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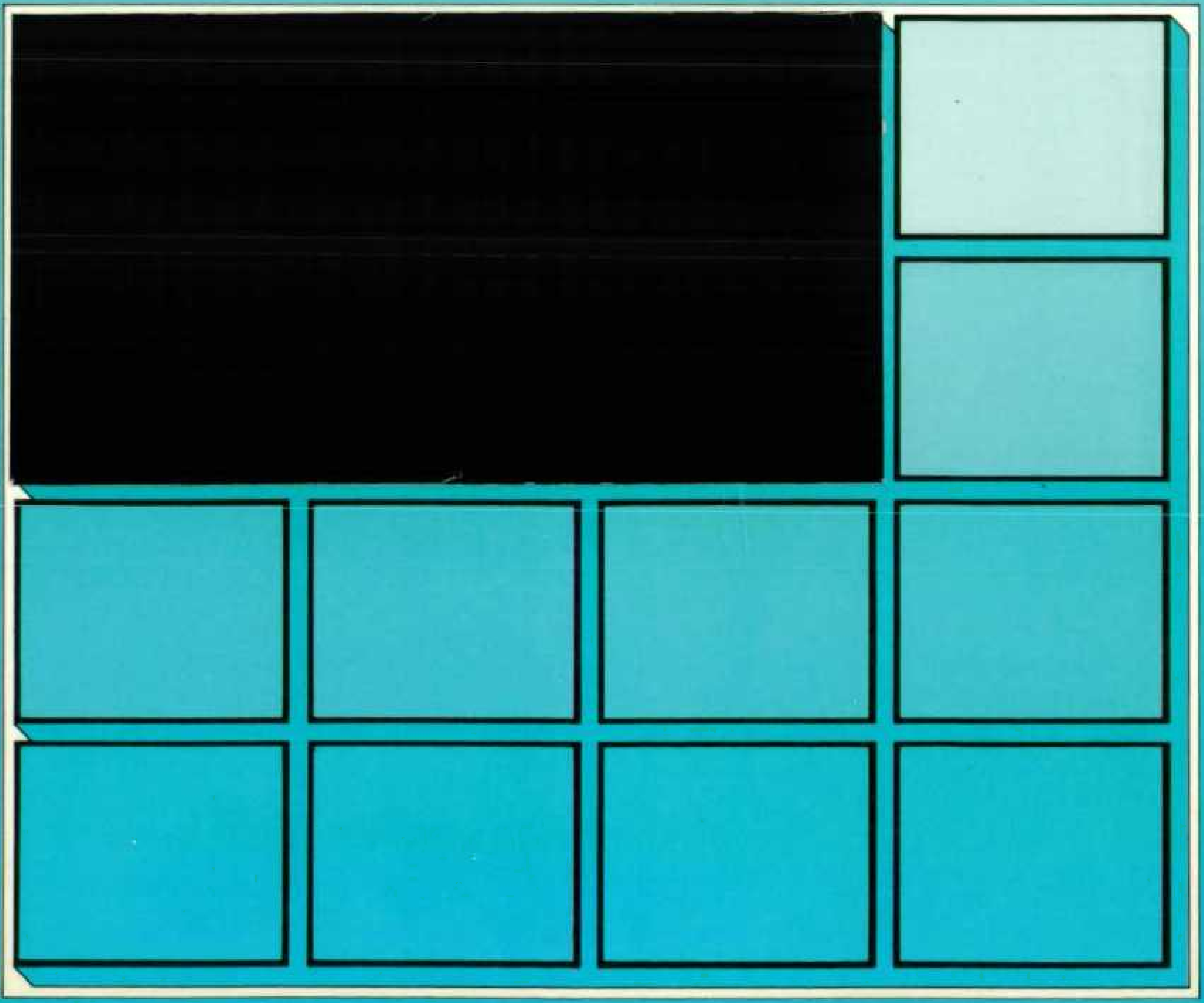

REGIONAL MODELLING OF ACIDIFICATION AND PREDICTING REVERSIBILITY

by

P G Whitehead & A Jenkins

Interim Report on Contract
EV4V.0033 UK(H)
November 1988

PREFACE

This report describes research completed for the contract EV4V.0033.UK(H) between the Commission of the European Communities (CEC) and the Natural Environment Research Council (NERC), entitled 'Regional Modelling of Acidification and Predicting Reversibility'. The research has been carried out at the Institute of Hydrology (IH), a component body of NERC.

