INSTITUTE of
HYDROLOGY

Regional Modelling of Acidification and Predicting Reversibility

by

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Interim Report Number 2

On Contract EV4V.0033 UK(H)

February 1990

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Summary

(i) OBJECTIVES

The objectives of the research are many and full details are not given here. In summary, the objectives are to apply mathematical models of catchment acidification processes to several key sites, to extend the modelling to a regional scale, to link models to an air pollution model, to link models to biological models and to investigate the effects of different emissions reduction strategies on stream water quality.

The application of MAGIC to key sites in Scotland and Wales was detailed in the previous report, together with details of the regional MAGIC model applications to Wales and Scotland. This report looks in detail at validation and sensitivity of the MAGIC model. Substantial work has also been completed on the link between MAGIC and biological models. We also report progress to date on the linking of MAGIC to an atmospheric transport and pollutant deposition model.

(ii) MODEL VALIDATION

MAGIC has been applied to a range of catchments in Scotland subject to different pollution inputs and land uses. The calibration technique (see Section 2) developed now allows sensitivity bands to be constructed around the 'mean' MAGIC output. 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.

The MAGIC model results indicate that pollution inputs and land use, particularly conifer afforestation, have significant effects on surface water acidification. Moreover, the model indicates that reversibility may be occurring at several sites although this is not always consistent with the diatom reconstruction. Reversibility of acidification has been further explored using the model in predictive mode under a number of deposition reduction scenarios and indicate that substantial reductions will be necessary to achieve significant improvement in water chemistry. Details of this work are given in Section 1 of the report.

(iii) MODEL SENSITIVITY

MAGIC was applied to two sites in Scotland to assess the influence of model

structure on hindcast and forecast water quality variables. The sites modelled were the Allt a Mhorcaidh (see previous report) and the Round Loch of Glenhead. 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. This technique was developed in the previous year and represents our best method for describing uncertainty in both model parameters and in observed chemical data. 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 types of structure. The differences in simulation results among the model structures were small, however, compared to errors inherent in the measurement of soil and water chemistry. Given currently available data, a one-layer model structure is apparently sufficient for long term simulation of acid deposition effects on the sites studied.

The details of the calibration technique, fuzzy optimisation and results of the sensitivity analysis are given in Section 2 of the report.

(iv) LINKING CHEMICAL AND BIOLOGICAL MODELS

A preliminary approach to modelling the impact of acidification on the ecology of two Welsh streams is given in Section 3. Output from MAGIC was used to drive empirical models for predicting brown trout density, survival and invertebrate assemblages. The modelling showed 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 showed 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 4. Some sites in Wales showed increased pH and alkalinity following a 30% decrease in deposition from 1984, however, even under this improvement in water quality, further biological impoverishment occurred on the regional scale due to continued mobilisation of aluminium.

(v) REVERSIBILITY OF ACIDIFICATION

In Sections 1, 2 and 3 examples of reversibility have been detailed at several sites and even across whole regions in response to decreased atmospheric deposition of sulphate. It is encouraging to see that this equates well with diatom reconstruction at some sites although widespread reversibility will not be evident unless sustained deposition reductions of the order of 60% are achieved. The modelled responses of biological systems is worrying insofar as the modest increases in pH and alkalinity predicted by the chemical model are not reflected in increased trout survival and density.

(vi) LINKING ATMOSPHERIC DEPOSITION AND CHEMICAL MODELS

Models of atmospheric deposition, hydrochemistry and biology now exist and this report goes some way towards developing the link between chemical and biological models. We have also developed a strategy by which the atmospheric deposition model can be incorporated. The overall structure of the integrated model is given in Figure 1.

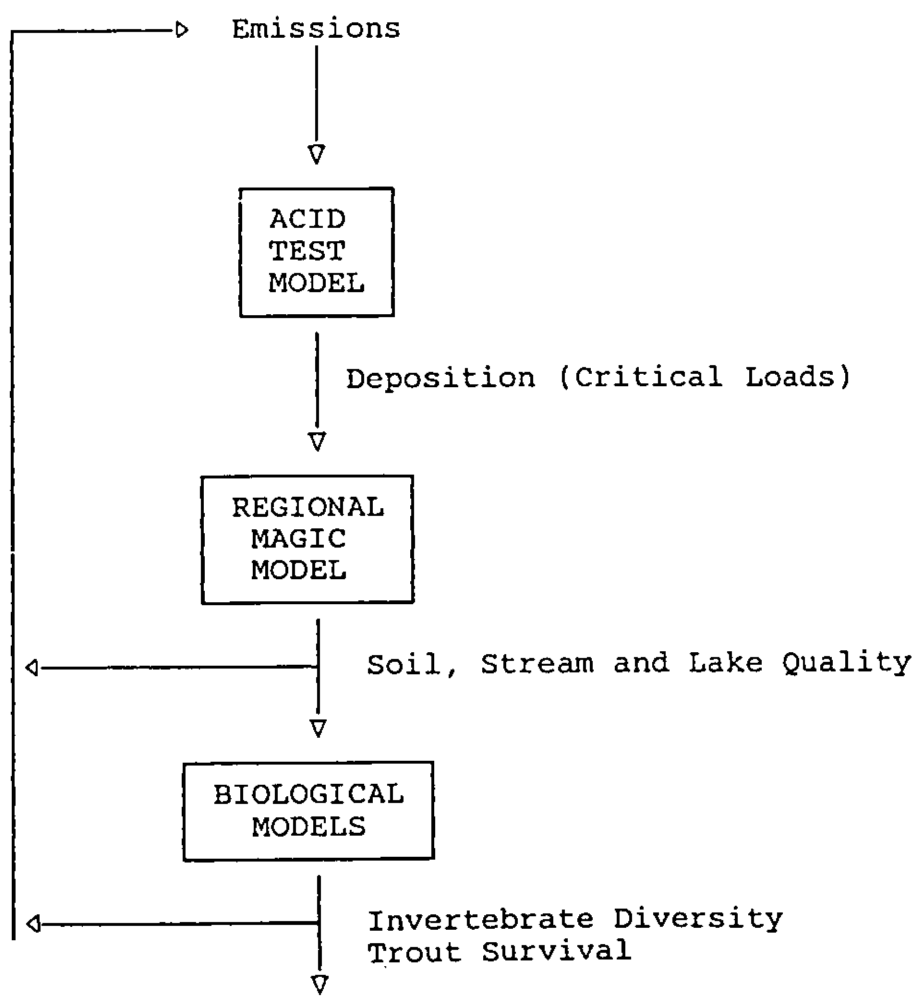

Figure 1 The flow of information in the proposed linked model.

The model will have two important uses; (i) to determine critical loads given specific objectives such as soil/water chemistry or biology, and (ii) to design the best strategy for emission reductions.

In designing critical load strategies it is important to take into account the cumulative effect of pollutant depositions and to assess the changes that will occur in the future. Catchments respond on different timescales and with different inherent delaying processes, as our completed research has shown. The proposed linked model will be able to evaluate trends in soil and water quality over time. The second application area of the model will be the design of an emission control strategy. Figure 1 shows the feedback loop being closed so that emission controls can be designed in an optimal manner to meet critical loads and, hence, biological or soil and water quality objectives.

(vii) FUTURE RESEARCH

The MAGIC model will be adopted for application to afforested sites to include processes such as; increased scavenging ability of the developing canopy; increased uptake of ions as the trees grow; and, increased evapotranspiration as the forest grows. This will enable us to address the question of the relative importance of acid deposition and afforestation in promoting surface water acidification.

Further sensitivity analysis will be carried out, in particular, a new two layer conceptualisation of the model constructed. This will employ flow routing, contain all mineral weathering in the bottom layer and all ion exchange in the top layer. This model will be compared with previous single layer site specific applications and the implications for reversibility will be addressed. This structure will also be adopted to enable us to reconstruct and predict short term, or storm event, changes in pH.

The proposed linked model will be further developed and applied to Wales in the first instance.

A statistical procedure will be developed to provide information on the range of chemical variations about the annual means predicted by MAGIC. Information on extremes of water chemistry has particular relevance from the biological viewpoint and in the establishment of Critical Loads for protecting aquatic biota.

SECTION 1

MODELLING LONG TERM ACIDIFICATION: A COMPARISON WITH DIATOM RECONSTRUCTIONS AND THE IMPLICATIONS FOR REVERSIBILITY

by

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ABSTRACT

A model of long term acidification (MAGIC) is applied to a range of catchments in Scotland 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 using the model in predictive mode under a number of deposition reduction scenarios.

1. 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 palaeoelimnological reconstructions. The two approaches differ in that the palaeoelimnological reconstruction may be viewed as a direct measure of a surrogate acidity indicator whilst the models, although having their roots in hydrochemical laws, draw largely on a conceptualised 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 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 1990). The results from the calibrated models are compared both historically and to present day water chemistry and the models are run forward to assess reversibility under a range of deposition reduction scenarios.

2. 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 (1990). 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 Springs Laboratory 1987). At L. Tinker and L. Uaine, because of the lack of a nearby DOE collector mean bulk precipitation data for 1987 for the Loch Chon (Jenkins _et al._ 1989a) 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._ 1990).

To achieve a charge balance in both input and output it was necessary in some cases to add or subtract cations or anions. Where this was necessary concentrations of chloride and/or sodium 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.

3. RECONSTRUCTION TECHNIQUES.

Details of diatom analysis (Jones _et al._ 1990, Kreiser _et al._

1990), dating procedures (Appleby et al. 1990) and techniques for reconstructing historical pH (Birks et al. 1990) are fully documented in this volume. A full description of the MAGIC model is given by Cosby et al. (1985a, b, 1986) and details of the optimisation 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 TOC in the surface water.

4. 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, and the "true" pH value may lie anywhere within the envelope. These uncertainty bands encompass the range of variable values which were simulated given the specified uncertainty in the fixed parameter values and measured target values used in the optimisation procedure (Jenkins & Cosby 1989). pH inferred from the diatoms is represented 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. 1990). 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 c.0.3 pH units for both methods. The background pH derived from both techniques are in close agreement (Figure 2a) and neither method shows a systematic bias. Comparison of observed and simulated present day pH (Figure 2b), however, shows that both the MAGIC reconstructions, and to a lesser extent the diatom reconstructions, tend to underestimate observed mean pH. This problem 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 2b).

5. REVERSIBILITY OF ACIDIFICATION

All of the MAGIC reconstructions demonstrate some degree of reversibility since the late 1970's (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 Springs 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 there is an agreement between the two techniques. A possible recovery is also indicated in the diatom reconstruction at L. Tinker and Battarbee et al.

(1988) note a trend towards improved pH conditions at a number of 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.

MAGIC predicts that under a range of deposition reduction scenarios reversibility of 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 2037 and assume no deposition reduction from present day; a linear decrease to 30% of present day deposition by the year 2000 and held constant at that level until 2037; and, a linear decrease to 60 % of present day deposition by the year 2000 and held constant at that level until 2037. At Round Loch, 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. (1989b) 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 1920's and 1950's 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. (1989b). 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 neutralising capacity which will recover only slowly (cf. L. Doilet).

7. ACKNOWLEDGEMENTS

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

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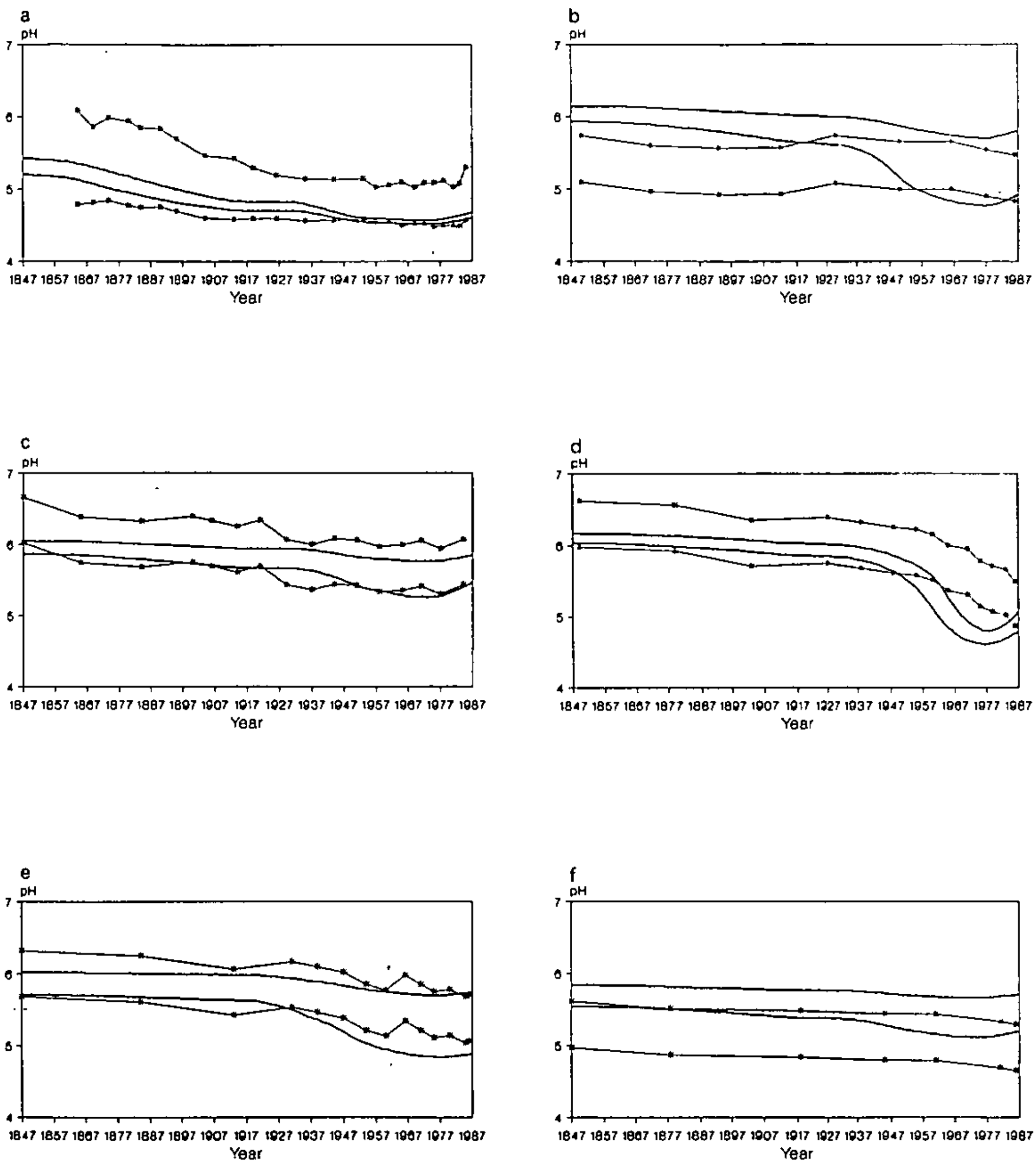
Table 1. MAGIC simulations of mean pH under three future deposition reduction scenarios.

