidification in southern Norway: calibration and validation using survey data', in J. Kämäri (ed), *Impact Models to Assess Regional Acidification,* Kluwer Academic Publisher, Dordrecht, The Netherlands

Harriman, R., D.E. Wells, E. Gillespie, D. King, E. Taylor, and A.W. Watt: 1987, 'Stream chemistry and salmon survival in the Allt a Mharcaidh, Cairngorm, Scotland'. *SWAP mid-term review conference*, Bergen, Norway

Hornberger, G.M., B.J. Cosby, and J.N. Galloway: 1986, *Water Resour. Res.* **22**, 1293.

Howells, G.D. (ed.): 1986, *The Loch Fleet Project: A report of the pre-intervention phase 1984-1986.* Central Electricity Generating Board. Leatherhead, U.K.

Jenkins, A., P.G. Whitehead, and A. Whitcombe: 1987, 'The hydro-chemical response of the Allt a Mharcaidh'. *SWAP mid-term review conference*, Bergen, Norway

Jenkins, A., R. Ferrier, T.A.B. Walker, and P.G. Whitehead: 1988, *Water Air Soil Pollut.* **40**, 275

Mason, B.J. and H.M. Seip: 1985, *Ambio.* **24**, 49

Rosenbrock, H.H.: 1960, *Comput. J.* **3**, 175

Warren Spring Laboratory: 1983, *Acid Deposition in the United Kingdom.* Warren Spring Laboratory, Stevenage, U.K.

Warren Spring Laboratory: 1987, *Acid Deposition in the United Kingdom 1981-1985.* Warren Spring Laboratory, Stevenage, U.K.

Wheater, H., S. Langen, J.D. Miller, and R.C. Ferrier: 1987, 'The determination of hydrological flowpaths and associated hydrochemistry in forested catchments in central Scotland'. in *Proceedings of the IAHS Symposium on Forest Hydrology and Watershed Management*, Vancouver, 433

Wright, R.F., B.J. Cosby, G.M. Hornberger, and J.N. Galloway: 1986, *Water Air Soil Pollut.* **30**, 367

3. PALEOECOLOGICAL COMPARISONS WITH MODEL SIMULATIONS

3.1 Round Loch

Cell-division sequence motif

SIR—We wish to point out that a structural motif shared among three transforming protein classes, the papovaviral large-T antigens, the adenoviral E1A proteins and the v- and c-myc oncoproteins[1,2] is also present in the E7 transforming proteins of human papillomaviruses[3] and the CDC25 gene, that is a mitotic regulator of yeast. The region encoding the shared motif has recently been demonstrated to be required by the large-T antigen of simian virus 40 (SV40) both for transforming function and for its specific binding to the 'negative oncoprotein' RB[4], the putative human retinoblastoma gene product, to which the E1A protein also binds specifically[5]. In addition, this region of SV40 large-T, E1A and human c-myc has been shown to be required for co-transformation with *ras* oncogenes of primary cells (see bibliography in ref. 1).

The motif is:

$$\begin{bmatrix}N\\D\end{bmatrix}\ - - \overbrace{C - \begin{bmatrix}S\\T\\E\end{bmatrix}}^{\text{Beta turn}}\ X\ \overbrace{\begin{bmatrix}D\\E\end{bmatrix}\begin{bmatrix}D\\E\\S\\T\end{bmatrix}\begin{bmatrix}D\\E\end{bmatrix}\ - - -}^{\text{Alpha helix}}$$

where the brackets indicate alternatives at a given position; the dashes, any amino acid; N, asparagine; D, aspartic acid; C, cysteine; E, glutamic acid; S, serine; T, threonine; and X, a spacer of 1–8 amino acids, often containing a proline and serines. There is a strong correlation between the presence of an aspartic acid in the first position and a hydrophobic amino acid in the second position. The predicted alpha helix is dominated over the remainder of its length by polar residues. Studies on the SV40 large-T and the adenoviral E1A proteins show that mutation of the glutamic acid in the sixth position of this descriptor to a positive amino acid inactivates the transforming activity of the proteins[1]. In one of the v-myc oncoproteins, at least one serine/threonine site in this region is phosphorylated[6]. This may also be how the region is activated in normal cellular proteins that contain the motif, while in some oncoproteins activation may be the result of the substitution of serine or threonine by glutamic acid or aspartic acid. This fits the apparent and unusual equivalence of all four amino acids in at least one position in the motif.

Using a sequence regular-expression handler and a modified Chou–Fasman secondary-structure prediction algorithm to annotate sequences with potential secondary structure, all matches to the descriptor within the NBRF protein sequence database (release 16) and the translated Genbank database (release 55) were identified out of over 11,000 proteins. They included nearly all of the v-myc and c-myc proteins, nearly all of the E1A and large T proteins, and six of the eight E7 proteins. Additional matches among proteins related to either cell transformation or division include a deer papillomavirus protein, a glycoprotein of Rift Valley fever virus and, perhaps most importantly, the CDC25 protein of yeast[7]. Only 12 functionally unrelated proteins were clearly identified. It is difficult to assess whether or not the pattern fails to match other known transforming proteins (for example, fos, jun and myb) because their molecular mechanisms are different or because the pattern itself is incomplete. Given the functional complexity of oncogenesis, we currently favour the former and therefore, believe the pattern's specificity to be nearly 100%. In which case, this may be one of the most diagnostic protein functional patterns known.

The importance of the match with the CDC25 protein is that it interacts with a known protein kinase WEE1+ and apparently modulates the activity of CDC2, another mitotic regulator protein[7]; interestingly, the ability of CDC25 to initiate cell division shows dosage effects, which are compatible with a protein–protein binding titration, such as is now known for the interaction of SV40 large-T or E1A with RB.

Thus, we propose that the majority of proteins containing the motif carry out one of the required steps in the cell division competency cascade of deactivating a cell division repressor (or activating a cell division activator). That these proteins will only transform primary cells in the presence of *ras* oncogenes suggests that at least one other cell-division signal transduction pathway exists.

JAMES FIGGE
TEMPLE F. SMITH

Dana-Farber Cancer Institute,
Harvard University,
44 Binney Street,
Boston,
Massachusetts 02115, USA

1. Figge, J., Webster, T., Smith, T.F. & Paucha, E. *J. virol.* 62, 1814–1818 (1988).
2. Stabel, S., Argos, P. & Philipson, L. *EMBO J.* 4, 2329–2336 (1985).
3. Phelps, W.C., Lee, C.L., Munger, K. & Howley, P.M. *Cell* 53, 539–547 (1988).
4. DeCaprio, J. *et al. Cell* (in the press).
5. Whyte, P. *et al. Nature* 334, 124–129 (1988).
6. Bister, K., Trachmann, C., Jansen, H.W., Schroeer, B. & Patschinsky, T. *Oncogene* 1, 97–109 (1987).
7. Russel, P. and Nurse, P. *Cell* 49, 569–576 (1987).

Reversal of acidification

SIR—Battarbee *et al.*[1] recently provided a reassuring account, based on diatom and lake-water records, that lake acidification in Scotland has either been reduced or has been reversed because of reductions in SO_2 emissions since 1970. Our recent modelling results simulating long-term changes in the acidity of Scottish lake and stream waters[2-4] also suggest a recent stabilization for some catchments.

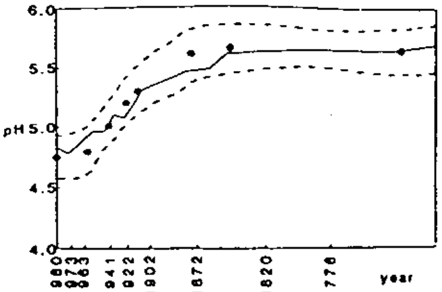


Fig. 1 Round Loch of Glenhead simulation of *p*H compared with palaeoecological data[4]. Solid line, palaeoecological reconstruction; dashed line, MAGIC reconstruction with 95% confidence bounds; dot, MAGIC reconstruction.

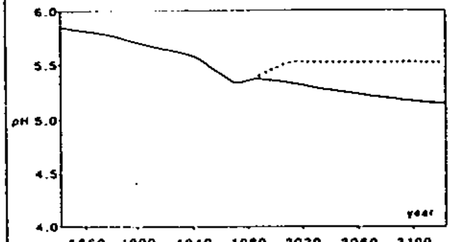


Fig. 2 Dargall Lane stream *p*H MAGIC simulation[7]. Solid line, prediction with future emissions at 1985 values; dotted line, prediction with emissions declining a further 50% from 1985 values over the next 20 years.

Figure 1, for example, shows a *p*H simulation for Round Loch of Glenhead (south-west Scotland), using the MAGIC model, which compares well with the diatom reconstructed *p*H[4]. Figure 2 shows the *p*H response for Dargall Lane, a stream draining into Loch Dee in the Galloway region of south-west Scotland, which shows similar declines over the past 100 years up to the 1970s. The model response also indicates a recovery in the 1980s which corresponds closely with the recovery of Battarbee *et al.*

Long-term predictions with the MAGIC model suggest that the recovery or stabilization is probably temporary, provided recent (1985) deposition levels are maintained. Qualitatively, this result may seem surprising. But the predicted decline results from the low rate of weathering and the highly base-depleted cation-exchange store which continues to be depleted at current acidic-oxide deposition rates. To avoid further declines in stream *p*H and ensure a significant recovery, for Dargall Lane, larger reductions in deposition of acidic oxides are required. To stabilize stream *p*H to provide a very modest improvement at Dargall Lane, for example, a further 50 per cent reduction in deposition from 1985 levels is needed, according to the estimates in Fig. 2.

Different catchments will show different responses dependent on factors such as soil-base saturation levels, sulphate adsorption and release mechanisms, weathering rates, hydrological factors and deposition rates. Although there are many uncertainties in the MAGIC model[1], the diatom records suggest that the model is applicable under these circumstances. Indeed, the model provides the only means of making site-specific or regional predictions of long-term future behaviour of stream and lake acidity.

On this basis, the observed improvements in Scotland, which are also suggested by the MAGIC model, should not be viewed as a case against further controls of acidic oxide emissions. Indeed, the modelling evidence suggests that further large-scale reductions are required and the amelioratory effects will be relatively rapid. Preliminary estimates for the United Kingdom, using the MAGIC model, indicate deposition reductions of around 50 per cent from 1985 levels are required to obtain significant long-term recovery[4-8] for much of the British uplands.

COLIN NEAL
PAUL WHITEHEAD
ALAN JENKINS
Institute of Hydrology,
Crowmarsh Gifford,
Wallingford OX10 8BB, UK

1. Battarbee, R.W. *et al. Nature* 332, 530–532 (1988).
2. Cosby, B.J., Wright, R.F. Hornberger, G.M. & Galloway, J.N. *Water Resour. Res.* 21, 1591–1601 (1985).
3. Whitehead, P.G. & Neal, C. *Trans. R. Soc. Edin. Earth Sci.* 78, 385–392 (1987).
4. Neal, C.; Whitehead, P.G., Neale, R. & Cosby, B.J. *J. Hydrol.* 86, 15–26 (1986).
5. Cosby, B.J., Whitehead, P.G. & Neale, R. *J. Hydrol.* 84, 381–401 (1986).
6. Cosby, B.J. *Proc. Reversibility of Acidification Workshop* EEC DGX11/G-1, 137–148 (1986).
7. Neal, C. & Whitehead, P.G. *Hydrol. Sci. Bull.* 33, 103 (1988).
8. Whitehead, P.G. *et al. J. Hydrol.* (in the press).
9. Flower, R.J. & Battarbee, R.W. *Nature* 305, 130 (1983).

Punctuation and selection

SIR—Radical theoretical positions in science are like programme trading in the securities markets: during euphoric uptrends their authors are not averse to taking full credit; but in the downward spiral that inevitably follows when reason returns, those associated with the movement no longer wish to be acknowledged.

This parallel came to mind as I read Steven Stanley's charge[1] that John Maynard Smith, in his criticism[2] of Eldredge and Gould's punctuational model of evolution, has seriously misrepresented Stanley's writings on species selection. Actually, Maynard Smith mentioned Stanley only twice. The second mentioned deals with a dispute over whether the evidence for punctuation has been in the form of measured morphological change or, instead, the duration of named taxa in the fossil record. Stanley does not mention this in his reply, so we can assume that his discomfort focuses on the other point: the decoupling of macroevolution from microevolution, and the role of random elements therein.

Specifically, Maynard Smith is charged with having "quoted out of context" a statement of Stanley's that refers to a "strong random element" in speciation. I have checked the passage in question (p.187 of ref. 3) and find my reading to be the same as Maynard Smith's. Indeed, shortly afterwards (p.193 of ref. 3) Stanley makes the case that species selection should not be considered as a subdivision of natural selection, and he asserts (p. 212) that "transitions are opportunistic in nature, reflecting the 'experimental' nature of speciation".

In the matter of quotes out of context, however, readers should consider Stanley's own statement that "although he never considered the process in detail, Wright asserted that selection operates at the level of the species...." Wright's paper[4] thus referenced is his classic *Modes of Selection*, in which the concluding sentence takes the rather more eclectic stance that "The course of evolution of vertebrate life and of life in general has been guided throughout by a hierarchy of processes of selection ranging from selection between genes to selection between orders, classes and even phyla." Significantly, the same paper opens with what Wright called the dogmatic statement of his general position with regard to evolution: "Adaptation rather than mere change seems to me to be the central problem. The only mechanism for evolutionary adaptation that has held up under investigation is natural selection." In Stanley's main publication on patterns of evolution[3], the concept of adaptation is conspicuous by its virtual absence.

ROBERT B. ECKHARDT
The Pennsylvania State University,
University Park,
Pennsylvania 16802, USA

1. Stanley, S.M. *Nature* 333, 214 (1988).
2. Maynard Smith, J. *Nature* 330, 516 (1987); 332, 311 (1988).
3. Stanley, S.M. *Macroevolution* (Freeman, San Francisco, 1979).
4. Wright, S. *Am. Nat.* 90, 5 (1956).

Understanding aggression

SIR—Had Melvin Konner been willing to take our book (*Aggression: Conflict in Animals and Humans Reconsidered*) a little more seriously, he might have understood it rather better[1]. We are not, as he suggests, anti-sociobiological; on the contrary, we endorse the sociobiological enterprise and attempt to reassess the significance of evolutionary theory for an understanding of aggression.

In this process of reassessment we do indeed criticize the work of several sociobiologists, including Konner himself (though not, as he suggests, either Robert Axelrod or Richard Dawkins). Our quarrel with Konner has to do with his use of selected ethnographic material to support the view that "no cultural training, however designed, can eliminate the basic core of capability of violence that is part of the makeup of human beings"[2]. Since our book was sent to press, the authors of the relevant ethnographic material have themselves complained about this misuse of their work[3].

The proper response to criticism is counter-criticism. Konner ignores this and all other substantive issues, contenting himself instead with a rhetorical plea: "Respected critics of sociobiology! Surely you can do better than this!". The answer is obvious: "Respected sociobiologists! Surely you can do better than Konner!".

JOHN R. DURANT
Department for External Studies,
University of Oxford
Oxford OX1 2JA, UK

1. Konner, M. *Nature* 333, 405 (1988).
2. Konner, M. *The Tangled Wing*, 207 (Heinemann, London, 1982).
3. Robarchek, C.A. & Dentan, R.K. *Am. Anthropol.* 89(2), 356–365 (1987).

Segregation of cystic fibrosis allele

SIR—Kitzis *et al.* (*Nature* 333, 215; 1988) suggest that the high frequency of the cystic fibrosis (CF) mutant gene in Caucasian populations may have arisen from the preferential inheritance of the CF chromosome from male to male. This intriguing hypothesis was based on the haplotyping of 60 asymptomatic siblings of CF patients by DNA probes. Twenty of 22 normal homozygotes were girls, 16 of 21 paternal CF chromosomes were inherited by boys. This is at odds with our own haplotyping of 60 unaffected siblings from 41 German CF families. Ten girls and 10 boys were typed homozygous normal. Eight of 17 paternal CF chromosomes and 15 of 23 (65%) maternal CF chromosomes had been passed to boys.

If one compiles the data from the two studies, the proportion of maternal and paternal CF alleles is about 1 to 1 in both male and female CF carriers, as expected for autosomal mendelian inheritance. Hence, an unfortunate sampling bias may be the most likely explanation for the unexpected segregation of the CF allele to the male germline observed by Kitzis *et al.* The data still do not exclude the possibility of a slightly more frequent transmission of CF chromosomes to males. More extensive data from pedigree analyses and population studies on unrelated individuals should settle the issue.

B. TÜMMLER
A. ASCHENDORF
T. PARNEDDE
J. HUNDRIESER
Zentren Biochemie und Humangenetik,
Medizinische Hochschule Hannover,
D-3000 Hannover 61, FRG

3.2 A Comparison for Six Sites

Phil. Trans. R. Soc. Lond. B 327, 435–440 (1990)
Printed in Great Britain

Modelling long-term acidification: a comparison with diatom reconstructions and the implications for reversibility

By A. Jenkins[1], P. G. Whitehead[1], B. J. Cosby[2] and H. J. B. Birks[3]

[1] *Institute of Hydrology, Wallingford, Oxfordshire OX10 8BB, U.K.*
[2] *Department of Forestry and Environmental Studies, Duke University, Durham, North Carolina 22706, U.S.A.*
[3] *Botanical Institute, University of Bergen, Allégaten 41, N-5007 Bergen, Norway*

A model of long term acidification (MAGIC) is applied to a range of catchments in Scotland that are subject to different pollution inputs and land uses. The simulated historical trends in pH are compared with data from palaeolimnological reconstructions undertaken at the same sites. Both techniques produce similar historical acidification trends and, with some exceptions, closely match observed present day pH. The MAGIC model results indicate that pollution inputs and land-use, particularly afforestation, have significant effects on surface water acidification. Moreover, the model indicates that reversibility may be occurring at several sites. Reversibility of acidification is further explored by using the model in predictive mode under several scenarios for reduction deposition.

INTRODUCTION

In recent years many lakes and streams in upland Scotland have demonstrated increased surface water acidity (Harriman & Morrison 1981). This has been attributed to the effect of increased anthropogenic sulphur deposition since pre-industrial times in both moorland catchments and afforested systems (Flower *et al.* 1987). The timing of response of the surface water to increased input of anthropogenic sulphate is thought to be controlled by the physiochemical characteristics of the catchment, namely, bedrock, soils and vegetation. Evidence for the processes and mechanisms involved in the titration of acidity from catchment inputs to outputs is still being gathered, but a quantification of the change in water acidity and the timing of changes in acid status has been derived from two approaches: long-term hydrochemical simulation models and palaeolimnological reconstructions. The two approaches differ in that the palaeolimnological reconstruction may be viewed as a direct measure of a surrogate acidity indicator whereas the models, although having their roots in hydrochemical laws, draw largely on a conceptualized representation of the major processes thought to be operating, and so at best can only be regarded as a simplification of the catchment system. Given this situation, model hindcast simulations require validation against long-term water-quality data sets. Clearly, few data sets of sufficient time period exist with which to test and validate either approach but increased confidence in both techniques would be gained if the reconstructions from the two are found to be consistent. Furthermore, the international concern over the problem of surface water acidification and its ecological effects and a stated policy of promoting amelioration strategies (Mason & Seip 1985) demands that predictions of surface water quality are made to assess the ability of systems to reverse acidification under different emissions and land-use strategies.

We use the model of acidification of groundwater in catchments (MAGIC) to simulate historical water quality and to compare the pH reconstruction to those determined by diatom analysis of sediment cores from the same lake sites. Six sites are chosen to cover a range of deposition loadings, land-use and bedrock geology in Scotland (Battarbee & Renberg, this symposium). The results from the calibrated models are compared both historically and to present-day water chemistry; the models are run forward to assess reversibility under a range of scenarios for deposition reduction.

THE STUDY SITES AND DATA SOURCES

The sites selected are Round Loch of Glenhead, Lochan Uaine, Loch Tinker, Loch Chon, Loch Doilet and Lochan Dubh (Battarbee & Renberg, this symposium). Rainfall amount and chemistry are taken, wherever possible, from nearby collectors operated by the Warren Springs Laboratory under the Department of the Environment monitoring network (Warren Spring Laboratory 1987). At L. Tinker and L. Uaine, because of the lack of a nearby D.O.E. collector, mean bulk precipitation data for 1987 for the L. Chon (Jenkins *et al.* 1989*a*) and Allt a Mharcaidh (Jenkins *et al.* 1988) catchments were used, respectively. Sea-salts dominate rainfall at the sites in the west and although sulphate concentrations are at a consistent level at all of the sites, rainfall quantity is substantially greater on the west coast thereby increasing the total loading. Mean present day observed water chemistry is taken from the SWAP Palaeolimnology Programme data-base (Munro *et al.*, this symposium).

To achieve a charge balance to both input and output it was necessary in some cases to add or subtract cations or anions. Where this was necessary concentrations of chloride or sodium, or both, were adjusted and the result of the changes generally improved the sea-salt ratio. In all cases, the changes implemented were within the annual variation in chemistry at each site.

RECONSTRUCTION TECHNIQUES

Details of diatom analysis (Jones *et al.* and Kreiser *et al.*, this symposium), dating procedures (Appleby *et al.*, this symposium) and techniques for reconstructing historical pH (Birks *et al.*, this symposium) are fully documented in this volume. A full description of the MAGIC model is given by Cosby *et al.* (1985*a*, *b*, 1986) and details of the optimization and calibration procedure used for these applications are identical to those given in Jenkins and Cosby (1989). Partial pressure of CO_2 in soil and lake water was identical for all applications. Organic matter concentration in soil water was 100 mmol m^{-3} at all sites and proportional to measured total organic carbon (TOC) in the surface water.

COMPARISON OF RECONSTRUCTION TECHNIQUES

The historical pH reconstructions at each site are given in figure 1. The MAGIC pH reconstruction is shown as an envelope curve, the width of which represents uncertainty in the model output; the 'true' pH value may lie anywhere within the envelope. These uncertainty bands encompass the range of variable values that were simulated given the specified uncertainty in the fixed parameter values and measured target values used in the optimization procedure (Jenkins & Cosby 1989). Values for pH inferred from the diatoms are represented

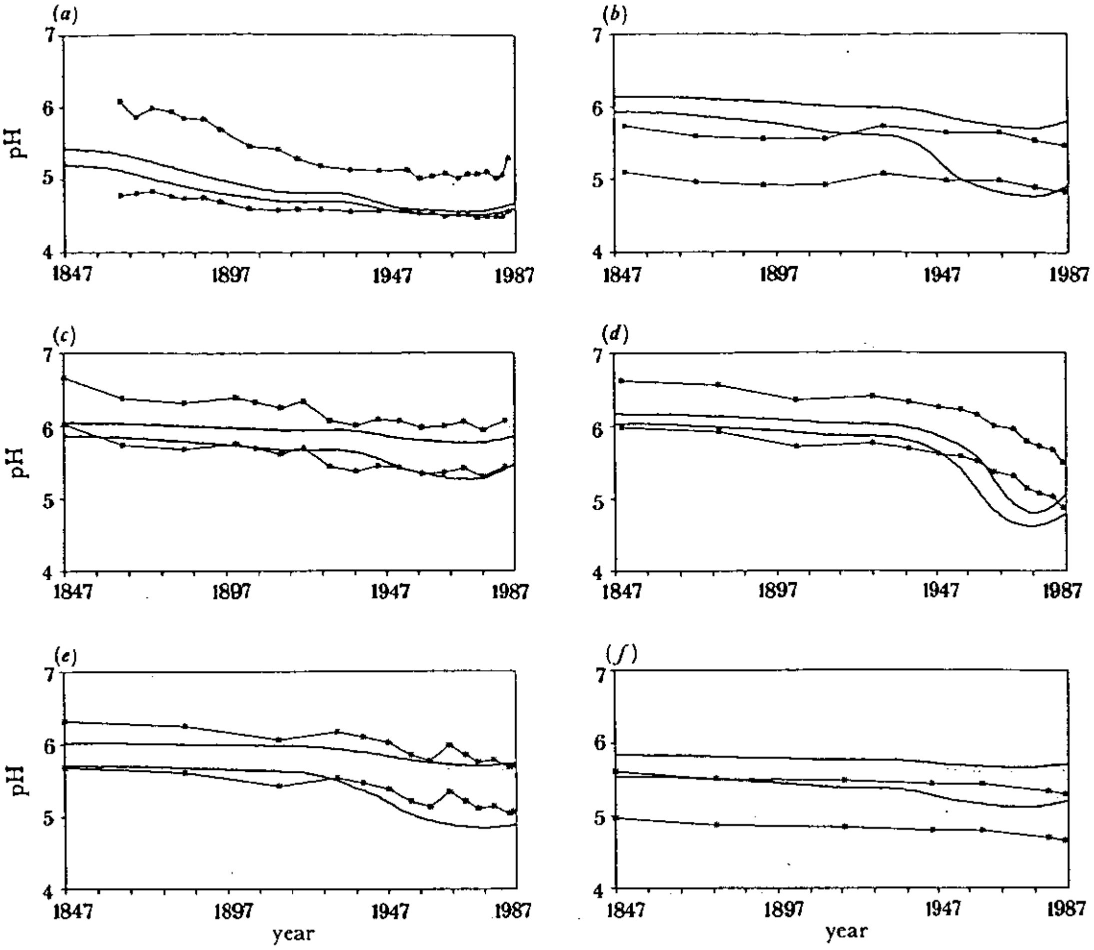


FIGURE 1. Historical pH trends reconstructed by MAGIC (thick lines) and diatoms (thin lines with asterisks) at (*a*) Round Loch of Glenhead, (*b*) Lochan Uaine, (*c*) Loch Tinker, (*d*) Loch Chon, (*e*) Loch Doilet and (*f*) Lochan Dubh.

as a series of points (asterisks), connected by thin lines. These represent the upper and lower standard errors of prediction for the weighted average pH reconstructions, estimated by bootstrapping (Birks *et al.*, this symposium). The overlap between the two reconstructions demonstrates a close agreement between the techniques in terms of the general pattern of historical acidification and timing of change. At L. Dubh and L. Uaine, however, the uncertainty bands from the two methods demonstrate the poorest agreement. These are high altitude sites where little pH change is predicted from a slightly acidic (pH 5.5–6.0) background (1847) level. At L. Uaine, MAGIC predicts a higher background pH although the uncertainty bands converge from 1940 onwards. At L. Dubh the diatom reconstructed pH is consistently lower than the MAGIC reconstruction. The predicted magnitude of pH change through the reconstruction period is consistent, however, being only *ca* 0.3 pH units for both methods. The background pH derived from both techniques for all lakes are in close agreement (figure 2*a*) and neither method shows a systematic bias. Comparison of observed and simulated present day pH (figure 2*b*), however, shows that both the MAGIC reconstructions, and to a lesser extent the diatom reconstructions, tend to underestimate observed mean pH. This problem

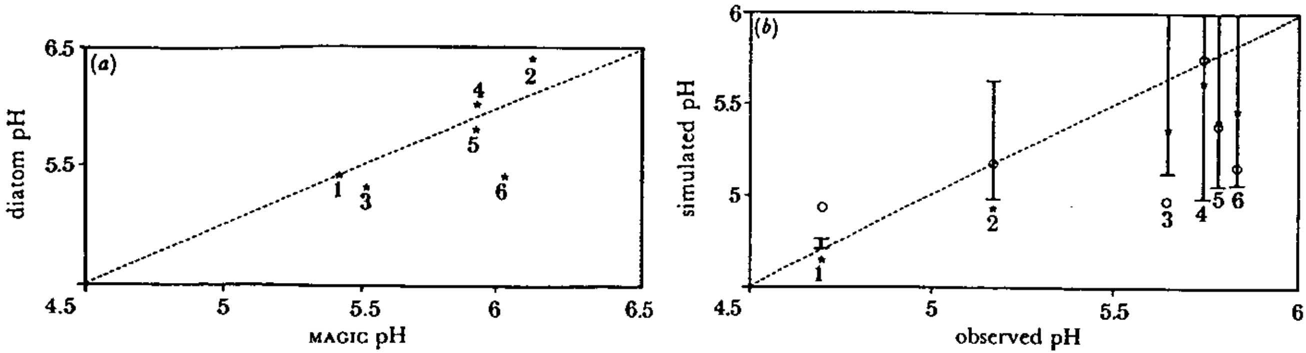


FIGURE 2. A comparison of (*a*) MAGIC and diatom reconstructed background (*ca.* 1850) pH and (*b*) present-day observed mean pH and that predicted from MAGIC (★) and diatom (○) reconstructions at Round Loch of Glenhead (1), L. Chon (2), L. Dubh (3), L. Tinker (4), L. Doilet (5) and L. Uaine (6). Solid bars represent the range of present-day measured pH values at each site.

tends to be exacerbated at pH greater than 5.5 although the simulated pH is almost always within the range of measured pH values at any site (figure 2*b*).

5. REVERSIBILITY OF ACIDIFICATION

All of the MAGIC reconstructions demonstrate some degree of reversibility since the late 1970s (figure 1) as a direct consequence of the reduction in sulphate deposition since 1970. The deposition trajectory used in the model is based on data from the Warren Spring Laboratory (1987), which reports an almost linear decrease to approximately 50% of the 1970 level. This simulated recovery in pH is not always consistent with the diatom reconstructions although at Round Loch of Glenhead there is an agreement between the two techniques. A possible recovery is also indicated in the diatom reconstruction at L. Tinker. Battarbee *et al.* (1988) note a trend towards improved pH conditions at several other moorland sites in Scotland. The implication at the other four sites included in this analysis, however, is that the deposition trajectory is not applicable at all of the sites or that the pH change is as yet too small to be identified by diatom analysis.

It is predicted by MAGIC that under a range of deposition reduction scenarios reversibility of surface water acidification will continue and that greater deposition reductions will lead to increased surface water recovery (table 1). The simulations are run forward for 50 years to

TABLE 1. SIMULATIONS FROM MAGIC OF MEAN pH BY YEAR 2037 UNDER THREE FUTURE DEPOSITION REDUCTION SCENARIOS

(See text for details.)

	deposition reduction		
site	no reduction	30% reduction	70% reduction
Loch Doilet	5.0	5.2	5.4
Loch Chon	5.0	5.4	5.7
Lochan Dubh	5.2	5.3	5.4
Round Loch of Glenhead	4.7	4.8	5.0
Lochan Uaine	5.6	5.7	5.9
Loch Tinker	5.6	5.7	5.8

2037 on the basis of three different scenarios: no deposition reduction from the present day; a 30% linear reduction to the year 2000, then held constant at that level until 2037; a 70% reduction to the year 2000, then held constant until 2037. At Round Loch of Glenhead, L. Chon and L. Doilet, a decrease of 70% does not return the surface water to its background pH level and indeed, the predicted pH may still be too low for a self-sustaining fish population to be maintained (i.e. mean pH < 5.5) although this will depend on other chemical and biological factors. It is clear that at these sites further recovery of the surface water pH will only occur following more rapid recovery of the soil-base exchange capacity. A modelling analysis of the L. Chon system by Jenkins *et al.* (1989*b*) demonstrates that soil recovery occurs more slowly than surface water, even with relatively large reductions in sulphate input. At L. Chon and L. Doilet, however, the simulated pH reported in table 1 depends not only upon sulphate deposition levels but also on land management. The reported pH assumes that the forest, planted in the 1920s and 1950s at L. Doilet and L. Chon, respectively, remains in place for a further 50 years. This is unlikely in a commercial forest where trees are normally harvested after about 60 years. The surface water pH will then depend upon whether the forest is replanted or not and such considerations are detailed by Jenkins *et al.* (1989*b*). Furthermore, at L. Chon the high degree of recovery, simulated by MAGIC, in recent years (figure 1) and the level of future recovery (table 1) is greatly influenced by the very high calcium weathering rates, associated with a doleritic dyke, within the catchment. From this point of view L. Chon is not necessarily typical of forested catchments on bedrock with very low acid neutralizing capacity, which will recover only slowly (cf. L. Doilet).

Soil physical and chemical data were provided by Bob Ferrier, Bruce Walker, Basil Smith and Cyril Bown of the Macaulay Land Use Research Institute.

REFERENCES

Battarbee, R. W., Flower, R. J., Stevenson, A. C., Jones, V. J., Harriman, R. & Appleby, P. G. 1988 Diatom and chemical evidence for reversibility of acidification of Scottish lochs. *Nature, Lond.* 332, 530–532.

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

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

Cosby, B. J., Hornberger, G. M., Wright, R. F. & Galloway, J. N. 1986 Modelling the effects of acid deposition: control of long-term sulfate dynamics by soil sulfate adsorption. *Wat. Res.* 22, 1283–1291.

Flower, R. J., Battarbee, R. W. & Appleby, P. G. 1987 The recent palaeolimnology of acid lakes in Galloway, southwest Scotland: Diatom analysis, pH trends and the role of afforestation. *J. Ecol.* 75, 797–824.

Harriman, R. & Morrison, B. R. S. 1981 Forestry, fisheries and acid rain in Scotland. *Scott. Forest.* 36, 89–95.

Jenkins, A., Ferrier, R. C., Walker, T. A. B. & Whitehead, P. G. 1988 A modelling study of long term acidification in an upland Scottish catchment. *Wat. Air Soil Pollut.* 40, 275–291.

Jenkins, A. & Cosby, B. J. 1989 Modelling surface water acidification using one and two soil layers and simple flow routing. In *Regional acidification models* (ed. J. Kamari, D. Brakke, A. Jenkins, S. Norton & R. Wright), pp. 253–267. Heidelberg: Springer-Verlag.

Jenkins, A., Cosby, B. J., Miller, J. D., Ferrier, R. C. and Walker, T. A. B. 1989*a* Modelling stream acidification in afforested catchments: long term reconstructions at two sites in central Scotland. *J. Hydrol.* (In the press).

Jenkins, A., Cosby, B. J., Ferrier, R. C., Walker, T. A. B. & Miller, J. D. 1989*b* Modelling stream acidification in afforested catchments: a comparison of the relative effects of acid deposition and afforestation. *J. Hydrol.* (In the press.)

Mason, B. J. & Seip, H. M. 1985 The current state of knowledge on acidification of surface waters and guidelines for further research. *Ambio* 14, 45–51.

Warren Spring Laboratory 1987 *Acid deposition in the U.K.* Stevenage, U.K.: Warren Spring Laboratory.

Discussion

D. F. Charles (*Indiana University, Indiana, U.S.A.*). A concern has been raised at this meeting and elsewhere that computer models such as MAGIC do not account well for organic acids, especially for any change in output of organic acids from watersheds that may occur in response to increased acidic deposition.

A. Jenkins. The MAGIC model incorporates only a simple representation of the effects of organics on water chemistry. Organic matter concentrations for the soil water and stream water are specified, usually in proportion to TOC, together with dissociation constants derived from empirical relations. Organic concentrations are held constant at the specified level throughout the model simulation. In this form, the model has been applied to a Finnish lake (Liuhapuro) with high DOC (17.2 mg l^{-1}) and succesfully reproduces the pH decline indicated by palaeolimnological reconstruction. At present, the effect of increased acid deposition on the output of organic acid is not well documented and so cannot be represented in the model.

4. MODELLING DYNAMIC RESPONSE IN THE LONG-TERM

4.1 A Method of Predicting Future Extremes of Water Chemistry

A METHOD FOR PREDICTING THE EXTREMES OF STREAM ACIDITY AND OTHER WATER QUALITY VARIABLES

A J Jakeman[1], P G Whitehead[2], A Robson[2],

A Jenkins[2] and J A Taylor[1]

ABSTRACT

A hybrid deterministic statistical approach is proposed for modelling the extremes of water quality in catchments subjected to long-term acidification. The approach is based on process models describing the long term variations in mean chemistry. Superimposed on these mean projections are distributions providing information on the extremes of water quality. The distributions are fitted to catchment data using maximum likelihood techniques. The approach is general and can be applied to the prediction of other water quality variables where samples can be regarded as belonging to a parametric probability distribution. A simple implementation of the approach using chemical data and a calibrated deterministic model for the Allt a Mharcaidh is used as an illustrative method.

[1] Centre for Resource and Environmental Studies,
Australian National University, GPO Box 4,
Canberra ACT 2601.

[2] Institute of Hydrology
Crowmarsh Gifford, Wallingford,
Oxon OX10 8BB, United Kingdom

INTRODUCTION

Mathematical models of complex environmental processes are often only capable of reasonable prediction of long term mean values of some quantity of interest. In the area of acidification modelling, long term models such as MAGIC (Model of Acidification of Groundwater In Catchments) have been developed to simulate long term trends and have been applied to a wide range of catchments (Cosby et al, 1985a,b, 1986; Wright et al, 1986; Jenkins et al, 1988, 1989; Whitehead et al, 1987, 1988). Whilst MAGIC may produce acceptable historical and future trends based on average annual chemistry, there are difficulties in modelling acidification at time scales of the order of hours and days (Neal et al, 1988). On this short time scale severe acid pulses are associated with hydrograph events.

Predictions of the extremes of behaviour during storm periods are difficult to obtain. Yet knowledge of the extremes is required in order to assess the likely biological effects of increased acidification in certain catchments or, alternatively, the biological recovery given reductions in acid deposition (Ormerod et al, 1988).

Process knowledge gaps, spatial heterogeneity and the cost of data acquisition contribute substantially to the difficulties besetting the prediction of extremes solely from process models. Nevertheless there are strategies at our disposal to provide information on extremes even when the environmental processes are very complex.

Much prior information may be obtained from statistical analysis of the characteristics of data already accrued. There are many examples where modellers analyse historical data to find a prescriptive solution to their problem. Simple parameterisations of probability density functions are fitted to outputs of processes for river flow management (Chow, 1964) air quality management (Jakeman and Taylor, 1989) and industrial manufacturing (Bain, 1978). In these cases, analysis should be undertaken to guarantee that the data being fitted are sufficiently independent and identically distributed (i.i.d.) so that the models can be used to synthesise more random samples or to extrapolate extreme values with acceptable confidence. Another example where modellers ignore physically based process knowledge is the use of purely stochastic models. A great deal of attention has been paid to the construction of autoregressive moving average models for forecasting (El-Shaarawi and Esterby, 1982) and, in application, the analysis depends on the stationarity (or absence of trend) of the data being fitted.

In the case of stream acidification the associated time series often contain long term trends. We cannot solely appeal to stationarity properties over the longer term to make predictions. Furthermore, if we wish to improve understanding of the processes associated with acidification and if we wish to assess control strategies, then we do need a process based description which is sensitive to, or largely determined by, the major forcing factors.

Fortunately, it is possible to combine the advantages of deterministic and statistically based-approaches into one that is hybrid. This has been constructed by Jakeman et al. (1988) for predicting extremes of air pollutant concentrations but the approach is a generic solution to many modelling problems.

In this paper we show a deterministic model, MAGIC, that predicts the long term trend of stream acidity variables in combination with probability distribution models that characterise the variability of the trend. These probability distributions must belong to some parametric family, our choice here being among two and three parameter Weibull, gamma and lognormal forms (see Jakeman and Taylor, 1989, for their mathematical definition). We develop and apply this hybrid model using data from the Allt a Mharcaidh catchment purely to illustrate the approach. It is stressed that insufficient years of data were available to confirm the validity of all the assumptions underlying the hybrid approach.

The paper is organised as follows. The general hybrid approach is stated in the next section. This is followed by a brief description of MAGIC used to predict the mean annual stream concentrations. Another section is devoted to analysis of the characteristics of stream concentration data. The statistical results allow us to subsequently devise a particular implementation of the hybrid approach. Predictions of the hybrid model are given and some analysis is reported of the sensitivity of the method to its underlying assumptions. We illustrate the practical use of the model by applying it to output from the MAGIC model. The conclusions suggest how the approach could be further explored and developed.

THE HYBRID APPROACH

The hybrid deterministic - statistical distribution approach of Jakeman et al (1988) can be stated in four steps as:

(1) Select a deterministic or physically-based process model of the phenomenon of interest to make predictions at the desired intervals (eg annually as in MAGIC).

(2) Identify, from a range of alternatives, the parametric form of the probability distribution (ie 2 or 3 parameter Weibull, gamma or lognormal) of historical observations within individual intervals (eg weekly) and assess its consistency over all intervals;

(3) For each prediction interval, fit the predictions of the model output in (1) to the parametric form identified in (2) so that its parameters can be estimated;

(4) Calculate the extremes of the probability distribution function (pdf) for each interval from a knowledge of the estimated parameter values.

The major assumptions of the approach are:

(A1) Within an interval, the probability distribution can be characterised by a simple parametric form;

(A2) The parametric form (but not the parameter values) of the pdf at a fixed site remains consistent from one interval to another;

(A3) The deterministic model yields sufficiently accurate properties of the pdf, such as the mean, to determine the parameter values.

In the case of stream acidification MAGIC is not presently capable of predicting any properties of the pdf other than the mean. Therefore, additional assumptions related to the values of some of the pdf parameters must be made.

The analytical tools required for the statistical component of the hybrid approach are:

(a) parameter estimation or fitting methods for probability density functions;

(b) identification criteria for discriminating among pdf alternatives.

THE DETERMINISTIC MODEL MAGIC

MAGIC (Model of Acidification of Groundwater In Catchments) is explicitly designed to perform long term simulations of change in soilwater and streamwater chemistry in response to changes in acidic deposition (Cosby et al, 1985a, b). The processes on which the model is based are:

- anion retention by catchment soils (eg sulphate adsorption);

- adsorption and exchange of base cations and aluminium by soils;
- alkalinity generation by dissociation of carbonic acid (at high CO_2 partial pressures in the soil) with subsequent exchange of hydrogen ions for base cations;
- weathering of minerals in the soil to provide a source of base cations;
- control of Al^{3+} concentrations by an assumed equilibrium with a solid phase of $Al(OH)_3$.