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Summary

Objectives

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

Modelling Long Term Trends in Acidification

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

Section 1 of this report describes the application of MAGIC to the Llyn Brianne catchments in South-West Wales and to the Plynlimon Catchments in Mid-Wales. In both areas MAGIC is shown to provide an excellent description of long term catchment acidification processes. For both grassland and forested catchments the model reproduces observed chemistry and can be used to assess the impacts of land use change such as afforestation. It is shown that afforestation increases the sulphate loading into catchment by up to 80% and this has a major detrimental effect increasing water acidity and increasing aluminium levels.

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

Regional Modelling Studies

In order to assess the impact of acidification across a country or region it is necessary to employ a Monte Carlo strategy coupled to the MAGIC model. In this approach key parameters are identified and their variability across a region assessed. For example, soil base saturation levels will range from low levels on thin granitic systems to high levels on calcareous soils. Similarly hydrological and chemical inputs will vary across a region. These regional variations are incorporated into the Monte Carlo approach and distributions of water quality across a region are simulated. The regional simulations for South-West Scotland and Wales are presented in section 3 of the report and for both areas the observed distributions match the simulated distributions. The Monte Carlo approach provides a particularly useful technique for simulating regional behaviour.

. Effects of Deposition Reductions and Reversibility of Acidification

In sections 1, 2 and 3 examples are given of the effects of deposition reductions on stream water quality. At sites in Scotland and Wales and in the regional studies reversibility is shown to be feasible although there is evidence that a significant and sustained reverse will only be achieved by major reductions in deposition levels of the order of 60%. For catchments with particularly thin soils and low buffering capacity a smaller reduction will produce a short term recovery but the continuing loss of buffering capacity will eventually lead to increased stream water acidification.

. Future Research

The site specification applications of MAGIC will be continued with particular emphasis on comparison with palaeoecological data for model validation.

The regional analysis will be extended to other areas of the UK and, to this end, data bases are being collected for Scotland, Northern Ireland and South-West England.

The MAGIC results will be linked with biological models to investigate the reversibility of both chemical and biological behaviour. In addition, a statistical procedure will be developed to provide information on the range of chemical variations about the annual means predicted by MAGIC. Information on the extremes of behaviour will be particularly important from the biological viewpoint.

SECTION 1

STREAM ACIDIFICATION IN THE WELSH UPLANDS

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

[3]

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

P.G. WHITEHEAD[1], S. BIRD[2], M. HORNUNG[3], J. COSBY[4], C. NEAL[1] and P. PARICOS[1]
[1] *Institute of Hydrology, Maclean Building, Crowmarsh Gifford, Wallingford, Oxon. OX10 8BB (U.K.)*
[2] *Welsh Water, Tremains House, Coychurch Road, Bridgend, Wales (U.K.)*
[3] *Institute of Terrestrial Ecology, Bangor Station, Peurhes Road, Bangor, Wales (U.K.)*
[4] *Department of Environmental Sciences, University of Virginia, Charlottesville, VA (U.S.A.)*