Site	Deposition Reduction		
	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

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.

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 (o) reconstructions at Round Loch (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 at each site.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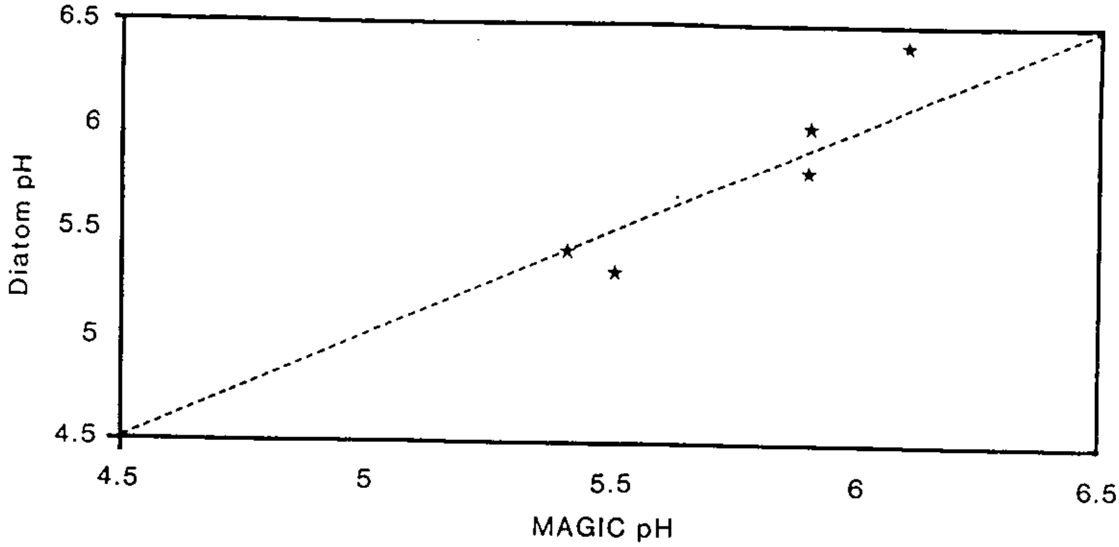

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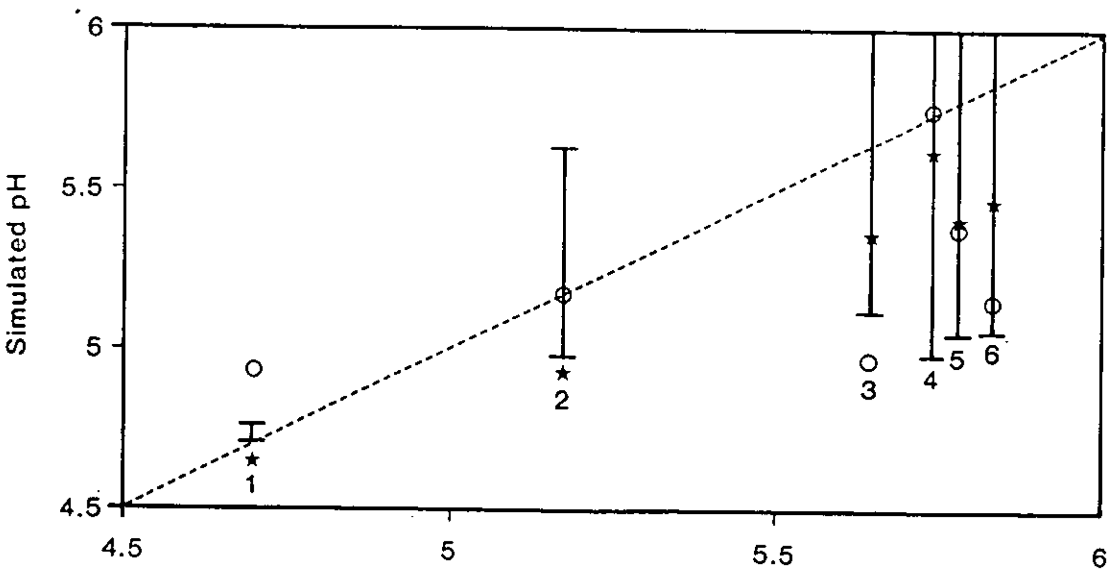

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Observed pH

SECTION 2

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.

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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).

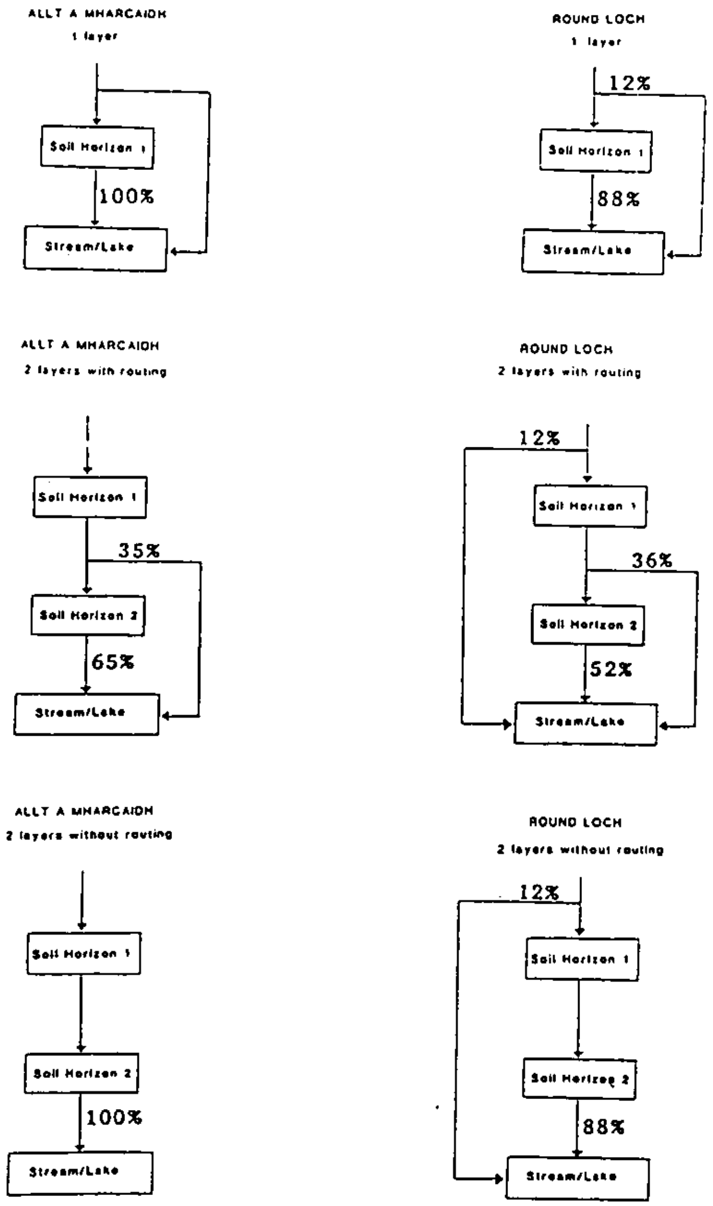

Figure 19.1. The model structures used at Allt a Mharcaidh and Round Loch; (top) one-layer, (middle) two-layer with flow routing and (bottom) two-layer without flow routing.

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 $\mu eq\,l^{-1}$ 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 inter-comparison of model structures is the primary interest. Our evaluation of the inter-comparisons 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 $\mu eq\,l^{-1}$ 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

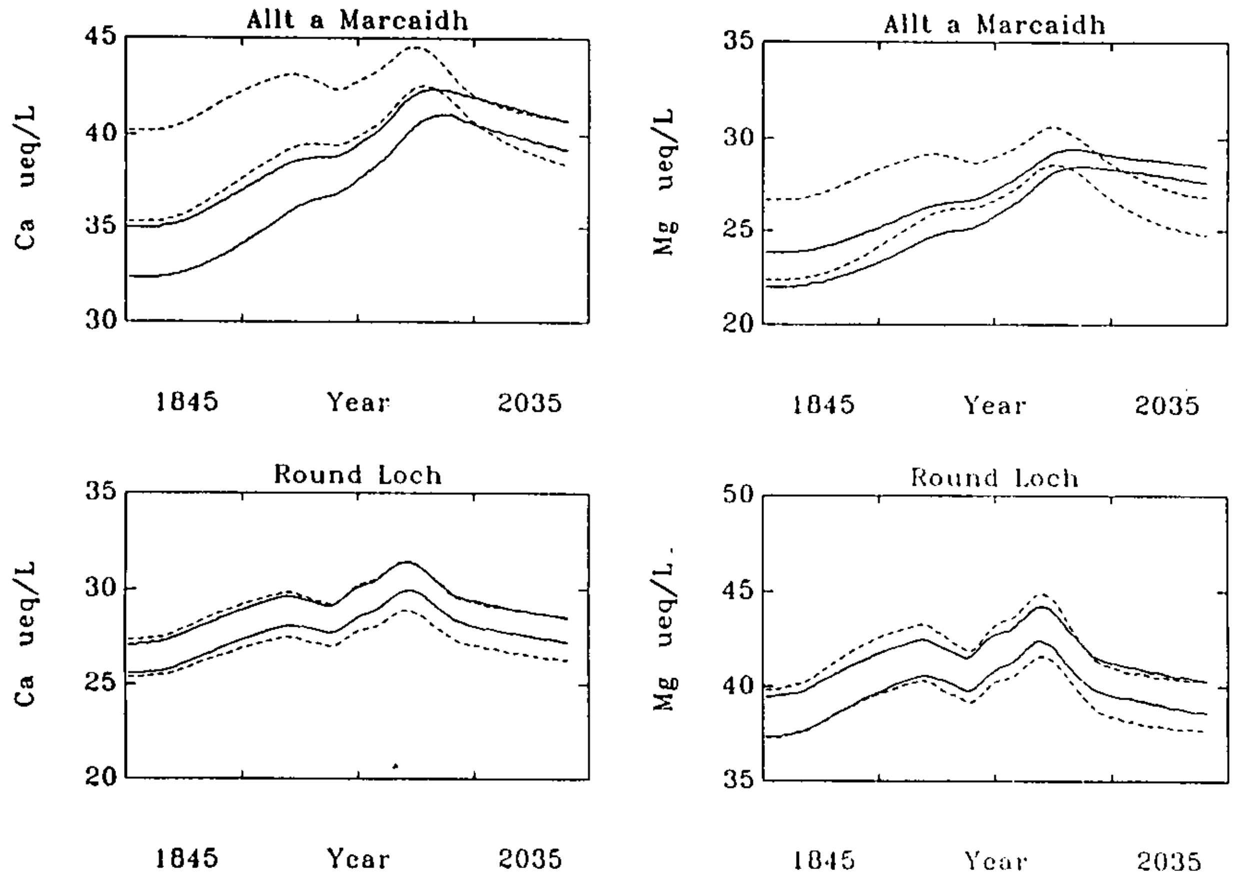

Figure 19.2. Simulated annual average Mg and Ca concentrations for Allt a Mharcaidh and Round Loch of Glenhead. Solid lines are maximum and minimum values for the one-layer structure; dashed lines are maximum and minimum values for the two-layer