A sequence of atmospheric deposition and mineral weathering is assumed for MAGIC. Current deposition levels of base cations, sulphate, nitrate and chloride are needed along with some estimate of how these levels have varied historically. Historical deposition variations may be scaled to emissions records (Cosby et al, 1986) or may be taken from other modelling studies of atmospheric transport into a region (Derwent, 1987). Weathering estimates for base cations are extremely difficult to obtain. Nonetheless, it is the weathering process that controls the long term response and recovery of catchments to acidic deposition, and some estimate is required. An optimization scheme is used to determine key parameters (Jenkins and Cosby, 1989).

The MAGIC programme has been applied extensively to a range of catchments as mentioned previously and details of the model and its application are presented elsewhere (see Cosby et al, 1985a,b, 1986)

The approach suggested in this paper, to investigate the extremes of water quality behaviour, is to analyse the observed chemistry data from a catchment and quantify the inherent variability in such data. The data used here are taken from the Allt a Mharcaidh catchment in the Cairngorm region of Scotland and represent a site which is not at present chronically acidified but is subject to severe acid pulses during high flow events.

DATA, DESCRIPTION AND PRIOR ANALYSIS

The Allt-a-Mharcaidh catchment lies on the western flank of the Cairngorm Mountains draining an area of approximately 10km^2. Vegetation is mainly a mixture of heather and fescue grassland. The soils are essentially of three main types with c60% alpine and peaty podsols and 40% blanket peat. The site was selected as a transitional site, that is, a catchment which is not acidified but is thought to be at risk as regards future acidification problems.

Two years of approximately biweekly chemistry data are available from the catchment. For each year, two and three parameter versions of the Weibull, gamma and lognormal distributions were fitted and compared. These distributions are skewed shape-scale location distributions which were felt to cover a large range of possible shapes from which the historical data could be assumed to be derived. The normal distribution was not fitted to the data because it will predict negative (and hence physically meaningless) values of concentration for its lowest extremes. Furthermore, the three selected distributions are capable of fitting a symmetric bell-shaped density ie near enough normal.

Table 1 lists the chemical species studied together with basic statistics (mean, standard deviation etc). Figures 1 and 2 are time series plots of Alkalinity and Calcium over the two year period of 1986 and 1987. For some of the measurements such as alkalinity, pH and sulphate there appears to be a reasonably constant trend over the two years. For most of the remaining, there are higher levels on average in the first half of 1986 while the trend is reasonably constant but lower for the remaining one and a half years. This category includes conductivity, sodium, calcium, potassium, magnesium and nitrate.

TABLE 1 The Allt a Mharcaidh Catchment Chemistry Data for 1986 and 1987

	N	Mean	Standard Deviation	Min.	Max.
1986					
Alkalinity	120	46.0	21.8	3	97
Ph	90	6.0	0.4	4.7	6.5
Conductivity	97	27.3	5.2	18	45
Na	117	129.5	21.5	81	196
Ca	117	43.3	10.3	25	70
K	117	7.4	2.0	5	13
Mg	117	31.0	8.1	19	66
SO4	114	53.8	8.7	34	83
NO3	114	1.6	2.7	0	16
1987					
Alkalinity	99	51.0	14.0	17	76
Ph	97	6.0	0.3	4.8	6.4
Conductivity	95	24.5	2.5	17	29
Na	102	124.8	12.6	92	145
Ca	102	40.5	5.5	25	57
K	102	6.5	2.5	3	20
Mg	102	26.4	3.8	14	37
SO4	102	53.6	7.4	32	79
NO3	102	1.0	1.4	0	6

In terms of the assumptions required to fit probability distributions to these data, two points should be made. First, the data sets generally appear generally stationary (ie of constant trend) in 1987, and for some of the sets, this property also applies in 1986. Second there appears to be only a modest level of autocorrelation in all the data. Although application of probability distribution models to the data assumes independent random samples, Jakeman et al (1988) point out that quite high levels of autocorrelation can be tolerated and provide some quantification of the errors to be expected for varying degrees of autocorrelation. Jakeman et al (1989) also demonstrate that non-stationarity in time series of data does not represent a problem provided the samples can be regarded as belonging to a well-identified probability distribution.

Table 2 shows some of the likelihood values obtained from fitting our range of pdf models to the chemical species available for the Allt a Mharcaidh. Various criteria which trade off model fit against model complexity are available for using the likelihood to discriminate among model (parametric) alternatives. The criteria chosen should reflect the intended use of the model. A well known criterion which is biased towards overfitting is the Akaike Information Criterion (Akaike, 1972). The AIC is defined as

$$AIC(m) = -2 \log(likelihood) +2m$$

where m is the number of independent parameters. This criterion therefore only accepts a three parameter model if its log likelihood is more than one unit higher than a two parameter model. We have used this criterion to indicate our preliminary choice of superior model for each chemical species and each year in Table 2. The results for only two years are expectedly mixed, there not being enough years to determine if there is a consistently superior parametric model for any particular pollutant. The same distribution type is identified in each year for alkalinity, Na, Ca and NO_3. For SO_4 the two parameter gamma is the superior one for 1987, for 1986 this distribution is almost as good an assumption as the two parameter lognormal. For the other

TABLE 2 Log-likelihood values obtained from fitting different distributions to some of the chemical species measured in 1986 and 1987

Distribution	Alkalinity	pH	Conductivity	Na	Ca	K	Mg	SO_4	NO_3
Weibull-3 1986	*	**	-292.2	-524.1	-433.6(/)	-178.3	-389.4	-406.8	289.4
1987	*	-20.70	-218.4	-417.8	-319.3(/)	-210.8	-281.2(/)	-350.7	23.6
Weibull-2 1986	-537.6(/)	-44.40(/)	-304.0	-529.7	-441.1	-248.7	-417.6	-417.3	-139.8
1987	-399.3(/)	-562.4	-218.5(/)	-829.8	-321.4	-236.0	-282.5	-357.1	-69.6
Lognormal-3 1986	*	*	-292.2	*	*	*	-382.3(/)	-403.3	*
1987	*	*	*	*	*	-187.9(/)	*	*	*
Lognormal-2 1986	-555.0	-55.32	-293.1(/)	-524.9	-435.1	-236.2	-391.3	-403.4(/)	-124.3
1987	-413.7	-19.35	-224.4	-407.2	-321.6	-192.6	-283.7	-347.3	-66.9
Gamma-3 1986	*	*	-292.1	*	-434.8	-155.8(/)	-385.1	-403.6	295.1(/)
1987	*	*	*	*	*	-197.3	*	*	35.9(/)
Gamma-2 1986	-543.0	-54.15	-294.2	-524.2(/)	-435.2	-238.6	-396.7	-404.2	-137.6
1987	-408.0	-17.65(/)	-223.2	-405.5(/)	-320.3(/)	-205.3	-282.2(/)	-346.9(/)	-67.7

* denotes negative parameter value(s) obtained, usually location
(/) denotes superior model(s)
** denotes lack of convergence

chemical species, pH, conductivity, K and Mg, the distribution identified depends upon the year. Finally for 6 of the 9 species, a two parameter assumption is preferable to a three parameter in both years, the exceptions being K, Mg and NO_3. As will be seen, this is an advantage in constructing a hybrid model because a two parameter model requires less information for calibration.

Figure 3 shows the fit of the two parameter Weibull distribution to the empirical cumulative distribution function of the alkalinity data for the years 1986 and 1987. The agreement between the observed and fitted distribution functions is good in both cases.

A HYBRID METHOD AND PREDICTIONS

We demonstrate one possible implementation of the hybrid approach using the alkalinity data set only. The intention is to illustrate the method as simply as possible rather than draw conclusions about the extremes of acidification in the Allt a Mharcaidh catchment. Alkalinity is the obvious species to select for this purpose since both the 1986 and 1987 data sets visually conform to the i.i.d. assumption and a two-parameter Weibull distribution is preferred for both years. However, it is stressed that independence and stationarity of the time series of a variable are not necessary conditions to obtain good parametric fits and hence hybrid model results.

In choosing a method it must first be appreciated that the deterministic model MAGIC at present predicts only mean annual values (see Jenkins et al, 1988). No variability of this mean is yet reliably available as the model output. Because the distribution identified for alkalinity is a 2-parameter version, two pieces of information are needed to describe it. An obvious strategy is to use the deterministic model to provide the mean of the identified distribution (Weibull for alkalinity) assume a range of values for the shape parameter of the distribution, compute the scale parameter from the mean and shape and look at the sensitivity of the result to values within the shape range.

Table 3 contains the parameter values for the model fit to the 1986 and 1987 Weibull alkalinity data sets. These were two extremely different years, in terms of snowfall. In other years we might therefore expect the shape parameter to lie between or nearby the 1986 and 1987 estimates. On this basis, we select a shape parameter range of 1.5 up to 6 in an attempt to cover most possibilities.

TABLE 3 Parameter values for Weibull model fit to alkalinity data set

Year	Shape parameter	Scale parameter
1986	2.230	51.81
1987	4.341	56.17

The mean of the Weibull distribution is given by

$$\text{mean} = \text{scale} \times \text{Gamma}\left(1 + \frac{1}{\text{shape}}\right)$$

so that knowledge of scale straightforwardly ensues from a fixed shape. Figure 4 shows the result of calibrating the scale parameter for a range of assumed shape parameter values, using the known mean alkalinities from 1986 and 1987 (ie we do not bother to use our deterministic model to predict the mean, accepting that this can be done to an acceptable accuracy). It demonstrates the nature of the above relationship that the scale parameter has a low sensitivity to changes in the value of the shape parameter and is largely determined by the mean, especially if the mean is large compared to the shape.

Figure 5 shows the sensitivity of percentile predictions to errors in knowledge of the shape parameter. The observed percentiles are indicated as are the predicted results if the best shape parameter value was that underlying the Weibull description of the 1986 or 1987 alkalinity data sets. Figure 6 shows the errors in the estimated 67% and 95% percentiles. The error is expressed as a percentage of the observed percentile values (assumed to be correct).

The results were obtained from the Weibull cumulative distribution function for a range of shape parameter values and the known mean. The 67% and 95% upper percentiles were arbitrarily chosen (5% and 33% percentiles, which in the case of alkalinity would correspond to harmful extremes, could equally well be considered). For both 1986 and 1987 the estimated 67% upper percentile was not sensitive to the choice of shape parameter value. However the 95% upper percentile expectedly showed more sensitivity particularly when the shape values were low (as was the case in 1986). With additional years of data it should be possible to determine a realistic range for the shape parameter and hence a range for each percentile. Even more desirable would be an extension of the deterministic model so as to calculate not only the mean but also accurate predictions of percentiles close to the mean which would enable improved estimation of the shape parameter. In any case the percentile value for a very low shape parameter choice serves as an upper bound on the extreme value.

In its simplest form the hybrid approach, as outlined in this paper, may be implemented using the mean value, M, the percentile, p, where 0<p<100 and the shape parameter, c, to estimate the percentile of interest, Lp, as follows:

$$Lp = \frac{M \left| \ln\left(\frac{100-p}{100}\right) \right|^{1/c}}{\text{Gamma}\ (1 + c^{-1})} \qquad (1)$$

or $$Lp = M \times F(c,p) \qquad (2)$$

where F(c,p) is a shape factor

Table 4 lists values of the factor F(c,p) for varying values of the percentile and the shape parameter. In order to implement the hybrid approach using Table 4 all that is required is an estimate, derived from the deterministic model, of M and an estimate of the shape parameter. If no estimate of the shape parameter is available then a middle range of c=2.5 could be assumed. Then, based on the percentile for which a prediction is required and the value of the shape parameter a value for F(c,p) may be selected from Table 4. The estimate of the percentile follows simply according to equation (2).

It should be noted that a bound of uncertainty could be approximated by estimating Lp at the highly skewed c=1 and nearly unskewed c=6 shape parameter values.

APPLICATION TO THE MAGIC MODEL

MAGIC has been used to predict past and future mean alkalinity values. The hybrid approach has been applied to these predictions and estimates of the 95% and 5% percentiles have been derived. The predicted means and estimated percentiles are plotted in Figure 7. Two estimates of each percentile are plotted - these are based on shape parameter values for the years 1986 and 1987. The wide spread of behaviour reflects the variability associated with catchment chemistry especially those subject to snow melt and extreme hydrological events. Nevertheless the ranges provide valuable information to biologists to assess fishery survival in acid streams (Ormerod et

Table 4: The factor F(c,p) for the two parameter Weibull distribution calculated over a range of percentiles and shape parameter values.

	Percentile (p)							
	67	75	80	85	90	95	97	99
SHAPE PARAMETER (C)								
1	1.11	1.39	1.61	1.90	2.30	3.00	3.51	4.61
1.25	1.17	1.39	1.57	1.79	2.09	2.58	2.93	3.64
1.5	1.19	1.38	1.52	1.70	1.93	2.30	2.56	3.07
1.75	1.19	1.35	1.47	1.62	1.81	2.10	2.30	2.69
2	1.19	1.33	1.43	1.55	1.71	1.95	2.11	2.42
2.25	1.18	1.31	1.39	1.50	1.64	1.84	1.97	2.23
2.5	1.17	1.28	1.36	1.46	1.57	1.75	1.86	2.08
2.75	1.17	1.27	1.34	1.42	1.52	1.67	1.77	1.96
3	1.16	1.25	1.31	1.39	1.48	1.61	1.70	1.86
3.25	1.15	1.23	1.29	1.36	1.44	1.56	1.64	1.78
3.5	1.14	1.22	1.27	1.33	1.41	1.52	1.59	1.72
3.75	1.14	1.21	1.26	1.31	1.38	1.48	1.55	1.66
4	1.13	1.20	1.24	1.29	1.36	1.45	1.51	1.62
4.25	1.13	1.19	1.23	1.28	1.34	1.42	1.48	1.57
4.5	1.12	1.18	1.22	1.26	1.32	1.40	1.45	1.54
4.75	1.12	1.17	1.21	1.25	1.30	1.38	1.42	1.51
5	1.11	1.16	1.20	1.24	1.29	1.36	1.40	1.48
5.25	1.11	1.16	1.19	1.23	1.27	1.34	1.38	1.45
5.5	1.10	1.15	1.18	1.22	1.26	1.32	1.36	1.43
5.75	1.10	1.14	1.17	1.21	1.25	1.31	1.34	1.41
6	1.10	1.14	1.17	1.20	1.24	1.29	1.33	1.39

al, 1988)

Further years of data can be used to assess the general adequacy of assumption (A2) in the hybrid approach as well as the most likely range of shape values for the identified parametric form. Whenever sufficient years are available, the method then can be used to investigate important biological questions for a catchment of interest from more comprehensive analysis than is illustrated here.

CONCLUSIONS

In this paper we have seen how the hybrid approach can be used to supplement the predictions from process models such as MAGIC. Data from an existing catchment have been analysed and a preliminary form for the distribution has been chosen. The mean values produced by the MAGIC model have then been combined with this knowledge of the distribution and estimates of the extremes derived. The approach is general and can be applied to the prediction of other water quality variables where samples can be regarded as belonging to a parametric probability distribution.

Further work is required to examine the validity of our assumption that, for a given catchment, the selected form of distribution does not change substantially over time. Data from long term catchment sites such as that of Birkenes in Norway could profitably be studied (Christophersen et al, 1989). The approach also has potential use in the study of catchments where strong artificial perturbations have occurred such as at Llyn Brianne where liming has taken place (Whitehead et al, 1988). Finally, estimation of the extremes could be substantially improved if the process model were to yield accurate predictions not just of the mean but also the variance or a range of percentiles about the mean, however narrow that range. This type of additional information would aid calibration of the shape parameter value for the pdf that is assumed or statistically identified from historic data sets.

REFERENCES

Akaike, H. 1972 Use of an information theoretical quantity for statistical model identification. Proceedings of the Fifth Hawaii International Conference on Systems Science, Western periodicals, North Hollywood, California, pp 249-250.

Bain, L.J. 1978 Statistical Analysis of reliability and life testing models: theory and methods. Marcel Dekker, New York.

Chow, V.T. 1964 Handbook of Applied Hydrology. Section 8-IV Sequential Generation of Hydrologic Information, McGraw-Hill, New York.

Christophersen, N., Robson, A.J., Neal, C., Whitehead, P.G., Vigenst, B., Henriksen, A. 1989 Evidence for Soil Acidification and Long Term Deterioration in Streamwater Chemistry at the Birkenes Catchment, Southern Norway. Submitted for Publication.

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

Cosby, B.J., Whitehead, P. and Neale, R. 1986 A preliminary model of long-term changes in stream acidity in South Western Scotland, J.Hydrol. 84, 381-401.

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. Water Resources Res. 21, 1591-1601.

Derwent, R.G., Dollard, G.J. and Metcalfe, S.E. 1987 On the nitrogen budget for the United Kingdom and north west Europe, AERE R-12616, Harwell.

El Shaarawi, A.H. and Esterby, S.R. (eds) 1982 Time Series Methods in Hydrosciences. Developments in Water Science, Vol 17, Elsevier, Amsterdam, 614 pp.

Jakeman, A.J., Simpson, R.W. and Taylor, J.A. 1988 Modelling Distributions of Air Pollutant concentrations - III. The Hybrid Deterministic-Statistical Distribution Approach. Atmospheric Environment, Vol 22, No 1, 163-174.

Jakeman, A.J. and Taylor, J.A. 1985 A Hybrid ATDL-Gamma distribution model for predicting area source acid gas concentrations. Atmospheric Environment, 19(11), 1959-1967.

Jakeman, A.J. and Taylor, J.A. 1989 Identification, Estimation and Simulation of frequency distributions of pollutant concentrations for air quality management. Chapter 4 in "Library of Environmental Control Technology" Volume 2, P.N. Cheremisinoff (ed), Gulf Publishing, Ca, Houston, pp 135-158.

Jakeman, A.J., Taylor, J.A. and Bai Jun 1989 Fitting probability distribution models to samples from non-stationary time series. Submitted for publication.

Jenkins, A., Cosby, B.J. 1989 Modelling surface water acidification using one and two soil layers and simple flow routing. In: J Kamari (Ed) Proceedings of the conference on Models to describe the Geographic extent and time evolution of acidification and air pollution damage. Avlanko, Finland, July 1988 (in press).

Jenkins, A.J., Ferrier, R.C., Walker, T.A.B. and Whitehead, P.G. 1988 A modelling study of long-term acidification in an upland Scottish catchment. Water, Air and Soil Pollution, 40, 275-291.

Jenkins, A.J., Whitehead, P.G., Cosby, B.J. and Birks, J.B. 1989 Modelling Long-term Acidification. A comparison with Diatom Reconstruction and the Implications for Reversibility. Proceedings of the Royal Society SWAP Palaeolimnology Programme.

Neal, C., Christophersen, N., Neale, R., Smith, C.J., Whitehead, P.G. and Reynolds, B. 1988 Chloride in precipitation and surface water for the upland catchment of River Severn, Mid-Wales: some consequences for hydrochemical models. Hydrol. Processes 2, 155-165.

Ormerod, S.J., Weatherley, N.S., Varallo, P.V. and Whitehead, P.G. 1988 Preliminary empirical models of the historical and future impact of acidification on the ecology of Welsh streams. Freshwater Biol. 20, 127-140.

Whitehead, P.G., Bird, S., Hornung, M., Cosby, B.J. Neal, C. and Paricos, P. 1988 Stream acidification in the Welsh uplands: a modelling study of the Llyn Brianne catchments. J.Hydrol. 101, 191-212.

Whitehead, P.G. and Neal, C. 1987 Modelling the effect of acid deposition in Upland Scotland. Earth Sciences 78, 385-392.

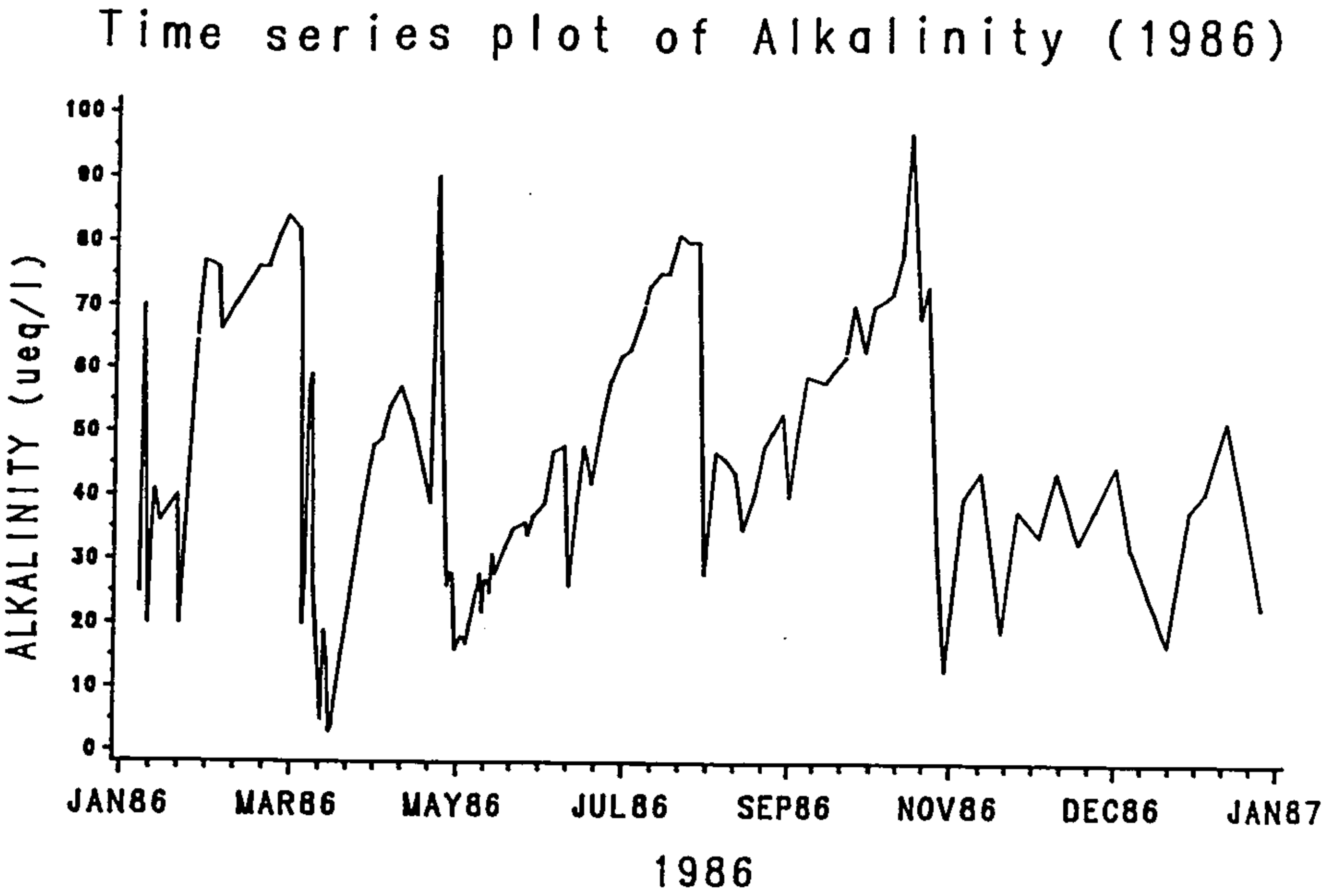
Wright, R.F., Cosby, B.J., Hornberger, G.M., and Galloway, J.N. 1986 Comparison of palaeolimnological with MAGIC model reconstructions of water acidification. Water Air Soil Pollut. 30, 367-380.

ACKNOWLEDGEMENTS

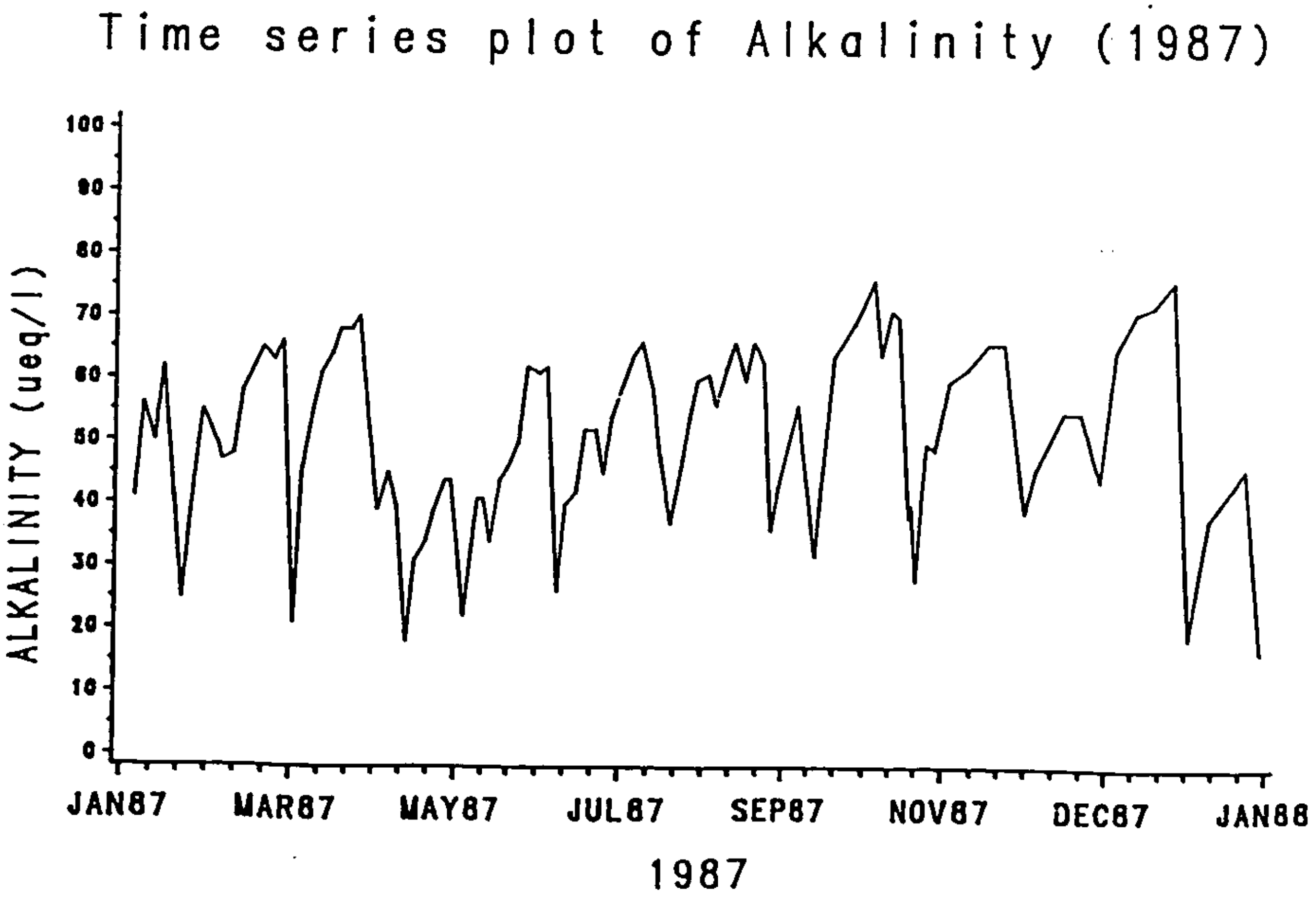
Research at the Allt a Mharcaidh has been conducted as a part of the Royal Society Surface Water Acidification programme.

We thank Jo Porter for collection of water samples and Ron Harriman (Freshwater Fisheries Laboratory, Pitlochry) for chemical analysis.

Figure 1.



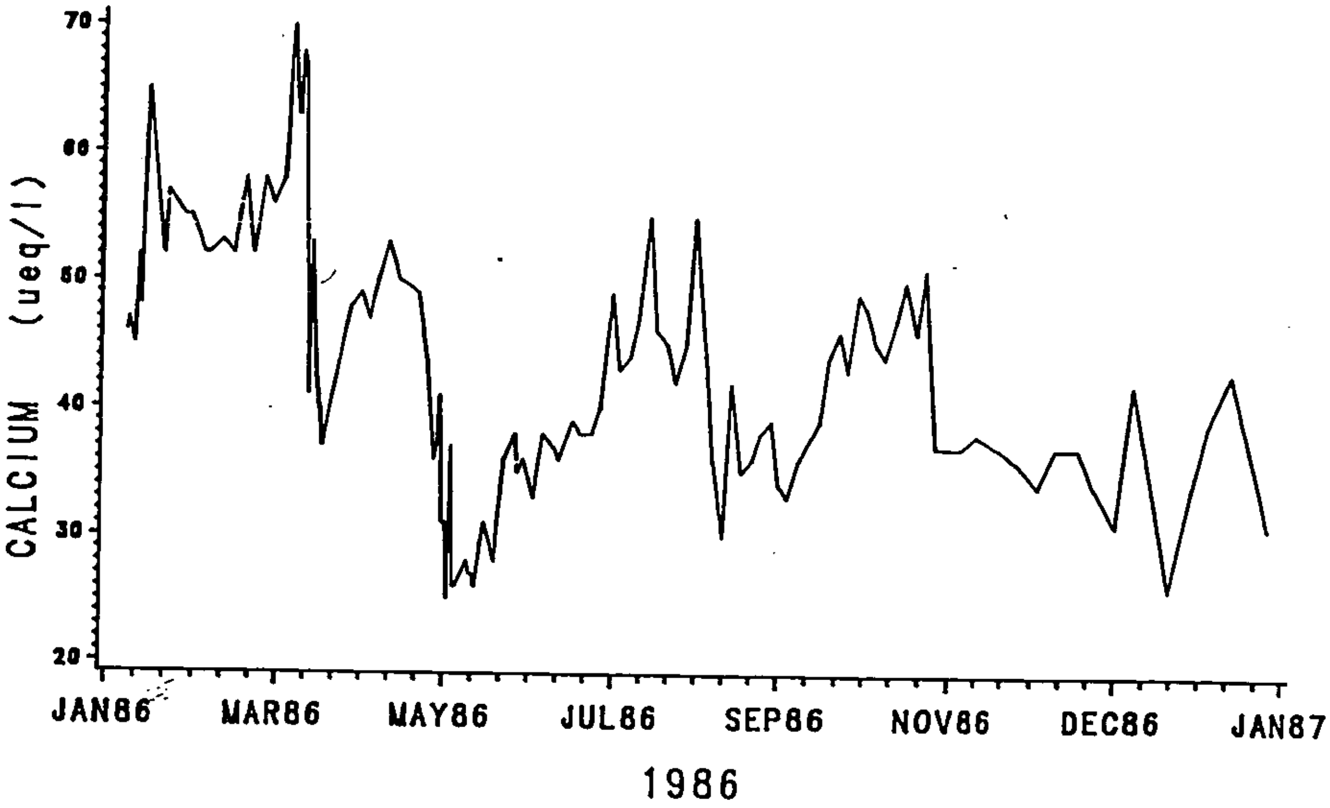
Time series plot of Alkalinity (1986)



Time series plot of Alkalinity (1987)

Figure 2.

Time series plot of Calcium (1986)



Time series plot of Calcium (1987)

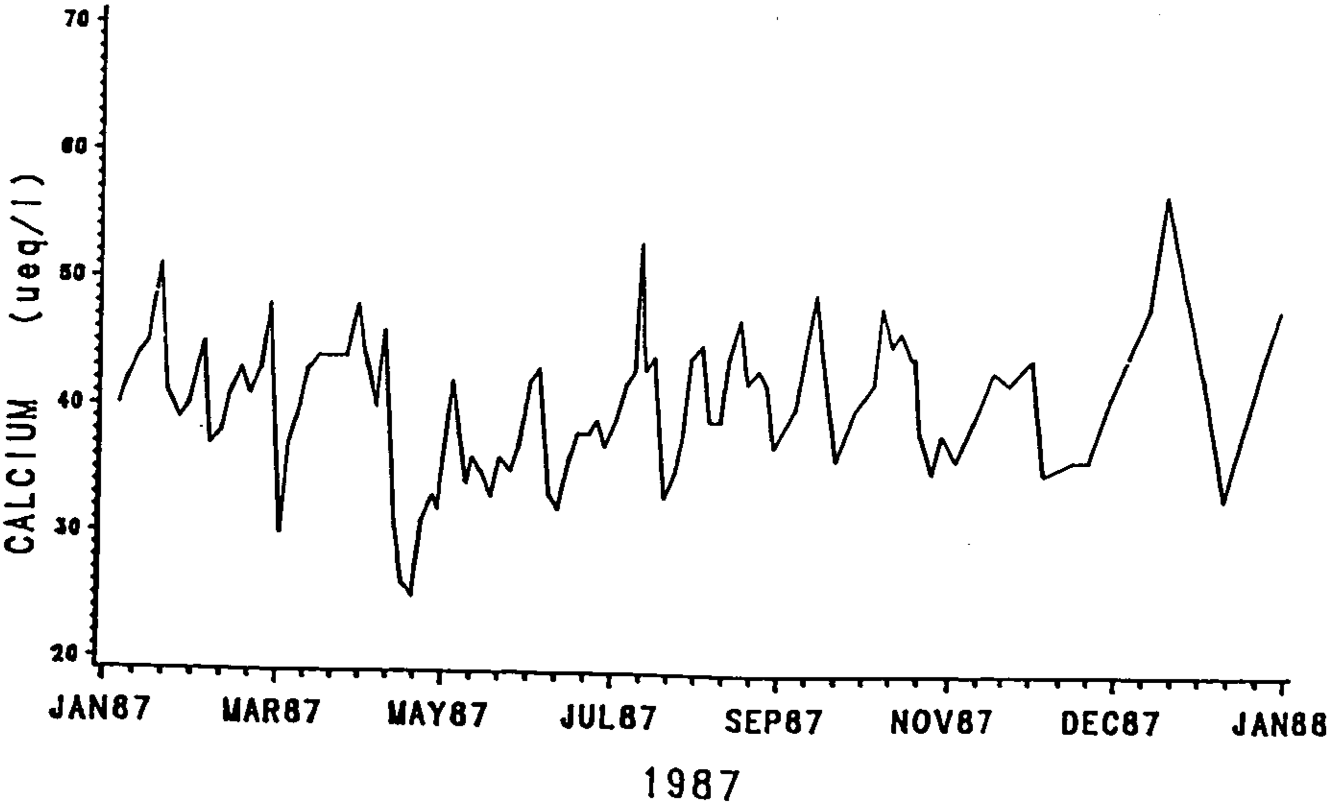


Figure 3.

Fit of the two parameter Weibull distribution to the empirical cumulative distribution function

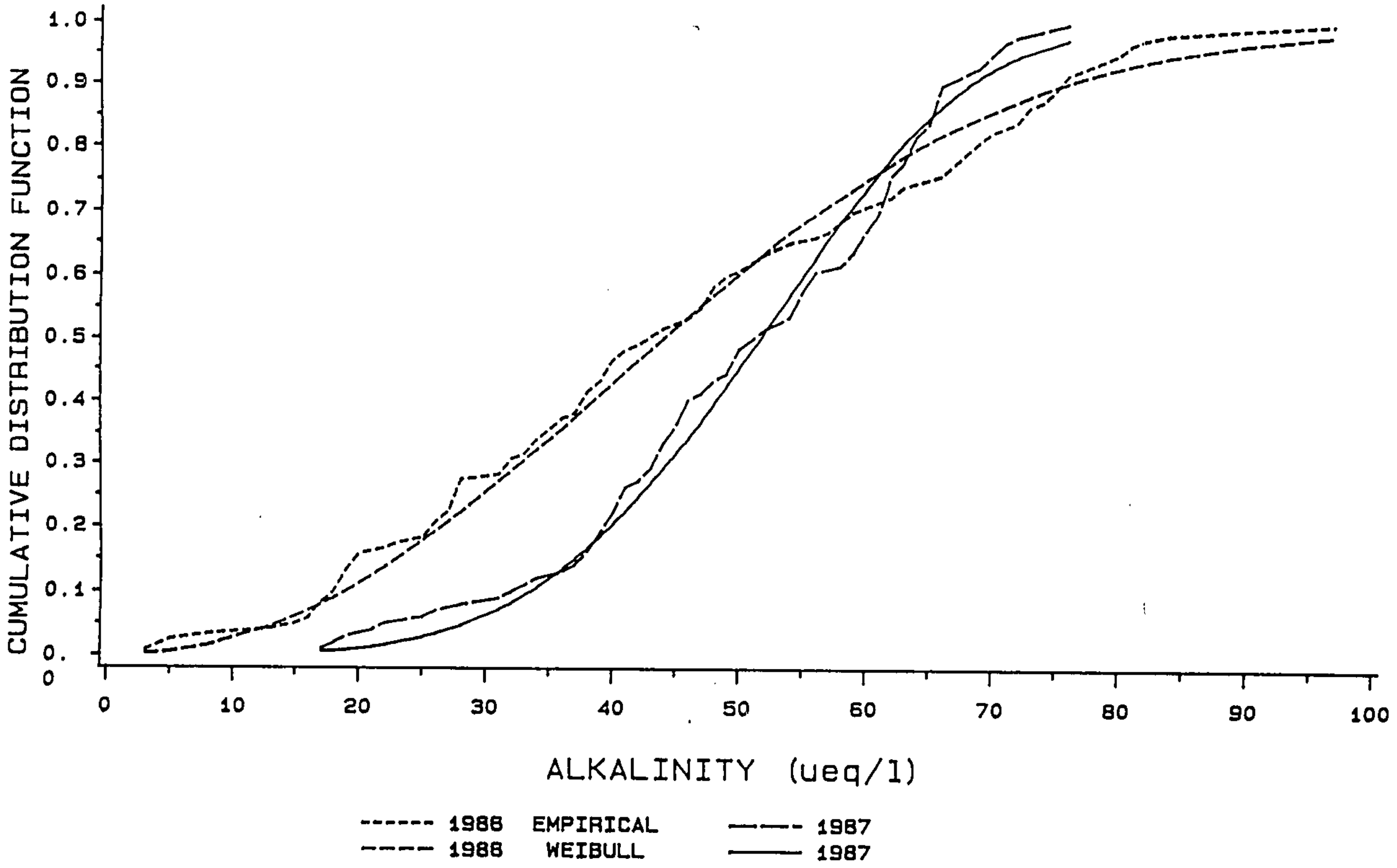


Figure 4.