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

ABSTRACT

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

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

INTRODUCTION

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

0022-1694/88/$03.50

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

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

THE LLYN BRIANNE CATCHMENT STUDY

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

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

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

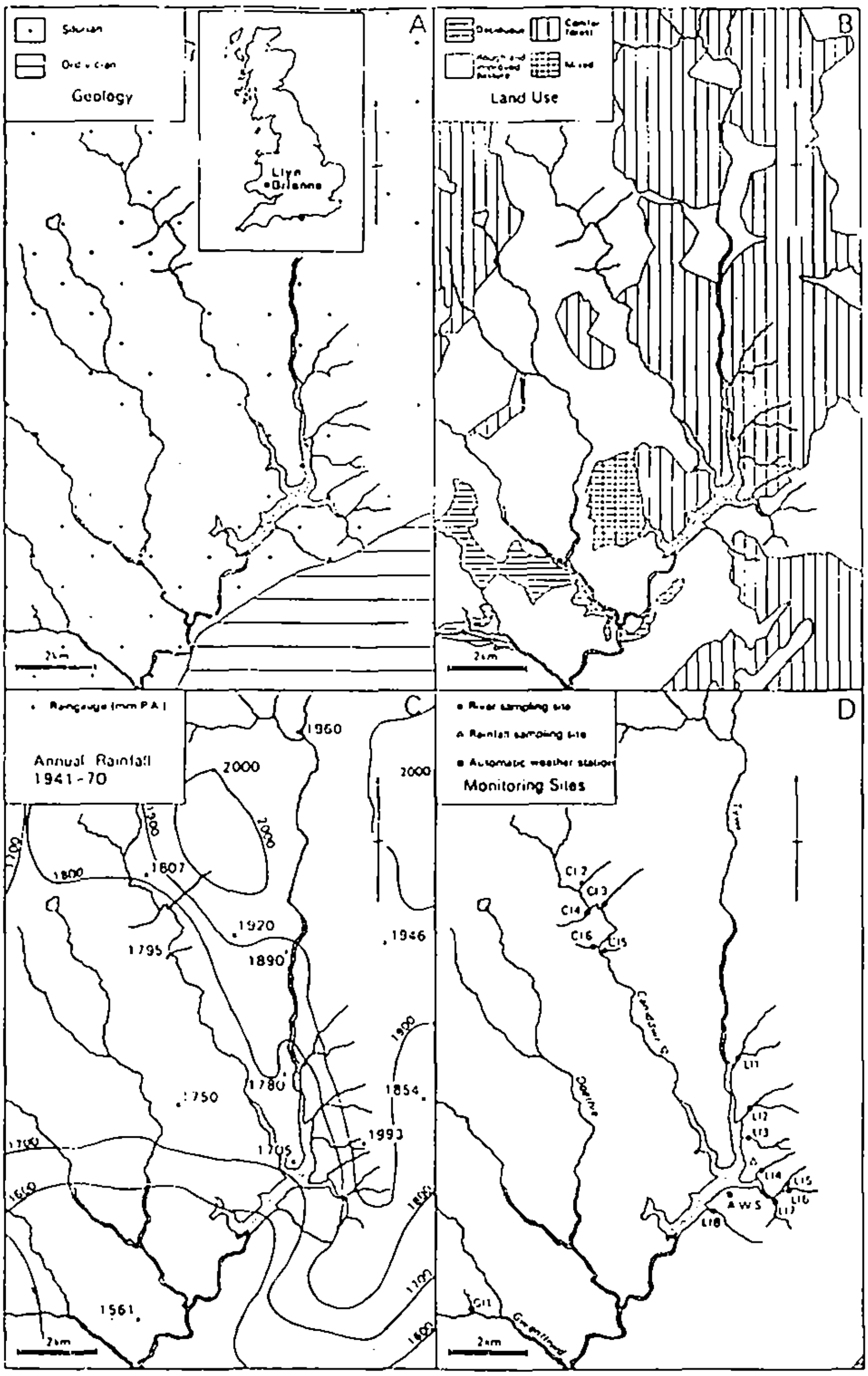
A
Silurian
Ordovician
Geology
Llyn Brianne
2km
B
Deciduous
Conifer forest
Rough and improved pasture
Mixed
Land Use
2km
C
Raingauge (mm P.A.)
Annual Rainfall
1941-70
1960
2000
2000
2000
1700
1800
1800
1607
1920
1795
1890
1946
1900
1780
1750
1854
1705
1993
1700
1650
1800
1700
1600
1561
2km
D
River sampling site
Rainfall sampling site
Automatic weather station
Monitoring Sites
Tywi
C12
C13
C14
C16
C15
Camddwr
Doethie
L11
L12
L13
L14
L15
L16
L17
AWS
L18
C11
Gwenffrwd
2km

TABLE 1

The study catchments: basic information

Site	Land use/treatment	Area (km^2)	Year of treatment
LI1	Close canopy conifer forest control	2.53	-
LI2	Bankside clearance and liming of close canopy forest	1.05	1986
LI3	Bankside clearance of close canopy forest	0.64	1983
LI4	Bomb liming of close canopy forest	0.33	1987
LI6	Unacidified moorland control	0.68	-
LI7	Moorland used for artificial acidification studies	0.68	1985, 1986
LI8	Juvenile open canopy forest	0.66	-
GI1	Acid oak woodland	0.18*	-
CI2	Strip liming of acidified moorland	0.59	1987
CI3	Land improvement of acidified moorland	0.84	1986
CI4	Ploughing without planting of moorland	0.49	1986
CI5	Surface liming of acidified moorland	0.34	1987
CI6	Acidified moorland control	0.72	-
UC4	Ploughing and planting of moorland	2.60*	1987

* Estimated.