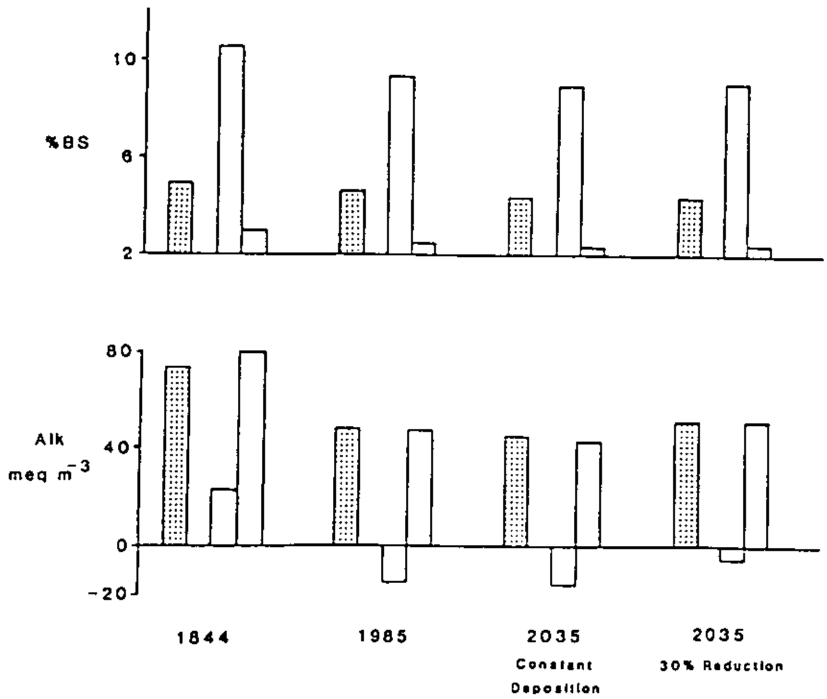

Figure 19.3. Simulated annual average soil water alkalinity and per cent base saturation for Allt a Mharcaidh for the hindcast year, calibration year and two forecast years. Shaded bars are for the one-layer structure; open bars are for the two-layer structure without flow routing.

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

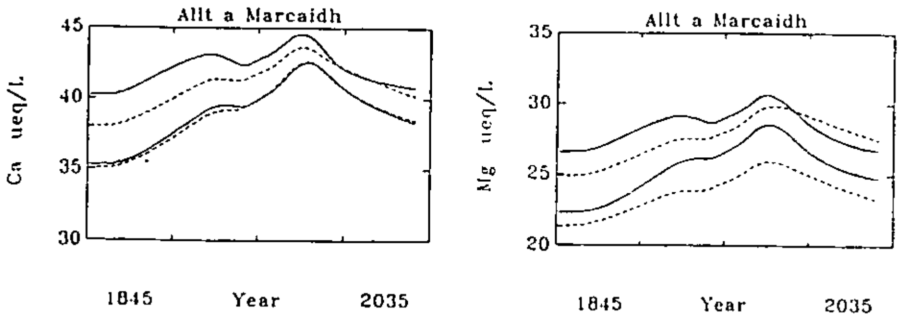

Figure 19.4. Simulated annual average Mg and Ca concentrations for Allt a Mharcaidh. Solid lines are maximum and minimum values for the two-layer structure without flow routing; dashed lines are maximum and minimum values for the two-layer structure with flow routing.

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

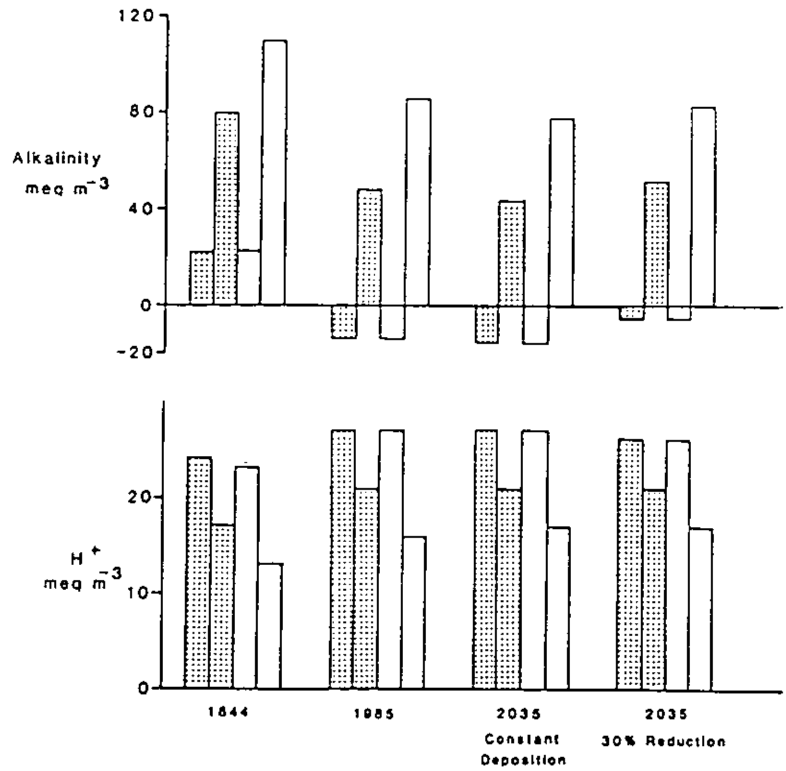

Figure 19.5. Simulated annual average soil water alkalinity and soil water hydrogen ion concentrations for Allt a Mharcaidh for the hindcast year, calibration year and two forecast years. Shaded bars are for the two-layer structure without flow routing; open bars are for the two-layer structure with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

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SECTION 3

Freshwater Biology (1988) 20, 127–140

OPINION

Preliminary empirical models of the historical and future impact of acidification on the ecology of Welsh streams

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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.

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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.

Determinand	MS	Model MS		FS	Model FS	
		Moorland	Forest		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

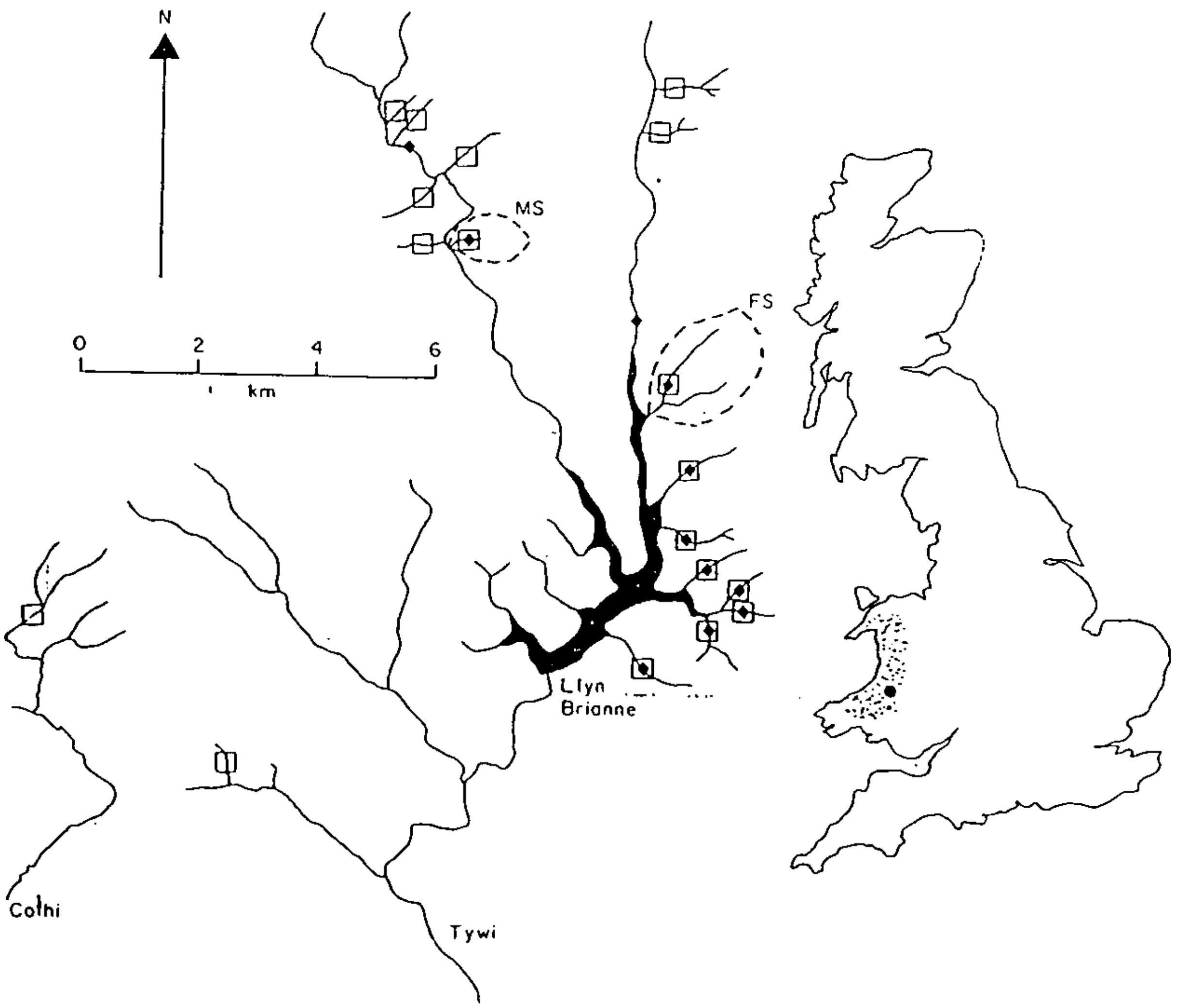

FIG. 1. The location of the study area (●). Data for the fish density model were drawn from the shaded area. On the large-scale map, FS and MS are the forested and moorland catchments, respectively, which were involved in the MAGIC simulations. Other sites marked were used to produce data for the invertebrate (□) and fish survival (◆) models.[4]

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:

$$\begin{aligned} L\ density = &-1.24-1.08\ L[Al_{filt}]\\ &+1.33\ L[Hardness]\\ &-0.22\ L\ A.D.F. \end{aligned}$$

(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

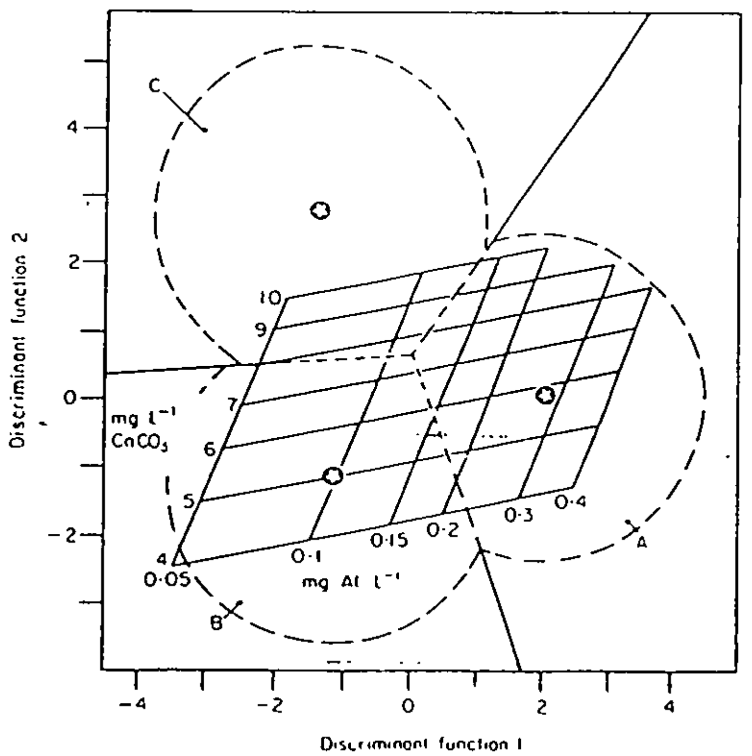

FIG. 2. The macroinvertebrate model, showing the 95% probability boundary (broken line) and centroid (stars) for each macroinvertebrate group (A, B, C) in discriminant space. The grid shows how a hypothetical stream, of catchment area 100 ha, would change location with increasing total hardness (y axis) 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).

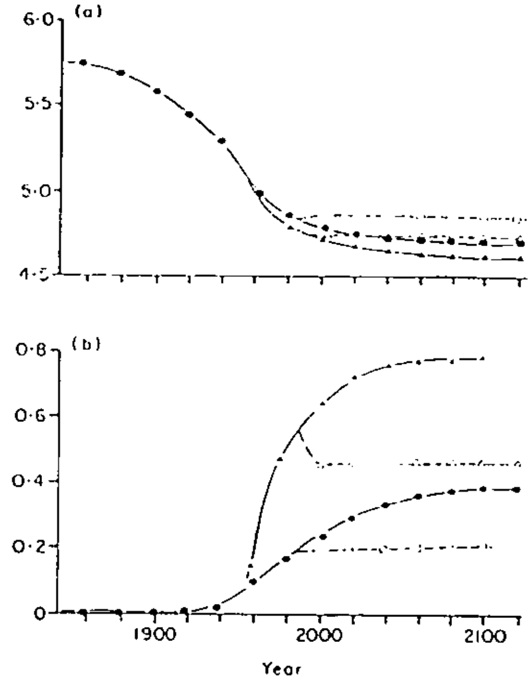

FIG. 3. Changes in (a) pH and (b) aluminium concentrations in MS between 1844 and 2124, simulated by MAGIC (broken line, 50% reduction in deposition from 1984; solid line, continued deposition at 1984 levels; ● ○, moorland; ▲ △, forest from 1958 onwards) (see Whitehead *et al.*, 1988).