Plot showing dependency of the scale parameter on the shape parameter using mean values from 1986 and 1987

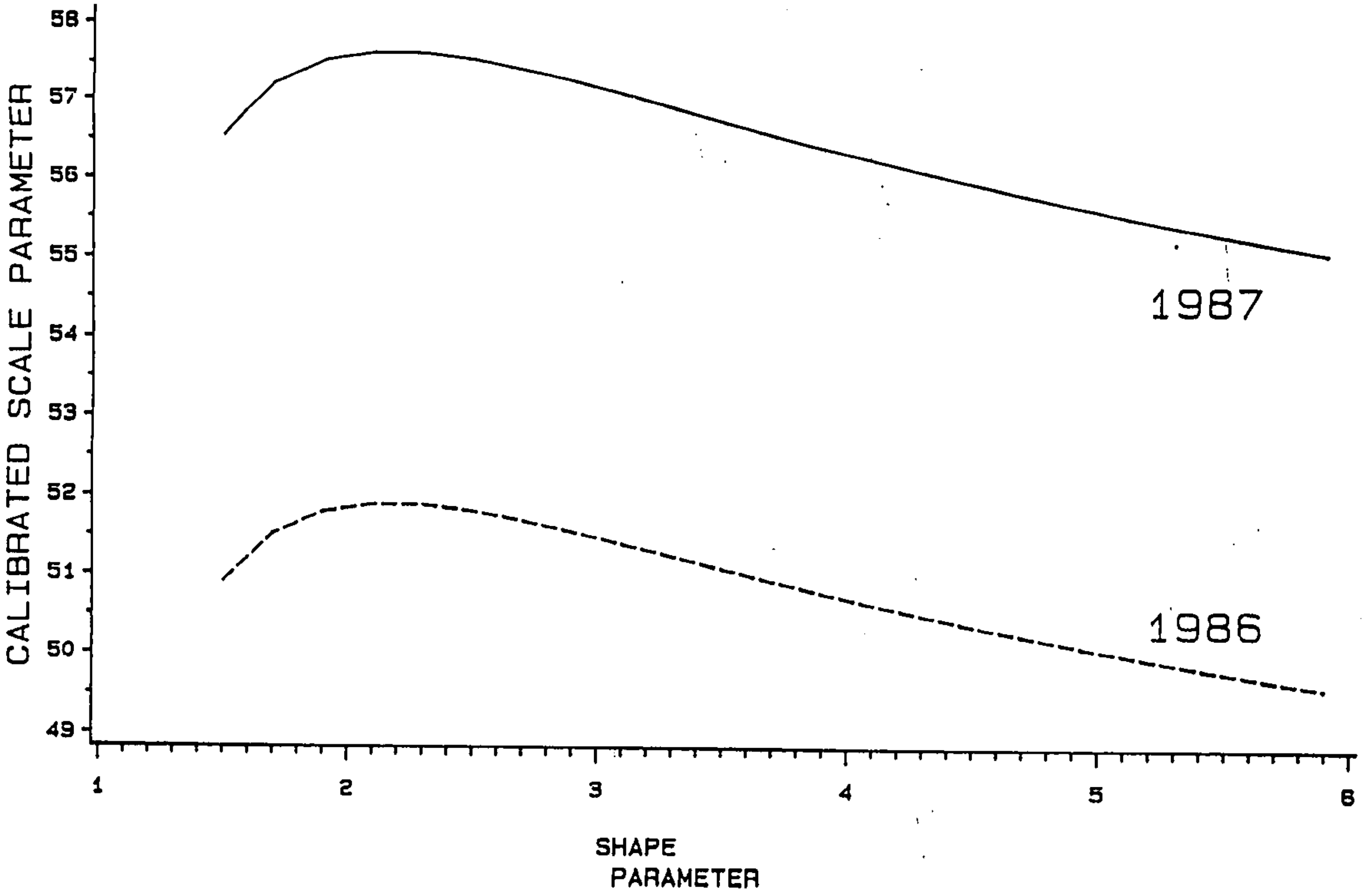
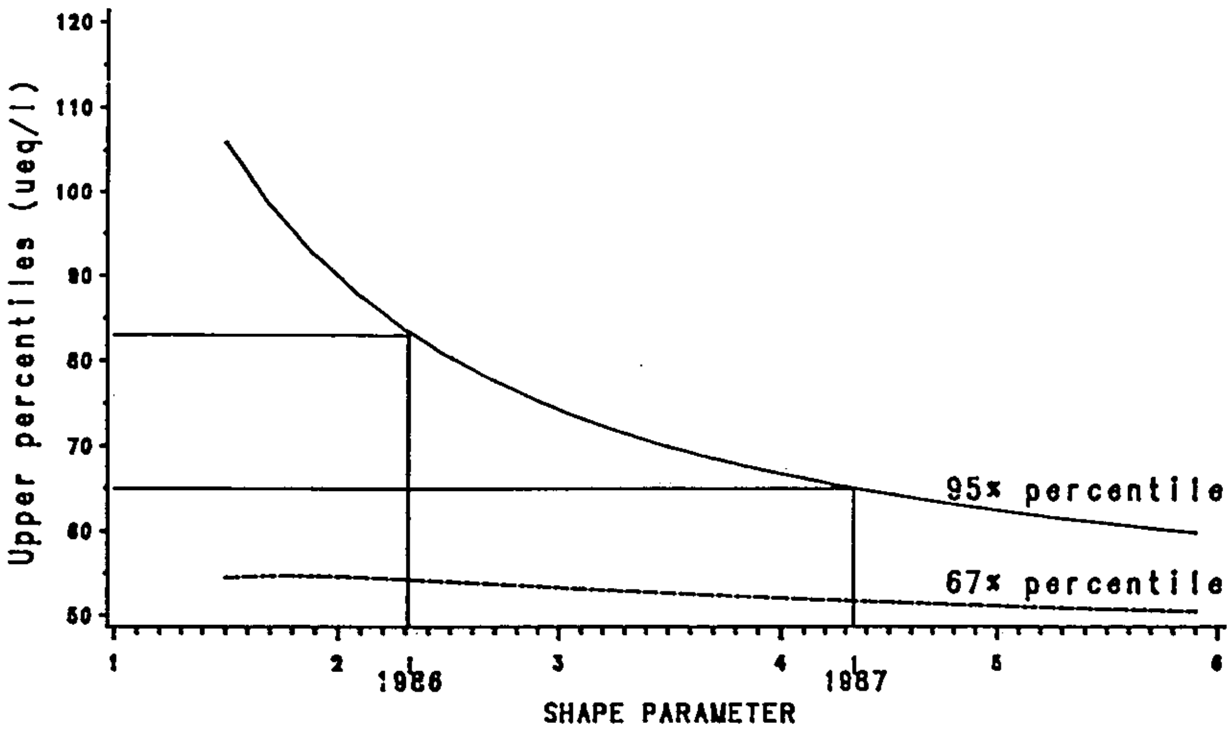
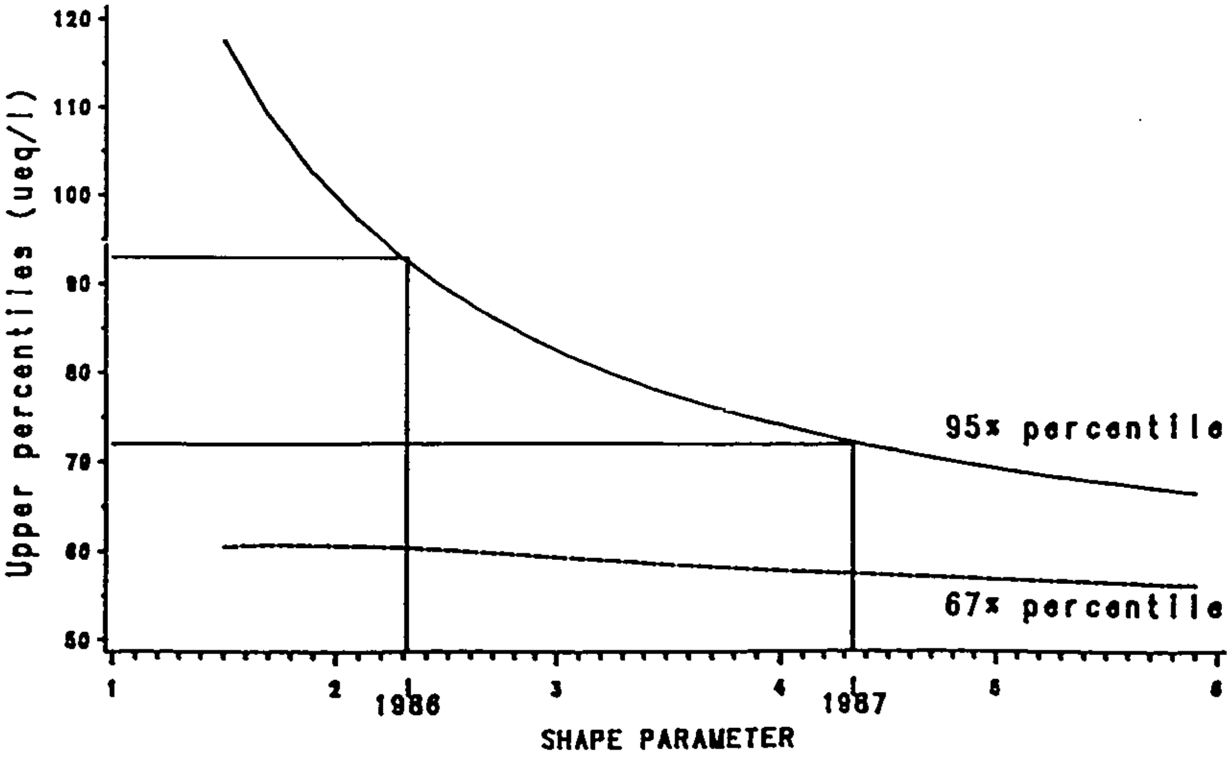


Figure 5.



Sensitivity of upper percentile to the shape parameter value - 1986

YEAR=1986



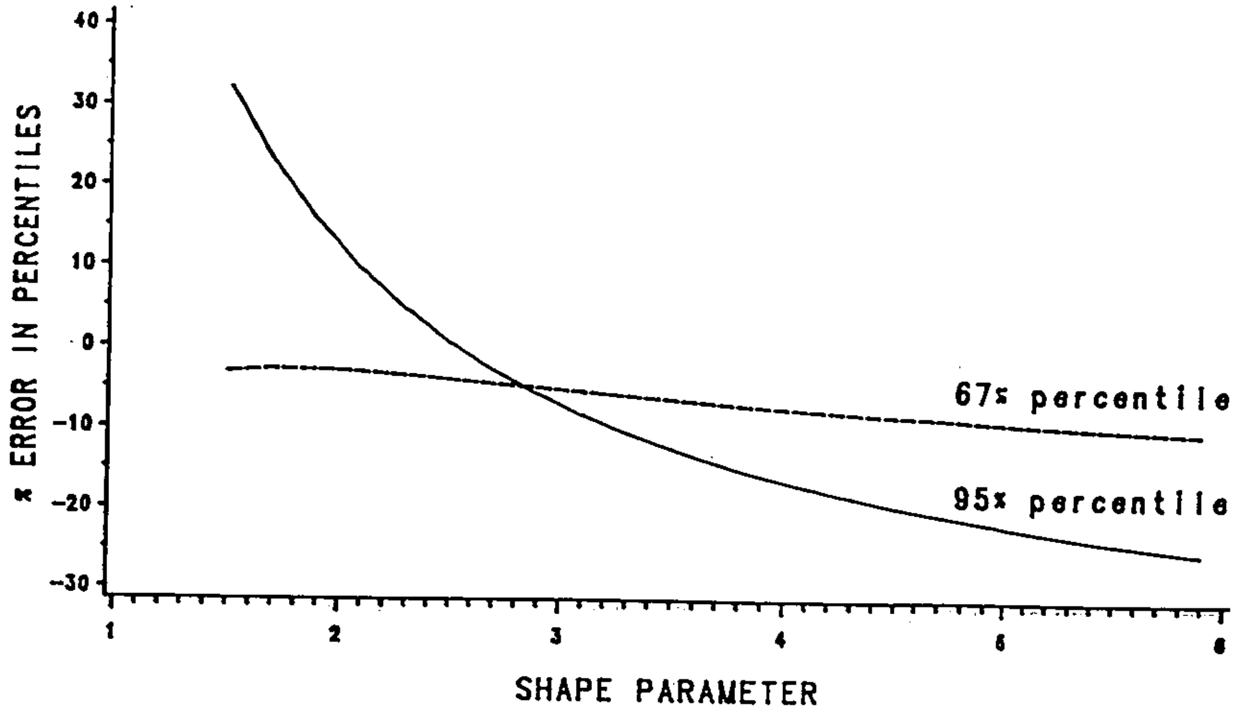
Sensitivity of upper percentile to the shape parameter value - 1987

YEAR=1987

Figure 6.

Plot showing effect of shape on errors in the percentiles for 1986, assuming that the observed percentiles are correct

YEAR=1986



Plot showing effect of shape on errors in the percentiles for 1987, assuming that the observed percentiles are correct

YEAR=1987

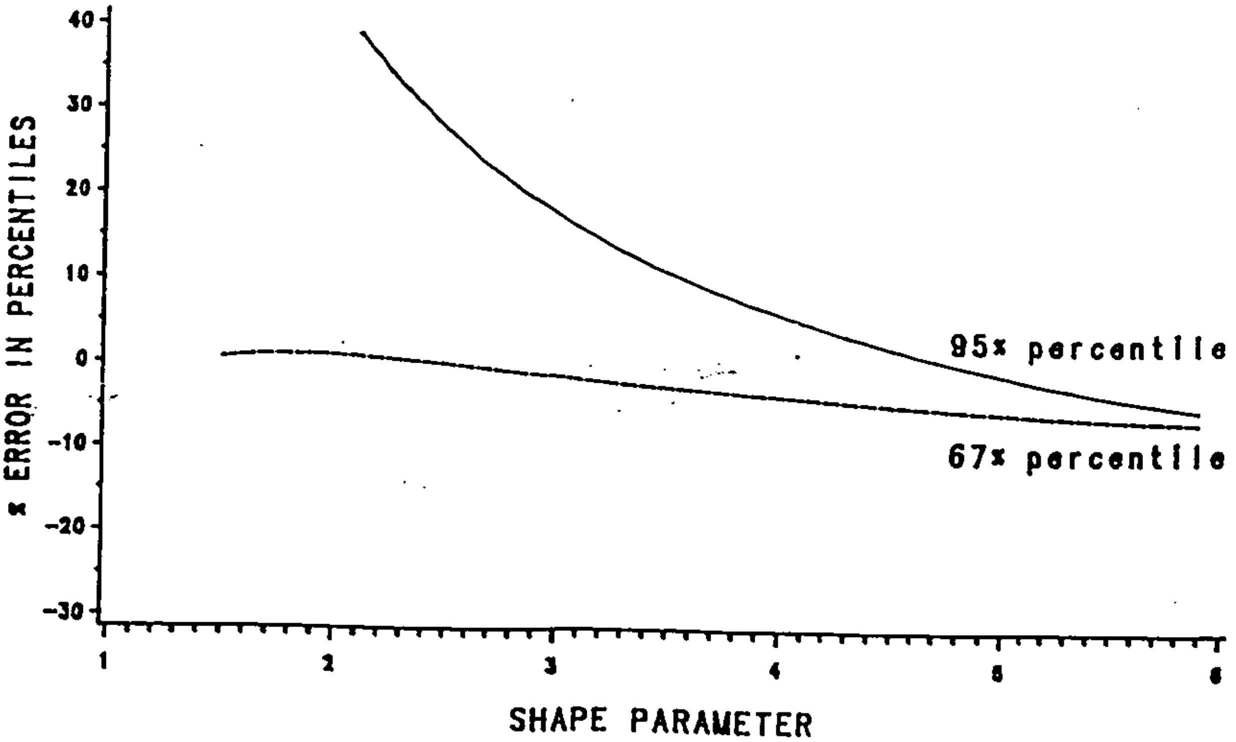
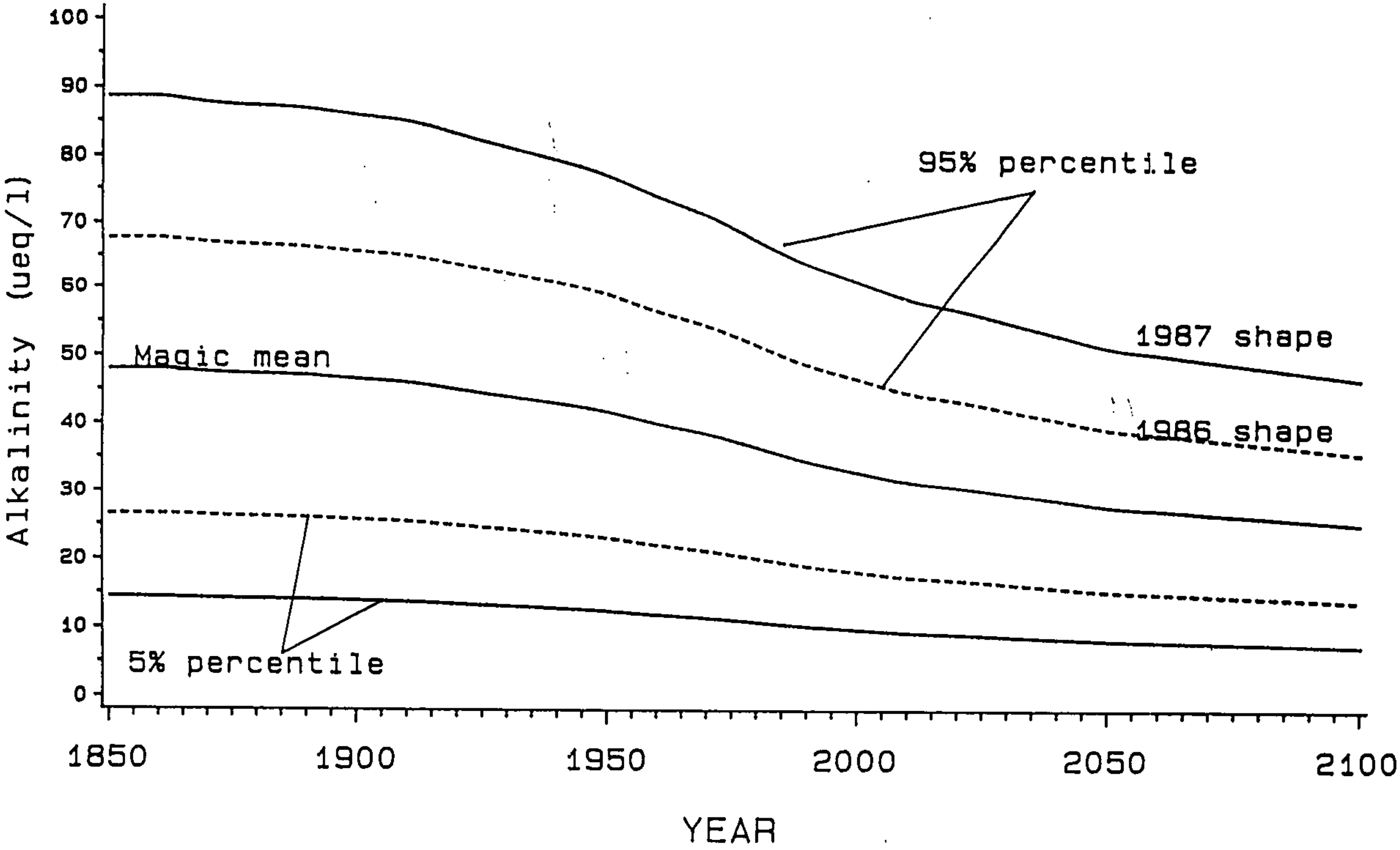


Figure 7.

Predicted means from MAGIC with estimated
95% and 5% percentiles



4.2 Towards Predicting Changes Through Storm Events in the Future

Towards predicting future episodic changes in stream chemistry.

Alice Robson, Alan Jenkins and Colin Neal.

Institute of Hydrology, Wallingford, Oxon, OX10 8BB, UK.

ABSTRACT

Short term stream chemistry response in a small stream in upland Wales is characterised by applying a mixing approach whereby the flow is assumed to be a mix of water from two distinct sources. Acidic water from the upper soil horizons and well buffered water from deeper 'groundwater' sources are used to represent the two endmembers and a chemical hydrograph separation technique is used to estimate the mean proportions of mix. A long term simulation model, the Model of Acidification of Groundwater In Catchments (MAGIC) is calibrated in its two layer mode to these two endmember chemistries. The model produces a good fit to observed present day stream, soil and baseflow chemistry. Future predictions of changes in endmember chemistry are made so as to enable future episodic response to be modelled. Under a 60 percent sulphate deposition scenario the model predicts a lowering of hydrogen ion concentrations associated with high flows and even a marginal recovery in baseflow pH.

INTRODUCTION

An assessment of the impact of surface water acidification on ecosystems requires an understanding of changes in stream chemistry over two timescales. That is, the long term build up of chronic acidity over periods of years and the short term acute changes associated with storm events. These short term acidic pulses are superimposed on long term trends and reconciliation of the two timescales is difficult. Hydrochemical models have been developed to simulate either long term changes in mean concentrations of water quality variables (MAGIC;Cosby et al. 1985a: RAINS;Kamari et al. 1984), or have focused on short term hydrologically driven responses (ILWAS;Chen et al. 1984: TRICKLEDOWN;Schnoor et al. 1984: BIRKENES;Christophersen et al. 1982). None of these models have proved sufficiently robust to work across the two timescales.

The link between long term build up of acidity and the extinction of fish populations in many surface water ecosystems is now well documented (Haines, 1986). It is also established that the survival of fish in upland streams is dependant not just on mean stream pH but the duration and severity of acid episodes (Turnpenny et al. 1987). Little is known, on the other hand, about the link between mean acidity and extreme values during episodes. A long term decrease in mean pH could theoretically be accompanied by two alternative episodic responses; both baseflow and peakflow waters show a corresponding drop in pH or, baseflow waters remain well buffered but the severity of the acid pulses at peak flow increases. To distinguish between these possibilities it is necessary to identify the mechanisms of flow generation and the source areas of the flow components comprising the flows at all discharge levels.

In this paper the link between long term and episodic response is examined through the development of a technique for modelling the changes important to short term stream water quality variations under continued acid deposition. This involves, (1) a mixing model approach to identify simple flow pathways and components of stream flow (endmembers), (2) a two layer version of MAGIC calibrated to present day endmember chemistry and used to predict the changes which will occur in the endmembers under acid deposition, and, (3) an assessment of future short term water quality variations using the predicted endmembers. The technique is applied to the Afon Gwy a small, moorland catchment at Plynlimon in mid-Wales.

THE STUDY SITE

The Afon Gwy catchment forms part of the headwaters of the river Wye. The geology consists of lower Palaeozoic mudstones, shales and grits with locally derived glacial and postglacial drift. Soil types include peats, brown earths, stagnogleys and stagnopodzols. The vegetation is acid grassland dominated by Nardus, Festuca and Agrostis species. Mean annual rainfall and runoff for 1983 - 1984, 1984 -1985 was 2385 and 2111 mm/year, respectively. Average rainfall, stream water and soil water chemistry is shown in Table 1 together with the stream water composition at baseflow, that is, from samples taken during very low flow periods when the water is assumed to originate from deeper, 'groundwater' sources and so is characterised by low acidity and high alkalinity.

THE MIXING APPROACH

The essence of the mixing approach is the concept that stream waters are generated by the mixing of chemically distinct water types (Christophersen et al., 1990; Hooper et al., 1990; Neal et al., 1990). The mean composition of each of these components (endmembers) is assumed to change only slowly and at most from year to year. The rapid chemical changes seen in the stream, in response to rainfall, are assumed to be the result of mixing varying proportions of the endmembers. The quantity or proportion of each endmember contributing to the stream is determined by changing catchment flowpaths as the storm intensifies and recedes.

The choice of characterisic endmembers for the catchment is based on the ion-flow relationships in the stream. Chemical response of the Gwy is typical of many British upland streams in that during high flow the pH falls, aluminium levels rise and base cation concentrations decrease (UKAWRG, 1988). At times of low flow the stream waters are well-buffered, of high pH and relatively rich in base cations. A simple interpretation of this can be made. During peak flows, when the water table is high, waters move through the acidic upper soil layers to the stream. During low flow, waters originate from deeper sources where weathering reactions with the bedrock occur (Neal et al., 1985). Only two components of flow are identified at this stage but this helps to limit the complexity of the modelling work and fits with observed variations (Neal et al., 1990; Robson and Neal, 1990; Kleissen et al., 1990). The natural choice is to take soil water as one endmember and a well buffered deep water (ground water) as the other. The rationale for the choice of these two components is discussed further in Neal et al. (1990). The soil water endmember chemistry is derived from L, O, E and B horizon soil water chemistry . The deep water component, however, has not yet been sampled directly and the composition of these waters is inferred from the chemistry of the baseflow waters seen in the stream.

To calibrate the MAGIC model, a mean annual proportion of mix between the two endmembers is required to fix the flow pathways in the model. This proportion of mix can be calculated by using a conservative chemical characteristic as a tracer such as the acid neutralising capacity (ANC). ANC is defined by:-

ANC = Sum "strong" base cations - Sum "strong acid anions"

and is determined from the chemical composition of the water, all terms being expressed in μEq/l. The ANC distinguishes well betwen the two chosen endmember water types and it is unaffected by CO_2 degassing. Extensive details of the use of ANC in hydrograph separation are given in Neal et al., (1990) and Robson and Neal, (1990). Calculated ANC for stream water, soil water and baseflow water is given in Table 2.

Since ANC is conserved during mixing the average proportion of soil water can be derived;

$$\text{Average proportion soil water} = \frac{\text{ANC deep water-ANC stream}}{\text{ANC deep water-ANC soil water}}$$

Using this relationship, the calculated mean flow-weighted proportion of soil water for the Gwy was approximately 0.48.

Clearly, a number of limitations exist in the use of this mixing approach and it is necessary to assume that, (1) streamflow is generated by water from two sources, (2) the direct contribution of rain to the stream is negligible, (3) a single soil endmember is representative of the upper soils even though the soils show heterogeneity both spatially and with depth, (4) the deep water component has uniform composition, and, (5) the chemistry of the endmembers remains constant during a storm.

Given the limitations of these assumptions and analytical error in the chemical measurements, a perfect match between the modelled and the observed chemical species in the stream is unlikely. The ANC gives a good indication of the overall composition of a water sample and whereas some deviations in individual determinands are acceptable, it is important that the modelled ANC is accurate.

THE MAGIC MODEL AND APPLICATION TO THE GWY

The MAGIC model uses equilibrium equations to describe soil processes and mass balance equations to describe catchment input-output relationships. Detailed descriptions of the conceptual basis of tha model and the equations on which it is based are documented elsewhere (Cosby et al.,1985 a,b). In this application a two layer version of MAGIC is used (Jenkins and Cosby, 1989) enabling the simulation of two chemically distinct waters. Here, the waters are chosen to correspond with the flow components identified from the mixing considerations outlined earlier. That is, the top layer represents the lumped L, O, E and B soil horizons while the bottom layer represents the C- horizon and deeper till layers. Similarly, the flow proportions included in the model are those suggested by the mixing approach. That is, all rain passes through the upper soils (top layer) and 42% of that percolate contributes directly into the stream whilst the remainder is routed via the deeper zones (bottom layer) to the stream (Figure 1.).

Concentrations of chloride and sulphate in the rainfall and stream were adjusted for occult and dry deposition of sea-salts and anthropogenic sulphur compounds. Between 1844 and 1984 the modelled rainfall inputs were varied according to the deposition sequence outlined by the Warren Springs laboratory (1983).

The two layers in the model were conceptualised such that different reaction mechanisms dominate each layer since they generate waters with distinct chemistries. The water from the upper soils is acidic and aluminium rich suggesting that ionic exchange mechanisms are the most important influence on soil water chemistry. Water from the deeper sources is rich in base cations indicating that it comes from a high weathering zone. In this application, therefore, it is assumed that ion-exchange occurs in only the top layer and that the ion exchange capacity of the lower soils and till layers is small enough to be neglected. On the other hand, weathering is assumed to take place predominantly in the deeper layers. A source of base cations was found to be essential in the upper soils, however, in order to fit the observed ANC. This may be attributed to biological activity or cycling. Only weathering inputs for calcium and magnesium were necessary in the top layer. Observations of throughfall chemistry support this: concentrations of calcium and magnesium are 15 and 18 μmol/l, respectively in throughfall compared with 4 and 10 μmol/l, respectively, in rainfall, allowing for evaporation: for sodium the throughfall concentration (94 μmol/l) is little different from rainfall (85 μmol/l) and so no extra input to the top layer is necessary.

The soil characteristics used in the model are given in Table 3. The depth of the upper soil (0.4m) corresponds to the average combined depth of the L, O, E and B horizons. An average depth of 1m is assumed for the remainder. The bottom layer is denser and of lower porosity. The partial pressure of carbon dioxide is assumed to be 30 times atmospheric for both layers (Neal and Whitehead, 1988). For the stream the pCO_2 was set to 3 times atmospheric pressure (Neal, 1988 a,b). The organic acid concentration in the two layers was calculated from the average observed DOC concentration assuming 9 carbon atoms per molecule. Dissociation constants were specified according to previously used values for similar sites in Scotland and are the same for each layer.

MODEL CALIBRATION

The model was calibrated to the chemistry of the stream water, the soil water and the deeper groundwater by adjusting weathering rates, uptake rates and the initial soil base saturation. The optimised values for the adjustable parameters are given in Table 4. Sulphate adsorption in the model is described by a Langmuir isotherm which has two parameters (Hornberger, 1986). These are calibrated on the assumption of a present day steady state condition with respect to sulphate input and output. Unique isotherms were calibrated for each layer under the assumption that the bottom layer has a greater capacity to adsorb sulphate than the top layer.

Nitrate and ammonia were modelled by calibrating catchment uptake to match the difference between inputs and outputs. Nitrate input was further increased to account for the high nitrate levels in the top layer resulting from a combination of dry deposition and biologically activated nitrogen mineralization.

RESULTS

The results from the calibrated model, shown in table 5, demonstrate a good agreement with stream chemistry although soil and groundwater chemistry are less well simulated. Given the variability of soil water chemistry with depth and aerially across the catchment, however, it is encouraging that each of the determinands falls within the measured range of soil water chemistry. The chloride concentration in the bottom layer is lower than observed in stream baseflow and is a consequence of the assumption of chloride conservativity in the model: this forces the chloride concentration in all of the model compartments to be constant. As a result of the low chloride level, simulated base cation concentrations are also lower than observed in the bottom soil layer.

Simulated stream ANC lies within 1 ueq/l of the value calculated from observed stream chemistry and the simulated ANC in the top soil layer is well within the observed range for soil waters. The simulated ANC for the lower box, however, is slightly higher than for stream baseflow water, probably because at baseflow the stream water includes a small soil water component. In this case the "true" groundwater endmember may be characterised by a higher ANC than that of stream baseflow.

The time trends of reconstructed soil, ground and stream water chemistry from 140 years ago, that is pre-acidification, up to the present day, are shown in figure 2. The pH (Figure 2a) of the stream falls rapidly as deposition increases in the 1950's and levels out in the 1980's in response to decreases in atmospheric deposition in recent years. The pH of the two endmembers changes similarly, but to a lesser degree, through the same period as a result of the higher partial pressure of carbon dioxide in the two layers. As a consequence of CO_2 degassing, the pH of the stream is not always bounded by the two endmember pH values, espescially at higher pH levels.

Sulphate concentrations in all three model compartments increase through time (Figure 2b) in line with the assumed increase in sulphate deposition. The variation in response between the endmembers reflects the sulphate adsorption constants chosen in the calibration whilst the stream concentration represents a direct mix of the two components. Calcium, magnesium (Figure 2c, d) and aluminium concentrations also increase in response to sulphate input whilst soil exchangeable bases (top layer) decrease (Figure 3). Exchangeable magnesium decreases most quickly, relative to the other exchangeable cations. This is a direct consequence of the Gaines - Thomas expression used to model ion exchange, whereby the most abundant ion is preferentially leached.

The model has also been used to estimate changes in stream, soil and deep water components into the future under two sulphate deposition reduction scenarios (Figure 2a-d); a reduction to 30% and 60% of present day levels by the year 2000 and held at a constant level thereafter.

Stream water pH improves in response to increasing pH in both soil layers and the greatest recovery occurs in response to the larger deposition reductions. Sulphate concentration in both endmembers decreases and the model predicts a reversal in sulphate concentration gradient between the upper and lower soils. Prior to the 1970's, modelled groundwater sulphate concentrations are lower than in the upper soils. In future years, as a consequence of the chosen sulphate adsorption constants sulphate concentration in groundwater takes longer to decline than the upper soil water. By the year 2100 the sulphate concentrations have equilibriated with the lowered input and there is no longer a variation between the layers.

Simulated aluminium concentrations fall, in line with sulphate reduction. The results give only a broad indication of likely trends since the cubic equilibrium conditions assumed in MAGIC may well not hold during episodes (Neal et al, 1989); this does not affect hydrogen ions or other base cations to any significant degree. The response of the base cation concentrations is more complex (Figure 2c, d). As sulphate input is reduced, fewer cations are exchanged from the soils and so cation concentrations decrease in both endmembers. The decrease is rapid for the first 10-20 years and then slows, directly reflecting the mobile anion input to the system. Under a 60% deposition reduction, some long term recovery is predicted but a 30% reduction is insufficient for any recovery in the model. In terms of the catchment soils (upper box), a 60% reduction in sulphate input produces a significant improvement in cation exchange capacity (Figure 3).

To assess the performance of the two layer model, a basic one-layer version of MAGIC was also calibrated to the Gwy catchment. Where possible identical values of the fixed parameters were chosen. The parameters for the aggregated soil layer were lumped according to standard practice (Jenkins and Cosby, 1989). As expected, the results show a broadly similar pattern of behaviour. The one-layer stream water chemistry falls well within the range spanned by the predicted endmembers from the two-layer model (Figure 4). However, the optimised one layer model estimates a significantly lower weathering rate than was found for the two layer version. As a consequence, the simulated background and predicted future stream chemistries from the one layer model are more acidic and the one layer model is less responsive to the variations in atmospheric deposition. The major differences between the approaches result from the inclusion of an additional body of well buffered water in the two-layer model.

DISCUSSION

During the next 140 years the predicted changes in endmember chemistry will produce a significant improvement, relative to present conditions, in the chemistry of the streamwater, especially at high flows. For example, the model predicts that whereas the difference in cation concentrations at high and low flows will remain the same, relative to each other, the predicted recovery in the upper soil water chemistry and the assumed dominant contribution from that source at high flows will lead to a decrease in the peak concentrations of hydrogen and aluminium. Concentration of both hydrogen and aluminium at baseflow is currently low and this situation will continue.

The incorporation of short term stream chemistry dynamics into models of long term response to changing acid deposition has obvious benefits in determining critical loads to ecosystems. At present, critical load estimation is based only on predictions of mean chemistry (Nilsson and Grennfelt, 1988) and yet stream biota can be seriously affected by short term acid pulses. This is not neccesarily a result of the peak levels of toxic species reached during an event, but may also be a function of the duration of the toxic conditions. If the critical load is to accurately represent the point at which biological life becomes seriously at risk then it must account for these dynamics. Through the technique developed here short term water quality responses can be quantified.

The two layer MAGIC model predicts enhanced recovery relative to the one layer model. Further work is required to see if this result holds in general as present day regional assessments may be too pessemistic.

CONCLUSIONS

1. A simple 2-layer model structure gives a good fit to observed endmember and stream water chemistry.

2. The model predicts that the chemistry of the endmembers has changed historically. Both soil waters and deep waters have acidified and the cation exchange capacity of the soils shows a large decrease.

3. Under reduced deposition the model predicts that the most significant changes in stream chemistry will occur at peak flow with greatly reduced levels of acidity and aluminium. Baseflow chemistry will also improve slightly. Recovery is greatly enhanced by a 60% reduction as opposed to a 30% reduction.

4. The approach may be expanded to model dynamic storm response using mixing principles and can provide valuable information for establishing an episodic basis for critical load estimation.

5. Greater recovery from reduced emission strategies are suggested with the two layer model in comparison with the one layer MAGIC model.

REFERENCES

Chen, C.W., Gherini, S.A., Dean, J.D., Hudson, R.J.M. and Goldstein, R.A. (1984) Development and calibration of the integrated lake-watershed acidification study model. In:Schnoor, J.L. (ed.), Modelling of Total Acid Precipitation Impacts, Vol. 9, Butterworth, Boston, Mass., 175-203.

Christophersen, N., Seip, H.M., and Wright, R.F., 1982. A model for streamwater chemistry at Birkenes, Norway. Water Resour. Res., 18, 977-996.

Christophersen, N., Neal, C., and Hooper, R.P., 1990. Modelling streamwater chemistry as a mixture of soil water endmembers, a step towards second generation acidification models. Journal of Hydrology. Special issue: transfer of elements through the hydrological cycle. 307-321.

Cosby, B.J., Wright, R.F., Hornberger, G.M., and Galloway, J.N., 1985a. Modelling the effects of acidic deposition: assessment of a lumped-parameter model of soil water and stream water chemistry. Water Resour. Res., 21, 51-63.

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

Haines, T.A. 1986. Fish population trends in response to surface water acidification. In, Acid deposition, Long-term trends, National Academy Press, Washington, D.C., 1986, pp 300-334.

Hooper, R.P., Christophersen, N., and Peters, J., 1990. Endmember mixing analysis (EMMA): an analytical framework for the interpretation of streamwater chemistry. J of Hydrology. Special issue: transfer of elements through the hydrological cycle. 321-345

Hornberger, G.M., Cosby, B.J. and Galloway, J.N. (1986) Modeling the effects of acid deposition: uncertainty analysis and spatial variability in the estimation of long-term sulfate dynamics in a region. Water Resources Res.22:1293-1302.

Jenkins, A. and Cosby, B.J. 1989,Modelling surface water acidification using one and two soil layers and simple flow routing.Ch 19 In:Kamari et al.,Regional acidification models, Springer-Verlag Berlin Heidelberg.

Kamari, J., Posch, M., and Kauppi, L. (1984) Development of a model for analyzing surface water acidification on a regional scale:Application to individual basins in southern Finland. NHP 10,151-170.

Kleissen, F.M., Wheater H.S., Beck M.B. and Harriman R. (1990). Conservative mixing of water sources: analysis of the behaviour of the Allt a'Mharcaidh catchment. J of Hydrology. Special Issue:transfer of elements through the hydrological cycle.365-

375.

Neal, C., Musgrove, T., and Whitehead, P.G. (1989) Predicting the long-term variations in stream and lake inorganic aluminium concentrations for acidic and acid sensitive catchments. Science of the total Env. 80 205-211.

Neal, C., 1988a. Determination of Dissolved CO_2 in Upland Streamwater. J. Hydrol. 99, 127-142.

Neal, C., 1988b. pCO_2 variations in streamwaters draining an acidic and acid sensitive spruce forested catchment in mid-Wales. Sci. of the Total Environ., 76, 279-283.

Neal, C., Reynolds, B., Stevens, P. and Hornung, M., 1989. Hydrogeochemical controls for inorganic aluminium in acidic stream and soil waters at two upland catchments in Wales. J. Hydrol., 106, 155-175.

Neal, C., Robson, A.J., and Smith C.J.,in press. Acid Neutralisation Capacity variations for Hafren forest streams: Inferences for hydrological processes. Journal of Hydrology

Neal C., and Whitehead P.G., 1988.The role of CO_2 long term stream chemistry acidification processes: a modelling viewpoint. Hydrolgical sciences journal,33,1.

Nilsson, J. and Grennfelt, P.(eds) 1988 Critical loads for Sulphur and Nitrogen - Nordic council of ministers. Miljorapport.1988:15 Copenhagen, 418pp.

Reynolds, B., Neal, C., Hornung, M., Hughes, S., and Stevens, P.A., 1988. Impact of afforestation on the soil solution chemistry of stagnopodzols in mid-Wales. Water, Air and Soil Poll., 38, 55-70.

Reynolds, B., Hornung, M. and Hughes, S.(1989) Chemistry of streams draining grassland and forest catchments at Plynlimon, mid-Wales. Hydrological Sciences Journal.34:6 667-685

Robson, A.J. and Neal, C.(1990). Hydrograph separation using chemical techniques: an application to catchments in Mid-Wales. Journal of Hydrology. Special issue: transfer of elements through the hydrological cycle. 345-365.

Schnoor, J.L., Palmer Jr, W.D. and Glass, G.E. 1984. Modelling impacts of acid precipitation for northeastern Minnesota In: J.L. Schnoor (ed.) Modelling of Total Acid Precipitation Impacts, Vol. 9, Butterworth, Boston,Mass., 155-173.

Turnpenny, A.W.H., Sadler, K., Aston, R.J., Milner, A.G.P. and Lyman, S.1987. The fish population of some streams in Wales and Northern England in relation to acidity and associated factors. J. Fish. Biol. 31, 415-434.

Warren Spring Laboratory.1983 Acid deposition in the United

Kingdom. Warren spring laboratory, Stevenage, U.K.

United Kingdom Acid Waters Review Group. Second report. 1988. Acidity in United Kingdom fresh waters.H.M.S.O. London.

Table 1.

Rainfall, stream water, soil water and baseflow water chemistry. Units are μEq/l except Al and Si (μmol/l) and pH.

	Rainfall	Stream	Baseflow	Soils		
				Oh	Eag	Bs
Ca	8	36	58	14	20	14
Mg	10	54	70	40	44	40
Na	85	143	166	100	187	173
K	2	3	2	8	4	4
NH_4	17	<5	<5	<5	<5	<5
Si	<2	35	54	18	42	36
SO_4	42	72	74	68	87	71
Cl	106	155	170	124	209	184
NO_3	12	15	4	29	39	28
H	21	13	1	77	55	44
pH	4.7	4.9	6.3	4.1	4.3	4.4
HCO_3	<1	35	27	–	–	–
Al	<2	3	2	10	18	15

Table 2.

Stream water, soil water and baseflow Acid Neutralisation Capacity. Units are µEq/l.

	Stream	Soil			Baseflow
		Oh	Eag	Bs	
Sum cations	236	162	255	231	295
Sum anions	242	221	335	283	248
ANC	-6	-59	-80	-52	47

Table 3.

Soil characteristics used in the two-layer MAGIC model

	Units	Top Layer	Bottom Layer
depth	m	0.4	1
porosity	frac	0.55	0.35
bulk density	kg/m^3	1060	1460
CEC	meq/kg	70	0.1
Organics	µmol/l	56	10
Temperature	°C	7.6	7.6
PCO_2	atm	0.009	0.009
$\log_{10}(K_{Al(OH)_3})$		7.8	8.6

Table 4.

Calibrated parameters for the two-layer MAGIC model

		Top Layer	Bottom Layer
SO_4 Halfsat	µEq/l	80	5
SO_4 MAXcap	µEq/l	2	9
pk1 (organics)		4	4

Weathering/Uptakes	Top Layer	Bottom Layer
NH_4	-92	0
NO_3	0	-88
Ca	2	43
Mg	14	28
Na	0	36
K	0	0

Selectivity coefficients

Ca	2.7
Mg	3.27
Na	-0.65
K	-4.7

Initial base saturation: 35.0

Table 5.

Modelled stream and endmember chemistry. Bracketed values are the field measurements. A range is given for the O-B horizons in the soil.Units are μEq/l except pH.