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

CATCHMENT DESCRIPTIONS

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

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

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

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

TABLE 2

Major soil type chemistry at Llyn Brianne

	Moorland catchments									Forest catchments							
Type.	Integrade brown podzolic			Ferric stagnopodzol				Raw peat valley bottom		Integrade brown podzolic and ferric stagnopodzol				Ironpan stagnopodzol			
Vegetation.	*Festuca agrostis* grassland			*Molinia*						Sitka spruce (25 yr old)				Sitka spruce (25 yr old)			
Horizon	A	Bs	BC	O	E	B	C	O	P	Ah	E	B	C	O	E	B	C
pH (*water*)	4.44	4.61	4.63	3.64	3.94	4.23	4.35	3.93	4.20	3.78	3.85	4.00	4.26	3.35	3.45	3.51	3.63
*CEC** (meq 100 g^{-1})	7.64	4.64	4.40	16.53	11.62	6.92	4.95	14.07	14.72	14.45	8.06	5.04	3.21	16.90	9.45	5.12	4.79
Base sat. (%)	15.3	11.4	11.6	23.1	5.3	6.2	7.9	50.7	47.0	15.7	12.8	15.7	24.6	16.1	6.50	11.3	11.7
Exchangeable cations																	
Na	0.15	0.10	0.12	0.79	0.28	0.27	0.25	1.04	0.96	0.77	0.29	0.29	0.27	1.04	0.27	0.27	0.24
K	0.29	0.08	0.09	0.73	0.12	0.07	0.06	0.99	0.41	0.35	0.20	0.11	0.10	0.36	0.06	0.05	0.05
Ca	0.37	0.17	0.15	0.97	0.15	0.09	0.08	2.47	3.90	0.57	0.29	0.27	0.28	0.60	0.19	0.19	0.20
Mg	0.33	0.18	0.15	1.29	0.07	0	0	2.60	1.61	0.49	0.19	0.09	0.13	0.72	0.09	0.07	0.07
Al	6.47	4.11	3.89	10.23	10.16	5.89	4.09	5.41	6.70	10.65	6.58	3.96	2.25	11.24	8.18	4.19	3.89

* Cation exchange capacity.

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

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

PRESENT DAY RAINFALL AND STREAM QUANTITY AND QUALITY

Rainfall quantity and quality

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

TABLE 3

Bulk precipitation chemistry at sites C7 and L3 for 1984

	C7				L3			
	n	mean	wt.m	sd	*n*	mean	wt.m	sd
pH	34	4.7	4.2	0.8	33	4.9	4.1	0.9
NH_4	35	31	31	37	34	40	39	48
NO_3	35	44	44	71	34	38	37	49
Cl	35	177	142	241	34	144	113	183
SO_4	35	76	71	56	34	86	77	65
Na	34	147	114	198	32	109	90	108
K	34	8	8	8	32	7	7	8
Mg	34	36	28	48	32	30	25	30
Ca	33	21	17	22	32	30	28	36
H^+	34	63	59	143	33	44	50	73

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

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

ACKNOWLEDGEMENTS

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

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HYDROLOGICAL PROCESSES, VOL. ◀, ◀◀◀-◀◀◀ (1988)