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.

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

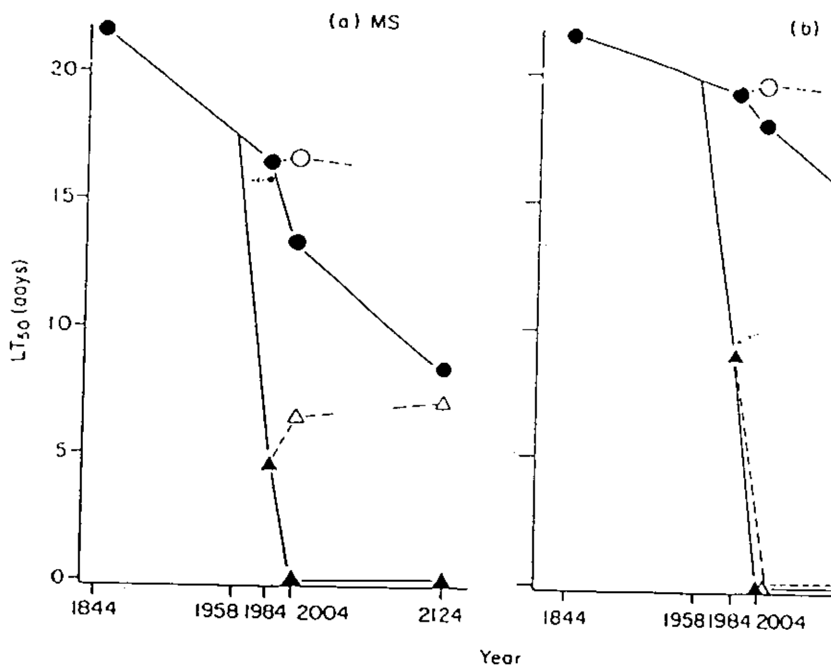

FIG. 4. Changes in the survival time of brown trout in two soft-water streams in the upper Tywi according to MAGIC simulation. The actual values in each stream in 1982 are arrowed. Conventions as in Fig. 3.

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 $100\,m^{-2}$, 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.

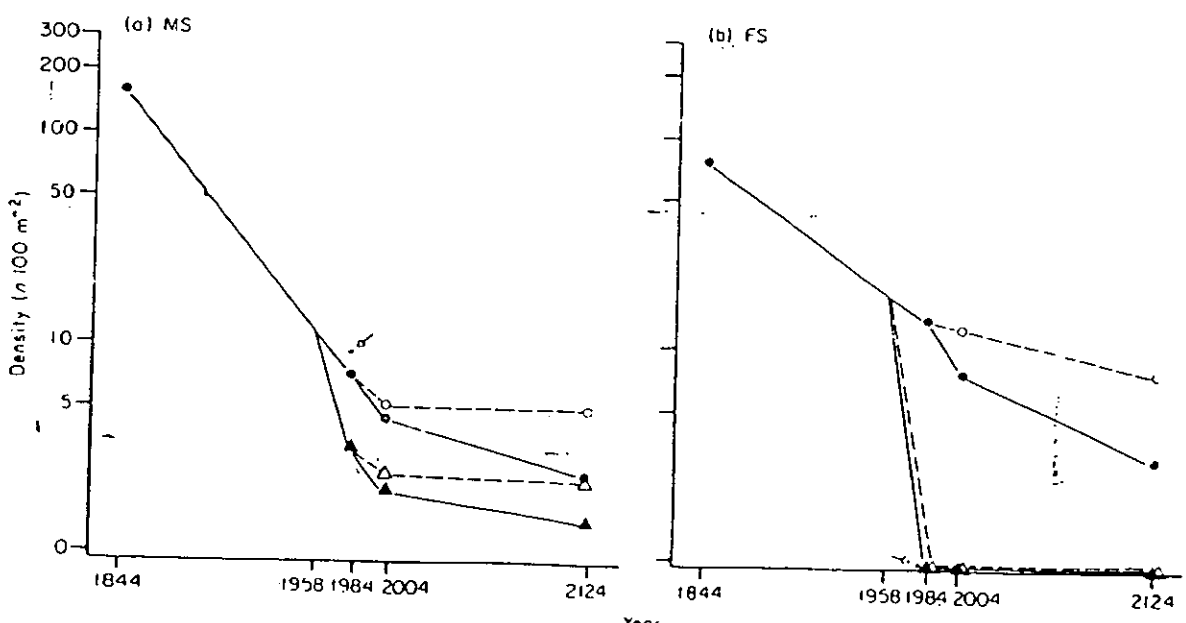

FIG. 5. Changes in the density of brown trout in two soft-water streams in the upper Tywi according to MAGIC simulation. Conventions as in Fig. 3. The actual values in 1984 are arrowed.

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

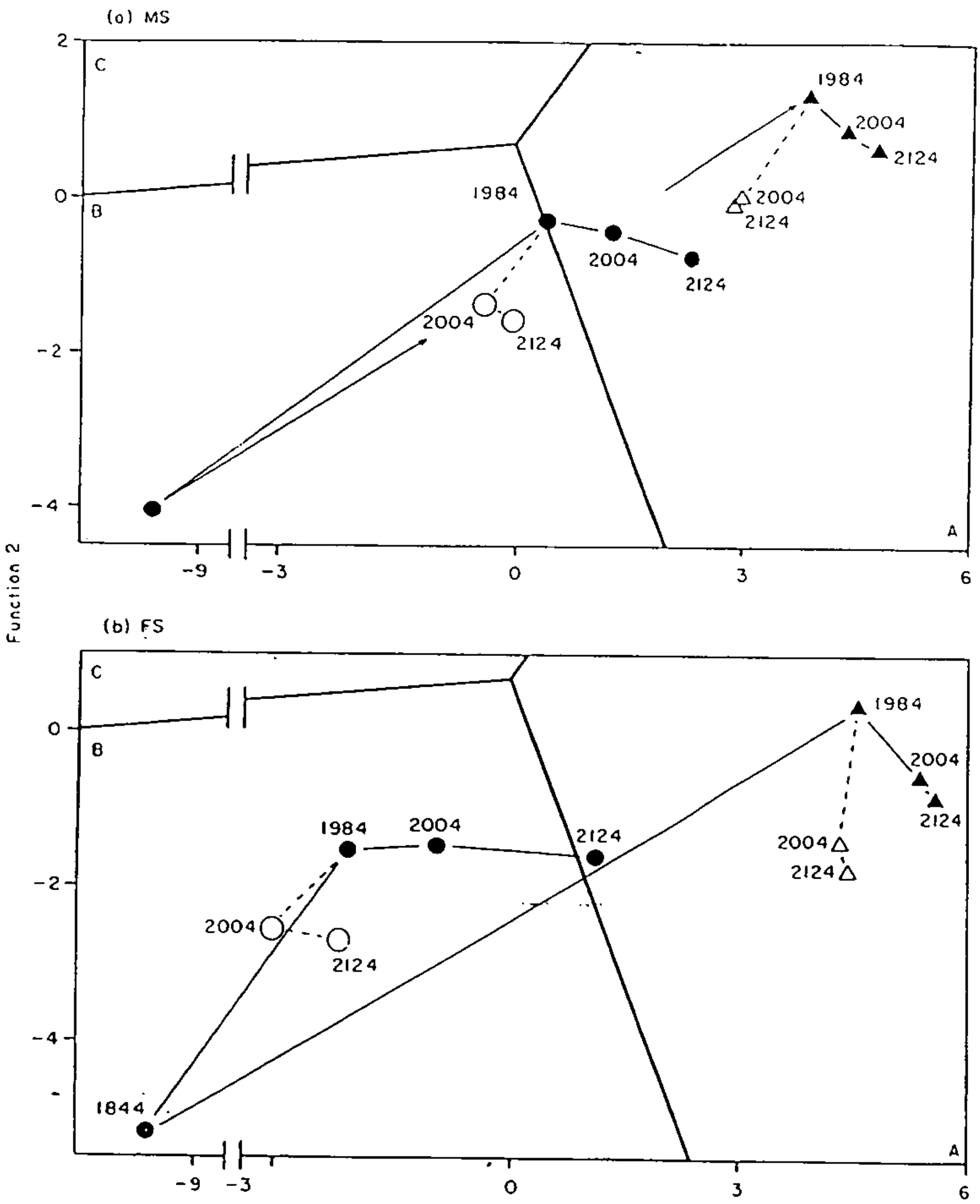

FIG. 6. Changes in the types of macroinvertebrate assemblages in two soft-water streams in the upper Tywi according to MAGIC simulation. The assemblages (A, B, C), described in the text, were judged from the position of each site in discriminant space. Conventions as in Fig. 3.

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.

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(Manuscript accepted 5 February 1988)

MODELLING THE CHEMICAL AND BIOLOGICAL RESPONSE OF WELSH STREAMS TO CHANGES IN ATMOSPHERIC DEPOSITION AND LAND USE

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Summary

We describe how the Model of Acidification of Groundwaters in Catchments (MAGIC) has been applied to a Welsh catchment, and to the acid sensitive region of upland Wales, to simulate long-term trends in acidification between 1844 and 2124. Output was used to drive biological models concerning fish, invertebrates and macroflora, thereby providing a unique combination of hydrochemical models and biological simulation.

In a stream at Llyn Brianne, the model showed marked acidification and aluminium mobilization between 1844 and the present which resulted in biological change. Loss of salmonids and impoverishment of the invertebrate fauna was most pronounced under simulated plantation forest. Biological recovery did not occur under the forest scenario despite a 50% reduction in deposition from 1984 onwards, although moorland streams retained fish when deposition was reduced.

The regional model also indicated acidification between the 19th century and present day, with concomitant biological change. Whilst some sites in the model showed increased pH and alkalinity with a 30% reduction in deposition from 1984, further biological impoverishment occurred on a regional scale due to continued mobilization of aluminium.

Introduction

The acidification of surface waters is a complex phenomenon, involving interactions between atmospheric deposition and catchment factors such as hydrology, geology, soil and vegetation. Moreover, time scales range from episodes of a few hours, to the changing balance between buffering capacity and deposition which occurs over decades (e. g. Battarbee et al., 1989). Despite this complexity, however, there is an increasing need to model the processes of acidification, both to understand past changes, and to permit forecasts of the likely effects of future management strategies. Not only do these strategies involve alterations in atmospheric deposition, but also changes in uses of the land which exacerbate or mitigate the effects of acidification (e.g. Stoner, Gee & Wade, 1984).

The modelling of biological changes in acid waters is also receiving increasing emphasis (Minns et al., 1986; LaCroix, 1987; Ormerod et al., 1988). It is now widely accepted that biological effects are amongst the most pronounced consequences of acidification, with most taxonomic groups showing differences in composition between acidic and circumneutral freshwaters (e.g. Altshuller & Linthurst, 1984). Often these differences have consequences for ecosystem function, and implications for the economic, amenity, conservation and aesthetic status of aquatic systems. Only recently, however, has it been recognized that there is a need for ecologists to model the biological effects of changing acidity and thereby provide some assessment of the environmental costs and benefits of alternative management strategies.

In this paper, we provide an overview of hydrochemical and biological models currently being used to simulate the effects of acid deposition and changing land use on surface waters in upland Wales. We apply the Model of Acidification of Groundwaters in Catchments, MAGIC (Cosby et al., 1985a, b, c) to one specific watershed, and to that part of the Welsh region known to be sensitive to acidification. We also use the output from MAGIC to simulate biological change at these catchment and regional levels.

An outline of the hydrochemical models

There has now been considerable use of mathematical models to describe the dominant interactions and processes of acidification which operate over different time scales. These include steady state models, which investigate the long-term effects of changing SO_x deposition (Cosby et al., 1985a, 1985b, 1985c; Kamari et al., 1984), and dynamic models, which combine chemical and hydrological behaviour (Christophersen et al., 1982, 1984). Whilst originally developed for the Norwegian Birkenes catchment, the latter model has now been extended and applied to catchments in Canada (Seip et al., 1986), and Sweden (Grip et al. 1986).

Of particular interest in our study, however, is the Model of Acidification of Groundwaters in Catchments, MAGIC, for examining long-term trends in acidification. MAGIC provides a tool by which soil processes can be simultaneously and quantitatively linked to examine the impact of acid deposition on surface water chemistry over time scales of years to decades. The model was originally developed and tested for catchments in the Shenandoah National Park, Virginia (USA), but it has now been adapted for catchments in Scotland (Loch Dee, Loch Grannoch), Wales (Plynlimon, Llyn Brianne) and Norway (Lake Hovvatn, and The RAIN project catchments at Songdal and Risdalsheia). Regional studies, using MAGIC, have also been undertaken in Scotland, Wales and Norway.