	Stream		Top Layer		Bottom Layer	
Ca	36	(36)	16	(14-20)	55	(58)
Mg	54	(54)	41	(40-44)	66	(72)
Na	143	(143)	126	(100-183)	159	(166)
K	3.2	(3)	3.2	(4-8)	3.3	(2)
NH_4	1.5	(<5)	1.5	(<5)	1.5	(<5)
SO_4	72	(72)	71.0	(68-87)	73	(74)
Cl	155	(155)	155	(124-209)	155	(170)
NO_3	16	(15)	29	(28-39)	3.5	(4)
H^+	18	(13)	60	(44-77)	3.6	(1)
pH	4.8	(4.8)	4.2	(4.1-4.4)	5.4	(6.3)
Al^{3+}	7	(9)	46	(28-55)	1.0	(5)
ANC	-5	(-6)	-69	(-52 - -80)	54	(47)

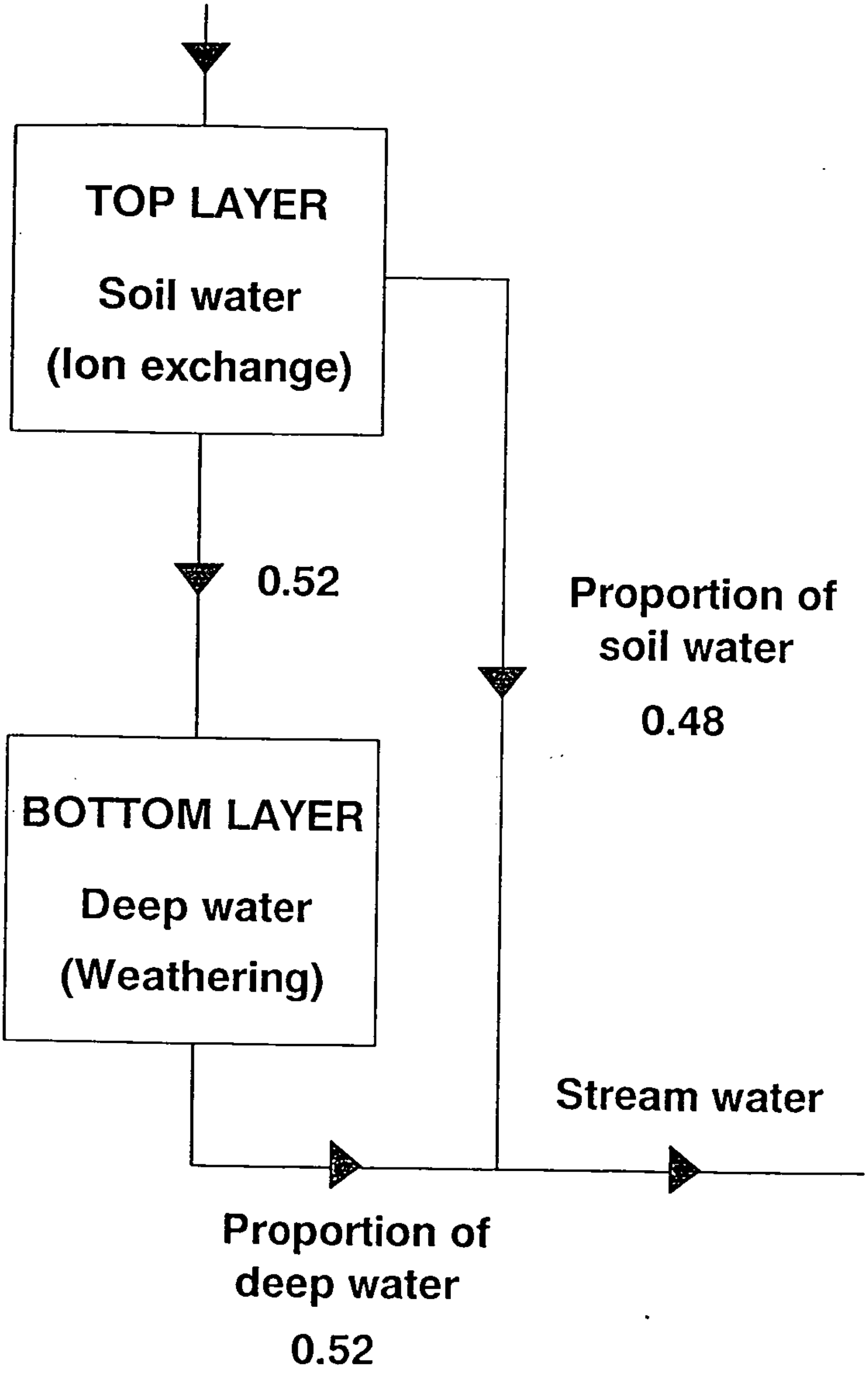
Figure Legends

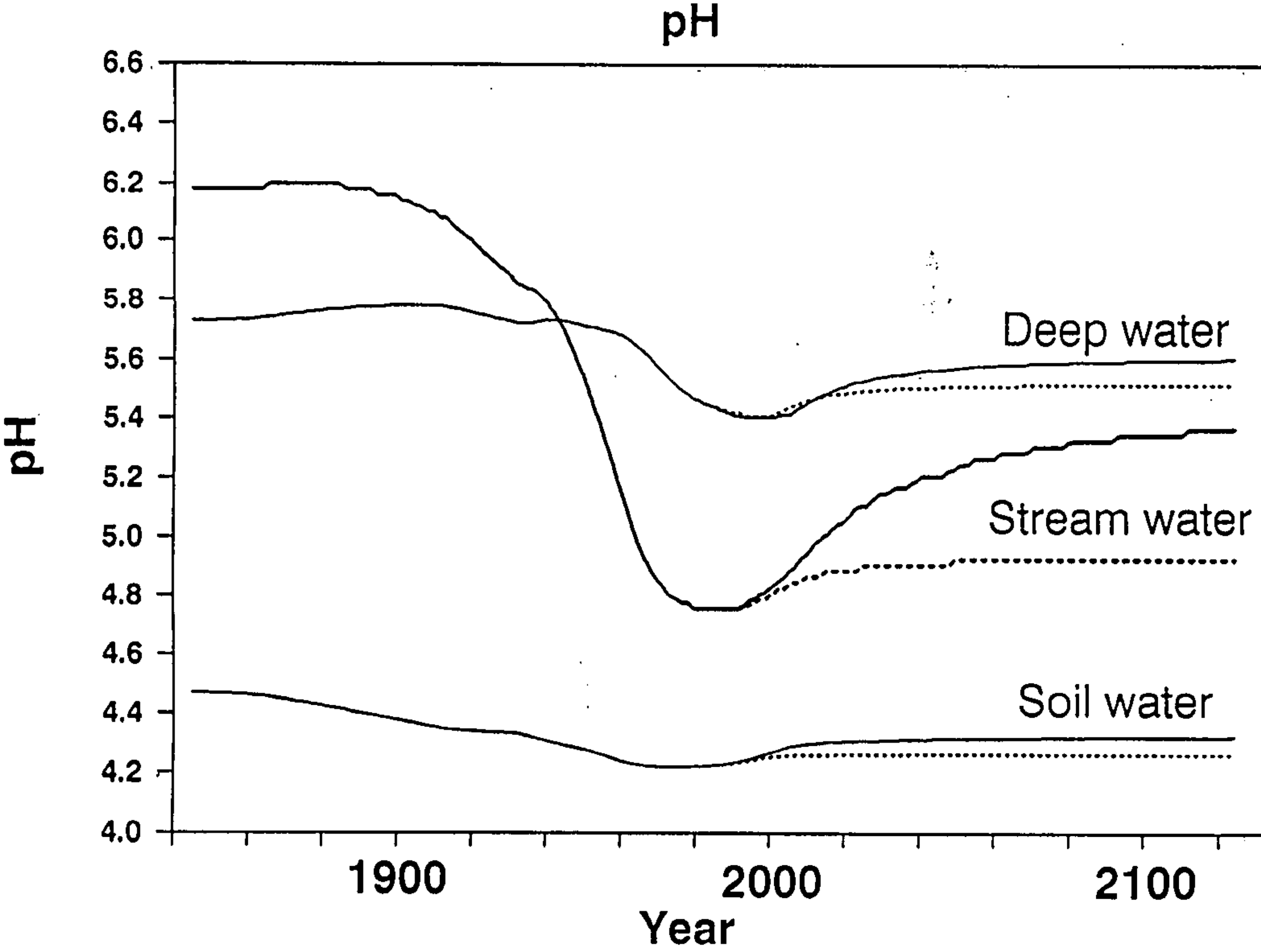
Figure 1. Flow routing for the two-layer MAGIC model.

Figure 2. Modelled stream and endmember chemistry; (a) pH, (b) sulphate, (c) magnesium, (d) calcium. For a, c and d solid lines show the predictions for 60% and the dotted lines for 30% reduction.

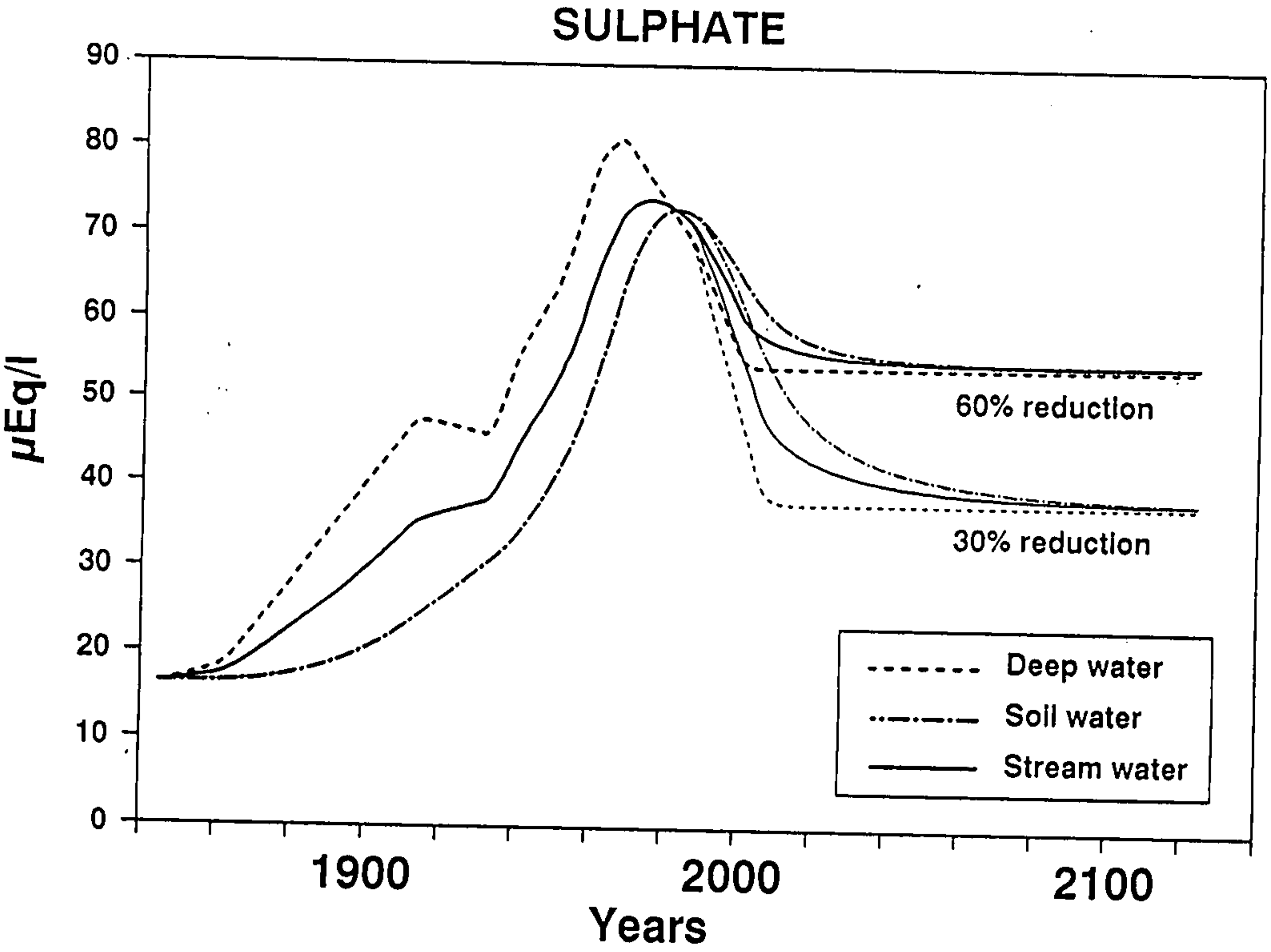
Figure 3. Simulated cation exchange capacity in the top soil layer.

Figure 4. Comparison of Acid Neutralisation Capacity for the one layer (line with markers) and two layer (no markers). Solid lines show the predictions for 60% reduction and dotted lines for 30% reduction.

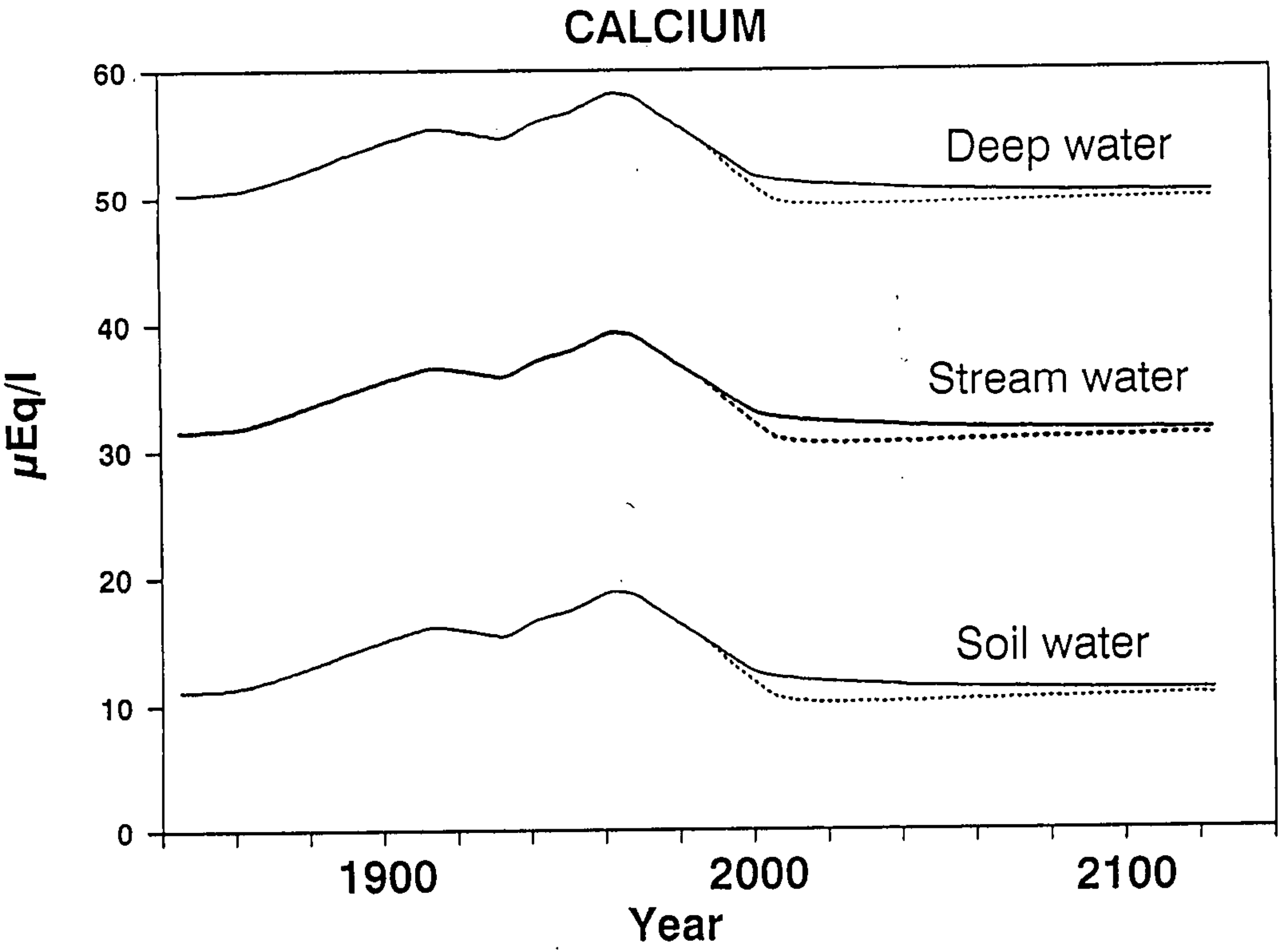

TOP LAYER
Soil water
(Ion exchange)
0.52
Proportion of soil water
0.48
BOTTOM LAYER
Deep water
(Weathering)
Stream water
Proportion of deep water
0.52


pH
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
pH
Deep water
Stream water
Soil water
1900
2000
2100
Year

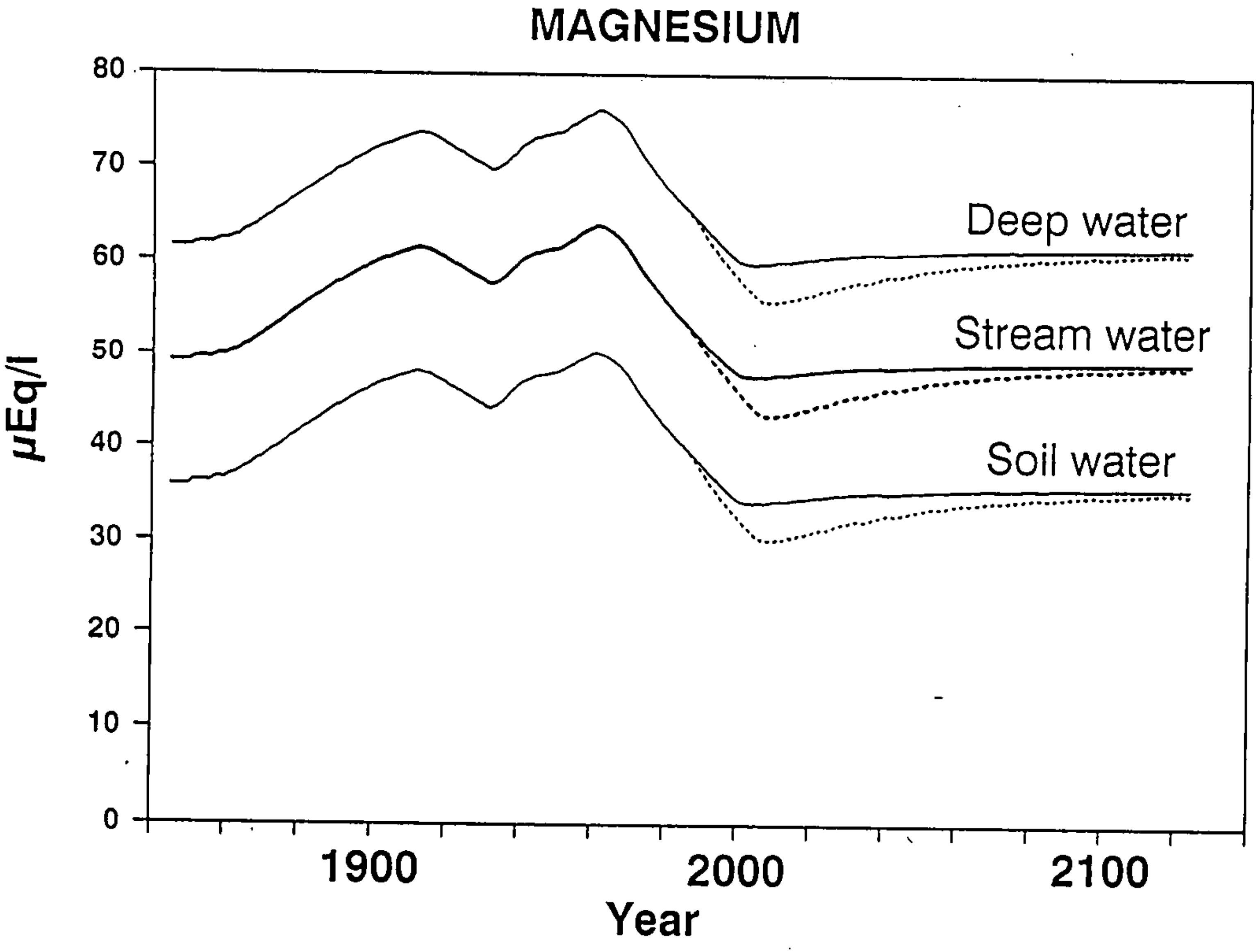
2b

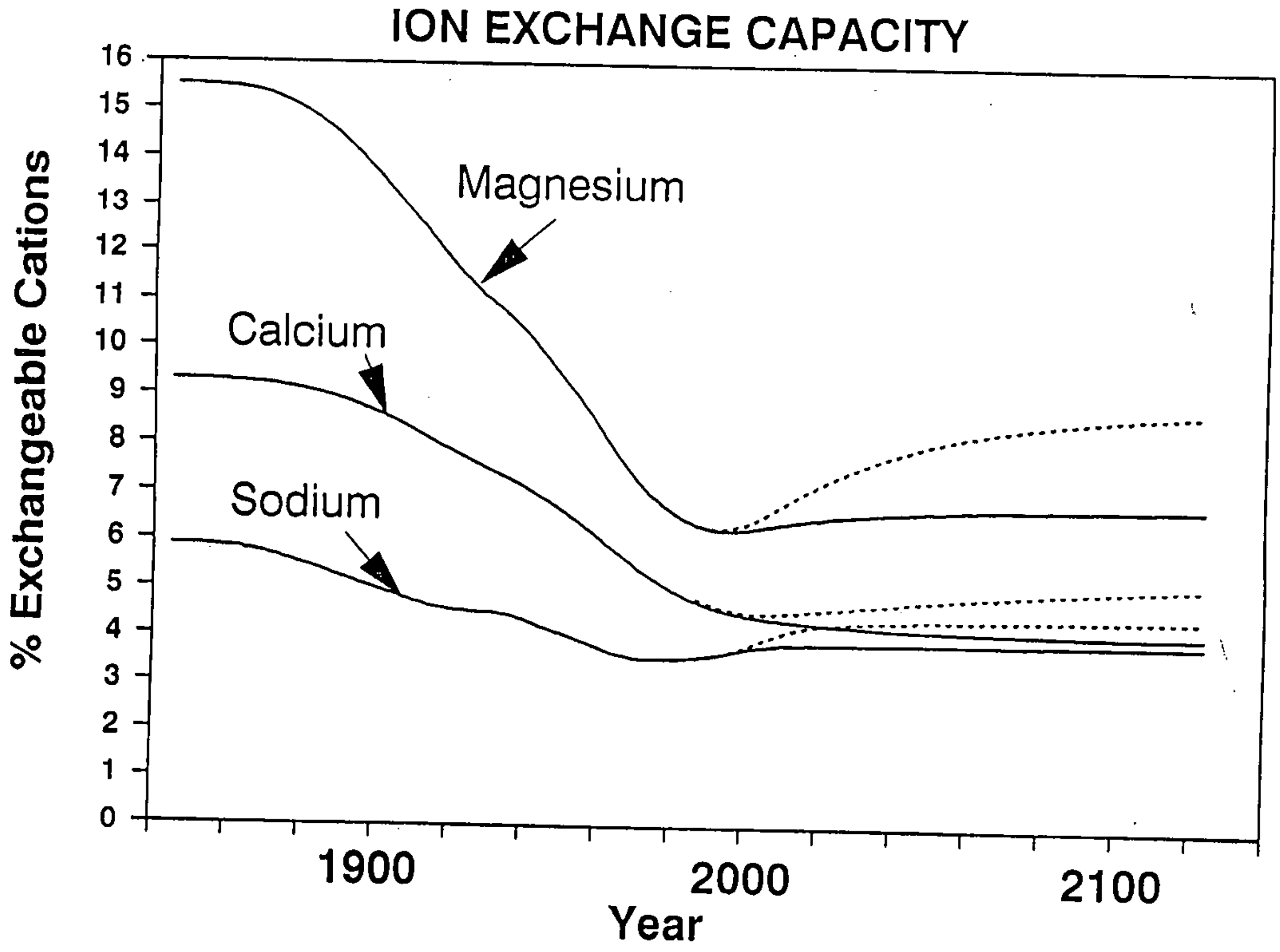

SULPHATE
μEq/l
0
10
20
30
40
50
60
70
80
90
1900
2000
2100
Years
60% reduction
30% reduction
Deep water
Soil water
Stream water

2c


CALCIUM
μEq/l
0
10
20
30
40
50
60
1900
2000
2100
Year
Deep water
Stream water
Soil water

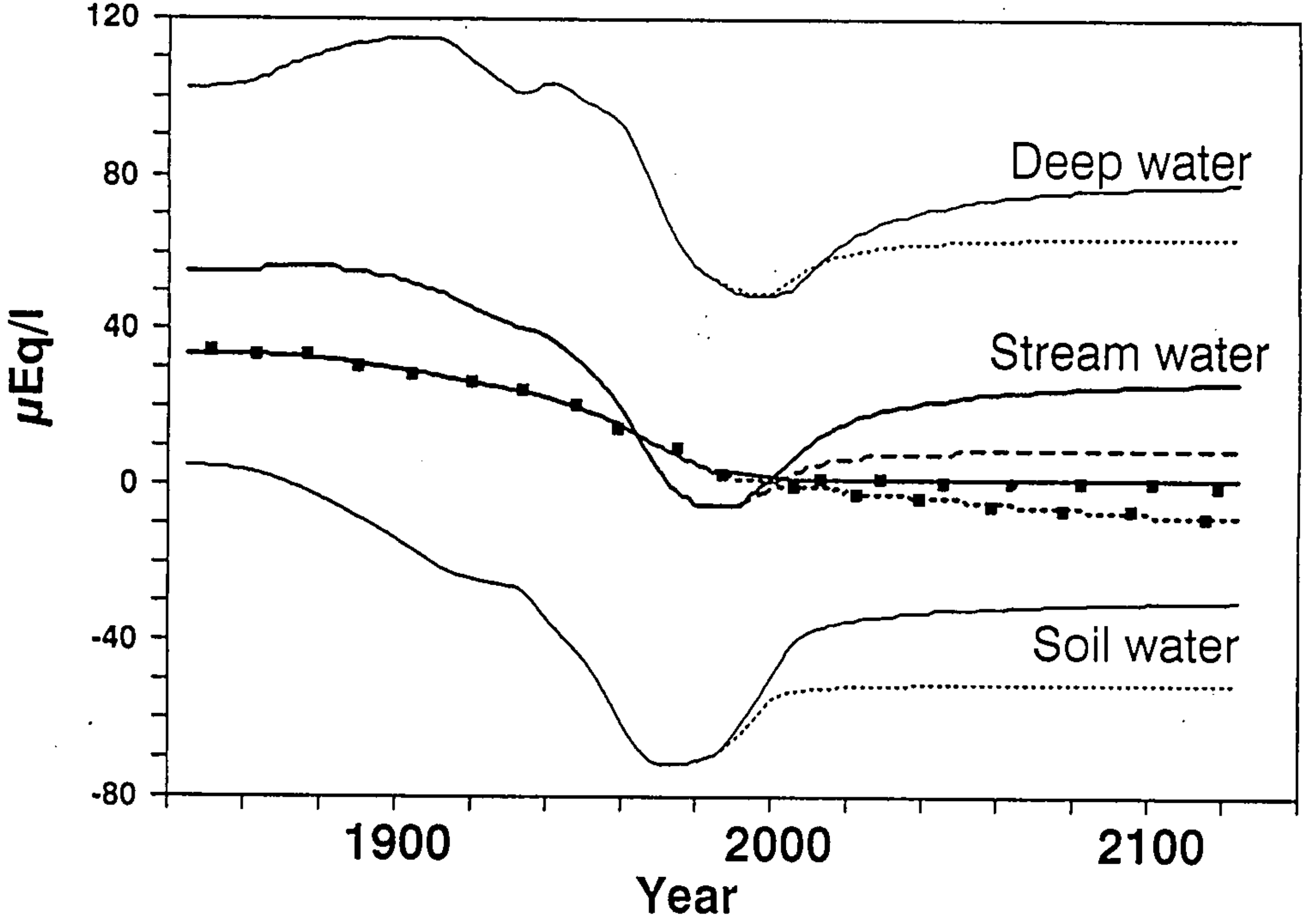
2d


MAGNESIUM
μEq/l
80
70
60
50
40
30
20
10
0
1900
2000
2100
Year
Deep water
Stream water
Soil water


ION EXCHANGE CAPACITY
% Exchangeable Cations
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
Magnesium
Calcium
Sodium
1900
2000
2100
Year

ACID NEUTRALISATION CAPACITY

COMPARISON OF ONE-LAYER AND TWO-LAYER MAGIC



5. REGIONAL HYDROCHEMICAL MODELLING AND REVERSIBILITY

5.1 Regional Analysis of Wales

Journal of Hydrology, 116 (1990) 403–416
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

[3]

A REGIONAL MODEL OF ACIDIFICATION IN WALES

A. JENKINS[1], P.G. WHITEHEAD[1], T.J. MUSGROVE[1] and B.J. COSBY[2]

[1]*Institute of Hydrology, Wallingford, OX10 8BB (U.K.)*
[2]*Department of Forestry and Environmental Studies, Duke University, Durham, NC 22706 (U.S.A.)*

ABSTRACT

Jenkins, A., Whitehead, P.G., Musgrove, T.J. and Cosby, B.J. 1990. A regional model of acidification in Wales. J. Hydrol., 116:403–416.

A regional assessment of streamwater quality in Wales is presented which reconstructs the historical trend for acidification and predicts the effect of several pollutant deposition reduction policies, using the model of acidification of ground water in catchments (MAGIC). The regional methodology used is a two-stage coupling of Monte Carlo simulations with a calibration procedure designed to produce a coarse fit to the joint distribution of the key streamwater quality variables. The regional model is based on data from the Welsh Water Authority Survey of 1983–1984 during which streams and lakes were sampled weekly for one year. The modelling results reveal a significant decline of water quality across the region since industrialization. The model indicates that 40% of the streams and lakes within the region have suffered a decline of mean annual pH of > 0.5 pH units. Predictions indicate that a 30% reduction of deposition would maintain present-day stream quality levels. Reductions of the order of 60% are required to ensure a significant recovery at most sites across the region.

INTRODUCTION

There is now considerable weight of evidence linking emissions of sulphur and nitrogen compounds with acidification of surface water and soil. A need to identify the acid sensitive areas still exists, however in order to assess the potential environmental damage and to investigate methods to halt or reverse the trend in affected areas. Two methods have been highlighted as being capable of relieving the impact of acidification: (1) a reduction in the emission of pollutants; and (2) addition of a neutralizing agent to sensitive sites. The prescription of the most effective remedy requires assessment of the different management strategies proposed in terms of financial and environmental costs.

An important link between emissions and ecological impact is the transmission of acidity from deposition to stream and lake waters. This focuses upon the chemical status of soil matrix and soil water which greatly affect streamwater quality. The soil accumulates changes induced by the addition of pollutant through time emphasizing the importance of historical trends for emission and deposition. These trends must be incorporated into any

0022-1694/90/$03.50

estimation of the rate and magnitude of acidification, and the likely recovery. The complexity of the problem necessitates the use of mathematical models for accurate evaluation of management strategies. These models must represent the key processes influencing the long-term acidification of the soil and must be applicable for long-term regional analyses. We use the model of acidification of ground water in catchments (MAGIC) for long-term prediction of soil and water acidification across a region. MAGIC is a soil-based model which represents the processes of major importance to soil acidification and is driven by acid deposition trends (Cosby et al., 1985a,b). The results of the MAGIC model have been used to drive biological models of trout density and survival, and intervertebrate species (Ormerod et al., 1988). The model has been widely applied to individual sites in Scotland, North America and Europe and accords well with historical pH reconstructions derived from diatom assemblages (Jenkins et al., 1990). This study uses MAGIC to make a regional simulation of the acid sensitive areas within Wales and to make a preliminary assessment of the ability of the region to recover.

DESCRIPTION OF SURVEY REGION

The study area is underlain by rocks of Cambrian, Ordovician and Silurian age. In the upland areas the soils are thin and base-poor; the combination of rocks resistant to weathering and thin, poor soils gives the region its vulnerability to acid deposition. Evidence of acidification in Wales has been derived from studies of fisheries, forest and moorland soils, geology and hydrochemistry (Stoner et al., 1984; Hornung et al., 1986). In 1984 the Welsh Water Authority investigated the extent of surface-water acidification throughout Wales by conducting a survey of streams and rivers. The area sampled was selected as being the region of greatest acid susceptibility (Fig. 1). During the same period, rainfall quality was monitored at 44 sites throughout Wales. The mean annual rainfall concentrations are summarized in Table 1. A breakdown of the results by region shows the most acidic rainfall in the uplands of Mid-Wales and North Wales (Donald and Stoner, 1989). The east of Wales receives the highest concentrations of SO_4 and NO_3; it also receives high levels of NH_4 and Ca, which partially buffer the rainfall. Mean pH across the region varied from 4.4 to 5.0.

Mean annual stream chemistry is presented in Table 2. The pH of streams varies across the region from 4.2 to 7.3 with a mean of 5.6. The very high maximum Ca level of 862 $\mu eq\,l^{-1}$ and the maximum Mg concentration of 393 $\mu eq\,l^{-1}$ were both measured at the site on the Isle of Anglesey where there is a large Al smelter. At this site, the alkalinity is also a maximum for the region at 1104 $\mu eq\,l^{-1}$.

The mean annual Na and Cl levels are strongly correlated ($R^2 = 0.93$) and sea-salt concentrations are high. The area is mountainous and rainfall is high with a large orographic input. The predominant weather pattern sweeps westerly air from the Atlantic Ocean and the Irish Sea over Wales. The high

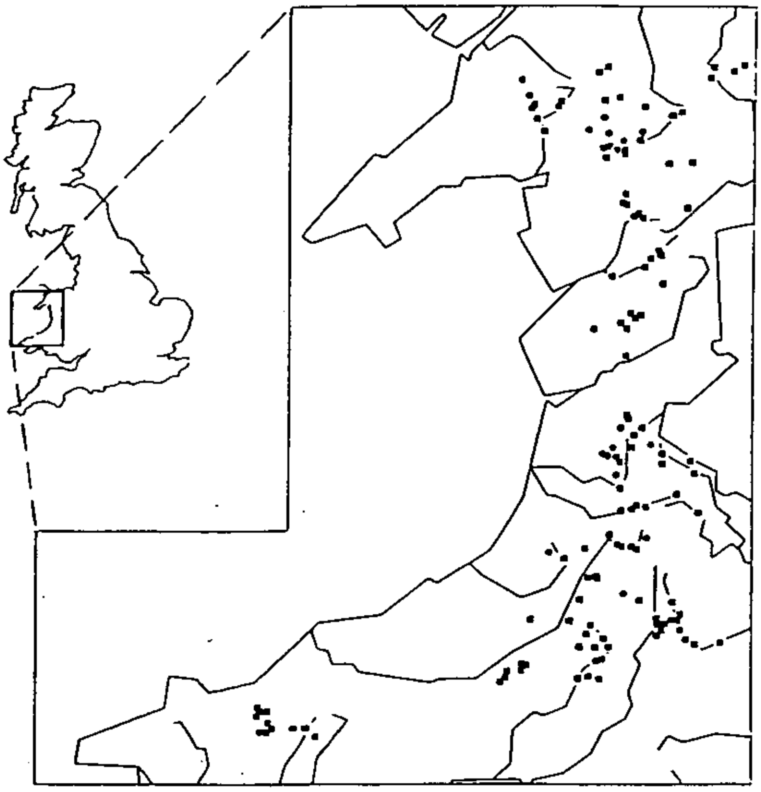


Fig. 1. The study region and sampling locations

mean SO_4 concentration in the streams includes a large component in excess of SO_4 of marine origin. The presence of the SO_4 in the streams is balanced by base cations in the well-buffered catchments and by hydrogen and Al at the more acidic sites.

TABLE 1

Rainfall chemistry (μeq l^{-1} except pH) at 44 sites in Wales 1983–1984

	N	Mean	Median	Standard deviation	Minimum	Maximum
pH	44	4.7	4.7	0.56	4.4	5.0
Ca	44	47.7	41.0	38.6	9.9	102.2
Mg	44	42.6	33.4	43.8	17.4	177.8
Na	44	137.0	124.5	171.2	62.5	510.9
K	44	8.6	7.3	5.4	4.7	21.8
SO_4	44	118.7	110.8	34.3	52.0	217.1
Cl	44	176.1	162.1	192.5	96.8	525.0
HCO_3	44	51.3	38.7	49.9	22.9	114.9

TABLE 2

Mean annual stream chemistry for the 130 sampling sites in the Welsh regional survey

	Mean	Standard deviation	Minimum	Maximum
pH	5.6	0.7	4.2	7.3
Ca	130.9	91.7	40.4	862.3
Mg	111.5	113.4	44.4	393.2
Na	220.1	62.0	149.1	640.0
K	13.4	9.8	5.4	89.0
SO_4	153.7	64.4	49.1	507.4
Cl	267.4	86.2	167.0	918.0
HCO_3	75.5	87.3	0.7	604.1
H	1.9	3.4	0.05	24.0
Alk	30.6	125.4	−206.9	1103.9
pCO_2	7.25	7.6	1.0	51.2
Al_T	6.3	4.3	0.7	24.3

Units are $\mu eq\,l^{-1}$, except Al ($\mu mol\,l^{-1}$), pH and pCO_2 (atmospheres × $10^{-3.5}$).

REGIONAL APPLICATION OF THE MAGIC MODEL

The MAGIC model may be adapted for modelling on a regional basis by the introduction of Monte Carlo techniques which assimilate regional variability. Weathering rates for base cations, soil depths and porosities, rainfall, cation exchange capacities, exchangeable base fractions on cation exchange sites, and chemical inputs from precipitation will vary across the region. In the model these factors are each represented by a model parameter and the Monte Carlo technique allows the parameters to vary across a wide range. The essence of the technique is to run the model repeatedly until sufficient information is obtained. For each of a large number of model runs, random values of the parameters are drawn from previously defined population distributions. When a sufficient number of successful runs are completed the calibrated set of model runs has a distribution of parameters that matches the distributions of the observed equivalents. Any knowledge of the likely covariation of parameters may be built into the model by specifying joint distributions for the varying parameters. For example, if there existed correlations between rainfall and elevation and between depth of soil and elevation, then a relation between rainfall and soil depth may be deduced; usually little is known of the parameter covariation and they are assumed to be independent. The Monte Carlo runs provide many simulations which, if the parameter ranges are sufficiently wide, span the range of observed chemistry across the region. These simulations are employed in a calibration procedure to discard simulations with predictions that are not observed within the region and to tighten the model fit.

To achieve the regional calibration, a large pool of simulations are accumulated and a relative frequency count is made on the observed discrete joint distributions. Weights are assigned to each simulation to provide a weighted relative frequency count that is identical with the observed. Hornberger et al. (1989) presented a detailed description of this technique.

APPLICATION TO WALES

MAGIC has been applied to several individual sites within the study region (Whitehead et al., 1988a,b), and the calibrated set of parameters for those studies formed the basis of the regional application. A one-soil layer version of MAGIC was used as the added complexity of a two-layer version has not been found to produce significantly different simulations of surface water chemistry (Jenkins and Cosby, 1989). Twelve parameters were subject to Monte Carlo uncertainty (Table 3). The mean precipitation volume per year (Q_p) is assumed to fall uniformly across the region and is held constant throughout the simulation. Variability of Q_p, therefore, incorporates variability of soil depth and porosity to some extent. 15% of the rainfall is assumed to evaporate. The 1984 rainfall concentrations of Cl and excess NO_3 and SO_4 were set for each model run by randomly sampling pre-set distributions. Within the model, Cl is assumed to be conservative and so the rainfall Cl concentration distribution can be calculated from knowledge of the stream Cl distribution and the runoff. Background (1844) precipitation was set equal to the present-day sea-salt concentrations.

The trend of excess SO_4 and NO_3 deposition through time is scaled to present-day deposition levels. The shape of the trend is taken to be equal to the overall mean emission curve for the U.K. reported by Warren Springs Laboratory (1983). The time trend in the remaining chemical concentrations in

TABLE 3

Ranges for the parameters used in the Monte Carlo simulations. The parameters are defined in the text

Parameter	Units	Monte Carlo ranges		Accepted simulations			
		Minimum	Maximum	Weighted mean	S.D.	Minimum	Maximum
Q_p	cm	120.0	230.0	177.3	29.5	122.4	229.8
Cl	$\mu eq\ l^{-1}$	167.0	400.0	243.4	34.0	175.8	379.2
SO_4	$\mu eq\ l^{-1}$	20.0	225.0	79.7	34.9	20.3	211.0
NO_3	$\mu eq\ l^{-1}$	2.4	140.0	46.5	22.0	4.1	125.7
CEC	$meq\ m^{-2}$	10.0	300.0	148.7	87.0	10.0	299.4
WE_{Ca}	$meq\ m^{-2}\ year^{-1}$	0.5	150.0	83.5	38.0	1.1	149.9
WE_{Mg}	$meq\ m^{-2}\ year^{-1}$	0.5	50.0	21.3	13.9	0.9	49.9
WE_K	$meq\ m^{-2}\ year^{-1}$	0.5	10.0	5.3	2.7	0.5	9.9
E_{Ca}		0.5	20.0	11.1	5.3	0.6	19.9
E_{Na}		0.5	5.0	2.8	1.3	0.5	0.5
E_K		0.5	5.0	2.7	1.2	0.5	0.5
E_{Mg}		0.5	20.0	9.2	5.9	0.5	19.9

precipitation was determined by using the present-day excess concentrations over sea-salt to scale the trend line. The present-day rainfall concentrations used are shown in Table 1. These concentrations are the same for each model run. Nitrate in the soil was assumed to be taken up by plants at a constant rate of 45% of NO_3 input. A wide variation of the cation exchange capacity (CEC) was used in the Monte Carlo simulations reflecting the high variability of measured data. Each soil horizon within the catchment may have a different CEC value and the lumped model parameter must allow for uncertainty by specifying a wide range in value (Table 3); WE_{Ca}, WE_{Mg} and WE_K are the weathering rates of Ca, Mg and K, respectively. The Na weathering rate was set to zero and the soil and stream Na set directly from the Na vs Cl regression line.