MODELLING LONG TERM STREAM ACIDIFICATION TRENDS IN UPLAND WALES AT PLYNLIMON

P. G. WHITEHEAD
Institute of Hydrology, Wallingford, Oxon OX10 8BB, U.K

B. REYNOLDS AND M. HORNUNG
Institute of Terrestrial Ecology, Bangor Research Station, Penrhos Road, Bangor, W

C. NEAL
Institute of Hydrology, Wallingford, Oxon OX10 8BB, U.K

J. COSBY
Department of Environmental Science, University of Virginia, Charlottesville, U

AND

P. PARKOS
Institute of Hydrology, Wallingford, Oxon OX10 8BB, U.K.

ABSTRACT

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

Acidification Modelling Wales Afforestation

INTRODUCTION

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

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

0885-6087/88/000000-00$00.00

Received 8 September 1987
Revised 20 January 1988

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

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

THE PLYNLIMON EXPERIMENTAL CATCHMENT

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

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

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

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

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

CONCEPTUAL BASIS OF MAGIC

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

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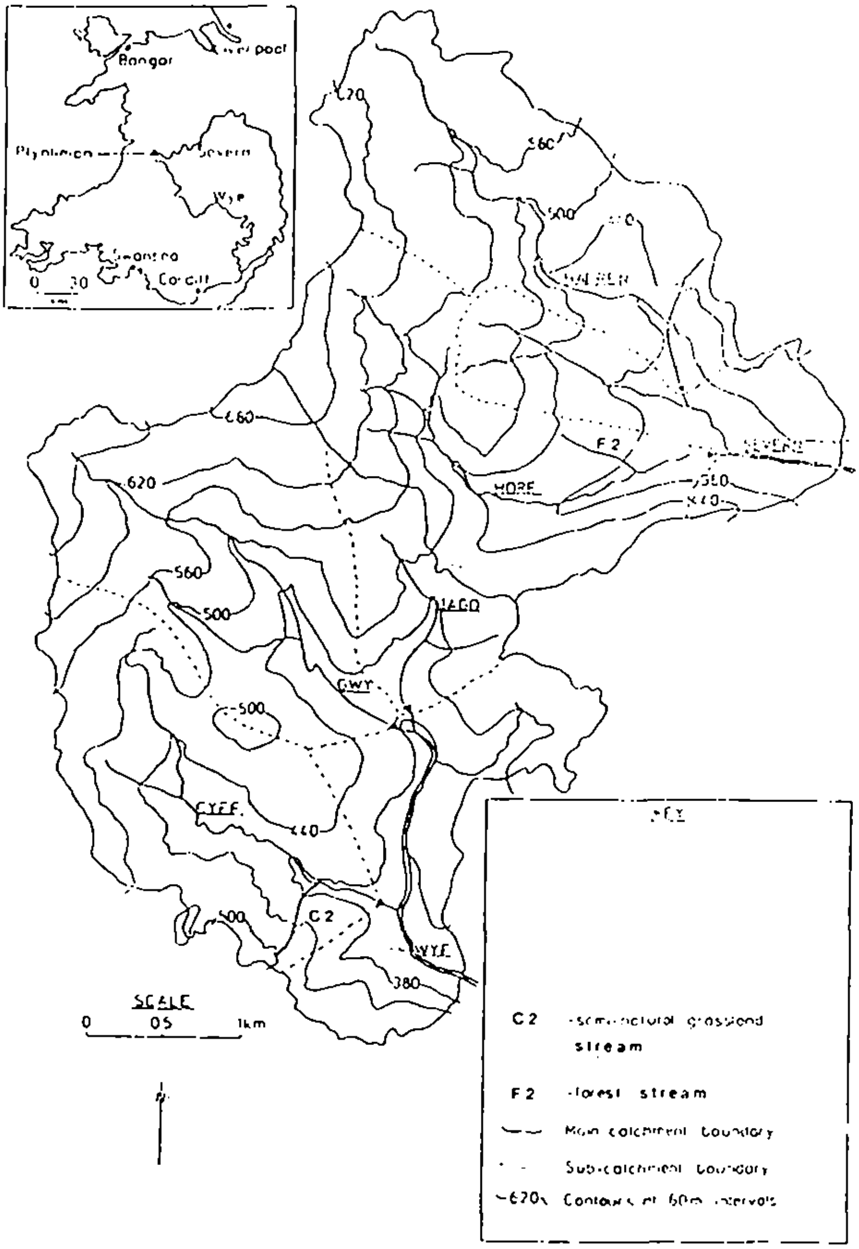


Figure 1. Location of the study sites

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

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

$$CO_2 + H_2O = H^+ + HCO_3^- \qquad (1)$$

Table 1. Rainfall and runoff chemistry

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

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

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

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

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

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

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

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

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

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

$$Al^3 + 3BCX(s) = AlX_3(s) + 3BC^+ \tag{5}$$

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

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

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

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

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

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

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

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

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

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

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

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

$$S_{Al\,BC} = \frac{\{BC^{2+}\}^3 E_{Al}^2}{\{Al^{3+}\}^2 E_{BC}^3} \quad \text{or} \quad S_{Al\,BC} = \frac{\{BC^+\}^3 E_{Al}}{\{Al^{3+}\} E_{BC}^3} \qquad (8)$$