The processes on which MAGIC 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 partial pressures of CO_2 in the soil), with subsequent exchange of hydrogen ions for base cations

control of AL^{3+} concentrations by an assumed equilibrium with a solid phase of AL (OH).

MAGIC simulates these processes using:

A set of equilibrium reactions which quantitatively describe the equilibrium processes and the chemical changes which occur as soil water enters the stream channel

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

A set of definitions which relate the variables in the equilibrium equations to the variables in the mass balance equations

The principal data requirements of MAGIC are rainfall and runoff quality, an estimated sequence of atmospheric deposition over time, and information on soil characteristics (e.g. bulk density, depth, cation exchange capacity, sulphate adsorption rates, base saturation, temperature and pCO_2). Parameters such as selectivity coefficients, weathering, and nitrate and ammonia uptake, are determined by calibrating the model against catchment data. Details of the chemical processes involved in MAGIC are given by Cosby *et al.* (1985a, b, c; 1986).

Catchment vegetation can also be an important factor in freshwater acidification because of differences between plant species in the scavenging of dry particles and acidic mist. For example, planted conifer forests can enhance the acid loading to the soil surface by up to 80% by comparison with grassland. These forestry effects are incorporated into MAGIC by increasing terms for dry and occult deposition, and also by increasing evapotranspiration, which further concentrates scavenged material (Calder & Newson, 1979; Neal *et al.*, 1986).

An outline of the biological models

Our approach to biological modelling has been to assess empirical relationships between biological phenomena and stream physico-chemistry, and to develop these relationships into linear models which permit prediction under new conditions. Such new chemical conditions can be generated either using real data, using inferential data from diatom stratigraphy (e.g. Battarbee et al. 1988) or using hydrochemical models, such as MAGIC. Biological models currently available predict:

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 faunal community, using a multiple discriminant analysis of the environmental variables (aluminium concentration, total hardness and catchment area) which differentiated most strongly between communities, identified using a cluster analysis (TWINSPAN = Two Way Indicator Species Analysis). Three communities have been recognized representing highly acidic (type A), intermediate (type B), and circumneutral streams (type C).

4. Macro-floral community, also using a discriminant analysis between TWINSPAN groups, based on stream pH, altitude and slope.
Four communities have been recognized, and range from circumneutral (1) to acidic (4).

Statistical manipulation using the discriminant models, and methods developed by Moss et al. (1987), enables some estimate of the probability of occurrence of individual species under specified conditions.

More details of the development and use of the biological models are given by Ormerod et al. (1987, 1988, 1989), and Weatherley & Ormerod (1987, unpubl.). Examples of their use to predict likely biological change, for example following the liming of a catchment at Llyn Brianne, are shown in Figures 1 and 2, and Table 1.

Application of MAGIC to a specific catchment

The study site

The catchment modelling exercise for this paper was undertaken using chemical data from one catchment, CI 5, at Llyn Brianne (52° 7' N, 3° 43' W), 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, Gee & Wade, 1984; Ormerod et al., 1987; Whitehead et al. in press; Brown, this volume). The catchment has a soft-water stream (< 2 mg Ca l^{-1}, pH 4.8 - 5.2, 0.15 - 0.36 mg Al l^{-1} annual means) and the 0.34 km^2 is covered by moorland with *Molinia caerulea* (L.), *Festuca* spp. and *Nardus stricta* (L.). The catchment is underlain predominantly by shales and mudstones of lower Silurian age, and soils consisting predominantly of brown podzolics (21%), ferric stagnopodzols (23%), and humic or stagnohumic gleys

(25%). CI 5 had 10 fish 100 m^{-2} in 1984 and 1985, whilst its invertebrate fauna was of type B, intermediate between highly acidic and circumneutral. Fuller details are given elsewhere (Ormerod et al. 1988; Whitehead et al. 1988).

MAGIC application

Trends in the catchment 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 either moorland or planted conifer forest from 1958 onwards. In the model the forest scenarios were 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).

An optimization routine, using progressive iterations, was initially applied to provide the best estimates of the key parameters in the model. These parameters include E_{mx}, the maximum sulphate adsorption rate, rates of nitrate and ammonia uptake, weathering, selectivity coefficients and the partial pressure of CO_2 (Table 2). E_{mx} in CI5 was particularly low, suggesting that soils in this catchment have a relatively low capacity to adsorb sulphate. Nitrate and ammonia uptake rates were high, reflecting nutrient utilization by vegetation. Weathering rates were low and, coupled with the low base saturation, indicate only a limited ability of the soils at CI 5 to buffer incoming acidity. The dry/occult deposition factor reflects the low rate with which moorland scavenges airborne material; modelled sulphate inputs through dry particles, aerosols and cloud water were only 0.2 X those in wet deposition. Under the forest scenario, these other inputs were 0.8 X wet deposition.

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 1984-5, although some overestimation of H^+ and aluminium concentration was apparent (Table 3). Simulated chemical trends showed a marked reduction in pH from around 1900 onwards (Fig 3), a pattern similar to trends inferred in Welsh lakes using diatom stratigraphy (Battarbee et al., 1988). 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 (Table 3; Fig. 3). Interestingly, the model's reconstruction of chemical changes in CI 5 under the forest scenario were very similar to the real conditions in several forest streams which are adjacent and drain similar soils to those in CI 5.

Reduced deposition onto CI 5 did not markedly affect pH, probably reflecting the low base saturation and weathering rates which characterized the catchment by 1984. Aluminium concentrations under the forest scenario, even with reduced deposition, never fell to those simulated in moorland. This pattern would indicate that a substantial reduction in sulphate deposition, of 50%, would be effectively offset in forest catchments due to the enhanced ability of conifers to scavenge airborne material.

Biological responses

Brown trout. MAGIC simulation indicated that, in 1844, trout would have survived for the duration of the calibration experiments (>22 d) in CI 5 (Fig. 4). However, a progressive reduction in both survival time and trout density occurred between 1844 and 1984 with the effects particularly pronounced in the presence of forest. In future simulations, further decline in trout density and trout survival was prevented only under the moorland scenario with reduced deposition.

Invertebrates. Simulated conditions for CI 5 prior to 1940, and after 2010 in the forest scenarios, involved extrapolation outside the range over which the invertebrate model was initially calibrated. Before 1940, this extrapolation reflected low concentrations of calcium and magnesium, coupled with pH > 5.7 and low concentrations of aluminium. Waters with these characteristics no longer occur in Wales, and reconstructing their likely fauna is not straightforward. As a consequence of these unusual conditions, simulation indicated that CI 5 probably did not have invertebrate group C in 1844 (Fig. 5).

Under the moorland scenarios, model conditions in CI 5 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 prevented.

By contrast, simulated chemical changes due to the presence of forest considerably advanced the change to assemblage type A. 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. Some species-specific changes accompanying these patterns are presented in Figure 6.

Macroflora. Macro-floral changes in all the scenarios were similar (see Fig. 1), and represented a transition from groups 3 (with *Fontinalis squamosa* present) to group 4 (*F. squamosa* absent, but with the acidophilic *Scapania undulata* and *Nardia compressa* present) between 1844 and the present day. No further change in these conditions occurred under any of the future scenarios of deposition and land use which were examined.

Application of MAGIC to the Welsh region

The study area

Around 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 and, as a result of these characteristics, much surface runoff is generally base poor and vulnerable to acidification. Between October 1983 and September 1984, 104 sites on sixteen river systems, all within this sensitive region, were sampled weekly by the Welsh Water Authority. General patterns were variable in both space and time, with mean pH values for the streams ranging from 4.6 to 7.2 (Table 4). Contemporaneous data on deposition quality were collected from 50 sites, which again were variable spatially; the most acidic rainfall, of volume weighted mean 4.4 - 4.5, fell in the uplands of mid and north Wales (Donald et al., 1988).

MAGIC application.

In the regional approach, the MAGIC model was repeatedly run using different sets of parameter values chosen randomly from given distributions. This technique, based on Monte Carlo Analysis, was developed by Cosby, Hornberger & Wright (in press) in an analysis of 700 Norwegian Lakes, and has been used also in the Galloway region of Scotland (Musgrove et al., 1988).
The ensemble results of the model runs was compared with the observed distribution of water chemistry from the Welsh Water regional survey, and input parameters were adjusted until the model and actual distributions were matched. Once derived, these input parameters were then used to assess changes in chemistry between 1844 and the present day. Forward prediction involved assessing the effect of a 30% reduction in deposition beginning in 1984 and phased over a 20 year period.

Chemical patterns

Of 3000 Monte Carlo runs, 532 were successful in producing variables that collectively satisfied behaviour criteria according to the observed values. In general, the observed and model distributions were in close agreement (Fig. 7). Changes in features such as sulphate and alkalinity have, according to the model, changed markedly between 1840 and the present day (Fig. 8).

In the future, reduced deposition in the model produced a slight increase in alkalinity, but this increase was restricted to sites which already had medium to high values. At sites with ALK < - 10 uq l^{-1}, model values continued to decline by up to 48 ueq l^{-1}, probably because the replenishment of bases from weathering was unable to buffer acid deposition even after the 30% reduction.

Biological responses

The biological consequences of these regional patterns have been demonstrated using the fish models (Fig 9). Survival in 1844 was, according to the models, high in all the streams; none had LT_{50} less than 19 days. Correspondingly, almost 80% of the sites modelled had simulated trout densities in excess of 10 fish 100 m^{-2}.

By 1984, LT_{50} 's at several sites fell markedly in the model, with approximately 20% having values less than 15 days (a survival value at which many streams in the study area become incapable of supporting trout populations). Simulated densities were also reduced by 1984, with 60% of sites showing values < 10 fish 100 m^{-2}. The survival and density patterns according to the simulated chemistry at this time were in close agreement with values based on actual chemistry.

Further falls in survival and density occurred in the model, in spite of the 30% reduction in deposition, by 2124. This pattern reflected the continued effect of sulphate deposition in mobilizing aluminium, which has a key role in the biological models.

Other biological changes accompanying simulated acidification included considerable impoverishment of the macroinvertebrate fauna in the Welsh region between 1844 and the present day: model indications were that no streams had community type A in 1844, whereas around 30% of sites had this fauna by 1984. These other biological changes will be the subject of a separate paper.

Discussion, implications and limitations in the models

Whilst this exercise demonstrates the potential usefulness of a combined hydrochemical and biological approach to modelling trends in acidity, it is nevertheless governed by several caveats. These have been discussed elsewhere with reference to both MAGIC (Reuss et al. 1986) and the biological models (Ormerod et al. 1988). In the case of MAGIC, uncertainties arise over:

- the estimated deposition pattern and its applicability to rural locations

- the assumption that soils are homogeneous within catchments

- the complex chemistry involved in the response of soils and surface waters to acid deposition, for example with respect to the chemistry of aluminium

- modelling acidification due to forestry with alterations only in evapotranspiration and dry/occult deposition, and not with alterations in hydrology

  the absence of relatively stochastic events such as acid episodes during flooding.

MAGIC has, nevertheless, been able to reproduce changes in pH similar to those indicated by palaeoecolgical data from both

Scotland (Musgrove et al. 1988), and Wales (Battarbee et al. 1989). The evidence presented here also shows how MAGIC can represent the catchment specific and regional chemistry of streams from moorland and afforested catchments. The chemistry generated under simulated forest accurately reproduced the real chemistry in adjacent forest streams and, together, these features enhance confidence in trends suggested by the model.

Caveats also apply to the biological models. Their empirical approach uses a 'black-box' system which excludes details such as biotic interactions between species (e.g. Gee et al. 1978; Ormerod, Wade & Gee, 1987), and dynamic population processes which occur between different life-stages and generations within species (LaCroix, 1987). Additionally, the biological models are, like MAGIC, limited because episodes are not incorporated. Welsh data indicate that fish, in particular, can be sensitive to acute changes in pH and aluminium concentrations (e.g. Ormerod et al., 1987; McCahon & Pascoe, in press), although the influence of chronic and episodic conditions are sometimes difficult to separate in the field, particularly for invertebrates (Weatherley et al. in press). One important feature for streams in the Welsh region is that their mean and minimum pH are closely correlated, hence the mean (as produced by MAGIC and used in the biological models) probably gives a good indication of liability to episodic change. Nevertheless, models which incorporate biotic and hydrological effects are currently undergoing development in Wales.

Notwithstanding caution over the models, our results have several important implications. Clearly, the biology and chemistry of upland Welsh rivers are significantly affected by acid deposition and recent changes in land use. The indications from MAGIC are that these effects would continue for some time and in some locations, even if deposition was reduced by around 30%. For 10% of the most acid sensitive sites, simulation indicated that a deposition reduction of this magnitude would result in an increase in pH and alkalinity. Biological impoverishment would continue on a regional scale, however. Deposition reduction by 50% onto some moorland catchments in the model could result in fish populations being retained, though severe biological impoverishment would remain under forest conditions. One conclusion would be that land management practices which offset these effects would be required under forest.