E_{Na}, E_{Mg}, E_{Ca} and E_K are the fractions of the cation exchange sites occupied by Na, Mg, Ca and K in 1844. These are required to initialize the model and the ranges specified are deduced from knowledge of present-day fractions and that base cation fractions have decreased owing to acidification. The total CEC within the soil is held constant during each run.

The CO_2 partial pressure (pCO_2) in the soil and stream was set to 40 and 4 times the atmospheric partial pressure, respectively. The stream pCO_2 represents the median value calculated from the observations of bicarbonate and hydrogen and these were held constant for each run. The value of the aluminium equilibrium constant in the soil was set at 8.55. Stream Al concentrations are usually represented in MAGIC by an equilibrium with $Al(OH)_3$. For the Welsh regional data, Neal et al. (1989) showed that the Al levels are better predicted by disallowing Al precipitation in the stream and this modification was used here. Soil SO_4 adsorption within the model was set from the single site analysis of Welsh catchments by Whitehead et al. (1988a) with a half saturation constant of 150 meq m^3.

The model was run 2000 times drawing the parameters from uniform distributions whose maxima and minima are given in Table 3. The results from these runs were used in the calibration phase of the analysis. Six streamwater variables were used to calibrate the model: Ca, Mg, SO_4, Cl, NO_3 and alkalinity. The remainder acted as free variables whose closeness of fit was used as a

TABLE 4

Bin sizes used for the final calibration procedure

Variable	Minimum (μeq l^{-1})	Maximum (μeq l^{-1})	Number of axis divisions
Ca	40	230	5
Mg	40	160	2
SO_4	50	300	5
Alkalinity	−250	160	5
Cl	160	400	5
NO_3	0	60	3

criterion for evaluating the model performance. The six variables were selected for their importance both in terms of their magnitude and variability in the observed data, and in terms of their influence on the biological species in the stream. The 'binning' procedure for forming the relative frequency structure for observed and simulated data entailed setting a maximum and a minimum limit for accepting simulations. The range formed on each axis was divided linearly to form the bins. The number of divisions on each axis was allowed to vary to form alternative calibration strategies. By taking many divisions the number of observations matched decreases as the bin size diminishes. By taking few divisions the model fit becomes coarse. The strategy that was accepted finally is shown in Table 4.

Calcium, SO_4, alkalinity and Cl were each apportioned five divisions, Mg had two and NO_3 three. Increasing the number of divisions for Mg or NO_3 greatly reduced the number of observations that were able to be simulated and so a coarser fit to these variables was accepted. An alternative would have been to run the model further to see whether the gaps in the mismatch could be filled. The total number of individual bins that had one or more observations in them was 74. Of these, 19 had no matching simulation. The observations lying in these 19 bins were thus unable to be represented in the regional simulation along with the observations at the extreme unacidic end of the distributions, which were precluded by the maximum cutoffs used in forming the bins. In total 35 of the observations could not be matched. These were mostly unacidified catchments apart from the three with the lowest pH values. These three observations had relatively high alkalinities for their corresponding pH, and the model could not predict this behaviour. Mean chemistry for the observed data set was then recalculated for the remaining 95 sites (Table 5). This 'tailored' data set was then used for matching simulated and observed. In total 252 of the original 2000 simulations were accepted by the calibrated filter.

TABLE 5

Comparison of simulated and observed stream chemistry. Observed data (in parentheses) are the 'tailored' data set used for model calibration

Variable	Mean	Minimum	Maximum
pH	5.6 (5.6)	4.5 (4.2)	6.5 (6.6)
Ca	105 (106)	42 (40)	202 (208)
Mg	87 (86)	40 (44)	160 (135)
Na	206 (202)	152 (149)	295 (289)
K	14 (11)	4.6 (5.4)	38 (35)
SO_4	138 (138)	52 (49)	284 (277)
Cl	246 (244)	176 (167)	379 (365)
Alkalinity	2.8 (2.9)	−127 (−141)	89 (90)
Total Al	0.16 (0.18)	0.01 (0.02)	0.96 (0.67)
NO_3	25 (20)	2.3 (7.1)	60 (60)

RESULTS

The parameters that led to the 252 successful simulations are presented in Table 3 and these successful parameters span the complete range specified in the Monte Carlo analysis. A comparison of observed and simulated chemistry is presented in Table 5 where the observed data represent the 'tailored' data set used in the calibration procedure. Good fits of mean value are obtained for each of the four variables that were assigned five axis divisions in the calibration procedure (Ca, SO_4, alkalinity and Cl). A good fit is also achieved for Mg despite only allowing for two divisions in the calibration phase. The closeness of the fit to the remaining variables is very good considering that they were set as free variables and did not take part in the calibration procedure (excepting NO_3).

Table 6 presents the observed and simulated correlation structure of the joint distributions. The table shows a close fit for most correlations, with the majority of simulated correlations being within 0.1 and most of the remainder within 0.2. The worst overall fit is for K, which was not used in the calibration procedure; this is not surprising given the potential biological controls not incorporated into the MAGIC model. The mean value of K (14 μeq l^{-1}) is small

TABLE 6

Stream chemistry correlation matrices for simulated data and observed data

	Cl	SO_4	Na	K	Mg	Ca	pH	Total Al	Alk	NO_3
Simulated data										
Cl		0.2	1.0	0.1	0.3	0.3	−0.1	0.1	−0.1	0.3
SO_4	0.2		0.3	0.2	0.4	0.5	−0.2	0.3	−0.2	0.1
Na	1.0	0.3		0.1	0.3	0.3	−0.1	0.1	0.0	0.3
K	0.3	0.2	0.1		0.0	0.0	−0.2	0.0	−0.1	0.0
Mg	0.3	0.4	0.3	0.0		0.5	0.5	−0.5	0.5	0.1
Ca	0.3	0.5	0.3	0.0	0.5		0.6	−0.4	0.6	0.3
pH	−0.1	−0.2	−0.1	−0.2	0.5	0.6		−0.8	0.1	−0.1
Total Al	0.1	0.3	0.1	0.0	−0.5	−0.4	−0.8		−0.9	0.2
Alkalinity	−0.1	−0.2	0.0	−0.1	0.5	0.6	1.0	−0.9		−0.2
NO_3	0.3	0.1	0.3	0.0	0.1	0.3	−0.1	0.2	−0.2	
Observed data										
Cl		0.3	0.9	0.1	0.3	0.4	−0.1	0.1	−0.2	0.3
SO_4	0.3		0.3	0.2	0.5	0.5	−0.2	0.1	−0.3	0.3
Na	0.9	0.3		0.2	0.5	0.3	0.2	0.0	0.0	0.5
K	0.1	0.2	0.2		0.5	0.5	0.4	−0.2	0.5	0.2
Mg	0.3	0.5	0.5	0.5		0.6	0.5	−0.3	0.5	0.4
Ca	0.4	0.5	0.3	0.5	0.6		0.4	−0.3	0.4	0.5
pH	0.1	−0.2	0.2	0.4	0.5	0.4		−0.7	0.7	0.2
Total Al	0.1	0.1	0.0	−0.2	−0.3	−0.3	−0.7		−0.6	0.1
Alkalinity	−0.2	−0.3	0.0	0.5	0.5	0.4	0.7	−0.6		0.0
NO_3	0.3	0.3	0.5	0.2	0.4	0.5	0.2	0.1	0.0	

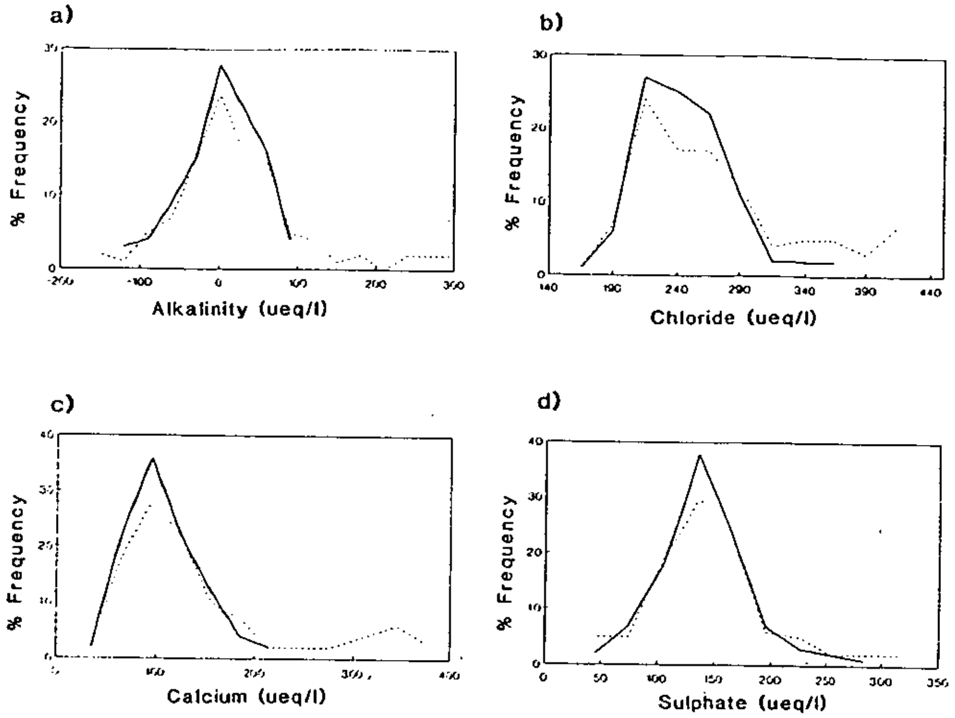


Fig. 2. Observed (- - -) and simulated (——) stream chemistry distributions using the full observed regional data set; (a) alkalinity, (b) chloride, (c) calcium and (d) sulphate.

compared with the other three base cations and the consequences of a poor fit to the correlation of K with the remaining variables are negligible. The very high simulated correlations for alkalinity with Al and pH reflect the strong model relationship. The fact that the observed correlations are also high indicate that these relationships are good approximations for this Welsh region.

Figure 2 shows the simulated marginal distributions for Cl, alkalinity, SO_4 and Ca compared with the distribution for the original data set containing 130 sites. Having calibrated the model to the 'tailored' data set of 95 sites, which the model was able to simulate, the match between simulated and observed is good. Although some fine structure is unable to be reproduced, the method of calibrating to a subset of the observed data is vindicated as the simulated distribution captures the general features of the water chemistry of the region.

The extent of acidification of the region since pre-industrial times can be seen by comparing the present-day stream chemistry with the stream chemistry reconstructed for 1844. From 1844 to 1984, mean pH dropped from 6.4 to 5.6; mean alkalinity has declined by an order of magnitude (from 63 to $3\,\mu eq\,l^{-1}$), and the mean sum of acid anions ($Cl + SO_4 + NO_3$) has more than doubled (from 278 to $584\,\mu eq\,l^{-1}$). Breaking down the pH changes reveals that 40 of the

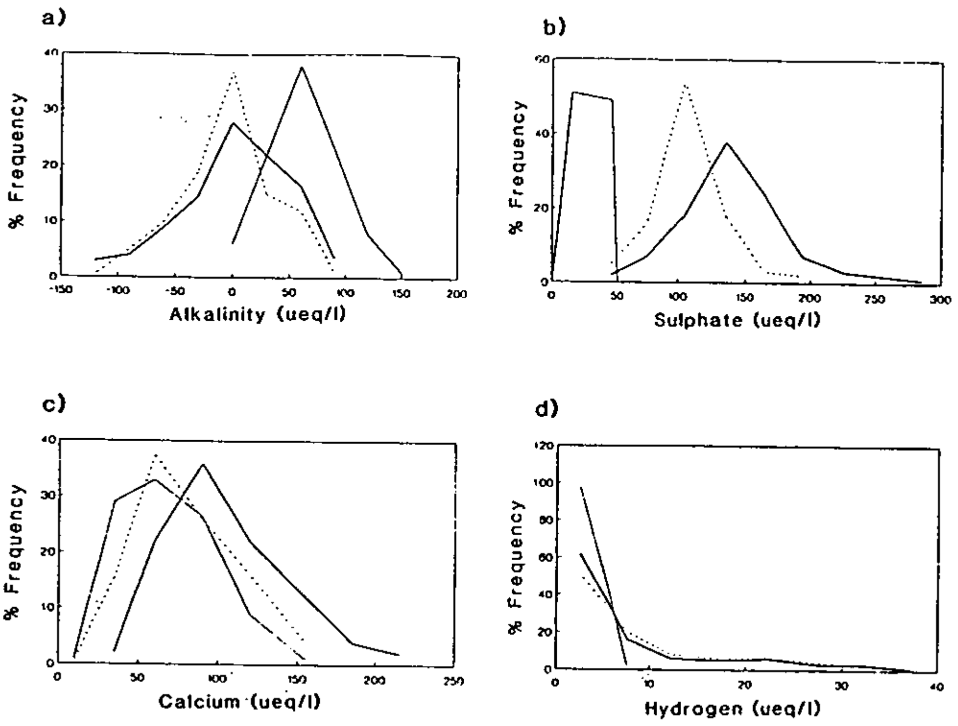


Fig. 3. Simulated background (——), present day (——) and future (– – –) stream chemistry assuming a 30% decrease in acid deposition; (a) alkalinity, (b) sulphate, (c) calcium and (d) hydrogen.

catchments have a simulated pH drop < 0.5, 37 catchments show a pH drop between 0.5 and 1.5, and 18 catchments show a drop in pH > 1.5 units. The number of catchments represented in any particular chemical class is determined by summing the weights of all the simulations falling within that class. Figure 3 shows the simulated regional weighted distributions in 1844 and 1984 for alkalinity, Ca, SO_4 and hydrogen. Also shown are model predictions into the future with a pollutant deposition loading of 70% of its present-day level. Calcium shows a slight return toward the 1844 conditions whereas the hydrogen remains more or less the same. The large change in SO_4 reflects the high pollutant loading since 1844.

The accepted model parameters were fed back into the model in an attempt to assess the ability of the region to recover from acidification. Several future deposition scenarios were used: Fig. 4 shows the effect of reduction in pollutant deposition on both alkalinity and pH. A 30% reduction of pollutant deposition is required to halt acidification in Wales and reductions greater than this may start to reverse the acidification at most sites. All sites show a pH recovery of at least 0.2 under a 70% reduction scenario. Table 7 shows the results for 30%, 50% and 70% reduction of deposition reflecting scenarios that are currently

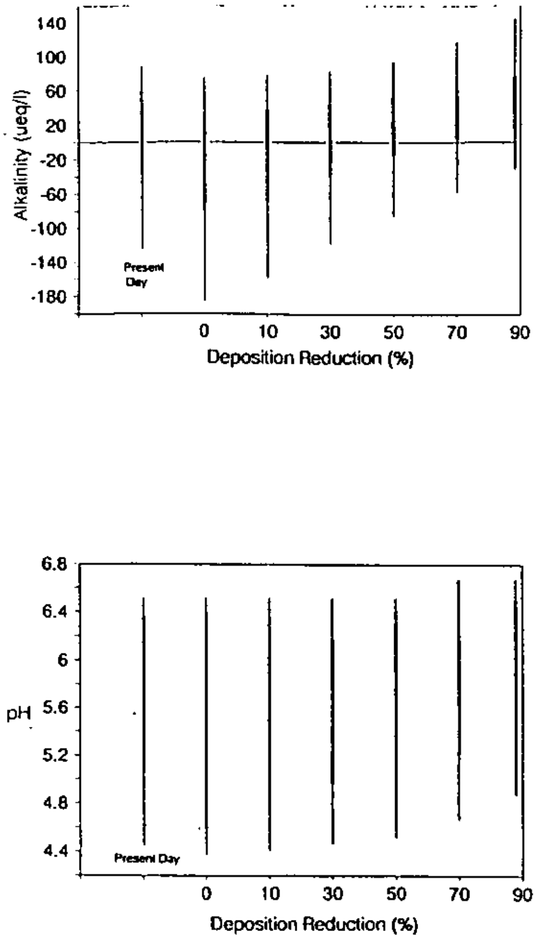


Fig. 4. Forecast stream pH and alkalinity (mean, standard deviation and extremes of the distributions) under a range of deposition reduction strategies.

believed to be achievable. Overall, by decreasing deposition of pollutants it is seen that the alkalinity and pH will rise whereas the base cation concentrations will fall. This decline in base cation concentration in the stream is the result of the decline of acid anion pollutants.

DISCUSSION AND CONCLUSIONS

A regional model of a part of Wales, believed to be sensitive to acid deposition, has been presented. The model has been used to predict the extent of acidification through the region and has enabled a dose-effect type of relationship, for reducing the deposition of acid pollutants, to be predicted. The model has been tested successfully against present-day joint distributions of

TABLE 7

Predicted stream chemistry under 70%, 50% and 30% deposition reduction strategies

	Mean	Standard deviation	Minimum	Maximum
70% deposition reduction				
pH	6.0	0.3	4.7	6.9
Ca	72.1	17.7	14.3	150.8
Mg	64.6	7.8	39.6	99.8
Na	201.7	16.0	152.6	293.5
SO_4	62.6	7.4	33.9	105.1
Cl	246.4	23.0	175.8	379.3
Alk	28.8	18.7	−60.2	118.2
Al	0.06	0.03	0.006	0.41
50% deposition reduction				
pH	5.7	0.3	4.5	6.5
Ca	77.1	18.0	16.8	151.6
Mg	67.7	8.3	40.2	102.2
Na	202.6	16.0	152.8	293.8
SO_4	83.8	11.4	38.8	155.7
Cl	246.4	23.0	175.8	379.2
Alk	12.3	20.9	−92.3	92.9
Al	0.09	0.06	0.009	0.63
30% deposition reduction				
pH	5.4	0.4	4.5	6.5
Ca	80.7	18.8	17.1	154.3
Mg	69.6	9.1	40.2	117.6
Na	203.2	16.0	152.8	294.2
SO_4	104.8	15.5	43.7	203.6
Cl	246.4	23.0	175.8	379.2
Alk	−6.8	25.7	−125.7	82.3
Al	0.17	0.10	0.01	0.90

All units in $\mu eq\, l^{-1}$, except pH and Al ($mg\, l^{-1}$).

water chemistry. The simulated range of pH decline across the region is compatible with that reported by Battarbee et al. (1988), who looked at the evidence for acidification of several lakes, in the same study region, using diatom analysis.

Assuming the catchments across the region to be broadly similar in response to acidification, the present-day chemistry may represent the response of any one site through time, i.e. all of the catchments will be at a different stage of acidification. Some were poorly buffered from the start and will be highly acidified whereas others will have been buffered to a greater extent. Collectively they may allow a substitution of space for time in the interpretation of the sampling variable. If this is the case then predictions using the same relationships may be assumed to be reasonable. Another indirect way of testing the model is to use the predictions to feed biological models of fish density, survival and floral and macroinvertebrate speciation (Ormerod et al., 1988). The results of this two-stage modelling may be compared with biological evidence for trends in acidification. Of crucial importance to these biological models is the stream Al concentration and its time trend. The submodel used here allows no net Al precipitation in the stream on a mean annual basis. Other hypotheses that could have been used include: (1) allowing precipitation only when saturation of Al occurs in the stream; (2) having a different phase of Al in each site; (3)having a depletable finite store of Al encompassing a range of solubilities in the pristine state so that as the catchment acidifies the more soluble phases are flushed from the soil; (4) ion exchange of Al in the soil, with a finite store; (5) using a two box version of MAGIC, with a mixing box at soil CO_2 partial pressure before release into the stream; (6) fitting an empirical curve to the data which is assumed constant through time. Each of the alternatives needs to be examined before concrete Al predictions may be made.

The timing of acidification in the region has not been presented because the key to the time trend is the deposition sequence of pollutants since 1844. The model uses emission data for the U.K. to predict the trend in deposition. This may not accurately represent the actual deposition trend for Wales. Further evidence is required and this may come from the record of historical deposition of carbonaceous soot particles in lakes. The model has been used to indicate possible future trends for acidification in Welsh catchments under a number of deposition reduction strategies. To see how these relate to reductions in emissions, a model of atmospheric pollutant transport must be applied across the region.

ACKNOWLEDGEMENTS

This work was carried out using joint funding from DOE (PECD 7/10/73), EEC (EV4V. 0033 UK(H)) and the Royal Society under the Surface Water Acidification Programme. Dick Wright and Juha Kämäri gave invaluable comments on an earlier draft of the paper.

REFERENCES

Battarbee, R.W., Anderson N.J., Higgit, S., Oldfield, F., Appleby, P.G., Jones, V.J., Patrick, S.T., Flower, R.J., Kreiser, A., Richardson, N.G., Fritz, S.C., Munro, M.A.R., Rippey, B., Hawarth, E.Y., Natkanjki, J. and Stevenson, A.C., 1988. Lake acidification in the UK 1800-1986. Report for Department of the Environment, ENSIS, London.

Cosby, B.J., Wright, R.F., Hornberger, G.M. and Galloway, J.N., 1985a. Modelling the effects of acid deposition: estimation of long term water quality responses in a small forested catchment. Water Resour. Res., 121: 1591–1601.

Cosby, B.J., Hornberger, G.M., Galloway, J.N. and Wright, R.F., 1985b. Modelling the effects of acid deposition: assessment of a lumped parameter model of soil water and stream water chemistry. Water Resour. Res., 121: 51–53.

Donald, A.P. and Stoner, J.H., 1989. The quality of atmospheric deposition in Wales. Arch. Environ. Contam. Toxicol., 18: 109–119.

Hornberger, G.M., Cosby, B.J. and Wright, R.F., 1989. Historical reconstructions and future forecasts of regional surface water acidification in southernmost Norway. Water Resour. Res., 25: 2009–2018.

Hornung, M., Stevens, P.A. and Reynolds, B., 1986. The impact of pasture improvement on the soil solution chemistry of some stagnopodzols in mid-Wales. Soil Use Manage., 2: 18.

Jenkins, A. and Cosby, B.J., 1989. Modelling surface water acidification using one and two soil layers and simple flow routing. In: J. Kämäri, D. Brakke, A. Jenkins, S. Norton and R. Wright (Editors) Regional Acidification Models. Springer-Verlag, Heidelberg.

Jenkins, A., Whitehead, P.G., Cosby, B.J. and Birks, H.J.B., 1990. Modelling long term acidification: a comparison with diatom reconstruction and the implications for reversibility. Philos. Trans. R. Soc. London Ser. B, 327: 435–440.

Neal, C., Musgrove, T. and Whitehead, P.G., 1989. Predicting the long-term variations in stream and lake aluminium concentrations for acidic and acid-sensitive catchments. Sci. Total Environ., 80: 205–211.

Ormerod, S.J., Weatherly, N.S., Varallo, P.V. and Whitehead, P.G., 1988. Preliminary empirical models of the historical and future impact of acidification on the ecology of Welsh Streams. Freshwater Biol., 20: 127–140.

Stoner, J.H., Gee, A.S. and Wade, K.R., 1984. The effects of acidification on the ecology of streams in the upper Tywi catchment in West Wales. Environ. Pollut., 35: 125–157.

Warren Springs Laboratory, 1983. Acid deposition in the United Kingdom. Report, Warren Springs Laboratory, Stevenage.

Whitehead, P.G., Reynolds, B., Hornung, M., Neal, C., Cosby, J. and Paricos, P., 1988a. Modelling long term stream acidification trends in Upland Wales at Plynlimon. Hydrol. Proc. 2: 357–368.

Whitehead, P.G., Bird, S., Hornung, M., Cosby, J., Neal, C. and Paricos, P., 1988b. A modelling study of the Lynn Brianne Catchments. J. Hydrol., 101: 191–212.

5.2 Regional Analysis of South West Scotland

CHAPTER 8

Regional Modeling of Acidity in the Galloway Region in Southwest Scotland

T.J. Musgrove, P.G. Whitehead, and B.J. Cosby

8.1. Introduction

The southwest region of Scotland (*Figure 8.1*) is believed to be particularly vulnerable to the effects of acidic deposition (Wright and Henriksen, 1979). Reports of long-term changes in acidic status of lakes and streams combine with reports of a decline in fish populations to present a picture of concern to freshwater fisheries and environmentalists alike (Battarbee and Flower, 1986; Burns *et al.*, 1984).

Action to reverse the observed trends can be effectively prescribed only once the processes within the catchment soils that transform acidic precipitation into stream water pollution are understood. Practical experimentation in the laboratory and in the field can help to explain part of the story. The picture for soils, however, is obscured in the field by their heterogeneous nature, and in the laboratory by the inability to reproduce field conditions exactly. Mathematical models are very useful as an aid to understanding the intrinsic processes in complex systems, such as the soil-water chemical interaction through time and space. By using models, hypotheses may be tested by simulating processes and the results compared with their measured counterparts. Useful information may often be deduced, irrespective of the outcome of the comparison.

In this chapter we use a well-documented and extensively used model of groundwater in catchments (the MAGIC model) to perform a regional analysis of lakes and streams in southwest Scotland. Instead of modeling each lake and stream separately, we pool them all and model the overall probability density

J. Kämäri (ed.), Impact Models to Assess Regional Acidification, 131–144.

Figure 8.1. Map of the British Isles showing location of the Galloway area.

functions of water chemistry variables. We use the Monte Carlo technique to run the model 880 times, taking for each run a different set of parameters randomly sampled from specified distributions. The runs that enable us to match the observed distributions are investigated to determine the sensitivity of the model results to the individual parameters. The changes that have occurred in the region as a result of increased deposition during the past 140 years are simulated, and a possible future scenario of deposition is investigated.

8.2. Analysis of Chemical Data for the Galloway Region

The Galloway Region in southwest Scotland contains many lochs and streams that drain moorland, forest, and pasture catchments. The bedrock consists mainly of lower Paleozoic rocks of Ordovician and Silurian systems with a few intrusions of granite of the Old Red Sandstone era (Harriman *et al.*, 1987). These catchments have only a thin covering of unconsolidated glacial till, often closely related to the nature of the underlying rocks (Greig, 1971). Many catchments in the region are covered by a blanket layer of peat of between 50 and 100 cm thickness. The southern part of the region is reported to have a higher calcite availability than the northern part (Welsh *et al.*, 1986; Edmunds and Kinniburgh, 1986b). The mean yearly rainfall ranges from 0.8 to 2.4 m with a mean of 2.0 m.

The concentrations of the major ions indicate three important sources: terrestrial input of Ca, Mg, Al, HCO_3 as products of weathering; atmospheric pollution input of H, NH_4, NO_3, and SO_4; and atmospheric input of seawater salts Na, Cl, Mg, and SO_4 (Wright *et al.*, 1980a). The distribution of these ions varies spatially with a regional character. Concentration of all the major ions is higher nearer the coast to the south. Pollutant concentrations are higher as a result of the location of the sulfur emission areas to the south and the southeast of Galloway. Weathering is highest in the more calcareous Silurian and Ordovician rocks to the south rather than in the slowly weathering, harder granitic intrusions to the north. Sea salts are more evident nearer the coast. The pH of precipitation is 4.1 to 4.4 and contains a large excess sulfate proportion (Wright and Henriksen, 1979). The region as a whole is believe to be highly sensitive to acidic deposition and is therefore a useful area for scientific study.

Data sets from four separate investigations in Galloway were used in the study. First, Edmunds and Kinniburgh (1986b) sampled sites during the wet summer of 1985 as part of a larger survey of groundwater throughout the United Kingdom. They took spot samples from springs, shallow wells, boreholes, and river baseflow from a 20 by 25 km area extending from Wigtown in the south to Loch Macaterick in the north and from the River Luce in the east to the Waters of Ken in the west. The study encountered the full range of Galloway bedrock, but sampled few coastal sites. Second, Wright and Henriksen (1979) took spot samples from 72 lochs and 39 streams during the wet period of 19–26 April 1979. The data were compared with an area of similar acidic susceptibility in Norway. The area of study was 70 km by 50 km and covered the entire Galloway region. These samples thus enveloped the complete spectrum of Galloway chemistry. Third, Flower *et al.* (1985) looked at the water quality and diatom content of 34 Galloway lochs in November 1984 and again in July 1985. The study area once again encompassed the whole of Galloway. Finally, Harriman *et al.* (1987) sampled 22 lochs and 27 streams, looking at their chemistry and their fish populations. The region of study was limited mainly to the granitic area between Loch Dee and Loch Doon in a 20-km by 15-km area.

A summary of each data set is presented in *Table 8.1*. The highest mean pH levels were recorded by Flower *et al.* (1985) in their July sample and by Edmunds and Kinniburgh (1986b), for whom the shallow well and borehole samples show the more alkaline groundwater chemistry. The latter study also shows the highest base cation concentrations. The data from Harriman *et al.* (1987) show low base concentrations indicative of the slowly weathering, acidic granite region away from the coast and the emission sources. Of the major anions, SO_4 levels are more or less similar at approximately 158 meq m^{-3}; but Cl is more variable, ranging from 148 to 385 meq m^{-3}.

Table 8.1. A summary of data from each study (minimum, mean, standard deviation, maximum).[a]

Data set		*pH*	*Al*	*Na*	*K*	*Ca*	*Mg*	*Cl*	SO_4	NO_3
Edmunds & Kinniburgh (1986)	Min	4.20	.01	96	0.0	19.0	16.5	28.2	37.5	0.0
	Mean	5.80	.21	277	26.7	329.0	158.0	253.0	159.0	49.5
	Std	.85	.21	153	65.3	38.7	171.0	192.0	112.0	125.5
	Max	7.30	.80	1,095	644.0	2,136.0	1,242.0	1,291.0	1.041.0	728.0
Wright & Henriksen (1980)	Min	4.30	.01	101	1.0	6.0	21.0	37.0	47.0	0.0
	Mean	5.40	.19	210	19.8	174.5	107.0	233.0	163.8	35.5
	Std	.92	.18	113	16.1	300.0	95.0	143.0	77.0	65.0
	Max	7.60	1.10	761	176.0	1,811.0	403.0	930.0	478.0	460.0
Harriman *et al.* (1986)	Min	4.20	.01	100	3.0	1.0	34.0	100.0	88.0	1.0
	Mean	5.20	.17	143	9.0	139.0	78.0	148.6	150.5	11.3
	Std	.60	.10	29	2.3	92.0	31.0	32.0	36.0	6.6
	Max	8.00	.62	257	13.0	1,325.0	429.0	232.0	279.0	45.0
Flower *et al.* (1985)	Min	4.40	.10	1,748	4.6	14.0	38.0	90.0	54.0	.7
	Mean	5.50	.21	286	13.4	134.0	121.0	385.0	161.5	17.0
	Std	.90	.11	138	12.0	114.0	83.0	179.0	85.0	31.0
	Max	7.00	.43	765	56.3	400.0	340.0	935.0	358.0	171.0
Flower *et al.* (1985)	Min	4.50	.07	135	3.1	23.0	37.0	87.0	70.8	.7
	Mean	6.00	.27	276	14.7	166.3	116.0	298.0	139.0	7.5
	Std	1.30	.40	164	14.6	142.0	88.0	163.0	67.0	7.2
	Max	7.20	.59	717	64.0	518.0	356.0	899.0	320.6	31.4
Overall	Mean	5.65	.21	248	21.5	248.6	132.0	250.4	158.0	37.0

[a] All values are shown in meq m^{-3} except for those for Al, which are mg l^{-1}.

The probability density distributions of corresponding chemicals within data sets are roughly triangular with a tail of varying length. The tail-values affect the mean results in *Table 8.1* by shifting them from their respective median values. This effect is greatest for the three data sets with a low number of samples. The distribution of pH has three peaks – at 4.5, 6.1, and 7.1 – for each of the studies except for that of Harriman *et al.*, who sampled the most acidic area and hence only show the lower two.

The data were pooled together to yield a large data set whose samples covered a variety of conditions produced by both spatial and temporal variation within the region. The samples were all taken within a five-year period, and it was assumed that the pooled set could represent the mean state of the region during those five years. The time scale of the model is longer, but the errors introduced by such an approach were considered to be outweighed by the benefit of utilizing all of the data to get a more accurate representation of region as a whole during that time. The overall mean results are presented in *Table 8.1*.

Probability density functions showing the three-peaked pH distribution and the long-tailed "triangular" distribution for calcium, but otherwise typical of each of the major ions, are shown in *Figures 8.2* and *8.3*.

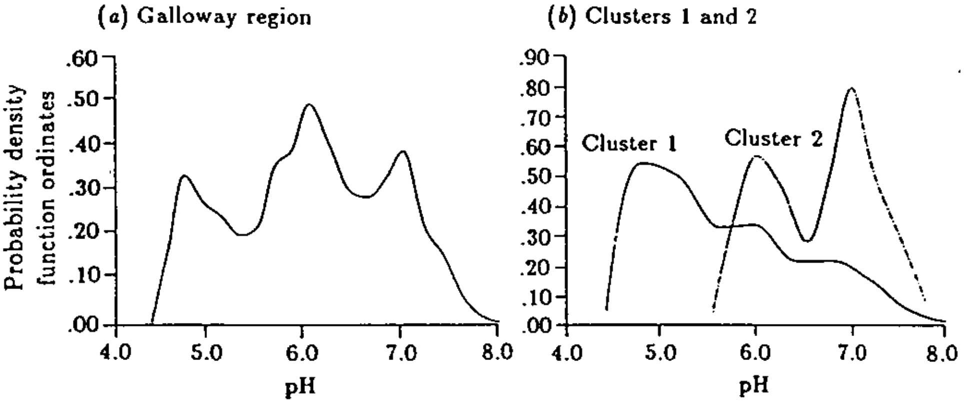


Figure 8.2. pH distributions in (*a*) Galloway region and (*b*) clusters 1 and 2.

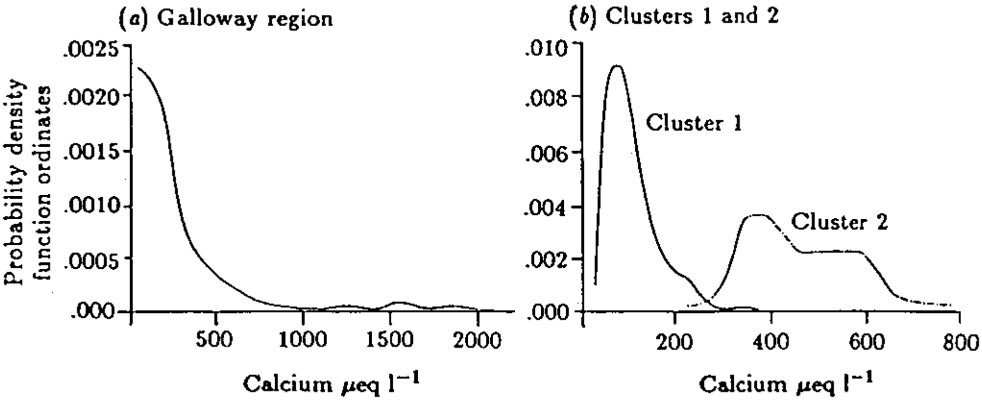


Figure 8.3. Calcium distributions in (*a*) Galloway region and (*b*) clusters 1 and 2.

A cluster analysis was performed in an attempt to categorize groups of data linked by a common chemical makeup. The minimum variance method of Ward (1963) was used to cluster the data, and the algorithms used were those available in the Statistical Analysis Systems computer package (*SAS*). The clearest division of the data was obtained by forming six clusters. Two main clusters contained 322 and 74 of the total sample of 453 sets of measurements, and four minor clusters effectively accounted for the long tails of the distributions for the appropriate chemicals.

Table 8.2 summarizes the two major clusters. Cluster 1 has a mean pH of 5.3 and includes all the low-pH sites. Concentration of all major ions is low, e.g., mean Ca is 83 meq m^{-3} and mean SO_4 is 120 meq m^{-3}. This contrasts with cluster 2, which has high values for ions (Ca is 412 meq m^{-3} and SO_4 is 216 meq

Table 8.2. Summary of the two major clusters.

Variable	*Number*	*Mean*	*Standard deviation*	*Minimum*	*Maximum*
Cluster 1					
Al	322	.312	.16	.01	1.05
Ca	322	82.90	52.90	6.00	339.30
Cl	322	189.80	80.10	28.20	541.50
SO_4	322	120.30	42.70	37.40	341.50
pH	322	5.34	.79	4.18	7.38
NO_3	322	8.75	13.30	3.57	89.00
Mg	322	69.00	31.70	16.50	310.20
Na	322	184.70	60.20	1.00	404.30
K	322	8.60	11.40	2.60	130.50
Cluster 2					
Al	74	.172	.11	.01	.42
Ca	74	412.10	120.00	196.10	748.50
Cl	74	332.20	135.50	87.40	631.70
SO_4	74	216.50	80.90	99.90	449.70
pH	74	6.40	.56	5.38	7.44
NO_3	74	54.80	57.80	3.57	298.40
Mg	74	204.90	73.10	90.50	477.20
Na	74	361.30	110.20	169.60	776.10
K	74	31.60	30.40	2.50	181.60

m^{-3}; see *Figure 8.2*), with a mean pH of 6.4. The differences may be interpreted by assuming that cluster 1 contains the more acidic sites on and around the granitic regions to the north of the Galloway region, and that cluster 2 represents the area with Silurian and Ordovician bedrock near the coast. Cluster 2 chemistry thus reveals the prevalence of higher deposition rate of sea salt and of atmospheric pollution and also the higher source of weathered minerals. The main interest focuses upon cluster 1, representing the most acid-sensitive subdivision. Therefore, only the simulation for cluster 1 is presented here.

8.3. Description of Modeling Techniques

The region was modeled using the Model of Acidification In Catchments (MAGIC), developed by Cosby *et al.* (1985a; 1985b). This is a lumped parameter, long-term simulation model of soil and surface-water quality. In the MAGIC model, five soil processes are identified as holding the key to understanding the acidification processes in soils:

(1) Formation of alkalinity in the soil from dissolution of carbon dioxide held at high partial pressure (Reuss and Johnson, 1985).
(2) Mineral weathering of base cations as a source within the catchment.
(3) Anion retention by the soil, e.g., sulfate adsorption.
(4) Aluminum mobilization and dissolution of aluminum minerals.
(5) Cation exchange by the soils.

Dynamic variation in the catchment soil condition is included in the model by forming a mass balance for each of the major anions and cations (presented by Cosby *et al.*, 1985b). Equilibrium is assumed for each time step, with changes between time steps monitored by the ion flux budgets. The sulfate subsection of the model is investigated in detail by Cosby *et al.* (1986a).

Initial conditions for the model are calculated by assuming an equilibrium with background chemistry prior to industrialization in 1844. This background chemistry is calculated using the present sea salt rainfall contribution as the 1844 precipitation concentration, and by taking the weathering rates to be constant throughout the time period considered by the model. Deposition of SO_4, Cl, and NO_3 are specified as an input to the model. The trend of sulfate deposition during the past 130 years is taken from findings of the Warren Springs Laboratory (1983). The effect of catchment flora is modeled as sink terms for the appropriate ions. Neal *et al.* (1986) and Whitehead *et al.* (1987) use this facility to simulate the effect of forest growth on stream acidity. The model has a simple component for the additional effect of organic chemistry, which has been applied by Lepistö *et al.* (1988) to simulate an organically rich catchment in eastern Finland.

An analysis of the uncertainties inherent in the model is proffered by Hornberger *et al.* (1986a). Verification of the model has been attempted by comparing model simulations to paleoecological reconstructions of pH for sites in Norway, Scotland, Sweden, and America (Wright *et al.*, 1986; Musgrove and Whitehead, 1988). The use of the model for regional analysis is illustrated by the study of Hornberger *et al.* (1987), who simulate the regional characteristics of the chemistry of 208 lakes in Norway.

For this study the model was set up for Monte Carlo analysis. In this technique, several arbitrary parameters are randomly selected from a prescribed parent distribution prior to running the model. This is repeated many times to build up a set of runs, each with a different set of parameter values. The statistical properties of the collection of runs are then analyzed. Examples of this technique applied to water quality problems are presented in Whitehead and Young (1979) and Spear and Hornberger (1980; 1983). The 12 independent model parameters that were varied are the mean annual precipitation, Q_p; the sulfate deposition rate for 1982, SO_4; the cation exchange capacity, *CEC*; the weathering rates of the base cations WE_{Ca}, WE_{Na}, WE_{Mg}, and WE_{K}; the $\log_{10}$ selectivity coefficients S_{AlCa}, S_{AlMg}, S_{AlNa}, and S_{AlK}; and the thermodynamic equilibrium constant for aluminum hydroxide dissolution, K_{Al}.

The results of the present analysis were investigated using the generalized sensitivity approach of Spear and Hornberger (1980). This method compares the simulations that accurately reproduced observed features of chemistry (the "behavior criterion") with those that did not. It then investigates the merits of the hypothesis in which the set of parameters giving rise to a successful simulation and the set of parameters failing to do so have the same parent distribution. This hypothesis is tested for each parameter individually, assuming them to be independent. The force with which the hypothesis is rejected is strongest for those parameters to which the achievement of a successful result is most sensitive. A pattern recognition technique based on the Fukunaga–Koontz transformation (1970) is employed to determine any linear combinations of parameters to which the model response is sensitive. This technique has been previously applied to MAGIC by Hornberger *et al.* (1986) and Cosby *et al.* (1987).

8.4. Monte Carlo Results

Cosby *et al.* (1986b) set up the MAGIC model to simulate one of the Loch Dee catchments. This catchment is located in the middle of the region described by cluster 1. For the present analysis, we initially set up the model in the same way to simulate cluster 1. *Table 8.2* indicates that for cluster 1 the effect of NO_3 is small. This is possibly due to a near equilibrium between the input sources to the catchments and the plant uptake sinks within the catchment. The uptake rate was set more or less to balance the source for this simulation.