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

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

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

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

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

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

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

The MAGIC model is composed of:

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

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

SIMULATION RESULTS

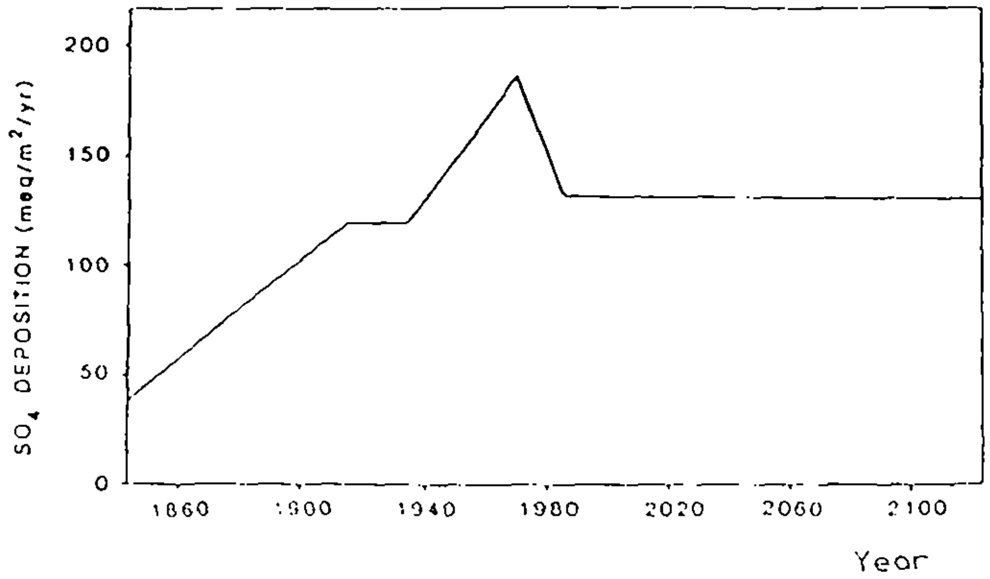
MAGIC had been applied to the grassland catchment, C2, using the pattern of emissions shown in Figure 2 to drive the model. The assumed deposition shows the significant increases in sulphate loadings since 1900 with a peak reached in 1970. Since 1970 levels have fallen by approximately 25 per cent.