Acknowledgements

The large data base employed during this study was compiled through extensive efforts by staff of the Welsh Water Authority, University College Swansea, Institute of Terrestrial Ecology and U.W.I.S.T. We are particularly grateful to Dr N. S. Weatherley and T. J. Musgrove for their efforts during the modelling exercise. Aspects of the study were funded by the Environment Programme of the Commission of the European Communities, the Department of the Environment,

the Welsh Office and the Welsh Water Authority, and it formed part of the Llyn Brianne Project

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Table 1. Simulated changes in the fish status of a Welsh stream following catchment liming. The chemical data are actual values, whilst the response of brown trout have been derived from empirical models.

	Before liming	After liming
Mean pH	5.2	6.4
Mean filterable Al u equiv l^{-1}	166	75
Mean total hardness mg l^{-1}	4.2	11.3
Trout survival LT_{50} d	16.7	26.4
Trout density n 100 m^{-1}	3.0	24.42

Table 2. Optimal parameters for MAGIC as applied to CI 5.

E_{mx}	0.01	meq kg^{-1}
Nitrate uptake	69.9	meq m^{-1} y^{-1}
Ammonia uptake	99.1	..
Weathering rates Ca	25.0	
Mg	15.0	
Na	10.0	
K	1.0	
Selectivity Coefficients:		
Log_{10} K Al/Ca	1.94	
Log_{10} K Al/Mg	1.67	
Log_{10} K Al/Na	-2.10	
Log_{10} K Al/K	-5.33	
Soil pCO_2	0.02	atm
Dry/Occult deposition factor	1.2	

Table 3 Observed and simulated runoff chemistry for CI 5. The values are ueq l^{-1} except for pH. Aluminium is assumed to be trivalent.

	Observed	Simulated (with moorland)		Simulated (with forest)	
	1984/5	1984/5	2124	1984/5	2124
Ca	44.0	43.7	36.8	54.1	44.8
Mg	56.0	55.3	43.0	71.6	56.0
Na	149.0	149.4	141.2	202.4	194.8
K	6.6	8.0	7.7	10.4	9.7
NH_4	1.5	1.6	1.6	2.3	2.3
SO_4	102.0	98.8	98.4	147.1	146.2
Cl	168.0	168.3	168.3	235.7	235.7
NO_3	15.0	15.3	15.4	21.5	21.5
Alkalinity	-	19.0	9.0	-64.8	-98.2
Al	18.0	19.2	41.9	53.7	85.0
pH	5.2	4.8	4.7	4.7	4.6
Soil % base saturation	5 - 10	9.6	8.0	9.0	7.0

Table 4. The observed chemistry of streams in the area of Wales sensitive to acidification. The values are pooled from 104 sites sampled weekly for one year.

	Mean	Median	S.D.	Minimum	Maximum
pH	6.1	6.1	0.54	4.6	7.2
Ca	130.9	107.8	91.7	40.4	862.3
Mg	111.5	89.7	113.5	44.4	1272.7
Na	220.1	205.6	62.0	149.1	640.0
K	13.4	11.0	9.8	5.4	89.0
SO_4	153.7	143.7	64.4	49.1	507.4
Cl	267.4	247.0	86.2	167.0	918.0
HCO_3	75.5	52.6	87.3	0.7	604.0
H	1.9	0.6	3.4	0.05	24.0
Alk	73.3	52.1	87.7	-15.7	603.8
Al	10.0	8.0	10.0	1.1	690.0

Figure 1. The macro-floral model, showing four community types in discriminant space. The communities range from acidic (1) to circumneutral (4). The symbols show how the floral community in one stream (CI 5) would be expected to change with liming (◆ ◇), unimproved moorland (○ ●) or forest (△ ▲) on its catchment. The open symbols are for a 50% reduction in deposition from 1984 onwards, whilst solid symbols are for continued deposition at 1984 levels.

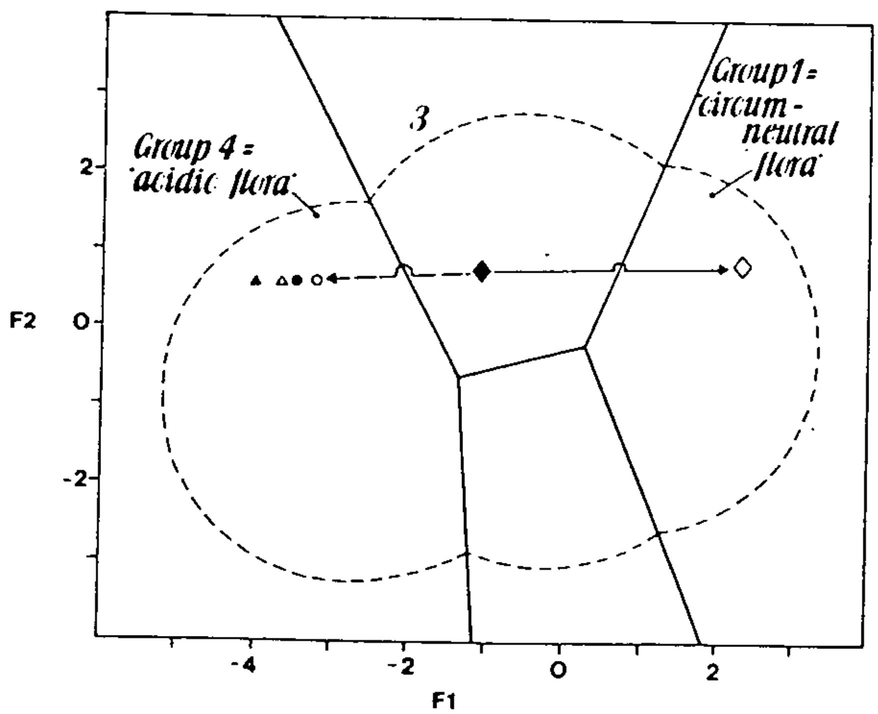
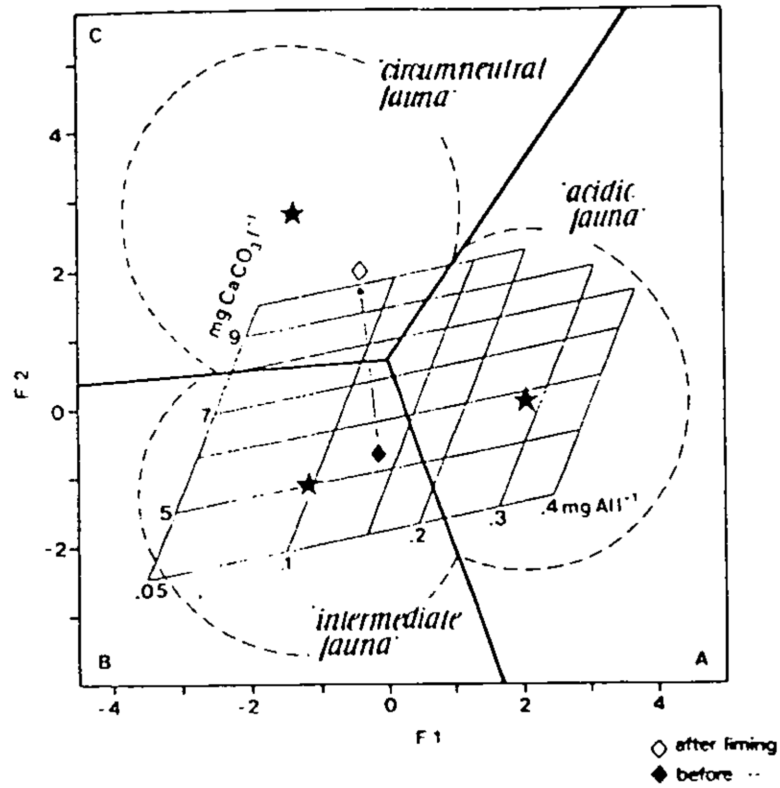


Figure 2. The invertebrate model, showing the three community types in discriminant space. The grid represents how stream CI 5 would be expected to change with alteration in hardness and aluminium concentration, exemplified by catchment liming. The dotted boundaries contain the range over which the model was calibrated (after Ormerod <u>et al.</u>, 1988).



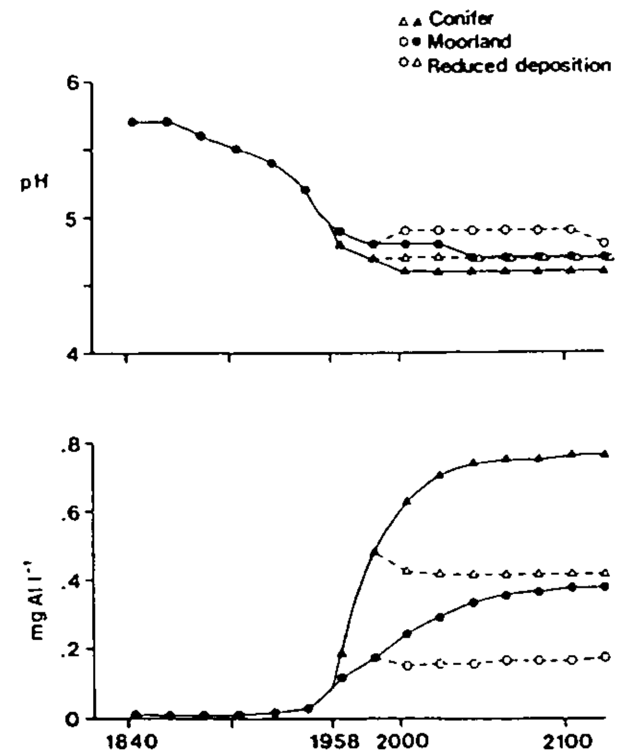


Figure 3. Changes in the pH and aluminium concentration in stream CI 5 according to MAGIC under different scenarios (after Ormerod <u>et al.</u>, 1988).

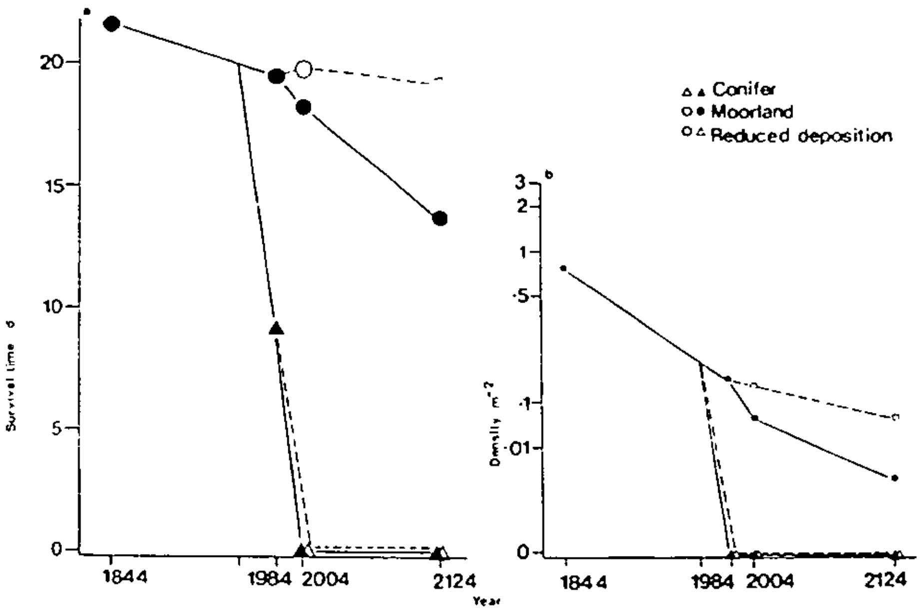


Figure 4. Changes in the survival and density of brown trout in stream CI 5 according to MAGIC under different scenarios (after Ormerod et al., 1988).

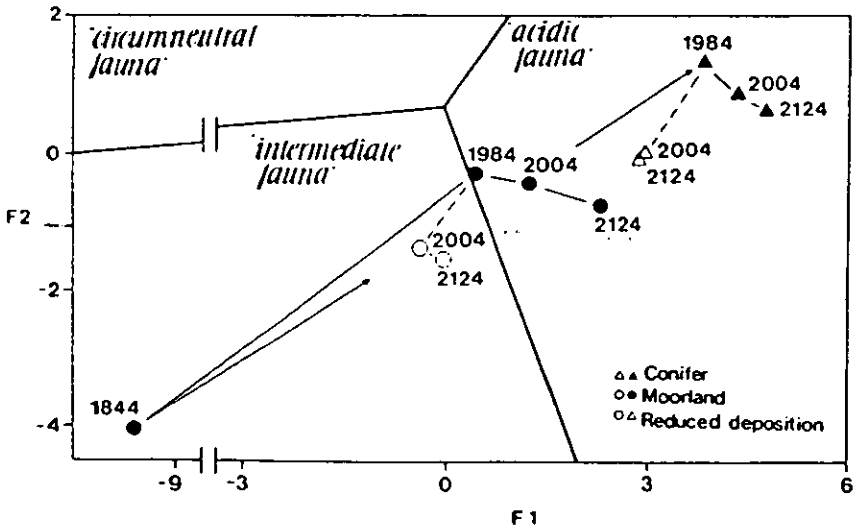


Figure 5. Changes in the invertebrate community in stream CI 5 according to MAGIC under different scenarios (after Ormerod et al., 1988).