The ranges from which the parameters were drawn in the Monte Carlo analysis are shown in *Table 8.3*. The mode indicates the peak for the triangular distributions (a negative mode indicates that the distribution was rectangular). The specified ranges are wide to encompass the entire spread of parameter combinations that are able to reproduce cluster 1 chemistry. The extent of the range is limited, however, to those values that may be experienced in the field. A behavior constraint was chosen such that a run was considered successful if its simulated chemistry for 1982 fell within the range of values between the appropriate 5 and 95 percentiles of the cluster 1 chemistry.

Table 8.3. Parameter variation for the Monte Carlo simulation.[a]

	Range for Monte Carlo variation			*Successful simulations*			
Parameter	*Min*	*Max*	*Mode*	*Mean*	*Std*	*Min*	*Max*
Q_p	1.2	3.0	2.0	1.7	.50	1.2	3.0
SO_4	50.0	220.0	150.0	121.50	32.40	52.2	184.1
CEC	40.0	250.0	120.0	178.50	119.90	40.0	229.0
WE_{Ca}	10.0	250.0	85.0	69.40	45.10	10.1	162.2
WE_{Mg}	0.0	50.0	25.0	13.40	8.90	6.5	39.4
WE_{Na}	0.0	50.0	25.0	10.30	6.93	.1	29.0
WE_{K}	0.0	30.0	10.0	3.70	2.53	.1	10.5
S_{AlCa}	–1.0	5.0	3.0	2.08	1.28	–.7	4.8
S_{AlMg}	–1.0	5.0	3.0	1.87	1.24	–.9	4.7
S_{AlNa}	–3.0	3.0	0.0	.08	1.22	–2.9	2.9
S_{AlK}	–3.0	3.0	0.0	.03	1.28	–2.8	2.9
K_{Al}	8.0	11.0	9.5	9.65	.6	8.1	10.9

[a] WE_{Ca}, WE_{Mg}, WE_{Na}, WE_{K}, and SO_4 have units of meq m^{-2} $year^{-1}$; Q_p is in meters depth over the catchment; CEC in meq/kg.

Of 880 runs, 530 were successful in reproducing the features of cluster 1 regional chemistry, and these are summarized in *Table 8.3*. *Table 8.4* shows the behavior constraint "windows" and a summary of the simulated chemistry.

Figure 8.4 shows the observed and simulated probability density functions of the cluster for Cl, SO_4, and Ca. Good fits about the mean value are seen for

Table 8.4. Summary of behavior criterion windows and the simulated chemistry (concentrations in meq m^{-3}) that satisfied the behavior criterion for cluster 1.

	Behavior criterion windows		*Successful runs*		
Variable	*Min*	*Max*	*Mean*	*Min*	*Max*
pH	4.4	7.6	5.4	4.3	6.5
Ca	20.0	245.0	91.5	21.5	224.0
Mg	18.0	190.0	27.0	19.0	85.0
Na	10.0	330.0	196.0	11.0	372.0
K	3.0	35.0	12.0	3.0	34.0
SO_4	40.0	245.0	115.0	39.0	242.0
NO_3	9.0	25.0	16.0	9.0	22.0
Cl	79.0	360.0	203.0	125.0	401.0

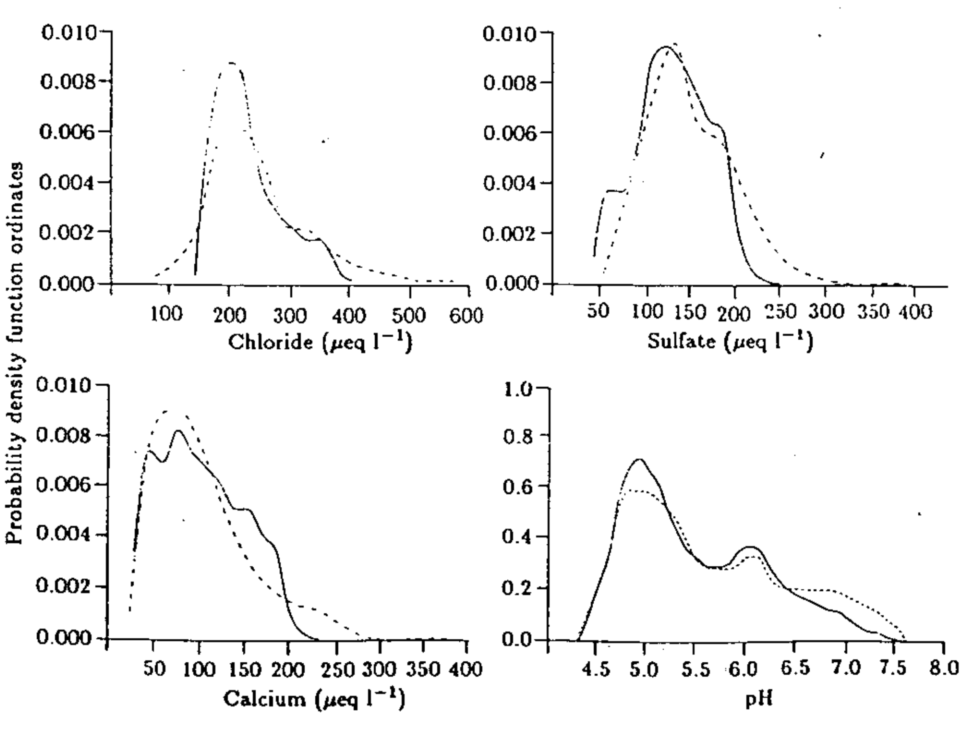


Figure 8.4. Cluster 1 distributions: simulated (——) and observed (——).

Ca, Cl, and SO_4; and the shapes of the simulated distributions for these three variables are also good. The fits are worst at the tail ends, resulting either from specifying a too narrow range of parameters for the Monte Carlo analysis or from failure to pick up the extremes in sampling the triangular distributions.

The simulated distribution for pH is compared with the observed distribution in *Figure 8.4*. The simulation enabled the complete range of pH value, present in the region defined by cluster 1, to be reproduced. The bias toward reproducing the lower pH chemistry possibly lies with the model being set up to reproduce a poorly buffered, highly acidic catchment response. While this is adequate for the majority of cluster 1 sites, it may be less good for the remainder. Alternatively, a better match might also have been achieved by selecting the parameters from more sophisticated distributions than the rather crude triangular ones that were used. By matching more closely the uppermost part of the pH distribution, the upper tail end of the other distributions would also have been better matched.

8.5. Regional Chemistry Changes over Time

Historical changes in the distributions of values of the simulated chemicals were ascertained by saving the output for 1844 and 1982. Future deposition was modeled as a linear decrease to 30% of the 1982 level by the year 2001. This is merely one of many possible scenarios and is used only to illustrate the potential use of the model for regional prediction. The regional levels of chemical concentrations in 2062, under this deposition sequence, were also looked at. The results are shown in *Figure 8.5*.

For cluster 1, the MAGIC model shows a large drop in both pH and alkalinity over the past 140 years. The pH level falls by 0.8 pH unit and alkalinity falls by approximately 70 meq m^{-3}. This is in accord with the findings of Battarbee and Flower (1986), who report changes in pH level of up to 1.0 pH unit during the same period, for those lochs in the granitic region of Galloway. A small recovery is seen during the future scenario. The small size of this recovery reflects the depletion in the soil of base cations (to between 2% and 5% in 1982). The low rate of soil weathering in the region enables only a slow recovery rate.

The sulfate distributions clearly show the shift in regional concentrations simulated as the result of industrialization. The preindustrialized levels are between 0 and 38 meq m^{-3}, whereas the 1982 levels are much higher with values between 42 and 190 meq m^{-3}. The 2062 levels are reduced by about 30%, closely matching the decline in sulfate deposition. This confirms the status of the soil as having low sulfate adsorption capability. Aluminum is seen to increase in extent over the years, up to 36 meq m^{-3} for the most acidic lakes. The majority of sites, however, shows only a small increase. Of the base cations, calcium levels are seen to rise only slightly, whereas magnesium levels show a much more substantial rise. The future scenario shows small decreases in these cations, as a result of the partial recovery of the soil.

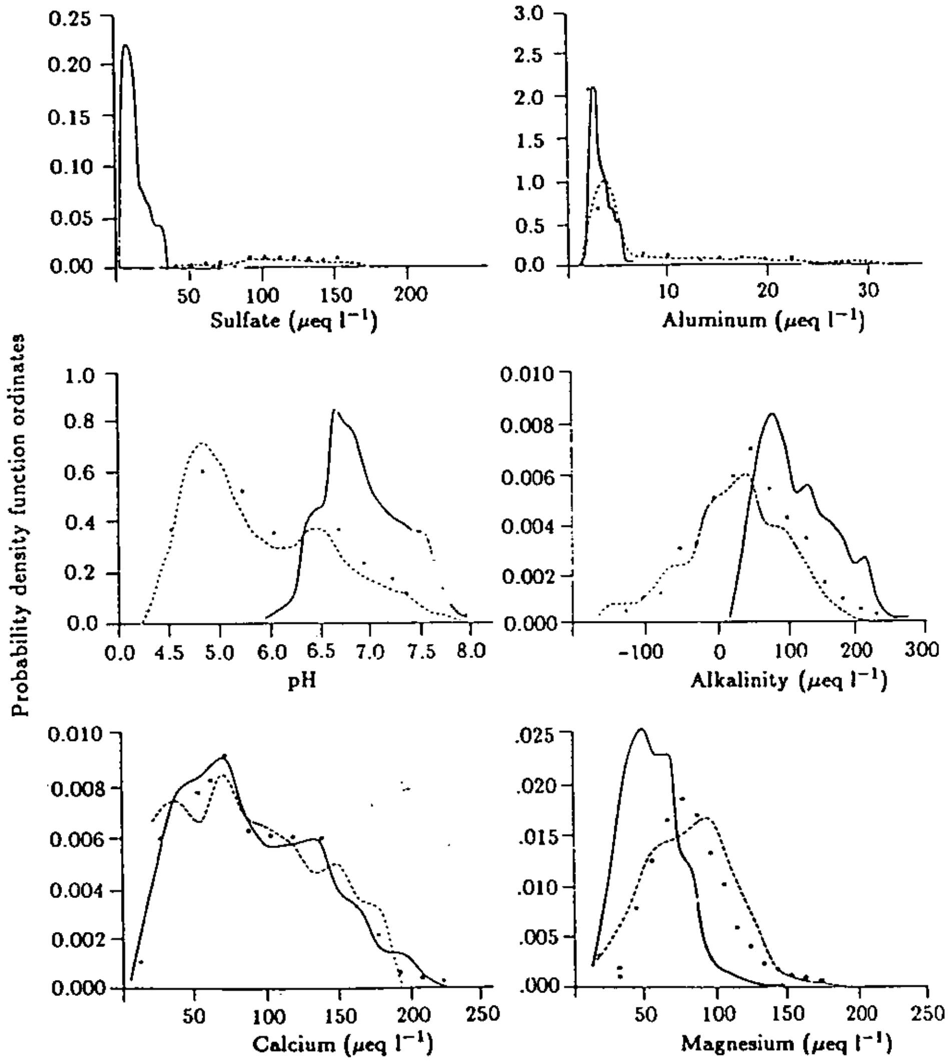


Figure 8.5. Cluster 1: simulated change through time (*** 2062 level; —— 1982 level; —— 1844 level).

8.6. Sensitivity Analysis

The results of the generalized sensitivity analysis are presented in *Table 8.5*, which describes the difference between the distributions of parameters that give rise to a "behavior" and those that do not. The Mann–Whitney statistic (M–W) indicates whether the distributions are significantly separated along the parameter axis, and the Kolmogorov–Smirnov statistic (K–S) gives the greatest separation of the two corresponding cumulative distribution functions. In both cases, a large number indicates a high significance and sensitivity of simulation to that parameter.

Table 8.5. Results of the generalized sensitivity analysis.

	Comparison of behaviors with non-behaviors	
Parameter	*Mann–Whitney z statistic*	*Kolmogorov–Smirnov d statistic*
Q_p	3.19	.139
SO_4	2.19	.204
CEC	1.59	.105
WE_{Ca}	.76	.219
WE_{Mg}	.51	.045
WE_{Na}	.26	.052
WE_{K}	.52	.065
S_{AlCa}	.26	.079
S_{AlMg}	1.21	.096
S_{AlNa}	.24	.042
S_{AlK}	1.08	.092
K_{Al}	.01	.054

The greatest sensitivity, as indicated by these two statistics, is seen for Q_p (M–W of 3.19) and for WE_{Ca} (K–S of 0.219), respectively. Parameter SO_4, the 1982 deposition level, is high in both cases. WE_{Ca} has a high value for the K–S statistic and a low value for M–W statistic. This indicates that one of the two distributions (behaviors or non-behaviors) is centrally placed within the domain of the other. The central distribution for WE_{Ca} is the one for behaviors, showing a peaked, triangular distribution with a well-defined band of acceptance. Thus, while the WE_{Ca} parameter was outside the range 10 to 162 meq $\mathrm{m}^{-2}\mathrm{yr}^{-1}$, there was no chance of a successful simulation.

A method based on the Fukunaga–Koontz pattern recognition technique was used to look at the sensitivity with regard to linear combinations of the parameters. This analysis reveals two eigenvectors of high sensitivity. The first was more sensitive than any individual parameter, with M–W of 3.63 and K–W of 0.214. The weight of each component of the normalized eigenvector indicates the relative importance of that component in explaining the variance associated with it. In this way the most important components were SO_4, explaining 63% of the variance, and WE_{Ca}, explaining 22%. The results indicate that the success of the model in reproducing the regional characteristics for areas of high acid susceptibility is strongly dependent on the selection of values for the WE_{Ca}, SO_4, and Q_p parameters (the weathering rate of calcium, the sulfate deposition rate in 1982, and the mean annual rainfall during the duration of the simulation).

8.7. Discussion

This analysis tends to confirm both the view that the Galloway region is susceptible to acidic deposition and the view that a significant change in soil conditions has occurred during the past 140 years. Falls in pH level of as much as 1.0 pH unit have been discovered for the Galloway by Battarbee and Flower (1986), using the method of reconstruction from study of diatom assemblage in the sediment of lochs. The simulation results show a drop in mean level of 0.8 pH unit. This is increased by the inability to match the highest portion of the 1982 pH distribution at the same time as matching its low end.

This inability also spills into the simulated distribution for alkalinity, by cutting off the highest levels in the simulation. A fair view of the changes caused by the acidification process can still be gleaned, however, by noting that the lakes with higher alkalinity in 1982 are also those with the higher alkalinity in 1844. Hence, the simulated results are valid for those lower alkalinity lakes that it represents well. The recovery under the scenario of a 30% deposition reduction is seen to be slight, owing to the depletion of base cation resources at the available cation exchange sites on the soil. In particular, alkalinity levels are seen to recover very little in the most highly acidified lakes.

Monte Carlo simulations are an excellent means of encountering the complete range of model response to uncertainty in parameters. Overall, the simulation was successful using triangular distributions for the parameters in the Monte Carlo analysis. Better reproduction of the present-day distributions could have been achieved using more complicated distributions to describe the parameters, noting that certain results in the behavior criterion are more in tune to particular parameters. For example, calcium levels are strongly affected by its weathering rate and selectivity coefficient.

The lack of available data for verification of the model calibration, however, limits the usefulness of such a study. Without verification, fine points raised by such a simulation might be mere quirks of the model. The simulations obtained work only under the assumption that the model structure is valid and that its lumped representation of parameters is valid on a regional basis. This is a difficult assumption to prove; one can only look at the simulations and see whether the model appears to represent the region well.

Given the validity assumptions, many uncertainties within the model itself need to be borne in mind when interpreting the results or when using the model to project assumed deposition scenarios into the future. Uncertainties arise in measurement of both precipitation and stream chemistry as a result of intrinsic imprecision both in the measuring technique and in the representative nature of the sampling plan used. In this study the results of five surveys are used, four of which are single-sample surveys. The findings of each survey have been pooled to produce an observed chemistry that may average out, to a degree, any unrepresentative feature of any one survey.

Each submodel within MAGIC also has an uncertainty associated with it. The true shape of the sulfate deposition trend curve, used to define the timing of precipitation pollutants, has only been estimated, and errors may seriously affect the timing of the onset of acidification. This aspect of the model has been investigated by Hornberger *et al.* (1986a) who looked at the effect of uncertainty on a single-site prediction using MAGIC. The aluminum submodel contains a cubic equilibrium between aluminum and hydrogen activities. Assuming an equilibrium model to be valid, there is uncertainty in the order of the relationship. A fit to observations at one point in time may be found for many different orders, and the future predictions and past reconstructions may be very different for each one.

8.8. Conclusions

The MAGIC lumped-parameter model of groundwater in catchments can be coupled with Monte Carlo techniques to provide a useful method of simulating long-term regional response to acidic deposition. The sensitivity of simulation to parameters in the model is seen to be dependent on the weathering rate of calcium, the level of deposition of sulfate, and the mean annual rainfall for a region with low weathering rates and low sulfate adsorption.

The response of the region to a future deposition scenario is also gleaned from the model. After a prolonged period of deposition, the ability of the region to recover is seen to decrease throughout the lifetime of the deposition sequence. Major future reductions in deposition are required to produce a significant recovery in the Galloway region of southwest Scotland.

Acknowledgments

The authors are particularly grateful to the Solway River Purification Board for providing data from the Loch Dee study and to the British-Scandinavian SWAP Committee and the Commission of the European Communities for providing research funding.

6. LINKING OF HYDROCHEMICAL AND BIOLOGICAL MODELS

6.1 Biological Responses at Llyn Brianne

Freshwater Biology (1988) 20, 127–140

OPINION

Preliminary empirical models of the historical and future impact of acidification on the ecology of Welsh streams

S. J. ORMEROD, N. S. WEATHERLEY, P. V. VARALLO* and
P. G. WHITEHEAD† Department of Applied Biology, University of Wales Institute of Science and Technology, Cardiff, *Welsh Water, Penyfai House, Furnace, Llanelli, Dyfed, and †Institute of Hydrology, Crowmarsh Gifford, Wallingford

SUMMARY. 1. We describe a preliminary approach to modelling the impact of acidification on the ecology of two Welsh streams. Output from the hydrochemical Model of Acidification of Groundwaters in Catchments (MAGIC) was used to drive empirical models which predicted brown trout *Salmo trutta* (L.) survival, trout density and invertebrate assemblage type. The models were used for hindcasts between 1844 and 1984 under conifer forest and moorland conditions. Forecasts involved each of these land uses with sulphate deposition either continued at 1984 levels or reduced by 50%.

2. Trout survival times and trout densities in the models declined markedly between 1844 and 1984. The most severe decline occurred under simulated forest, where high aluminium concentration led to the virtual elimination of trout in both streams.

3. In forecasts, only in simulated moorland with sulphate deposition reduced by 50% of 1984 levels, was further decline in trout population retarded. There was no marked recovery in trout density under any of the conditions examined.

4. Invertebrate assemblages in streams during the nineteenth century may have differed from those now existing in nearby moorland streams which are presently circumneutral. Past chemical conditions were unusual (<3 mg l^{-1} total hardness, but pH >5.7 and low aluminium) by present-day standards, and were outside the range of the invertebrate model until ~1940.

5. Between the 1940s and 1984 there was no change in invertebrate fauna under the moorland scenario despite some acidification. However, simulated forest advanced the appearance of the most impoverished assemblage type, which did not recover in spite of reduced deposition.

6. We discuss several uncertainties with the models in their present form, but suggest some methods for their testing and validation.

Correspondence: Dr S. J. Ormerod, UWIST, c/o Welsh Water, Penyfai House, Furnace, Llanelli, Dyfed SA15 4EL.

Introduction

Calls for a reduction in acidifying emissions are many and widespread. However, the costs and benefits of such a policy must be carefully appraised in both economic and environmental terms. As a result, freshwater ecologists are currently being asked to reconstruct past conditions, which might have occurred in waters which are now acidic (e.g. Flower & Battarbee, 1983; Battarbee & Charles, 1986), and to predict changes likely in the future. This element of forecasting is clearly desirable: many of the catchment processes which affect stream chemistry proceed slowly, over years or decades, hence management decisions on potential acidifying influences are required well in advance of perceptible change.

However, many uncertainties surround the causes and consequences of acidification. The chemical processes are intricate, involving interactions between atmospheric deposition, and catchment characteristics such as hydrology, geology, soil type, and vegetation (Overrein, Seip & Tollan, 1980; Altshuller & Linthurst, 1984). Biological responses to changing acidity are also complex, sometimes resulting from direct physiological effects by H^+, Ca^{++}, Al^{n+} or other ions (Altshuller & Linthurst, 1984), but sometimes involving indirect effects, such as trophic pathways (e.g. Hildrew, Townsend & Francis, 1984; Winterbourn, Hildrew & Box, 1985). Further complicating changes are imposed at the catchment level by man. In upland Britain, much climax vegetation has been removed over millennia (Pennington, 1984), in many places to be replaced recently by plantations of non-native conifer trees which exacerbate or add to the effects of acid deposition (Harriman & Morrison, 1982; Stoner, Gee & Wade, 1984; Ormerod, Mawle & Edwards, 1987). As with the regulation of acidifying emissions, this land-use component requires policy formulation and management decisions.

A possible solution to the problems of reconstructing or forecasting long-term trends is the development of models. The hydrochemical *M*odel of *A*cidification of *G*roundwater in *C*atchments (MAGIC) has now been used to simulate changes in surface-water acidity under various scenarios of sulphur deposition and catchment afforestation (Cosby *et al.*, 1985; Cosby, Whitehead & Neal, 1986; Neal *et al.*, 1986; Whitehead *et al.*, 1988). However, because biological resources are amongst those most at risk from acidification, there is a need for a significant biological input into the forecasting procedure. So far, such biological modelling has not been widely attempted. The few studies undertaken have involved simulating changes in fish and invertebrate populations expected under given chemical conditions, often extrapolating from toxic responses in the laboratory (Howells, Brown & Sadler, 1983; Van Winkle, Christensen & Breck, 1986; France & LaZerte, 1987). Only Minns, Kelso & Johnson (1986) have attempted to forecast temporal patterns by modelling alkalinity, total dissolved solids and potential fish yield in lakes of the Canadian Shield.

In this paper we suggest an approach to modelling empirically the ecological impact of acidification in Welsh streams, illustrated with reference to two catchments. We also point out some weaknesses which must be overcome before this approach becomes widely accepted, but also suggest methods for testing the model's output over relatively short time periods.

Methods

General approach

Our approach has been to use the hydrochemical model MAGIC to formulate stream chemistry in the past, and in the future under various rates of atmospheric deposition and types of land use. The chemical output from MAGIC was then used to predict stream biology, based on empirically derived relationships with water chemistry in the present day. All the biological models were simple and linear, and gave: (1) The survival of brown trout *Salmo trutta* (L.), using a linear regression of survival time on aluminium concentration. (2) Brown trout density, using a multiple regression from aluminium concentration, total hardness and stream size. (3) Invertebrate fauna, using a multiple discriminant analysis of the environmental variables which differentiated most strongly between invertebrate assemblages, identified using a cluster analysis (TWINSPAN).

TABLE 1. A comparison between the actual chemistry of MS and FS, and values given by the MAGIC model in 1984–85 under moorland and forest scenarios. The values, in mg l^{-1} except for pH, are annual means.

		Model MS			Model FS	
Determinand	MS	Moorland	Forest	FS	Moorland	Forest
pH	5.2	4.8	4.7	4.9	5.0	4.6
Aluminium	0.162	0.173	0.483	0.378	0.068	0.637
SO_4	4.8	4.7	7.0	7.3	5.2	7.3
Ca	0.8	0.9	1.1	1.2	1.1	1.3
Mg	0.7	0.7	0.8	0.7	0.7	0.7

The study area

The modelling exercise was undertaken using chemical data from two catchments around Llyn Brianne (52°7′ N, 3°43′ W; Fig. 1), a large reservoir on the River Tywi in mid-Wales, and the site of several previous studies of the chemistry and biology of surface water acidification (e.g. Stoner *et al.*, 1984; Ormerod *et al.*, 1987; Weatherley & Ormerod, 1987; Whitehead *et al.*, 1988). Both catchments have soft-water streams (<2 mg Ca l^{-1}, pH 4.8–5.2, 0.15–0.36 mg Al l^{-1} annual means) and are covered, respectively, by planted sitka spruce

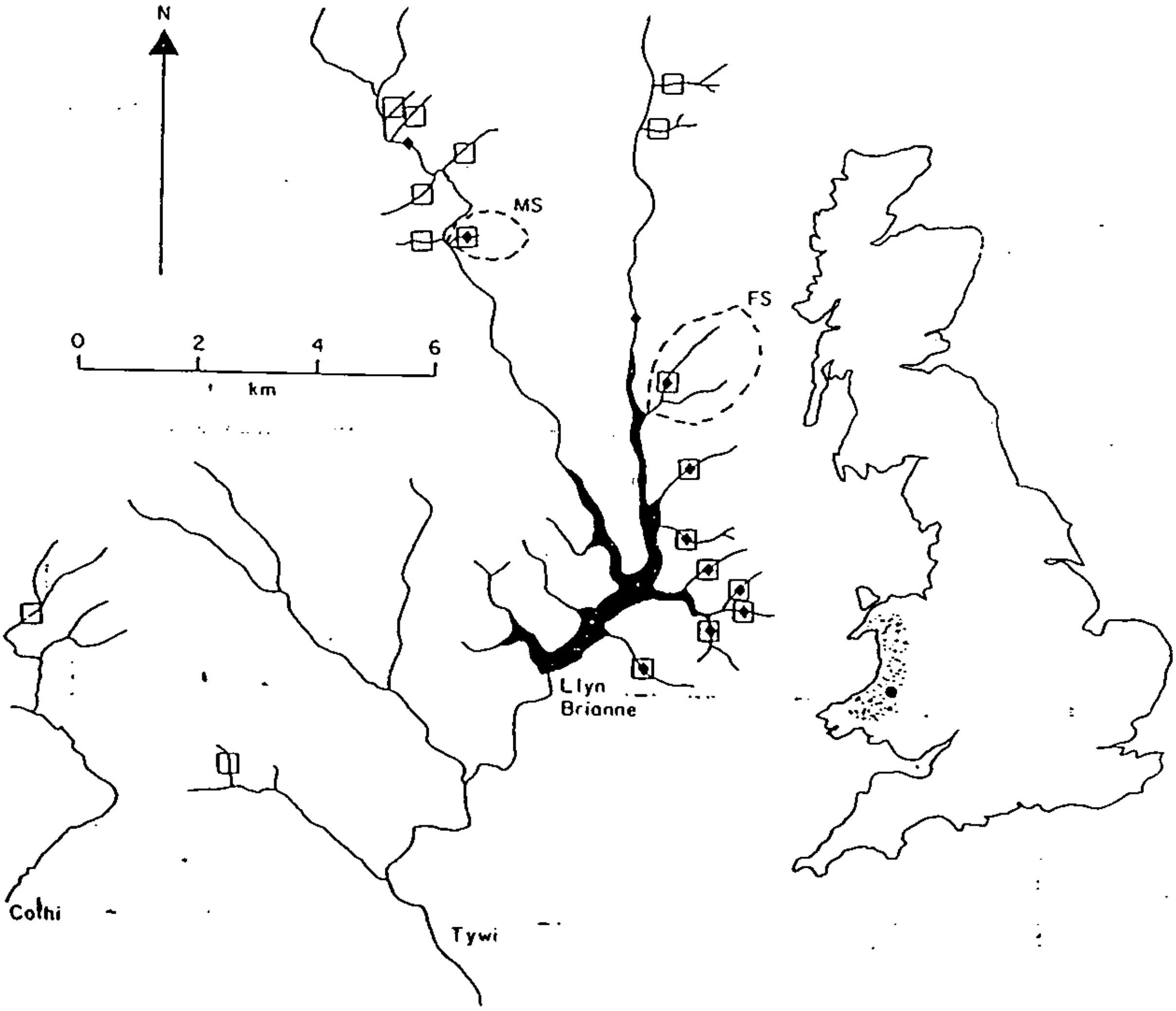


FIG. 1. The location of the study area (•). Data for the fish density model were drawn from the shaded area. On the large-scale map, FS and MS are the forested and moorland catchments, respectively, which were involved in the MAGIC simulations. Other sites marked were used to produce data for the invertebrate (☐) and fish survival (◆) models.

Picea sitchensis Carr. (FS=forestry stream), and by moorland (MS=moorland stream) with *Molinia caerulea* (L.). *Festuca* spp. and *Nardus stricta* (L.). Both catchments are underlain predominantly by shales and mudstones of lower Silurian age. Their soils are also similar, both being covered mostly by brown podzolics (34% in FS, 21% in MS), ferric stagnopodzols (19% in FS, 23% in MS), and humic or stagnohumic gleys (31% in FS, 25% in MS). The forestry stream is currently fishless, whilst MS had 10 fish $100\,m^{-2}$ in 1984 and 1985.

Depending on the model (see below), biological data were drawn either from streams around Llyn Brianne or from a wider geographical range of soft-water sites throughout $4000\,km^2$ of upland Wales (see Ormerod, Wade & Gee, 1987; Wade, Ormerod & Gee, 1988).

The fish models

The trout survival model was derived in 1982 by Stoner *et al.* (1984), who caged 0+ fish from wild stock in streams around Llyn Brianne (Fig. 1). Mean aluminium concentrations (filterable at $<0.45\mu m$) during exposure explained 96% of the variance in survival time giving a highly significant regression:

$$LT_{50}=22.2-36.2\,[Al_{filt}]$$

(LT_{50} in days, aluminium in $mg\,l^{-1}$).

In all cases where pronounced mortality occurred, pH was below 5, with most aluminium in the labile form (Welsh Water, unpublished).

To derive the density model, eighty-eight streams in the Welsh uplands (Fig. 1) were electro-fished between June and August 1984, and trout densities were estimated using catch-removal methods (Zippin, 1958; Seber & Le-Cren, 1967). Densities were related to water quality (from weekly spot samples) and other environmental data using stepwise multiple regression, and the following model explained 50% of the variance:

$$\begin{aligned} L\ \text{density}= & -1.24-1.08\ L[Al_{filt}] \\ & +1.33\ L[\text{Hardness}] \\ & -0.22\ L\ \text{A.D.F.} \end{aligned}$$

(Density in $n\ 100\,m^{-2}$, aluminium in $mg\,l^{-1}$, hardness in $mg\ CaCO_3\ l^{-1}$, A.D.F.=Average daily flow in $m^3\,s^{-1}$; L indicates $\log_{10}$.)

Alternative regressions, including zinc and pH (but not hardness) as predictors, explained a similar proportion of the variance, but were not used in this study; zinc concentrations are not raised in the streams being modelled, whilst pH and aluminium concentrations are highly correlated. Total hardness was incorporated because base cations are important in MAGIC, and also influence fish responses to acid stress (e.g. Brown, 1982).

The invertebrate model

Recent studies in the U.K. have revealed consistent and striking relationships between invertebrate assemblages and acid–base status in streams (Townsend, Hildrew & Francis, 1983; Wright *et al.*, 1984; Ormerod & Edwards, 1987; Weatherley & Ormerod, 1987; Wade *et al.*, 1988). Such relationships are clearly suitable for empirical modelling using techniques proposed by Green & Vascotto (1978). These methods have permitted important developments towards predicting the macroinvertebrate fauna expected under different environmental conditions (Wright *et al.*, 1984; Armitage *et al.*, 1987; Moss *et al.*, 1987). The procedure involves: (1) Classifying streams on the basis of their invertebrate faunas. (2) Assessing which environmental variables differ most strongly between site groups in the invertebrate classification. (3) Combining the environmental variables into a series of linear functions which then 'discriminate' between the *a priori* invertebrate grouping.

Prediction involves using new values of the discriminant functions to indicate which type of invertebrate fauna would be expected under the new environmental conditions.

The derivation of our invertebrate model has been described more fully by Weatherley & Ormerod (1987). Eighteen streams around Llyn Brianne were sampled for macroinvertebrates in April 1985 (Fig. 1). Streams FS (as site LI 1 in Weatherley & Ormerod, 1987) and MS (as site CI 5) were included in this earlier survey, but the modelling exercise is not constrained or circularized because wholly new sets of chemical data were generated in these catchments during the forecasts and hindcasts (see below). Invertebrate data were pooled from riffle and marginal habitats because of the extra information gained and precision achieved (Ormerod, 1987; Weatherley & Ormerod, 1987). Streams were then classified using Two-way Indicator Species Analysis (TWINSPAN: Hill, 1979), on the basis of species composition and relative abundance, into three groups:

Group A. Acidic streams (mean pH 5.0, total hardness 5.9 mg $CaCO_3$ l^{-1}, 0.29 mg Al l^{-1}), often draining afforested areas. Dominated by stonefly nymphs with mayflies absent.

Group B. Moderately acidic streams (mean pH 5.4, total hardness 4.8 mg l^{-1}, 0.1 mg Al l^{-1}), usually draining moorland catchments, and with a more diverse fauna than A including additional predaceous stoneflies (*Isoperla grammatica* (Poda), *Diura bicaudata* (L.)), some mayfly nymphs (e.g. *Leptophlebia marginata* (L.) and dragonfly nymphs (*Cordulegaster boltonii* (Donovan)).

Group C. Circumneutral streams (mean pH 6.7, hardness 13.0 mg l^{-1}, 0.05 mg Al l^{-1}), draining moorland or deciduous woodland, and with the most diverse fauna, dominated by grazing mayfly nymphs (*Baetis* spp., *Rhithrogena semicolorata* (Curtis)).

(Chemical characteristics were based on annual means from a weekly programme of spot sampling.)

In multiple discriminant analysis, the use of aluminium concentration, total hardness and catchment area (as an expression of stream size) permitted 100% precision in placing each stream into its correct invertebrate group (see Weatherley & Ormerod, 1987). Output from MAGIC was used to locate each modelled stream in discriminant function space, hence indicating the likely invertebrate assemblage (see Fig. 2), according to the following equations.

$$F1 = 6.58\,L[Al] + 4.12\,L[hardness] - 0.06\ L\ catchment\ area + 2.72$$

$$F2 = 9.93\,L[hardness] + 1.23\,L[Al] - 1.20\ L\ catchment\ area - 4.35$$

(concentrations in mg l^{-1}, area in hectares).

In part, the accuracy of the prediction will depend on whether a new site or new conditions are within the range of the existing TWINSPAN classification and discriminant analysis. This can be assessed from the Euclidean distance, in discriminant space, of the

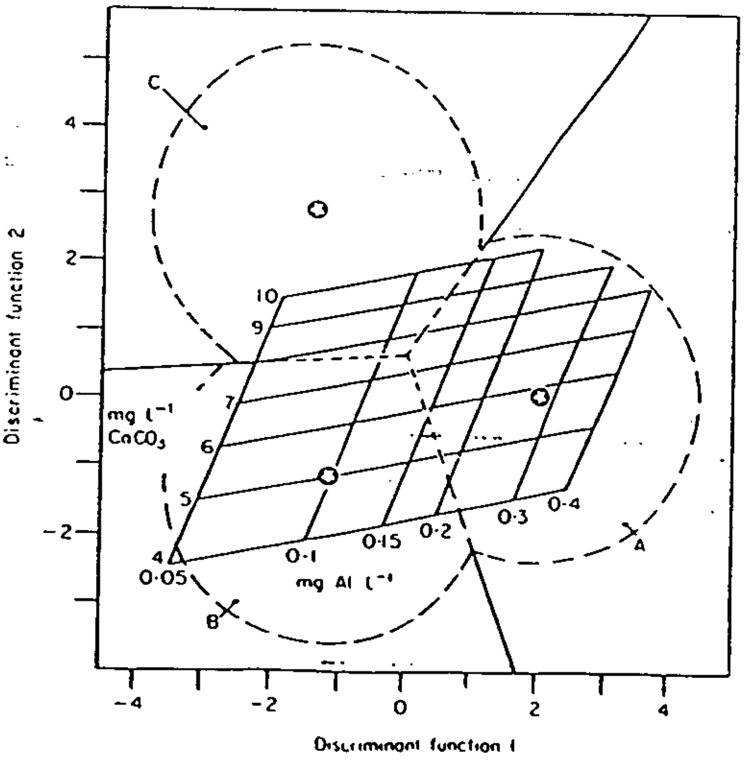


FIG. 2. The macroinvertebrate model, showing the 95% probability boundary (broken line) and centroid (stars) for each macroinvertebrate group (A, B, C) in discriminant space. The grid shows how a hypothetical stream, of catchment area 100 ha, would change location with increasing total hardness (*y* axis) and filterable aluminium (*x* axis).

new conditions from the mean location of each TWINSPAN group (see Moss *et al.*, 1987). Euclidean distance is a Chi-squared variable, with degrees of freedom equal to the number of discriminant functions. Hence, we have used a chi-squared value, at $P=0.05$, to calculate a Euclidean distance outside which the model involves extrapolation beyond the initial range of calibration (see Fig. 2).

MAGIC – a brief outline

The conceptual basis of MAGIC is that atmospheric deposition, mineral weathering and exchange processes in the soil and interstitial solutions are responsible for the observed chemistry of surface waters (Cosby *et al.*, 1985; Whitehead *et al.*, 1988). Output from the model includes pH, alkalinity, the concentrations of strong acid anions (SO_4^{2-}, Cl^-, NO_3^- and F^-), base cations, and aluminium. The following processes are important: (1) Dissolution of CO_2 in soil water, producing bicarbonate and free hydrogen ions. (2) Reaction between the free hydrogen ions and an aluminium mineral, producing trivalent aluminium. (3) Consumption of the trivalent aluminium as it is exchanged for base cations in the soil matrix. (4) Depletion of base-cations through leaching, affected mainly by the presence of strong acid anions (SO_4^{2-}, NO_3^{2-}, Cl^-, F^-). (5) Movement of soil water into stream water, accompanied by loss of CO_2 to the atmosphere (degassing) and hence rise in pH.

Because anions in acid deposition from the atmosphere are accompanied by H^+, base cations are initially displaced from the soil. However, if base cations in the soil are scarce or become depleted (process 4), less aluminium is removed by ion exchange (step 3), and increased aluminium concentrations and low base concentrations occur in runoff. Aluminium and H+ therefore become increasingly important in the charge balance of stream water. The precipitation of aluminium hydroxide also acts as a buffer against pH increase (step 5).

Long-term trends in base-poor catchments include the exhaustion of base cations in the soil, a process controlled by the relative rates of loss through leaching and re-supply by weathering. Catchments in which losses of base cations due to leaching exceed weathering rates are subject to acidification and to increased concentrations of aluminium. The balance between leaching and weathering is clearly affected by the atmospheric deposition of strong acids.

As a recent extension to MAGIC, some of the acidifying influences of conifer forest have been simulated by increasing the rate of dry and occult deposition, and evapotranspiration (Neal *et al.*, 1986; Whitehead *et al.*, 1988). These effects are particularly important in this study (see below).

MAGIC application to MS and FS

The application of MAGIC to any given catchment involves obtaining values for key parameters such as cation weathering rates, cation/aluminium exchange coefficients, sulphate adsorption capacity, nitrogen uptake rates and soil PCO_2. Once established, these parameters determine the chemical response of soil and runoff to deposition rates specified by the modeller. At FS and MS, MAGIC was calibrated from an extensive soil and streamwater data base from 1984 and 1985, and key parameters were determined by Whitehead *et al.* (1988).

Trends in MS and FS were simulated between 1844 and 2124. Deposition patterns up to 1984 involved sulphate loadings increasing between 1840 and 1970 to ~28 kg S ha^{-1}, and thereafter falling by 25% up to 1984 (see Whitehead *et al.*, 1988). From 1984 onwards, alternative scenarios involved, firstly, continued sulphate deposition at 1984 levels (~20 kg S ha^{-1}) and, secondly, a 50% reduction in sulphate deposition, beginning in 1984 but phased over a 20-year period. In addition, these different scenarios were applied to catchments under two different land uses.

In the 1950s and 1960s, many upland catchments in Wales were afforested with conifers (Ormerod & Edwards, 1985), with planting around the Llyn Brianne study area beginning in the late 1950s. In the model, therefore, alternative scenarios from 1958 onwards involved either moorland or conifer forest on each catchment, with forest simulated by linear increases in the dry/occult deposition of anthropogenic sulphate and sea salts over a 15-year period of tree growth and canopy closure (Whitehead *et al.*, 1988). Moorland

and forest treatments represented the actual sequence of development of MS and FS, respectively, whilst the converse (i.e. forest absence from FS and afforestation on MS) permitted a reversal of current land uses. This reversal was particularly useful in assessing the biological models, since simulated forest on MS enabled a comparison with the actual conditions in FS, whilst simulated moorland on FS permitted comparison with the actual conditions in MS.

Stream biology was simulated in the years 1844 (the origin), 1984 (the calibration year, following forest canopy closure), 2004 (the end of the 50% sulphate reduction period and approximately the time when the first forest crop would be harvested) and 2124. Catchment area was assumed to be constant in the invertebrate model, but average daily flow in the fish density model was adjusted by ±10% to mimic the average effect of conifer forest on water yield (Calder & Newson, 1979).

Results

Chemical changes

After running the model between 1844 and 1984, with the given deposition sequence, the chemical output for stream chemistry provided a reasonable match with the actual conditions for 1984–85, although some overestimations of H^+ and aluminium concentration were apparent. Comparing between the different catchments, simulated forest presence on MS gave similar chemical data to the real situation in FS.

Simulated chemical trends indicated slightly greater buffering capacity in FS than in MS, but the two were broadly similar and have been illustrated using MS (Fig. 3). pH values in all cases were below pH 5 by 1960, differing between only pH 4.6 and pH 4.9 in the scenarios from 1984 onwards. Of particular importance to the biological models, simulated aluminium concentrations increased markedly from 1940 onwards, most notably in the presence of forest.

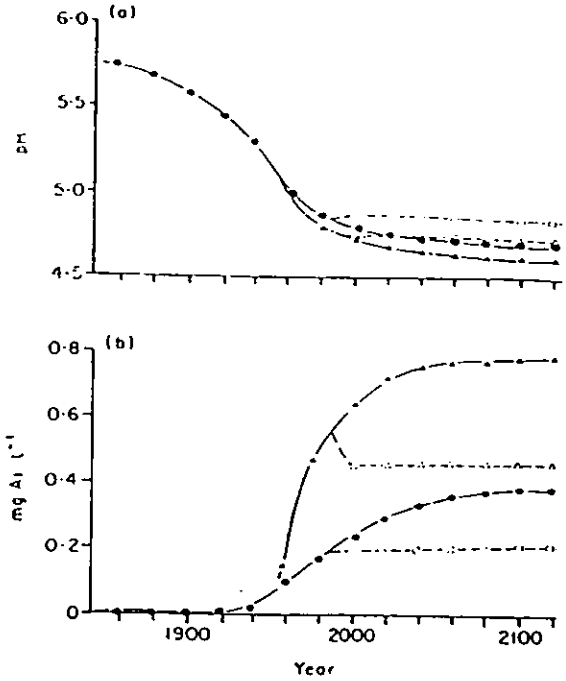


FIG. 3. Changes in (a) pH and (b) aluminium concentrations in MS between 1844 and 2124, simulated by MAGIC (broken line, 50% reduction in deposition from 1984; solid line, continued deposition at 1984 levels; ● ○, moorland; ▲ △, forest from 1958 onwards) (see Whitehead *et al.*, 1988).

The fish models

MAGIC simulation indicated that, in 1844, trout would have survived for the duration of the calibration experiments (>22 days) in both streams (Fig. 4). However, a progressive reduction in survival time occurred between 1844 and 1984 with the effect particularly pronounced in the presence of forest. During 1984, the simulated LT_{50} of 5 days in MS under the forest scenario was close to the actual value in the real forest stream of 9.2 days in 1982. Similarly, the absence of forest from FS gave a simulated LT_{50} of 19.7 days, close to the actual value for MS of 16.8 days.

Forecasts also indicated a marked influence by forest, LT_{50}s remained below 5–10 days in both streams in the forest scenario, irrespective of a 50% deposition reduction from 1984 onwards (Fig. 4). Under moorland, simulation showed that reduced deposition prevented survival times falling below 1984 levels.

Trout density in the model showed trends similar to those for survival time (Fig. 5). Both the streams had 80–150 fish $100\,m^{-2}$ in 1844. However, densities in MS and FS declined considerably by 1984: under the moorland scenario both streams had only 8–15 fish $100\,m^{-2}$, a range including the actual case in

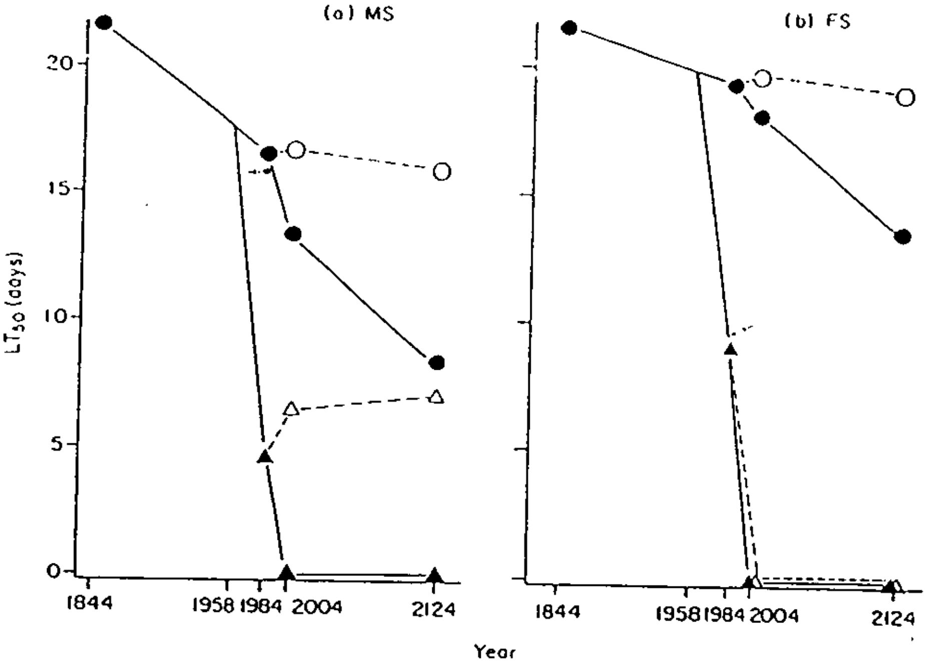


FIG. 4. Changes in the survival time of brown trout in two soft-water streams in the upper Tywi according to MAGIC simulation. The actual values in each stream in 1982 are arrowed. Conventions as in Fig. 3.

MS of 10 fish 100 m^{-2}. The reduction was even more marked under forest, values in MS and FS being 2 and 0 fish per 100m^{-2}, respectively, by 1984. This simulated condition in MS corresponded closely with the actual fishless status of FS.

In forward simulations, further pronounced decline in trout density was prevented only under the moorland scenario with reduced deposition.

The invertebrate model

Simulated conditions for each stream up to ~1940, and after ~2010 in the forest scenarios, were outside the 95% probability limits of the MDA, hence involving extrapolation.

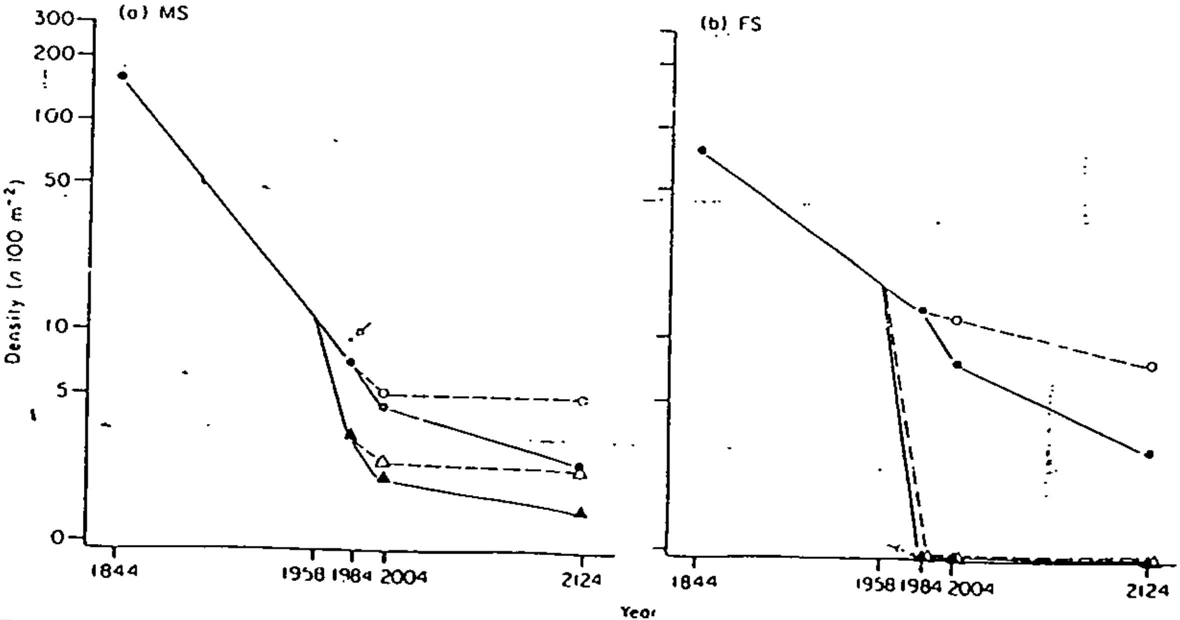


FIG. 5. Changes in the density of brown trout in two soft-water streams in the upper Tywi according to MAGIC simulation. Conventions as in Fig. 3. The actual values in 1984 are arrowed.

Interestingly, simulation indicated that MS and FS did not have invertebrate group C in 1844, reflecting low concentrations of calcium and magnesium at this time (Fig. 6). Under the moorland scenarios group B persisted in FS, even at 1984 levels of deposition, until shortly after 2124. This simulated return of moorland to FS, therefore, accurately recreated the real situation in MS during the calibration period. In MS, model conditions were borderline between groups B and A by 1984, with the transition occurring shortly after this date. With moorland and reduced deposition, change to the impoverished group A was

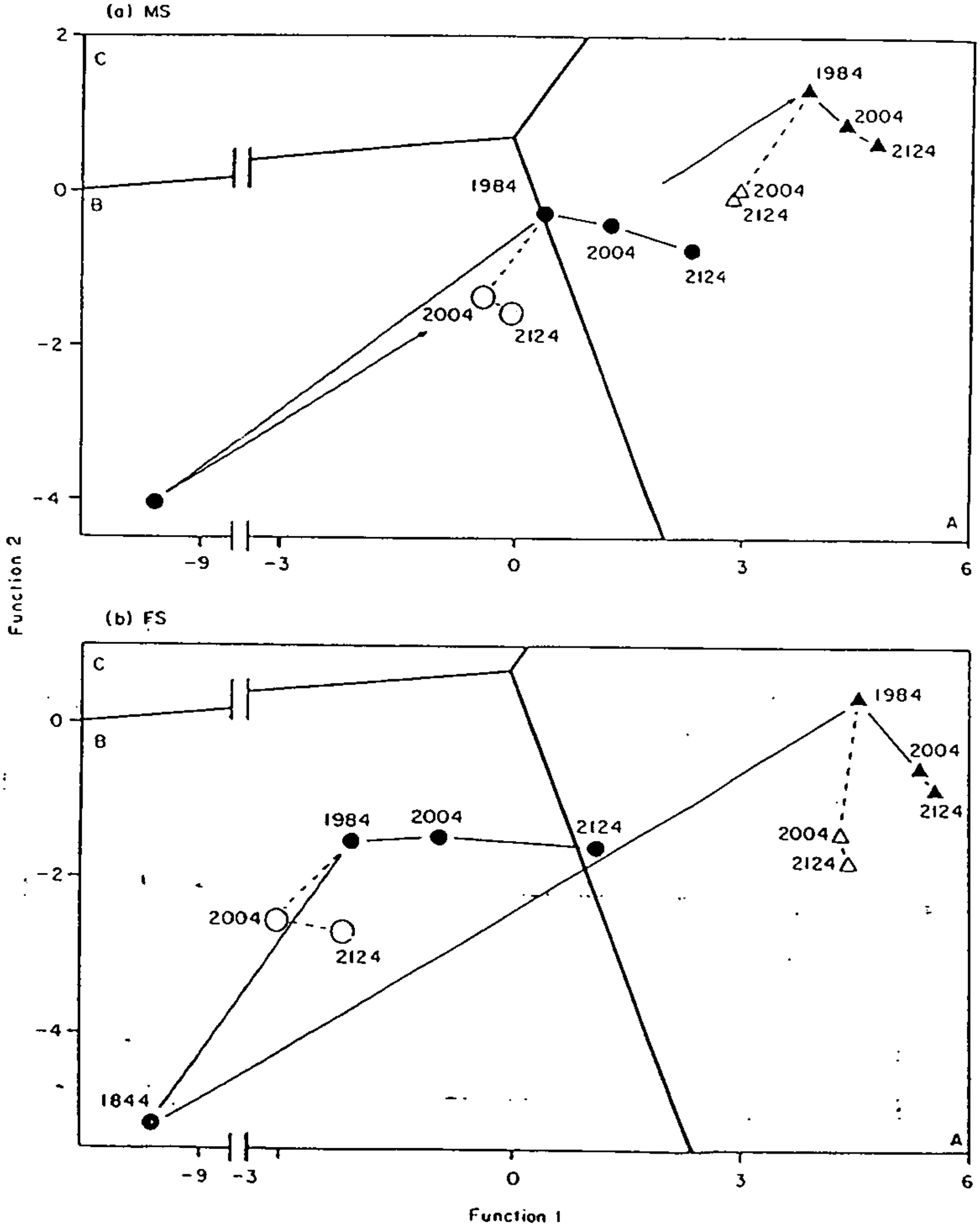


FIG. 6. Changes in the types of macroinvertebrate assemblages in two soft-water streams in the upper Tywi according to MAGIC simulation. The assemblages (A, B, C), described in the text, were judged from the position of each site in discriminant space. Conventions as in Fig. 3.

prevented in MS and delayed until almost 2124 in FS.

By contrast, simulated chemical changes due to the presence of forest considerably advanced the change to assemblage type A in both catchments (Fig. 6). This simulation in MS accurately re-created the actual situation in FS. A 50% reduction in deposition, under the forest scenario, was not sufficient to return the faunal type from A to B during any stage of future simulation.

Discussion

There are several caveats in a modelling exercise such as this, and we emphasize that our results represent simulation and not necessarily accurate representation of real phenomena. Such caveats apply not only to the ecological models, but also to MAGIC, whose design and operation is currently subject to debate (Reuss, Christophersen & Seip, 1986); even if the ecological models faithfully represented relationships with water quality, their predictive ability is dependent on the accuracy of the hydrochemical inputs.

Uncertainties over MAGIC

Uncertainties over MAGIC arise from the estimated deposition pattern, the assumption that soils are homogeneous within catchments, and from comprehension of the complex chemical processes involved in the response of catchments to acid deposition (Reuss *et al.*, 1986). For example, in MAGIC, the release aluminium is controlled largely by reactions which assume the solubility of gibbsite (Al $(OH)_3$), which is probably a scarce mineral in many catchments to which MAGIC has been applied. However, other aluminium sources may share similar solubilities to gibbsite, and this criticism of MAGIC may have been overstated (Ruess *et al.*, 1986; Whitehead *et al.*, 1988). Nevertheless, considerations of the model's aluminium chemistry remain an area of active development. Such developments could be particularly important to the ecological models in view of the importance of aluminium in the empirical relationships.

The use of MAGIC in studies that model acidification due to forestry carries a further major assumption, that the key acidifying processes under forest are increases in dry/occult deposition and evapotranspiration (Neal *et al.*, 1986). These processes do occur in afforested catchments around Llyn Brianne, leading respectively to enhanced deposition of sulphate and nitrate, and reduced dilution of the resulting acids (Stoner *et al.*, 1984; Hornung, unpubl.). However, other acidifying processes are possible in afforested conditions (Stoner & Gee, 1985). Pre-afforestation ploughing creates a drainage network which persists through the forest rotation, and the resulting alterations in hydrology may be particularly important for MAGIC, reducing the time available for weathering reactions (Reuss *et al.*, 1986). Ploughing would also change the mixing pattern of base-rich ground water with acidic surface water (Whitehead, Neal & Neale, 1986). Additionally, MAGIC appears to be particularly sensitive to changes in soil PCO_2, for which few field data are available from forested areas.

Despite the many cautions governing MAGIC, it has recently been able to reproduce accurately the acidification of Scottish lochs as shown independently by changes in the diatom flora (Musgrove, Whitehead & Cosby, unpubl.). Similar trends to those given by MAGIC for Welsh streams were also reconstructed from diatom cores taken from adjacent lakes, although Welsh data are so far only available from moorland situations (Battarbee *et al.*, 1988).

Problems in ecological modelling

A major assumption in operating the ecological models is that the empirical relationships (essentially correlations) between stream chemistry and biology represent a causal influence. Furthermore, cause–effect patterns from spatial relationships are implicitly assumed to equate with trends in time. Such assumptions are likely to be more robust in the trout toxicity model, where many data support direct toxicological effects by acid-related factors (see Witters & Vanderborght, 1987).

However, in the case of salmonid density or invertebrate distribution, other abiotic and biotic effects clearly could be important influences on the fauna. This caveat applies particularly to the trout density model, which explained only 50% of the overall variance. Of notable importance in our study, the effect of forestry on stream biology operates not only through chemistry, but probably also through changes in hydrology, sediment yields, energetic pathways and habitat structure (Ormerod *et al.*, 1987).

In addition, there is some evidence that salmonid abundance can be limited by habitat features (Milner, Hemsworth & Jones, 1985) or density dependent regulation and emigration (Chapman, 1962; Gee, Milner & Hemsworth, 1978; Elliott, 1985). These factors could restrict trout density in the study streams, keeping values below those given by the model for 1844 and indicating that the fishery decline in the model could be overstated. However, densities similar to those simulated in 1844 were found at about 25% of the sites during the calibration survey, undertaken on streams physiographically similar to FS and MS (Welsh Water, unpubl.). Moreover, other studies on Welsh hill-streams support a correlation between pH and fishery status (Sadler & Turnpenny, 1986). Low salmonid abundance in acid streams in Wales does not appear to reflect limited food availability (Turnpenny *et al.*, 1987). Nor does it reflect limited habitat because densities in streams with <25 mg $CaCO_3$ l^{-1} are often lower than expected from habitat characteristics (Milner *et al.*, 1985). The survival and density models (derived from different data-sets), and the trends they showed in simulation, were mutually supportive in indicating a chemical influence. However, further modelling exercises would benefit from the incorporation of parameters such as reproductive potential and the survival of eggs, fry, and older fish (Howells *et al.*, 1983; Van Winkle *et al.*, 1986). Comparisons between populations modelled in this way with those modelled empirically could be instructive.

Possible physical influences by forest on stream invertebrates were masked in our study because aluminium concentration represented the major detectable difference between afforested and moorland catchments (Weatherley & Ormerod, 1987). However, many data support an influence by acid related factors on invertebrates in Welsh upland streams. For example, the ordination and classification of invertebrate assemblages has repeatedly revealed pronounced correlations with pH, or related factors (for Welsh streams see Ormerod & Edwards, 1987; Weatherley & Ormerod, 1987; Wade *et al.*, 1988). While these correlations in themselves do not necessarily reflect cause–effect relationships, they persist amongst the fauna from different stream habitats (Ormerod, 1987; Weatherley & Ormerod, 1987), and are more pronounced than correlations between invertebrate ordinations and land use (Wade *et al.*, 1988); neither of these features would be likely if chemistry did not exert some causal influence. Direct effects on some species by low pH and high aluminium concentrations have been demonstrated in a Welsh stream (Ormerod *et al.*, 1987), although it is also possible that indirect chemical influences on invertebrates occur through 'bottom-up' (food availability) and 'top-down' (predatory) control (e.g. Hildrew, Townsend & Francis, 1984; Winterbourn *et al.*, 1985; Ormerod, Wade & Gee, 1987; Schofield, Townsend & Hildrew, unpubl.).

Whilst empirical models such as ours would take account of both direct and indirect pathways of chemical influence, the model could be inaccurate because of the relative effects of chronic versus episodic conditions. Acid streams are characterized by pronounced fluctuations in pH and aluminium concentrations during storm events or snow melt (Stoner *et al.*, 1984; Brown, McLachlan & Ormerod, unpubl.) and direct physiological effects on stream fauna could occur through such brief episodes of acid stress. However, all our ecological models were based on annual mean chemistry, partly because episodic influences could not be separated in our data-base, but also because MAGIC does not incorporate hydrological events or their associated pH change. The absence of episodes from the modelling procedure would be most problematic in situations where streams of differing mean pH had similar minima which exceeded toxic thresholds. Mean and extreme values for pH and aluminium are closely correlated, however, and means probably indicate the likelihood of episodic change (Ormerod & Tyler, unpubl.). Moreover, some of the indirect pathways of chemical influences on biology, such as those acting through trophic status, seem as likely to involve chronic effects as episodic. Nevertheless, the incorporation of episodes into MAGIC and biological models clearly require development for realistic simulation.

The invertebrate model used in this study follows the approach adopted by Wright *et al.* (1984), and indicates an extension to previous predictive studies (Moss *et al.*, 1987). The model, as we have used it, however, is constrained to predict faunal changes which occur in steps between TWINSPAN groups, rather than continuous change in species composition. In cases where species occurrences reflect direct chemical effects, faunal changes might be expected to occur incrementally as specific tolerance ranges are sequentially exceeded (e.g. Engblom & Lingdell, 1984). Moss *et al.* (1987) have now provided a method by which such specific changes can be modelled, and we are currently expanding our approach to include this development (Weatherley & Ormerod, unpubl.). However, if TWINSPAN groups reflect true aquatic communities, with functional relationships and interspecific dependence (e.g. Hildrew *et al.*, 1984; Ormerod *et al.*, 1987), even such species-specific modelling could be limited. Changes within sites are further influenced by the probability of colonization by 'new' species, a process of which little is known in upland streams (cf. Sheldon, 1984). Clearly, intensive monitoring of chemical and biological change in acid waters is required in order to assess how assemblage patterns develop.

Validating the model and testing the predictions

A sceptical view of an exercise such as this might be that only data spanning many decades would provide a test of the model predictions. However, an alternative would be to accelerate chemical changes at the catchment, or even lysimeter, level. For example, projects in Norway (Wright *et al.*, 1986) and the U.S.A. (Haines *et al.*, unpubl.) already involve experimentally increased or decreased acid deposition over whole catchments. At Llyn Brianne, catchment-scale manipulations include afforestation, partial deforestation and catchment liming (i.e. increased cation availability). Chemical and biological monitoring in these experiments is in progress to evaluate our hydrochemical and biological models.

Validation of historical reconstructions clearly presents a more insurmountable problem. Whereas past pH conditions in lakes, as indicated by MAGIC and diatom stratigraphy, are corroborative (Musgrove, Whitehead & Cosby, unpubl.), no similar method is readily available for obtaining data on the past biology of streams. For example, operation of the invertebrate model for the nineteenth century involved extrapolation beyond the range of the multiple discriminant analysis. MAGIC indicated that runoff modelled at this time was characterized by exceedingly low concentration of cations (~3 mg l^{-1} total hardness), but pH >5.7, and almost no aluminiun. At least in Wales, streams with these chemical features no longer exist, and it is impossible to assess from field data what their biological character might be.

General patterns

Notwithstanding the above caveats, several features of our models are of interest. Firstly, the results indicate a pronounced acidification and aluminium mobilization in soft-water streams in the upper Tywi between the nineteenth century and the present day. Such simulated change caused a considerable reduction in trout survival and density. Since brown trout are less sensitive to acid stress than salmon (Ormerod *et al.*, 1987), chemical changes indicated by the model would also affect the suitability of the upper Tywi as a nursery for this migratory species. Secondly, the most pronounced acidification occurred under the forest scenarios, with fish either totally eliminated (FS) or present at exceedingly low density (MS). In view of the reduced LT_{50} under forest conditions, it is unlikely that the few fish remaining in MS in the forest scenario would survive. Additionally, pronounced changes in the model invertebrate fauna were advanced under forest conditions. These simulated effects are supported by the observed impact of forestry on streams in Wales and Scotland (Harriman & Morrison, 1982; Stoner *et al.*, 1984). Lastly, and by contrast, the absence of forest with reduced deposition could at least support some salmonids in all the streams studied. If extrapolated to other upland areas, this feature could be important because of the nursery functions fulfilled by headwaters.

Acknowledgments

The field data used in calibrating the MAGIC and biological models were collected by field and laboratory staff of the Welsh Water Authority, University College Swansea and UWIST, to whom we are grateful. Professor R. W. Edwards, Dr A. S. Gee, Dr M. Hornung, Dr J. H. Stoner, Dr A. G. Hildrew and a referee commented on earlier drafts. The work was largely funded by the Department of the Environment and the Welsh Office, and formed part of the Llyn Brianne project. The views expressed are those of the authors and not necessarily those of the organizations they represent.

References

Altshuller A.P. & Linthurst R.A. (1984) *The Acidic Deposition Phenomenon and its Effects: Critical Assessment and Review Papers.* Volume 2, *Effects Sciences.* North Carolina State University Acid Deposition Programme, EPA, Washington.

Armitage P.D., Gunn R.J.M., Furse M.T., Wright J.F. & Moss D. (1987) The use of prediction to assess macroinvertebrate response to river regulation. *Hydrobiologia*, 144, 25–32.

Battarbee R.W. & Charles D.F. (1986) Diatom-based pH reconstruction studies of acid lakes in Europe and north America: a synthesis. *Water, Air and Soil Pollution*, 30, 347–354.

Battarbee R., Fritz S.C., Kreiser H. & Appleby P.G. (1988) Palaeoecological evidence for the acidification of Welsh lakes. In: *Acid Waters in Wales* (Eds J. H. Stoner, A. S. Gee and R. W. Edwards). Junk, The Hague.

Brown D.J.A. (1982) The effects of pH and calcium on fish and fisheries. *Water, Air and Soil Pollution*, 18, 343–351.

Calder I. & Newson M. (1979) Land use and water resources in Britain: a strategic look. *Water Resources Bulletin*, 15, 1628–1639.

Chapman D.W. (1962) Aggressive behaviour of juvenile coho salmon as a cause of emigration. *Journal of the Fisheries Research Board of Canada*, 19, 1047–1080.

Cosby C.J., Whitehead P.G. & Neale R. (1986) A preliminary model of long-term changes in stream acidity in southwestern Scotland. *Journal of Hydrology*, 84, 381–401.

Cosby C.J., Wright R.F., Hornberger G.M. & Galloway J.N. (1985) Modelling the effects of acid deposition: estimation of long-term water quality responses in a small forested catchment. *Water Resources Research*, 21, 1591–1601.

Elliott J.M. (1985) Population dynamics of migratory trout, *Salmo trutta*, and their implication for fisheries management. *Journal of Fish Biology* (Supplement A), 27, 33–43.

Engblom E. & Lingdell P. (1984) The mapping of short-time acidification with the help of biological pH indicators. Report 61 of the Institute for Freshwater Research, Drottningholm, pp. 60–68. National Swedish Board of Fisheries, Lund.

Flower R.J. & Battarbee R.W. (1983) Diatom evidence for recent acidification of two Scottish Lochs. *Nature*, 305, 130–133.

France R.L. & LaZerte B.D. (1987) Empirical hypothesis to explain the distribution of *Hyallela azteca* (Amphipoda) in anthropogenically acidified lakes. *Canadian Journal of Fisheries and Aquatic Sciences*, 44, 1112–1121.

Gee A.S., Milner N.J. & Hemsworth R.J. (1978) The effect of density on mortality in Atlantic salmon. *Journal of Animal Ecology*, 47, 497–505.

Green R.H. & Vascotto G.L. (1978) A method for the analysis of environmental factors controlling patterns of species composition in aquatic communities. *Water Research*, 12, 583–590.

Harriman R. & Morrison B.R.S. (1982) Ecology of streams draining forested and non-forested catchments in an area of central Scotland subject to acid precipitation. *Hydrobiologia*, 88, 251–263.

Hildrew A.G., Townsend C.R. & Francis J. (1984) Community structure in some southern English streams: the influence of species interactions. *Freshwater Biology*, 14, 297–310.

Hildrew A.G., Townsend C.R., Francis J. & Finch K. (1984) Cellulolytic decomposition in streams of contrasting pH and its relationship with the invertebrate community. *Freshwater Biology*, 14, 323–328.

Hill M.O. (1979) *TWINSPAN – A FORTRAN programme for arranging multivariate data in an ordered two-way table by classification of the individuals and attributes.* Department of Ecology and Systematics, Cornell University, Ithaca, New York.

Howells G.D., Brown D.J.A. & Sadler K. (1983) Effects of acidity, calcium and aluminium on fish survival – a review. *Journal of the Science of Food and Agriculture*, 34, 559–570.

Milner N.J., Hemsworth R.J. & Jones B.E. (1985) Habitat evaluation as a fisheries management tool. *Journal of Fish Biology* (Supplement A), 27, 85–108.

Minns C.K., Kelso J.R.M. & Johnson M.G. (1986) Large-scale risk assessment of acid rain on fisheries: models and lessons. *Canadian Journal of Fisheries and Aquatic Sciences*, 43, 900–921.

Moss D., Furse M.T., Wright J.F. & Armitage P.D. (1987) The prediction of the macroinvertebrate fauna of unpolluted running-water sites in Great Britain using environmental data. *Freshwater Biology*, 17, 41–52.

Neal C., Whitehead P., Neale R. & Cosby J. (1986) Modelling the effects of acidic deposition and conifer afforestation on stream acidity in the British uplands. *Journal of Hydrology*, 86, 15–26.

Ormerod S.J. (1987) The influences of habitat and seasonal sampling regimes on the ordination and classification of macroinvertebrate assemblages in the catchment of the River Wye, Wales. *Hydrobiologia*, 150, 143-151.

Ormerod S.J., Boole P., McCahon C.P., Weatherley N.S., Pascoe D. & Edwards R.W. (1987) Short-term experimental acidification of a Welsh stream: comparing the biological effects of hydrogen ions and aluminium. *Freshwater Biology*, **17**, 341–356.

Ormerod S.J. & Edwards R.W. (1985) Stream acidity in some areas of Wales in relation to historical trends in afforestation and the usage of agricultural limestone. *Journal of Environmental Management*, **20**, 189–197.

Ormerod S.J. & Edwards R.W. (1987) The ordination and classification of macroinvertebrate assemblages in the catchment of the River Wye in relation to environmental factors. *Freshwater Biology*, **17**, 533–546.

Ormerod S.J., Mawle G.W. & Edwards R.W. (1987) The influence of forest on aquatic fauna. In: *Environmental Aspects of Forestry Production in Wales* (Ed. J. E. Good). ITE symposium number 22, Institute of Terrestrial Ecology, Grange over Sands.

Ormerod S.J., Wade K.R. & Gee A.S. (1987) Macro-floral assemblages in upland Welsh streams in relation to acidity and their importance to invertebrates. *Freshwater Biology*, **18**, 545–558.

Overrein L.N., Seip H.M. & Tollan A. (1980) *Acid precipitation – Effects on forests and fish*. Final report of the SNSF project, 1973–1980. SNSF, Norway.

Pennington W. (1984) Long-term natural acidification of upland sites in Cumbria: evidence from post-glacial lake sediments. *Freshwater Biological Association Annual Report*, **52**, 28–46.

Reuss J.O., Christophersen N. & Seip H.M. (1986) A critique of models for freshwater and soil acidification. *Water, Air and Soil Pollution*, **30**, 593–599.

Sadler K. & Turnpenny A.W.H. (1986) Field and laboratory studies of exposures of brown trout to acid waters. *Water, Air and Soil Pollution*, **30**, 593–599.

Seber G.A.F. & LeCren E.D. (1967) Estimating population parameters from catches large relative to the population. *Journal of Animal Ecology*, **36**, 631–643.

Sheldon A.L. (1984) Colonization dynamics of aquatic insects. *The Ecology of Aquatic Insects* (Eds V. H. Resh and D. M. Rosenburg), pp. 401–429. Preager, New York.

Stoner J.H. & Gee A.S. (1985) Effects of forestry on water quality and fish in Welsh rivers and lakes. *Journal of the Institute of Water Engineers and Scientists*, **39**, 27–45.

Stoner J.H., Wade K.R. & Gee A.S. (1984) The effects of acidification on the ecology of streams in the upper Tywi catchment in west Wales. *Environmental Pollution* (Series A), **36**, 125–157.

Townsend C.R., Hildrew A.G. & Francis J. (1983) Community structure in some southern English streams: the influence of physiochemical factors. *Freshwater Biology*, **13**, 521–544.

Turnpenny A.W.H., Sadler K., Aston R.J., Milner A.G.P. & Lynam S. (1987) The fish populations of some streams in Wales and northern England in relation to acidity and associated factors. *Journal of Fish Biology*, **31**, 415–434.

Van Winkle W., Christensen S.W. & Breck J.E. (1986) Linking laboratory and field responses of fish population to acidification. *Water, Air and Soil Pollution*, **30**, 639–648.

Wade K.R., Ormerod S.J. & Gee A.S. (1988) Classification and ordination of macroinvertebrate assemblages to predict stream acidity in upland Wales. *Hydrobiologia* (in press).

Weatherley N.S. & Ormerod S.J. (1987) The impact of acidification on macroinvertebrate assemblages in Welsh streams: towards an empirical model. *Environmental Pollution*, **46**, 223–240.

Whitehead P.G., Bird S., Hornung M., Cosby C.J., Neal C. & Paricos P. (1988) Stream acidification trends in the Welsh uplands: a modelling study of the Llyn Brianne catchments. *Journal of Hydrology* (in press).

Whitehead P.G., Neal C. & Neale R. (1986) Modelling the effects of hydrological changes on stream water acidity. *Journal of Hydrology*, **84**, 353–364.

Winterbourn M.J., Hildrew A.G. & Box A. (1985) Structure and grazing of stone-surface organic layers in some acid streams in southern England. *Freshwater Biology*, **17**, 363–374.

Witters H. & Vanderborght O. (Eds.) (1987) Ecophysiology of acid stress in aquatic organisms. *Annales de la Société Royale Zoologique de Belgique*, **117**, Supplement 1.

Wright R.F., Gjessig E., Christophersen N., Lotse E., Seip H.M., Semb A., Sletaune B., Storhang R. & Wedum K. (1986) Project RAIN: changing acid deposition to whole catchments. The first year of treatment. *Water, Air and Soil Pollution*, **30**, 47–63.

Wright J.F., Moss D., Armitage P.D & Furse M.T. (1984) A preliminary classification of running-water sites in Great Britain based on macroinvertebrate species, and the prediction of community type using environmental data. *Freshwater Biology*, **14**, 221–256.

Zippin C. (1958) The removal method of population estimation. *Journal of Wildlife Management*, **22**, 82–90.

(Manuscript accepted 5 February 1988)

6.2 Regional Responses of Trout Survival and Invertebrate Diversity

Chapter 13

Temporal Patterns of Ecological Change During the Acidification and Recovery of Streams Throughout Wales According to a Hydrochemical Model

Steve J. Ormerod[1], *Neil S. Weatherley*[1] *and Paul G. Whitehead*[2]

Summary

The biological consequences of surface-water acidification are important and pronounced. There have, however, been few attempts at modelling biology in waters which are being acidified or restored. We describe a preliminary approach to modelling temporal patterns in the biology of acidic Welsh streams by operating linear empirical models in conjunction with the hydrochemical model, MAGIC. We apply the model to the Welsh region, and to one specific catchment. We simulate chemistry in the years 1844–1984, and in the future under different scenarios of reduced sulfate deposition. In each case, we use the chemical output from MAGIC to predict biological status. Historical reconstruction from 1844 onwards indicated substantial biological change, with declining fish populations, alterations in macroinvertebrate community structure, and reduced populations of riverine birds. Future scenarios, involving deposition reduced across the Welsh region by 0–90 %, showed that a reduction in sulfate of at least 50 % was required in the model to arrest change due to acidification. At sites covered by planted conifer forest, even this reduction did not permit the return of fish in the model. Many caveats apply to the models in their present form, not least, the dominant role of aluminum in the biological models means that they are sensitive to MAGIC's treatment of this poorly understood metal.

---

[1] Acid Waters Unit., School of Pure and Applied Biology, Univ. of Wales College of Cardiff, Cardiff, Wales UK

[2] Inst. of Hydrology, Wallingford, OX 10 8BB, UK

Introduction

Surface-water acidification affects important ecosystem processes and many organisms, from most trophic levels, are influenced either directly or indirectly. There are repercussions for the economic, aesthetic, and conservational status of affected systems (Altshuller and Linthurst 1984; Warren et al. 1988). Even semi-aquatic animals, such as birds which depend on freshwaters for food, are involved (Ormerod and Tyler 1987). As a result, biological criteria have figured prominently in discussions over water quality standards, and have acted as a focus in determining critical and target loads for the air pollutants which cause acidification (e.g. Brakke and Henriksen this volume).

Despite the obvious importance of biology, it has seldom been incorporated into model assessments of the geographic extent and temporal pattern of acidification (e.g. Minns et al. 1986; Ormerod et al. 1988). This is unfortunate because the development of biological models could be central to our understanding of how resources have been affected in acidified systems, and crucial to forecasting how biological resources will respond to future management action. However, many problems are often perceived with respect to modelling the biological effects of acidification. The chemical, physical and biological phenomena which lead to increased surface water acidity require models which are already highly complex. The addition of the dynamic, intricate and often unpredictable response of biological systems is thought by many as a difficult, if not an impossible, step. Nevertheless, there is a strong requirement for corporate models, combining emissions, deposition, hydrochemical responses, and biological effects, which could permit the analysis necessary for managers to reach decisions over future strategies on such issues as target loads.The approach to biological modelling adopted so far in Wales is a simple one, depending on relationships between biological phenomena and water chemistry. The resulting linear models are essentially empirical, adopting a 'black box' approach which avoids detailed understanding of processes. Historical reconstruction or forecasting requires a source of data on chemical change, derived for example from palaeoecology or hydrochemical modelling.

In this chapter, we demonstrate the use of biological models on both a catchment and regional scale in Wales. We have applied the Model of Acidification of Groundwaters in Catchments, MAGIC (see Cosby et al. this volume), at these two scales, and used the output to reconstruct biological change in the past, and to predict the future response under different scenarios of reduced deposition and changing land-use.

Study Area

About 4000 km^2 of Wales (19 % of the land area) is underlain by shales, grits, and mudstones of Silurian and Ordovician age. The accompanying soils are brown podzolics, ferric stagnopodzols and oligomorphic peats. Many surface waters are generally base-poor and vulnerable to acidification. Much land is now used for rough grazing, with deciduous woodland a minor component apart from remnant Oak woods *Quercus* spp. and stands of species such as alder *Alnus glutinosa* along stream banks. Planted forests of exotic conifers, mostly sitka spruce *Picea sitchensis*, now cover over 20 % of the land area above 250 m above sea level. Whereas studies of fossil diatoms in lake sediments indicate that some Welsh lakes in remote moorland areas have become more acidic since the industrial

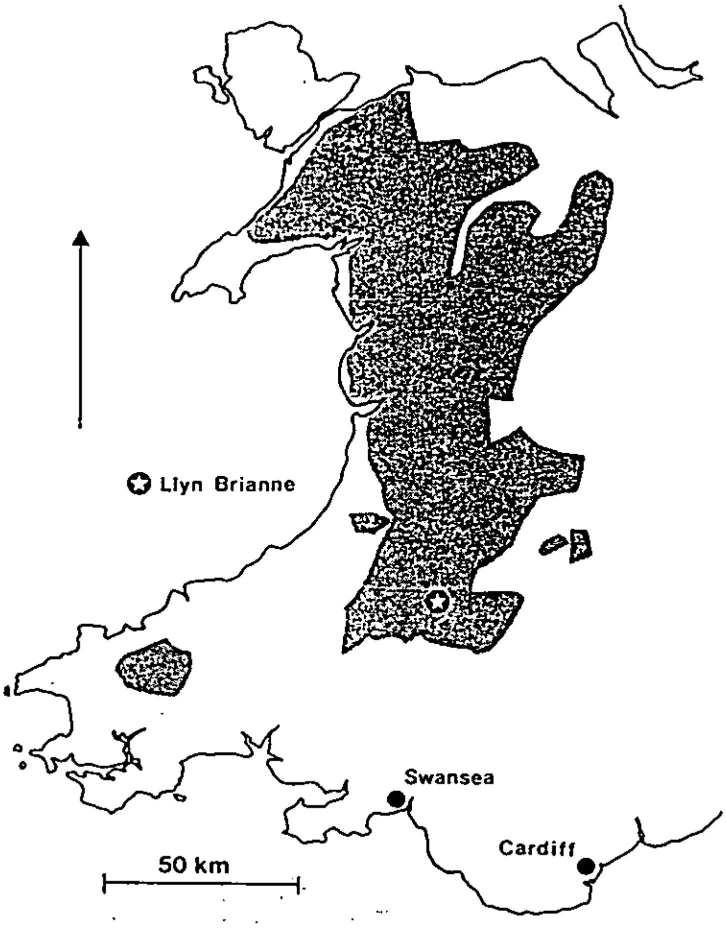


Figure 13.1. The acid sensitive area of Wales (shaded), in which acid waters occur at some or all flow levels, and the location of Llyn Brianne.

revolution (Battarbee et al. 1989), the increase in conifer forestry has represented a major acidifying influence on some water bodies (Stoner et al. 1984). Between October 1983 and September 1984, the Welsh Water Authority collected detailed chemical and biological data from 104 sites, all within the acid-sensitive area, and these form the basis of the regional modelling exercise reported here.

Within the acid-sensitive region, at Llyn Brianne, a major and multi-disciplinary project on acidification has been underway since 1984. Detailed studies aim to examine the process of acidification and its biological effects. The project involves manipulating several sub-catchments of the upper River Tywi (Figure 13.1), and comparing their biological and chemical responses with unmanipulated references. Brianne site CI 5 has provided the catchment application of MAGIC which is reported here (Whitehead et al. 1988), while some of the data for the biological models were derived from adjacent streams.

Methods

An Outline of MAGIC and its Application

Described widely elsewhere, MAGIC uses data on precipitation quality and quantity, soils and groundwater chemistry to simulate the likely change in stream chemistry which occurs over time scales of years to decades (Cosby et al. 1985; Cosby et al. this volume). The model can also be used to forecast the chemistry of streams under alternative future scenarios of acid deposition (e.g. 10, 20, 30 % reduction etc). Some of the acidifying influences of conifer forest have also been simulated, though this has been done only at the catchment level (Neal et al. 1986; Whitehead et al. 1988).