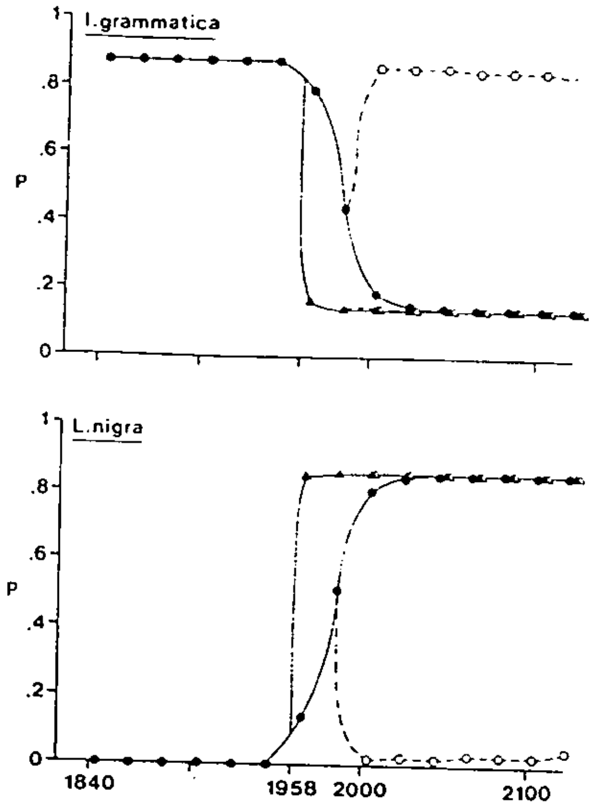
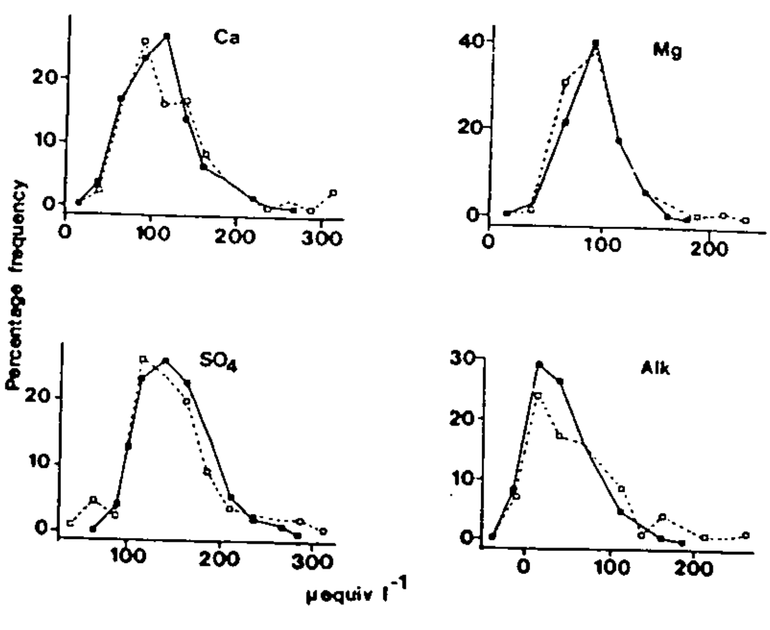


Figure 6. Changes in the probability of occurrence of some invertebrate species in stream CI 5 according to MAGIC under different scenarios.

Figure 7. Actual (■) distributions of selected parameters across the Welsh region in 1984, and those simulated by MAGIC (□).



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.

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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

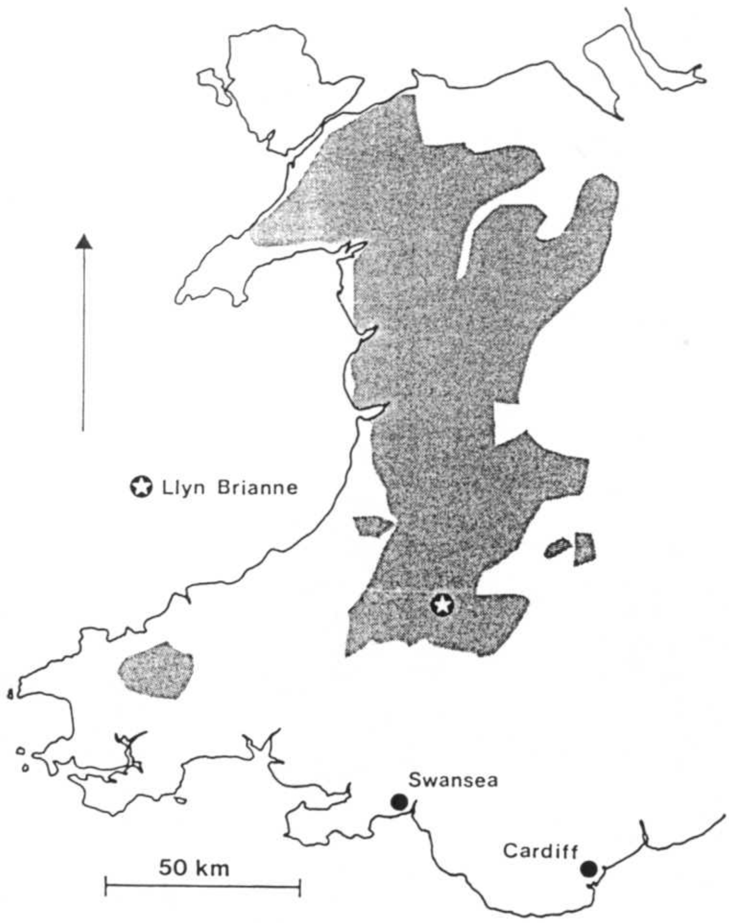

Figure 13.1. The acid sensitive area of Wales (shaded), in which acid waters occur at some or all flow levels, and the location of Llyn Brianne.

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 physico-chemistry in upland Wales. Notes: L indicates $\log_{10}$, Al is filterable at 0.45 μm in $mg\,l^{-1}$; Hd is total hardness in $mg\,l^{-1}$ SLOPE in $m\,km^{-1}$, AREA is catchment area in ha, ADF is average daily flow in $m^3\,s^{-1}$, 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

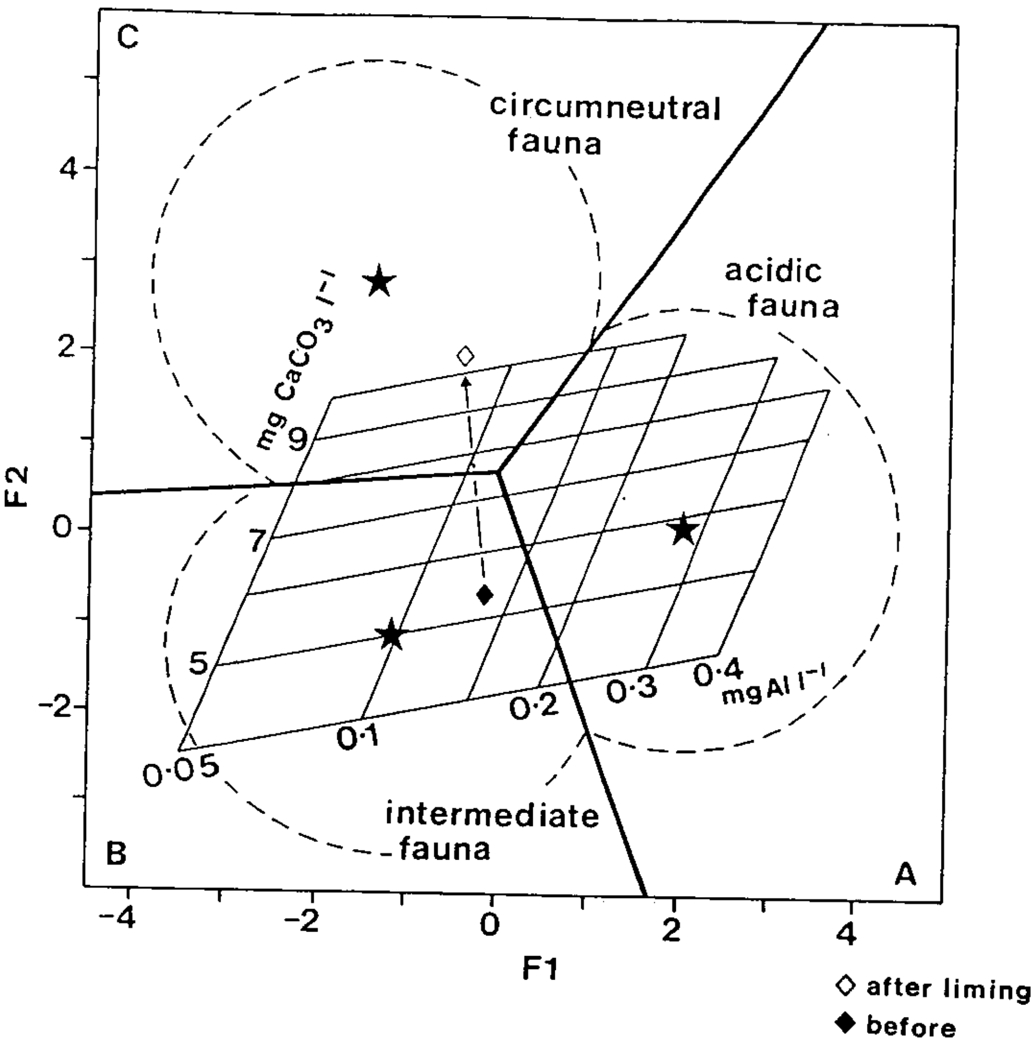

Figure 13.2. The macroinvertebrate model showing the location of the three invertebrate communities (A, B, C) in discriminant space. The grid shows how a hypothetical stream of catchment area 100 ha would change with increasing hardness (y axis) and increasing aluminum (x axis). The example is for a 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 mg l^{-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

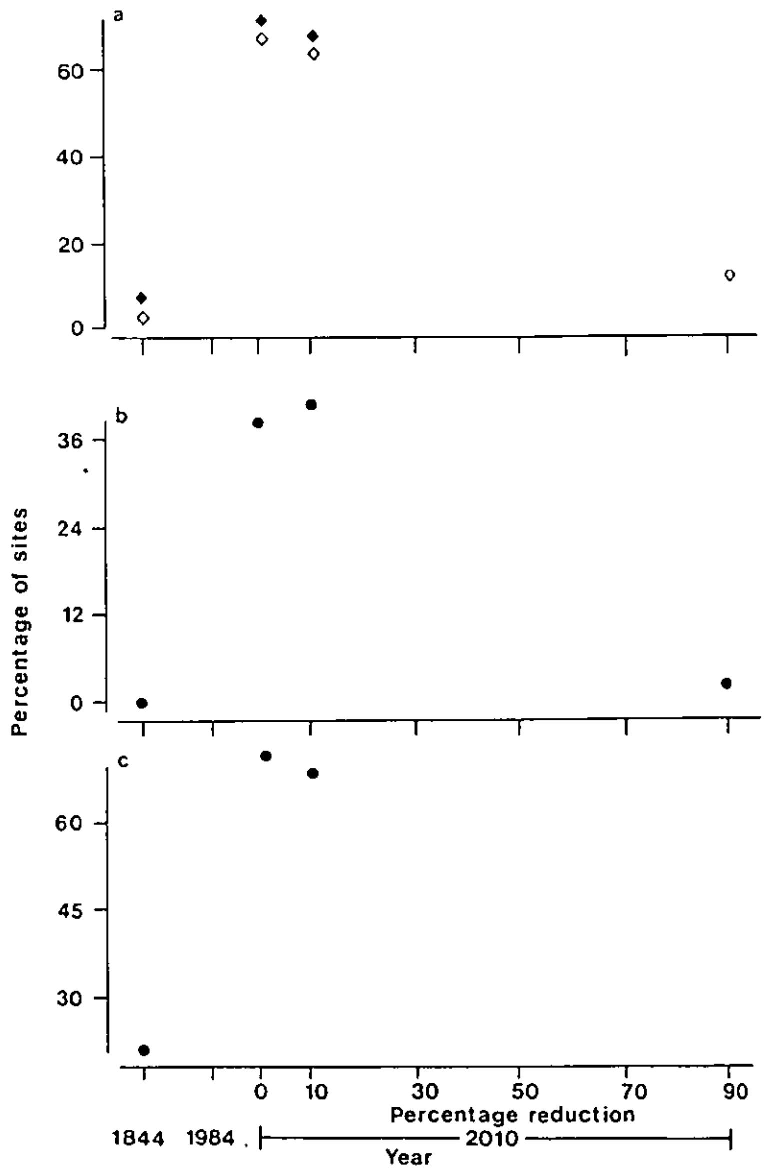

Figure 13.3. Changes in the chemical status of streams in the acid-sensitive region of upland Wales according to the MAGIC model, and consequences for trout biology. The x axis shows changes in time between 1844 and 1984, and simulated future conditions in 2010 under reductions in deposition between 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.