In this study, MAGIC was applied regionally to the acid sensitive area of upland Wales using techniques described by Whitehead et al. (in press). Historical reconstructions were made over the period 1844 to 1984 (the year used in calibrating the model), while forward prediction involved assessing the effect of different reductions in sulfate deposition (0 % to 90 %), beginning in 1984 and phased in over a 20 year period.

We have illustrated the effects of afforestation on one catchment at Llyn Brianne using the approach developed by Neal et al. (1986) and Whitehead et al. (1988). As with the regional application, historical trends were simulated between 1844 and 1984. From 1958 onwards, however, alternative scenarios involved either moorland or conifer forest, simulated by varying terms for sulfate deposition and evapotranspiration. These features are probably important in the acidifying effects of plantation conifer forest. From 1984 onwards, two alternative scenarios on each type of land use involved sulfate deposition either continued at 1984 levels or reduced by 50 %.

Biological Changes

Biological models currently available use physico-chemical features to predict the survival of first-year brown trout *Salmo trutta*, total trout density, macroinvertebrate community type, macro-floral community type, and chemical suitability of streams for a species of aquatic bird wholly dependent on rivers for food, the Dipper *Cinclus cinclus*. The development and use of these models are described in other papers (Ormerod et al. 1986, 1988; Ormerod et al. 1987; Weatherley and Ormerod in press) and only an outline is given here (Table 13.1). For any given year, chemical output from MAGIC is used as input to the biological models. In all but one of the biological models, aluminum concentration is a dominant component, reflecting its pronounced role in the biology of acid waters. The models for fish survival and density utilize combinations of aluminum concentration, total hardness, altitude, slope and stream size in regression analysis. The remaining three models use combinations of aluminum concentration, pH, total hardness and stream size in discriminant analysis, these variables being used to derive site positions on discriminant functions from which probable biological characteristics can be assessed. For example, the invertebrate model (Figure 13.2) indicates the likelihood that a site is occupied by a fauna typical of acid streams (A), intermediate (B) or circumneutral streams (C). The latter have the most diverse community.

For this study, trout survival, trout density, invertebrate community and chemical suitability for Dippers were predicted at each of 104 sites across the Welsh region in 1844, 1984, and in 2010 following fixed reductions in sulfate deposition by 0–90 % of 1984 values. For the catchment- specific application at Llyn Brianne, the trout models were run for

Table 13.1. A summary of the empirical models which relate stream biology to physicochemistry in upland Wales. Notes: L indicates $\log_{10}$, Al is filterable at 0.45 μm in $\mathrm{mg\,l^{-1}}$; Hd is total hardness in $\mathrm{mg\,l^{-1}}$ SLOPE in $\mathrm{m\,km^{-1}}$, AREA is catchment area in ha, ADF is average daily flow in $\mathrm{m^3\,s^{-1}}$, ALT is altitude in m.

Predicted variable:	Form of model:	Equations:
Trout survival time (d)	Linear regression	$LT_{50} = 22.2 - 36.2\,[Al]$
Trout density (n per 100 m^2)	Multiple regression	$L[Density] = -1.24 - 1.08\,L[Al] + 1.33\,L[Hd] - 0.22\,L[ADF]$
Invertebrate community	Discriminant functions	$F1 = 6.58\,L[Al] + 4.42\,L[Hd] - 0.06\,L[AREA] + 2.72$ $F2 = 9.93\,L[Hd] + 1.23\,L[Al] - 1.20\,AREA - 4.35$
Macrofloral community	Discriminant functions	$F1 = 2.60\,pH + 0.001\,ALT - 0.36\,L[SLOPE] - 16.11$ $F2 = 0.13\,pH + 0.01\,ALT - 1.46\,[SLOPE] - 2.29$
Suitability for Dippers	Discriminant function	$F1 = 4.76 + 3.68\,L[Al] - 0.08\,pH$

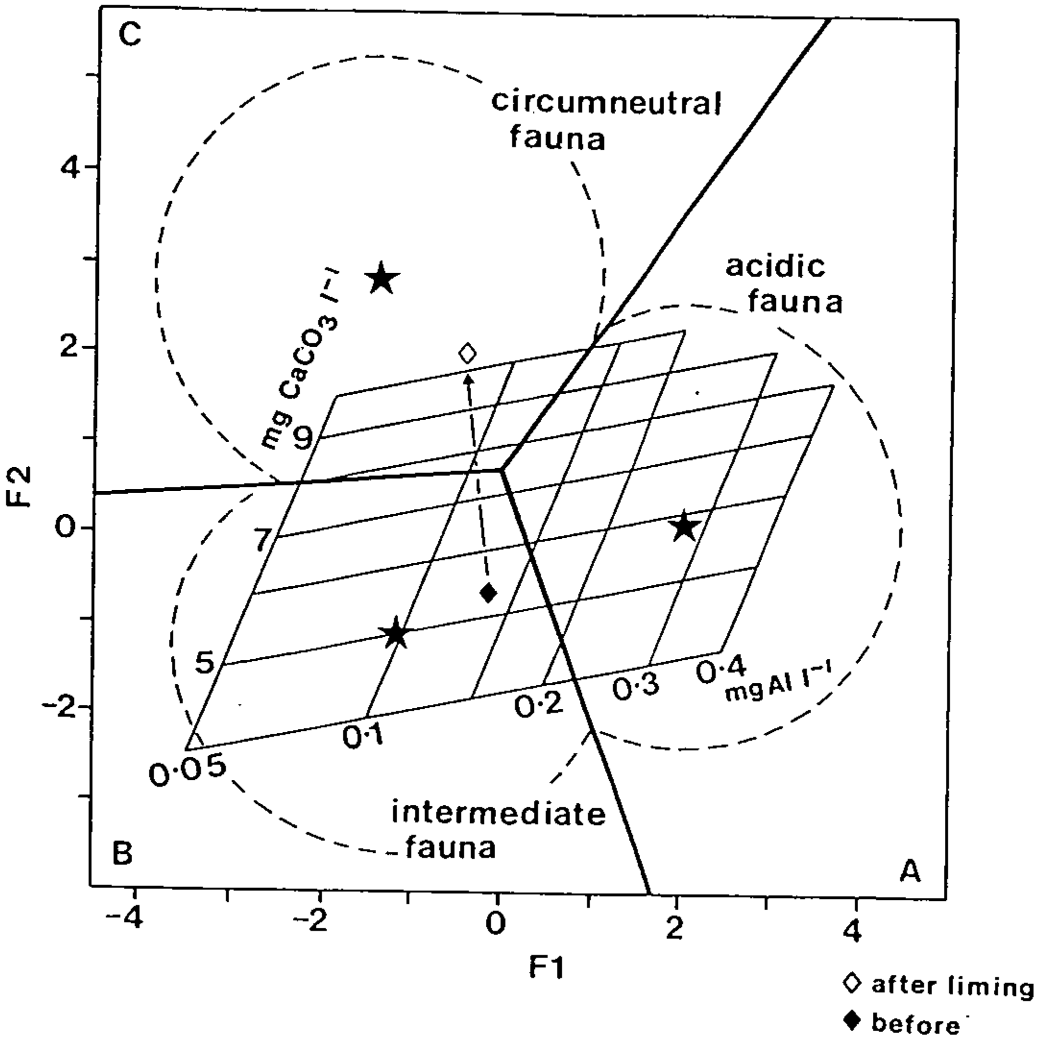


Figure 13.2. The macroinvertebrate model showing the location of the three invertebrate communities (A, B, C) in discriminant space. The grid shows how a hypothetical stream of catchment area 100 ha would change with increasing hardness (y axis) and increasing aluminum (x axis). The example is for a real stream before and after catchment liming.

1844, 1984, 2010 and 2124 in each of the alternative scenarios of land use change and deposition reduction.

Results

Regional Application

On a regional scale, MAGIC indicated a pronounced increase between 1844 and 1984 in the percentage of sites with total aluminum concentrations > 0.1 mgl^{-1} and pH < 5.5, conditions to which many organisms would be sensitive (Figure 13.3). The median pH fell from 6.2 to 5.8 over the same period. The consequences of such changes in chemistry for the biology of Welsh streams would, according to the models, be pronounced (Figure 13.3). Only 25 % of sites had trout densities < 10 fish per 100 m^2 in 1844, whereas over 45 % had densities below this value by 1984. Similarly, the survival time of trout fell markedly at many sites, and by 1984, over 20 % had values less than 15 days (Figure 13.3). Streams around Llyn Brianne which have survival times this low are typically fishless.

In 1844, invertebrate community A (typical of acidic sites) did not occur anywhere in the model region, but occupied 30 % of sites by 1984 (Figure 13.4). The percentage of sites with type B fell correspondingly. Interestingly, the occurrence of the faunal community typical of circumneutral streams in the present day (C) increased between 1844 and 1984, probably due to increased calcium concentrations atsome sites. Dippers, which feed on both invertebrates and fish, are indirectly sensitive to increasing aluminum and low pH, because their food supply is affected. According to MAGIC, over 95 % of the 104 sites in the acid-sensitive region in 1844 were chemically suitable for Dippers, but this value had been reduced to 44 % by 1984 (Figure 13.5).

In the regional predictions, reductions in sulfate deposition of at least 50 % were required to arrest further decline in pH and increase in aluminum. Continued deposition at 1984 levels led to a further increase in the percentage of sites which were highly acidic. A reduction in deposition of 50 % was required to prevent further acidification with concomitant biological change. At greater deposition reductions than this, there was some return to former conditions, although only at around 10 % of 1984 deposition values did they begin to approach those of the last century. At this deposition level, the model indicated some loss of the mayfly-rich community (type C), as calcium concentrations declined at some sites.

Catchment Application

Patterns of chemical change for individual streams in the Welsh region depend on catchment sensitivity, but the typical response from a sensitive case at Llyn Brianne was a progressive decrease in pH and increase in aluminum concentration from the early 20th century onwards (Figure 13.6). These changes were most pronounced under simulated forest, particularly for aluminum, where they persisted even with a 50 % reduction in sulfate deposition from 1984 onwards. Such elevated aluminum concentrations would clearly have biological consequences, and this was demonstrated by the fish survival and density models; values given by each declined markedly between 1844 and 1984, most of all under the forest scenarios. As with the regional models, deposition reduction of 50 % permitted the maintenance of some fish under moorland conditions. Such a reduction did not restore

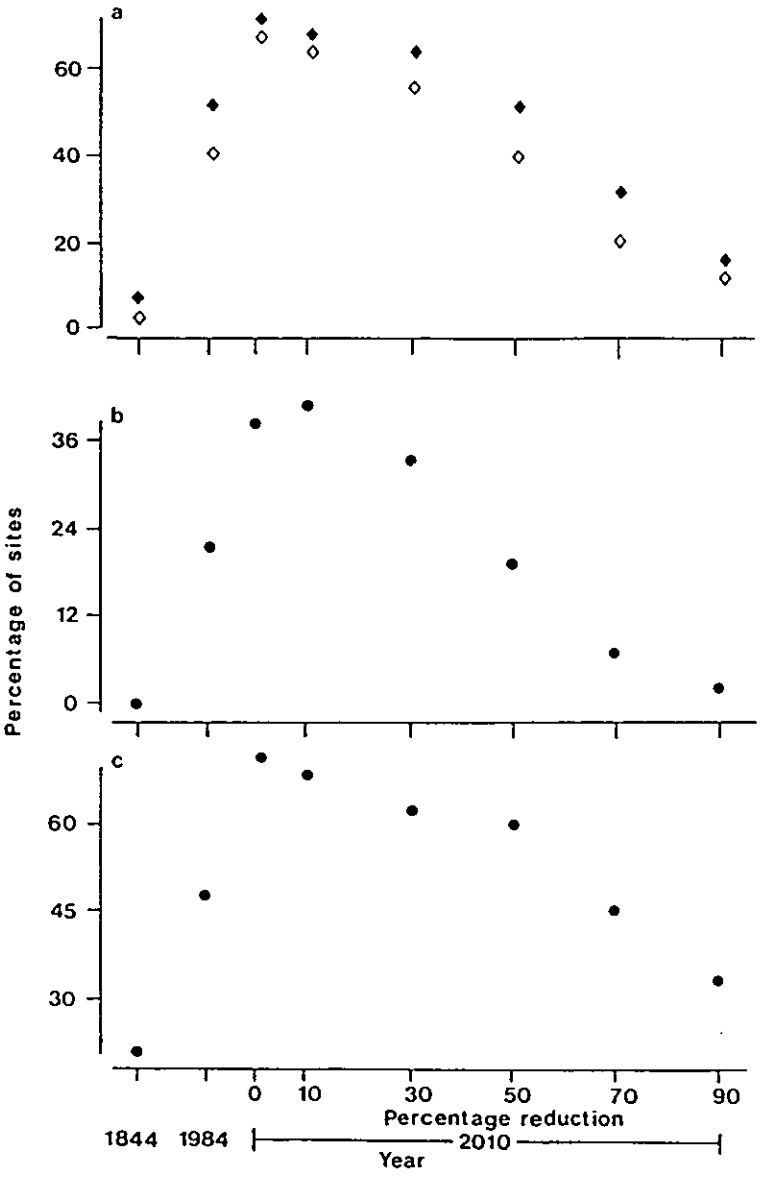


Figure 13.3. Changes in the chemical status of streams in the acid-sensitive region of upland Wales according to the MAGIC model, and consequences for trout biology. The x axis shows changes in time between 1844 and 1984, and simulated future conditions in 2010 under reductions in deposition between 0 and 90 % of 1984 values: a) the percentage of sites with > 0.1 mg l^{-1} aluminum (◆), and the percentage with pH < 5.5 (◇); b) the percentage of sites with < 10 trout per 100 m^2; c) The percentage of sites with trout survival < 15 days.

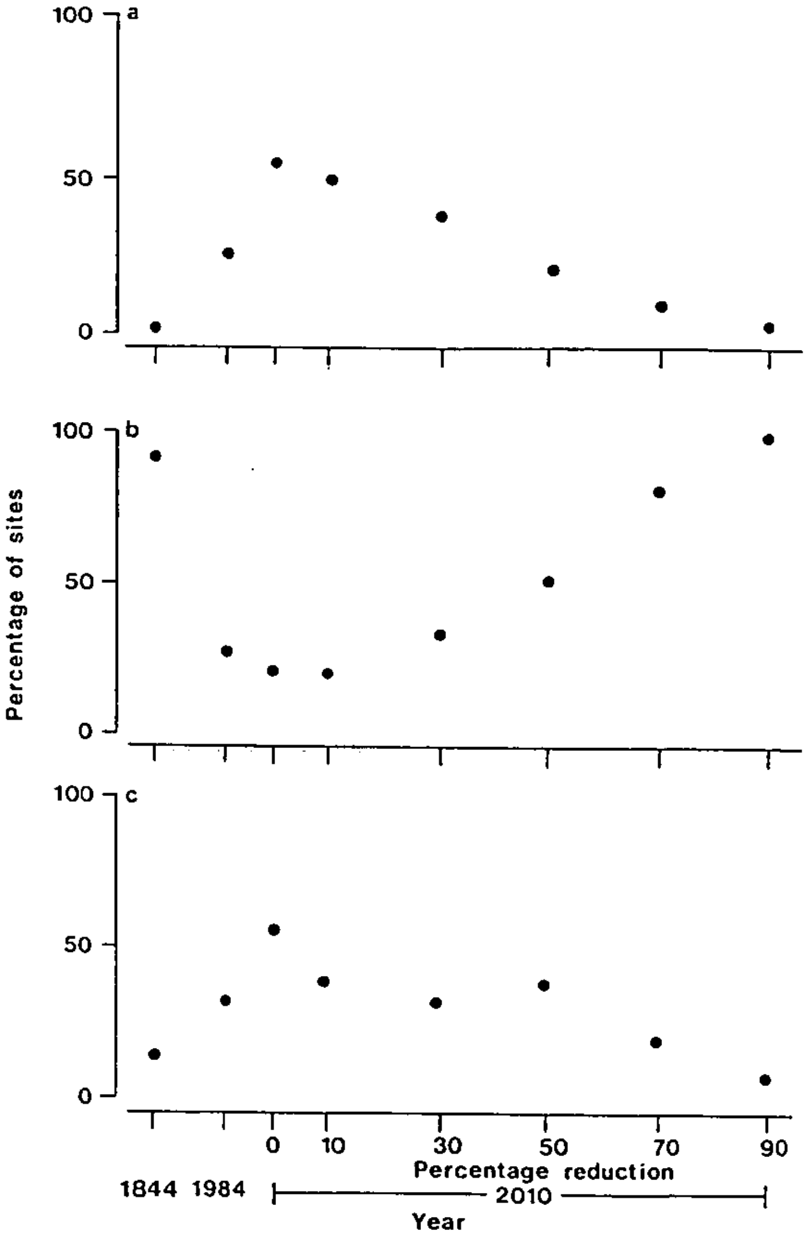


Figure 13.4. Changes in the percentage of sites in upland Wales with different invertebrate communities according to the MAGIC model. A (= 'acidic' community), B (= intermediate) and C (= circumneutral). Conventions for the x axis are as in Figure 13.3.

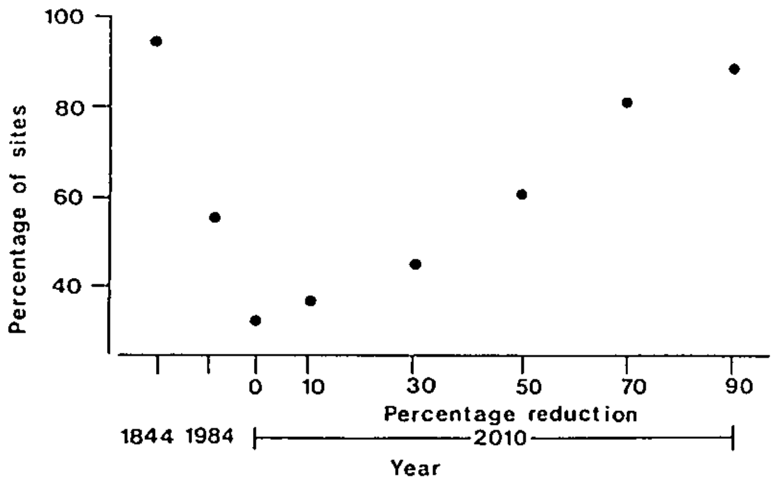


Figure 13.5. Changes in the percentage of sites in the acid sensitive region of upland Wales which would be chemically suitable for Dippers according to the MAGIC model. Conventions for the x axis are as in Figure 13.3.

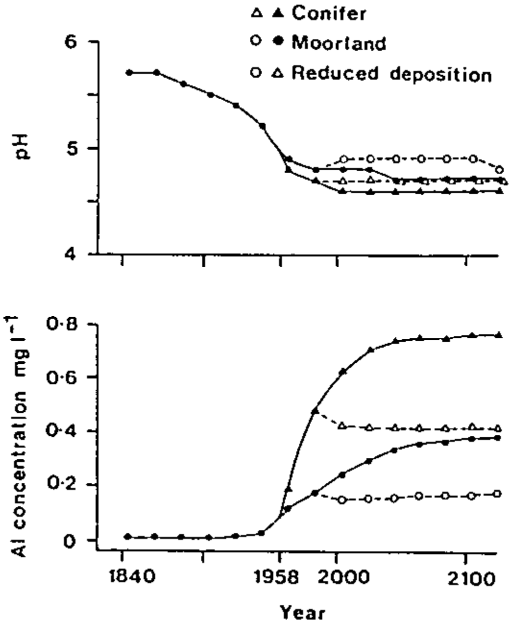


Figure 13.6. Changes in the pH and aluminum concentration in an acid-sensitive Welsh stream under different modelling scenarios as indicated by the MAGIC model: ●, moorland with deposition constant at 1984 levels; ○, moorland with deposition reduced by 50 % from 1984 onwards; ▲, forest from 1958 with deposition constant at 1984 levels; △, forest from 1958 with deposition reduced by 50 % from 1984 onwards (after Ormerod et al. 1988, with permission).

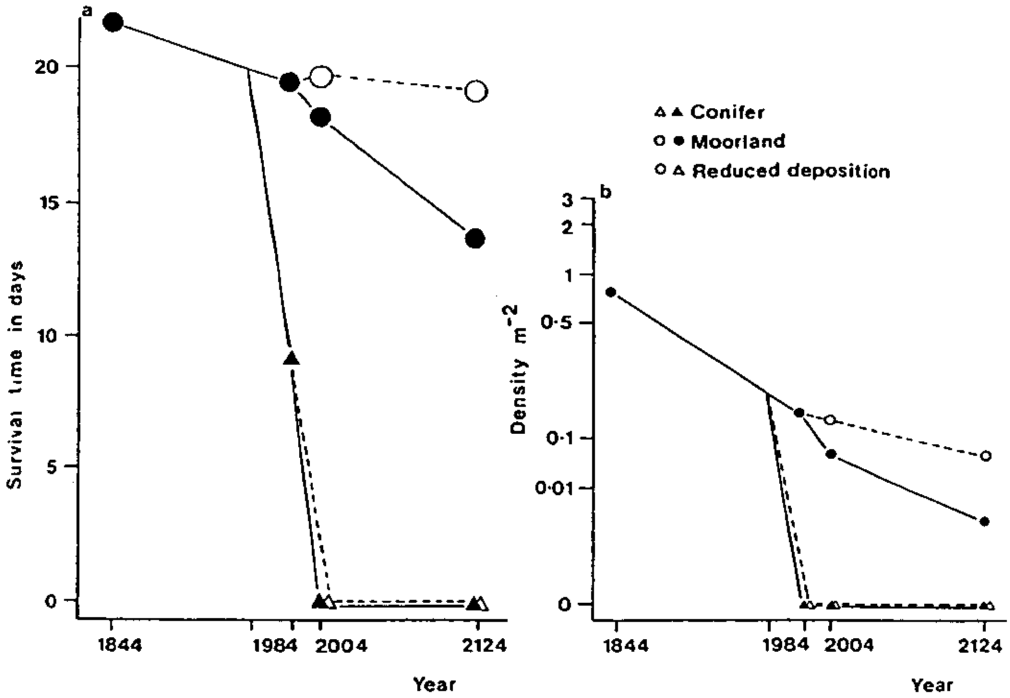


Figure 13.7. Changes in the survival time (a) and (b) density of brown trout in a soft-water streams at Llyn Brianne according to MAGIC simulation. Conventions as in Figure 13.6. After Ormerod et al. (1988).

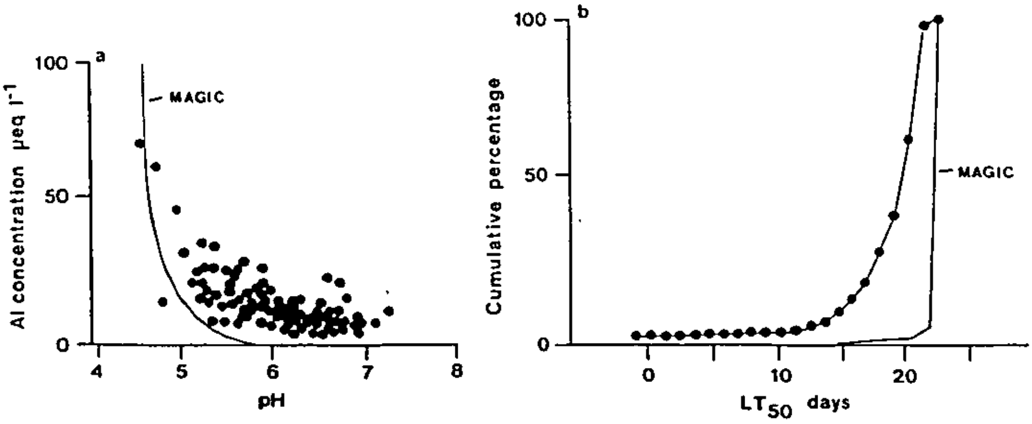


Figure 13.8. a) A possible relationship between aluminum concentration and pH at 104 sites in upland Wales in the absence of gibbsite equilibrium, and that predicted by MAGIC simulation. b) The different patterns of trout survival time, as cumulative percentage frequencies, which result from the two aluminum distributions in a.

the fish population in the forested catchment (Figure 13.7), indicating that the presence of conifer forest could cancel the effects of the reduced sulphate deposition, which prevented further acidification at the regional level.

Discussion

In previous papers, we have used MAGIC in individual catchments to reconstruct trends in fish populations, and to simulate changes amongst aquatic invertebrates and plants at both species and community levels (Ormerod et al. 1988, Weatherley and Ormerod in press). In one case, we outlined the possibility of simulating biological change in rivers across acid-sensitive regions (Whitehead and Ormerod in press), but this paper is our first comprehensive attempt at regional biological modelling. The prediction of biological impacts by acidification at this regional scale is clearly required to complement other models of air pollution, transport and deposition (e.g. Metcalfe and Derwent 1989; de Vries et al., this volume). Because the species composition and ecology of aquatic ecosystems will vary regionally, however, similar models now require development on a broader spatial scale.

Both MAGIC and the biological models also require attention to some areas of uncertainty. All models are imperfect representations of the real world which often require cautious interpretation. In the case of MAGIC, possible sources of error arise from the estimated historical pattern of changing deposition, the assumption that soils are homogeneous with chemical processes which can be 'lumped' on a catchment basis (see also Jenkins and Cosby this volume), and the difficulty in obtaining field data for important terms such as weathering rates (see e.g. Reuss et al. 1986). Such difficulties may be particularly important as MAGIC is applied increasingly to the regional level, although initial attempts at validating the model across regions are encouraging (Hornberger et al. this volume).

Despite some uncertainty, however, managers and politicians increasingly need information on which to reach decisions on emission reduction and land use policy. Although seen by many as a heuristic tool, MAGIC is being used with increasing confidence for the purpose of policy formulation. Such confidence has grown particularly because the shifts in pH which are indicated by MAGIC have been corroborated by diatom data from lake sediments. In Wales, all seven lakes so far investigated have shown a decline in pH, beginning after the industrial revolution and ranging from 0.5 to 1.8 units (Battarbee et al. 1989). These declines in pH seem almost unequivocal and are matched closely by the MAGIC simulations (e.g. Figure 13.6).

Nevertheless, despite confidence in pH trends indicated by MAGIC, some criticisms have arisen because the chemistry of aluminum in acidified catchments is not yet fully understood, and possibly not faithfully reproduced by the model. At present, aluminum in the soil and runoff of many hydrochemical models is assumed to be controlled by equilibrium with gibbsite, mediated by pH (Reuss et al. 1986). This assumption may be erroneous. For example, aluminum concentrations could be altered from those predicted by a simple gibbsite equilibrium because of mixing processes between acidic runoff and base rich groundwater (C. Neal, pers. comm), dissolution or ion exchange from stream sediments or plants (Norton this volume) and long-term change in the dynamics of aluminum dissolution (De Vries and Kros this volume). The result could be a trend in aluminum concentrations in the absence of pH change, or pH/Al relationships other than those predicted by MAGIC. Effects on the biological predictions would be pronounced in view of the dominant role of aluminum in most of the biological equations. An example of the kind of misfit which could occur is shown in Figure 13.8 and involves aluminum being retained in solution at pH from 5 to 5.5 at a greater concentration than expected from a gibbsite equilibrium at pH. The two patterns give markedly different indications of trout survival time (Figure 13.8). Complexation with dissolved organic substances is also liable to render some aluminum fractions biologically unavailable, or at least less toxic than labile aluminum (McCahon and Pascoe in press), and these processes are yet to be incorporated fully into models. One possibility would be to base biological prediction on the chemical features of MAGIC which are thought to be accurate, such as pH and alkalinity. Such developments would probably ignore a key toxic component of acid waters, however, and predictions might carry errors for the same reasons as those based on aluminum. For example, changing relationships between pH, aluminum and organic substances would mean that a given pH value does not always represent the same biological conditions. For these reasons, confidence in biological modelling using MAGIC, or other similar hydrochemical models, will only grow with developments in aluminum chemistry which permit robust predictions.

In cases such as this, where several models are operated together, the chance of error is probably compounded. As with MAGIC, the biological models are subject to some uncertainties and depend on assumptions. The greatest is that the empirical relationships (essentially correlations) between stream chemistry and biology represent a causal influence. Through such causality, temporal changes in stream chemistry bring corresponding changes in biology, either directly or indirectly. There is now considerable justification for making this assumption in all the models presented here. For example, ordination and classification of invertebrate assemblages has repeatedly revealed strong correlations with pH, or related factors (Ormerod et al. 1988). These correlations persist among the fauna from different stream habitats, which would be unlikely if chemistry did not exert some causal influence (Ormerod 1987; Weatherley and Ormerod 1987). More importantly, experimental episodes of increased acidity and aluminum concentration have confirmed the sensitivity of some species to such conditions (Ormerod et al. 1987). Even in the Dipper, an organism likely to be affected only indirectly by acidity and elevated aluminum, pairs at low pH show reduced clutch and brood size, reduced egg weight, moderate shell-thinning, reduced chick growth, impaired brood provisioning, and increased time spent foraging (Ormerod and Tyler 1987; Ormerod et al. 1988). These effects accompany alterations in the food supply as acidity increases, with reduction in the density of important prey types, general reduction in the size of prey available, and loss of calcium-rich food. In this modelling study, consistency between changes in the chemical suitability of streams for Dippers, and changes in their food supply, at least corroborates the indirect pathway through which Dipper distribution could be affected. For salmonids, many data support the direct toxicity of aluminum (Warren et al. 1989), while low fish density in acid streams in Wales does not appear to reflect either trophic effects (Turnpenny et al. 1987), or limited habitat (Ormerod et al. 1988). Despite such clear evidence of direct effects, however, the models would probably benefit from the inclusion of dynamic and biotic processes such as survival in different life stages, and density dependent regulation (Elliott 1985). Important developments in such modelling have recently been made in Nova Scotia (LaCroix 1987), though so far are applicable only to the colored organic wa-

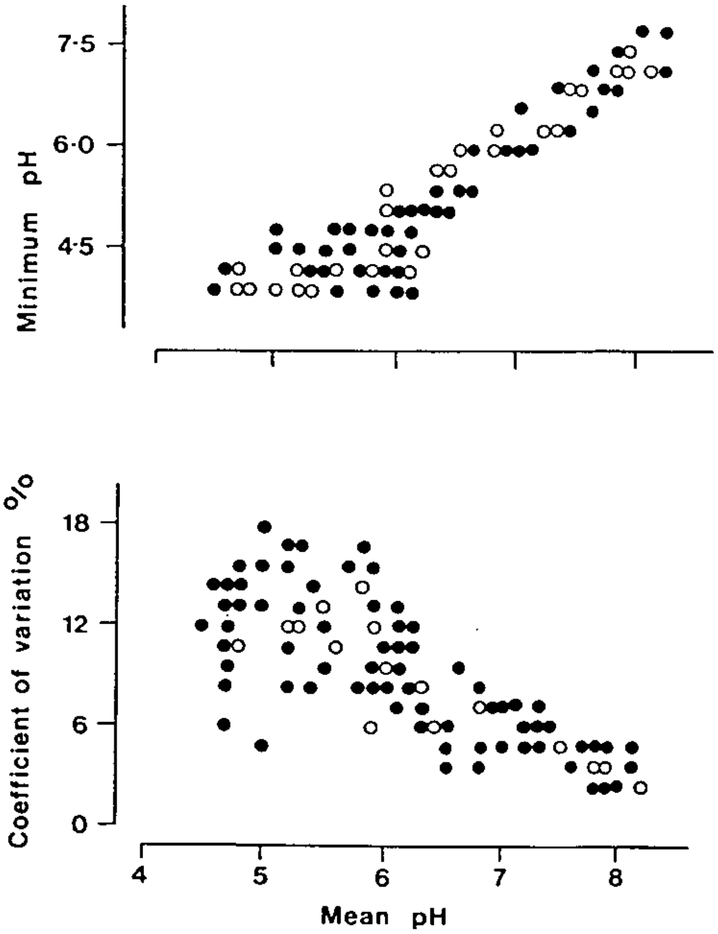


Figure 13.9. a) pH minima and b) coefficient of pH variation in relation to pH mean at 112 sites in upland Wales. All values are based on at least 1 year's data. Open symbols indicate > 1 point.

ters which occur there. Similar models are being developed in Wales in conjunction with detailed studies of aluminum speciation (e.g. Goenaga and Williams 1988).

While the assumption of biological effects by acidity and aluminum is supported, there is a potential source of error in the relative effects of chronic and episodic conditions. Episodic changes in pH, aluminum and calcium concentrations are usually marked in acid streams during storm events or snow melt (Stoner et al. 1984). Experimental investigations, and some field data, indicate that such events can affect fish and some invertebrates (Henriksen et al. 1984; Ormerod et al. 1987). However, all the ecological models presented here were based on mean chemical conditions, partly because of difficulties in assessing from the data the relative influences of chronic and acute chemistry, but also because MAGIC is not developed for analyzing episodes. As a consequence, the predictive ability of the models described here could be limited in situations where episodes control the fauna. This would be especially problematic if episodes occurred in streams of relatively high pH (5.5–6.0), and were sufficiently damaging to alter the biological conditions from those predicted from the mean chemistry. However, because mean and extreme values for pH and aluminum are closely correlated, the mean probably indicates the likelihood of episodic change (Figure 13.9). Additionally, there is some evidence that acidity affects some invertebrates only indirectly, through their food supply (see Ormerod et al. 1987), and this pathway is just as likely to involve chronic effects as episodic. In streams of about pH 6.5 at Llyn Brianne, isolated acid episodes during snow-melt or storm events have not substantially affected the invertebrate fauna or fish density (Weatherley et al. in press). Even in more acid waters, individual events with experimentally elevated aluminum were not sufficient to cause death in 'sensitive' invertebrates, though they have been in fish (Weatherley et al., in press). For these reasons, it is not yet clear whether episodes need to be built into our ecological models, though further consideration of extremes may be necessary for organisms like salmonids which can be especially sensitive.

Conclusions

A major conclusion in most modelling studies is that models are often imperfect. Notwithstanding such limitations and caveats in this study, there are two important indications. The first is that a large number of streams in the acidified region of Wales have, according to hydrochemical models, become more acidic since the last century. Their aquatic biology changed considerably in the models as a result. The model trends in pH are consistent with reconstructions of pH change based on fossil diatoms in Welsh lake sediments. Afforestation effects in the model accelerated the acidification, a trend again consistent with real data on the chemistry of forest treams, and on their biological status.

Second, the number of currently acidified streams might be returned to conditions similar to those prior to acidification only if sulfate deposition were reduced by over 50 % of 1984 levels. Models of air pollution transport have recently shown that a significant proportion of the sulfate reaching mid Wales originates from the UK, particularly in the British midlands (Metcalfe and Derwent 1989). However, the same models show that an emission reduction of 30 % in Britain might lead to a deposition reduction in mid Wales of only 10 %, and even emission reductions of 90 % could reduce Welsh deposition by only 30-40 % of full emission values. Pollutant sources in France, Belgium and Germany become increasingly important in the air pollution model as UK sources are reduced. Restoration of the chemistry and biology of acidic Welsh streams by the control of air pollution alone would thus require, according to model predictions, concerted action for reducing air pollutants across Europe. Moreover, the presence of forest cover on sensitive Welsh catchments, due to the effect of scavenging airborne pollutants and marine aerosols, could effectively cancel a 25 % reduction in European emissions or 75 % reduction in UK emissions alone (Warren et al. 1989). On this basis, the return of acidified Welsh rivers to chemical and biological conditions similar to the last century would, according to current models, require not only European-wide action on air pollution, but also a land use strategy which removed or ameliorated the impact of forestry.

Acknowledgements

Our thanks are due to numerous colleagues from Welsh Water, the Institutes of Hydrology and Terrestrial Ecology, and UWIST who assisted the field, laboratory and computing programmes. We particularly thank Tim Musgrove. The work was funded by the Department of the Environment and Welsh Office, and formed part of the Llyn Brianne project. The Surface Water Acidification Programme paid part of our costs to attend the conference on Models to describe the geographical axtend and time evolution of acidification and air pollution damage' where this paper. was first presented.

References

Altshuller, A. P. and Linthurst, R. A.: 1984, *The Acidic Deposition Phenomenon and its Effects.* Critical Assessment and Review Papers. Volume 2, Effects Sciences. US Environmental Protection Agency, Washington

Battarbee, R. W., Fritz, S. C., Kreiser, H. and Appleby, P. G.: in press, 'Palaeoecological evidence for the acidification of Welsh lakes'. In J. H. Stoner, A. S. Gee and R. W. Edwards (Eds). *Acid Waters in Wales.* Junk, The Hague

Brakke, D.F. and Henriksen A.: this volume

Cosby, B. J., Wright, R. F., Hornberger, G. M. and Galloway, J. N.: 1985, *Water Resour. Res.*, 21, 1591

De Vries, W., Kāmāri, J. and Posch, M.: this volume

De Vries, W. and Kros, J.: this volume

Elliott, J. M.: 1985, *Journal of Fish Biology (Supplement A)*, 27, 33

Goenaga, X. and Williams, D. J. A. : 1988, *Environmental Pollution*, 52, 131

Henriksen, A., Skogheim, O. K. and Rosseland, B. O.: 1984, *Vatten*, 40, 255

Hornberger, G. M., Cosby, B. J. and Wright, R. F.: this volume

Jenkins, A. and Cosby, B. J.: this volume

Lacroix, G. L.: 1987, 'Model for loss of atlantic salmon stocks from acidic brown waters of Canada'. In: R. Perry, R. M. Harrison, J. N. B. Bell and J. N. Lester (Eds). *Acid Rain: Scientific and Chemical Advances* pp 516

McCahon, C. P. and Pascoe, D.: 1989, *Archives of Environmental Contamination and Toxicology*, 18, 233

Metcalfe, S. E. and Derwent, R. F.: in press. 'Llyn Brianne: modelling the influence of emission reduction on deposition'. In: J. H. Stoner, A. S. Gee and R. W. Edwards. *Acid Waters in Wales*, Junk, The Hague

Minns, C. K., Kelso, J. R. M. and Johnson, M. G.: 1986, *Canadian Journal of Fisheries and Aquatic Sciences*, 43, 900

Neal, C., Whitehead, P. G., Neale, R. and Cosby, B. J. : 1986, *Journal of Hydrology*, 86, 15

Norton, S. A.: this volume

Ormerod, S. J. : 1987. *Hydrobiologia*, **150**, 143

Ormerod, S. J., Allinson, N., Hudson, D. and Tyler, S. J.: 1986. *Freshwater Biology*, **16**, 501

Ormerod, S. J., Boole, P., McCahon, C. P., Weatherley, N. S., Pascoe, D. and Edwards, R. W.: 1987, *Freshwater Biology*, **17**, 341

Ormerod, S. J., Bull, K. R., Cummins, C. P., Tyler, S. J. and Vickery, J. A.: 1988, *Environmental Pollution*, **55**, 107

Ormerod, S. J. and Tyler, S. J.: 1987, 'Dippers Cinclus cinclus and Grey Wagtails Motacilla cinerea as indicators of stream acidity in upland Wales'. In: A. W. Diamond and F. Filion (Eds) *The Use of Birds* ICBP Technical Publication No. 6., International Council for Bird Preservation, Cambridge

Ormerod, S. J., Wade, K. R. and Gee, A. S. : 1987. *Freshwater Biology*, **8**, 545

Ormerod, S. J., Weatherley, N. S., Varallo, P. V. and Whitehead, P. G. : 1988, *Freshwater Biology*, **20**

Reuss, J. O., Christophersen, N., Seip, H. M.: 1986, *Water, Air Soil Pollut.*, **30**, 593

Stoner, J. H., Gee, A. S. and Wade, K. R.: 1984. *Environmental Pollution (Series A)*, **36**, 125

Turnpenny, A. W. H., Sadler, K., Aston, R. J., Milner, A. G. P. and Lynam, S. : 1987, *Journal of Fish Biology*, **31**, 415

Warren, S. C., Alexander, G. C., Bache, B. W., Battarbee, R. W., Crawshaw, D. H., Edmunds, W. M., Egglishaw, H. J., Gee, A. S., Hildrew, A. G., Hornung, M., Howells, G. D., Hunt, D. T. E., Pugh, K. B., Wells, D. E., Whitehead, P. G., Cape, J. N., Harriman, R., Neal, C. and Ormerod, S. J.: in press, *United Kingdom Acid Waters Review Group Second Report*. Department of the Environment, London

Weatherley, N. S. and Ormerod, S. J. : 1987, *Environmental Pollution*, **46**, 223

Weatherley, N. S. and Ormerod, S. J.: in press, *Hydrobiologia*

Weatherley, N. S., Rutt, G. P. and Ormerod, S. J.: in press, *Archiv fur Hydrobiologie*

Weatherley, N. S., Thomas, S. P. and Ormerod, S. J.: in press, *Environmental Pollution*

Whitehead, P. G., Bird, S., Hornung, M., Cosby, C. J., Neal, C., and Paricos, P. : 1988, *Journal of Hydrology*, **101**, 191

Whitehead, P. G., Jusgrone, T.T. and Cosby, B. J.: in press, 'Hydrochemical modelling of acidificatopn in Wales', in R. W. Edwards, T. H. Srones and A. S. Gee (eds.) *Acid Waters in Wales*, Kluwer, Academic Publishers, Dordrecht, The Netherlands

Whitehead, P. G. and Ormerod, S. J.: in press, 'Modelling the chemical and biological response of Welsh streams to changes in atmospheric deposition and land use'. In: H. Barth (Ed). *The influence of land use on the acidification of streams.* Commission of the European Communities

Natural
Environment
Research
Council