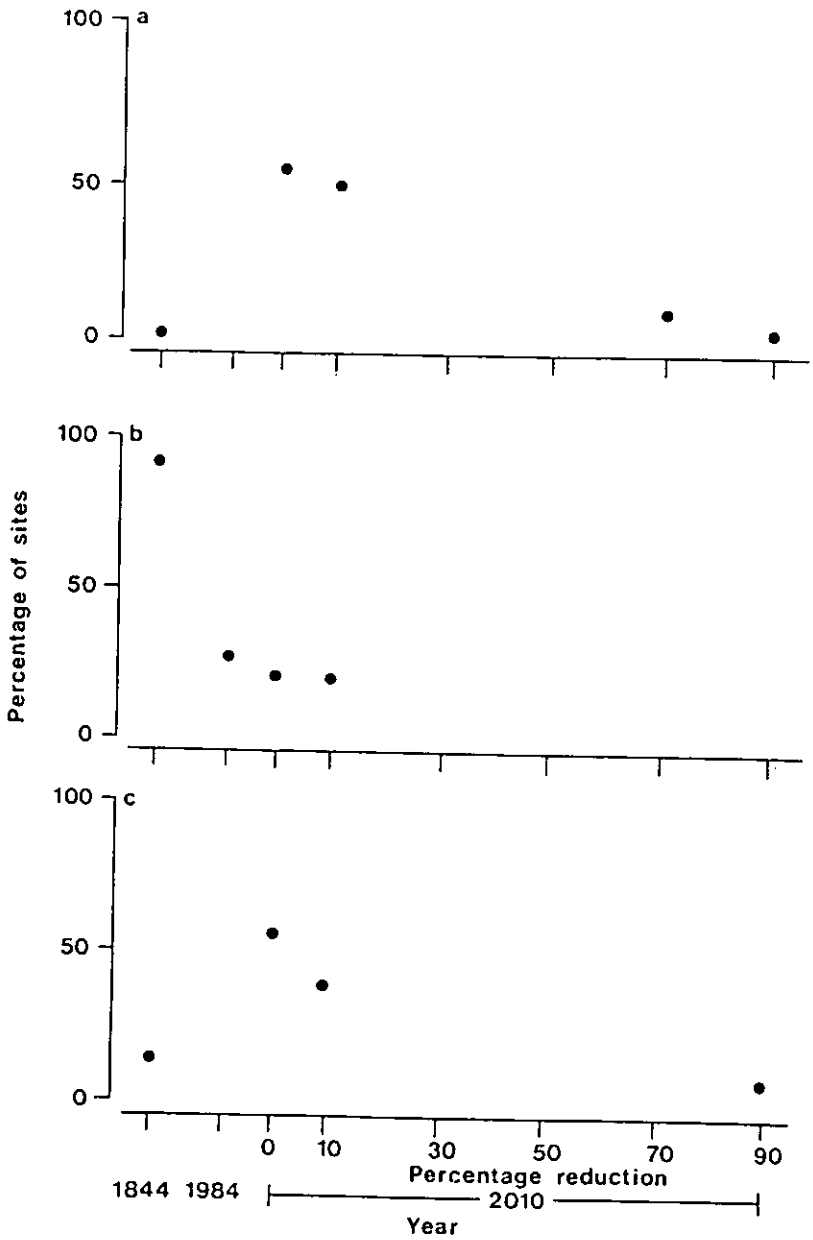

Figure 13.4. Changes in the percentage of sites in upland Wales with different invertebrate communities according to the MAGIC model. A (= 'acidic' community), B (= intermediate) and C (= circumneutral). Conventions for the x axis are as in Figure 13.3.

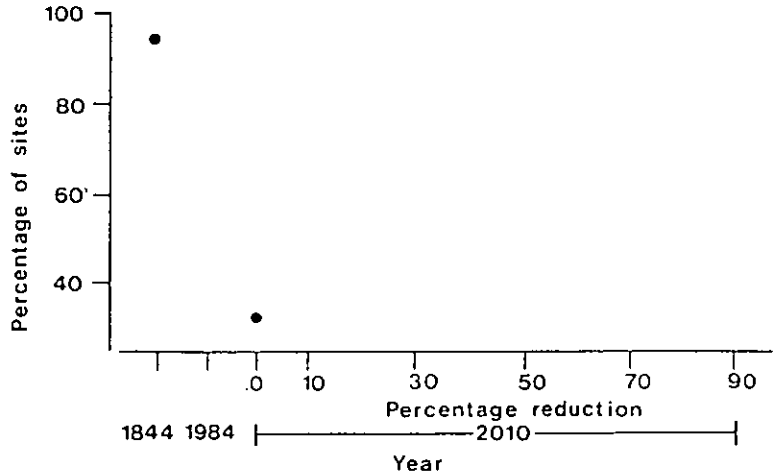

Figure 13.5. Changes in the percentage of sites in the acid sensitive region of upland Wales which would be chemically suitable for Dippers according to the MAGIC model. Conventions for the x axis are as in Figure 13.3.

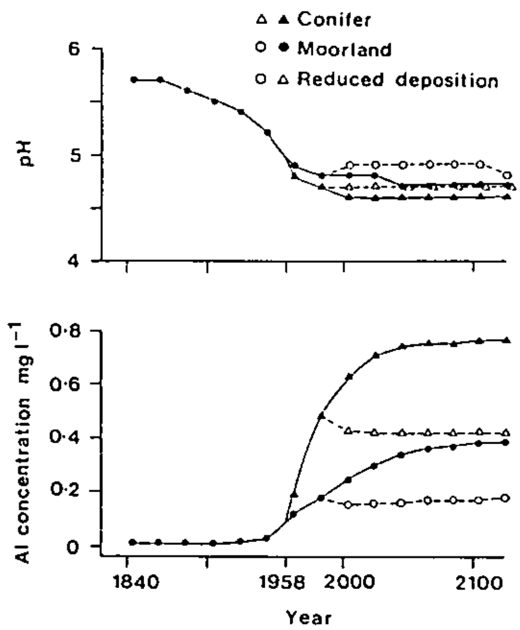

Figure 13.6. Changes in the pH and aluminum concentration in an acid-sensitive Welsh stream under different modelling scenarios as indicated by the MAGIC model: • , moorland with deposition constant at 1984 levels; o, moorland with deposition reduced by 50 % from 1984 onwards; ▲, forest from 1958 with deposition constant at 1984 levels; △, forest from 1958 with deposition reduced by 50 % from 1984 onwards (after Ormerod et al. 1988, with permission).

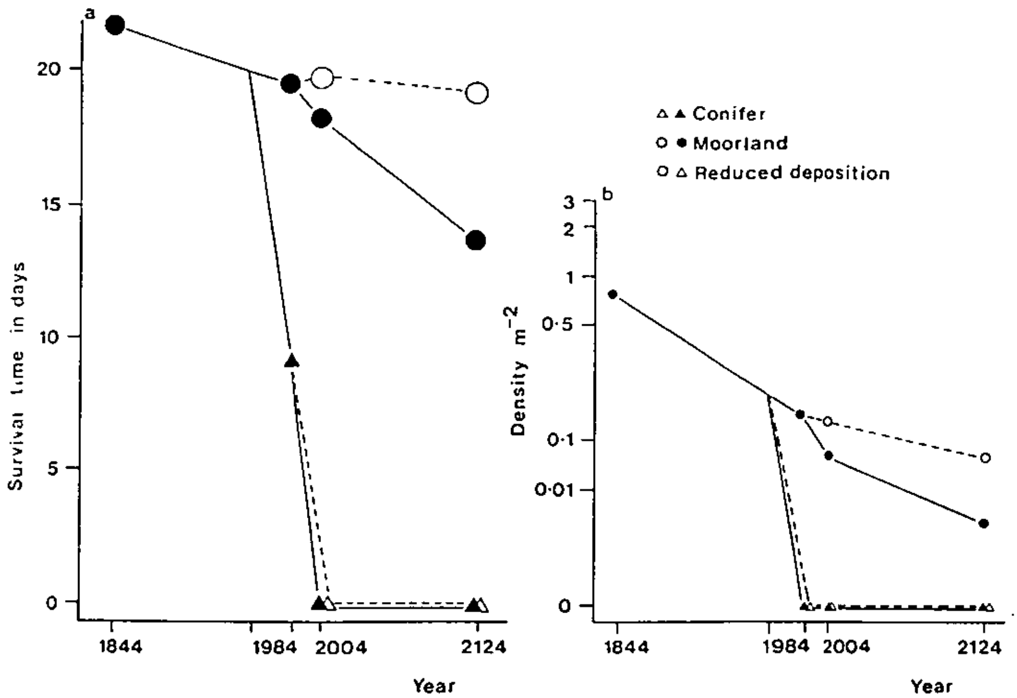

Figure 13.7. Changes in the survival time (a) and (b) density of brown trout in a soft-water streams at Llyn Brianne according to MAGIC simulation. Conventions as in Figure 13.6. After Ormerod et al. (1988).

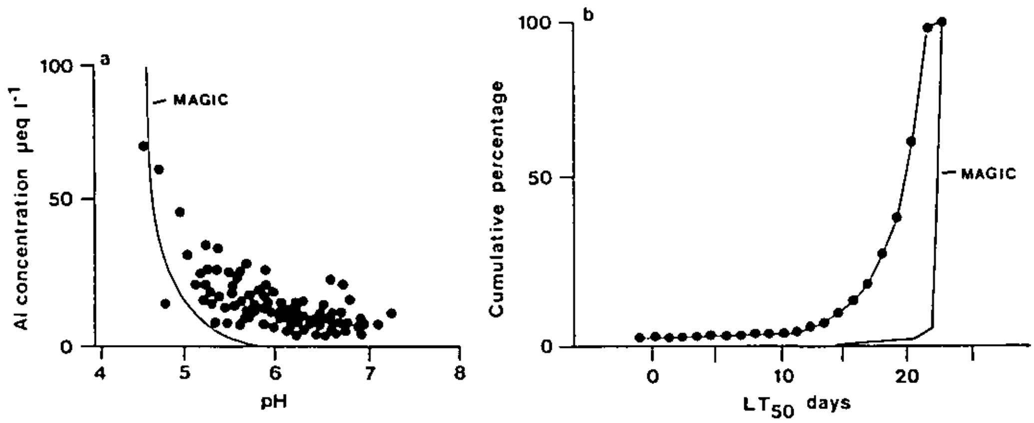

Figure 13.8. a) A possible relationship between aluminum concentration and pH at 104 sites in upland Wales in the absence of gibbsite equilibrium, and that predicted by MAGIC simulation. b) The different patterns of trout survival time, as cumulative percentage frequencies, which result from the two 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-

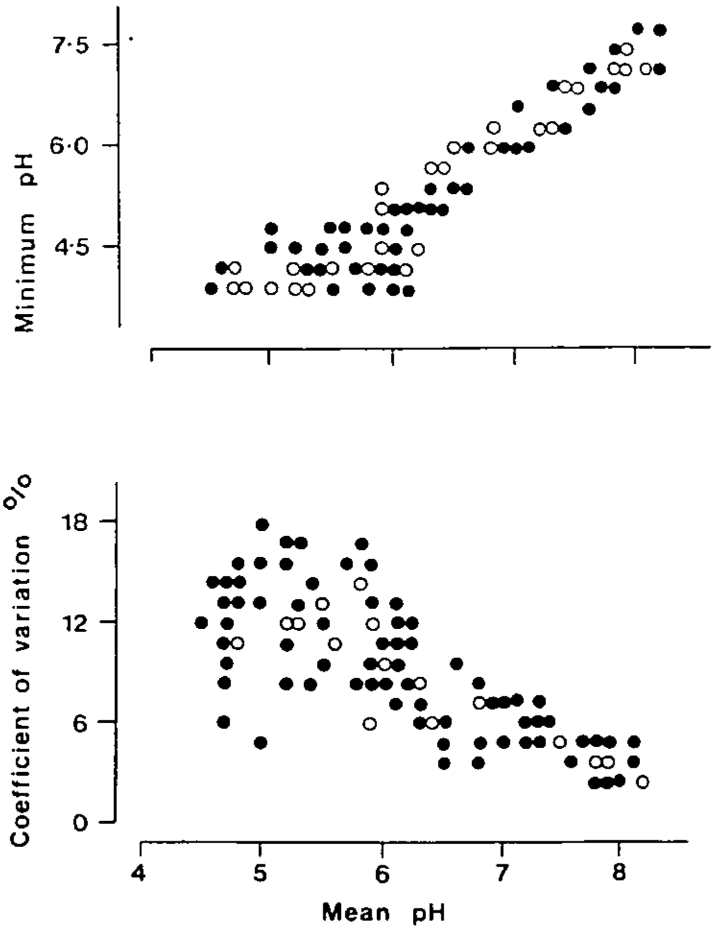

Figure 13.9. a) pH minima and b) coefficient of pH variation in relation to pH mean at 112 sites in upland Wales. All values are based on at least 1 year's data. Open symbols indicate > 1 point.

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.

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