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

These optimal parameter values indicate

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

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



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

Table II Optimal parameter values

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

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

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

EFFECTS OF AFFORESTATION

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

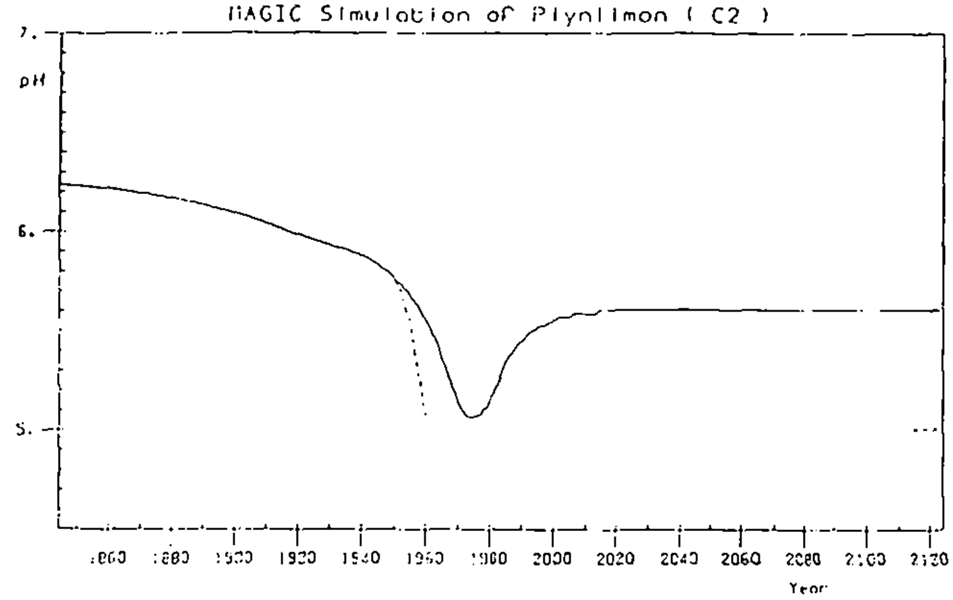


Figure 3. Simulated pH trends in moorland (——) and forest (··) catchments

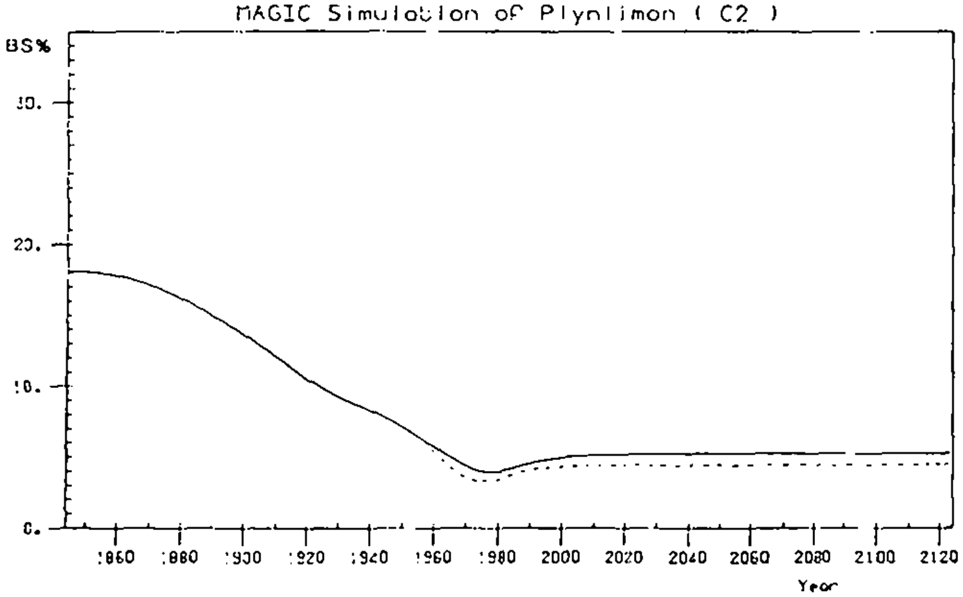


Figure 4. Simulated Base Saturation % trends in moorland (— -) and forest (···) catchments

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

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

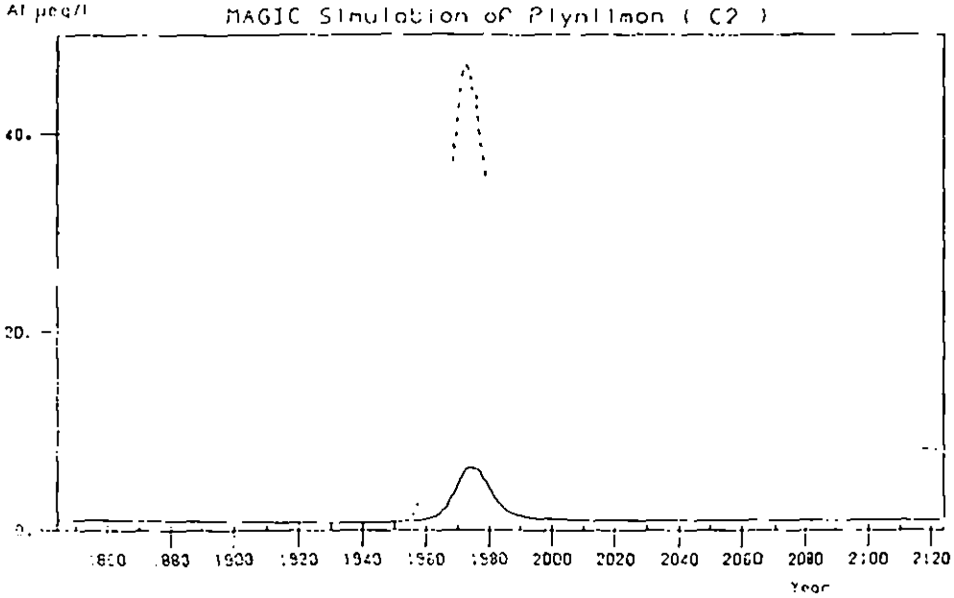


Figure 5. Simulated aluminium in moorland (—·–) and forest (···) catchments

Table III. Simulated stream chemistry

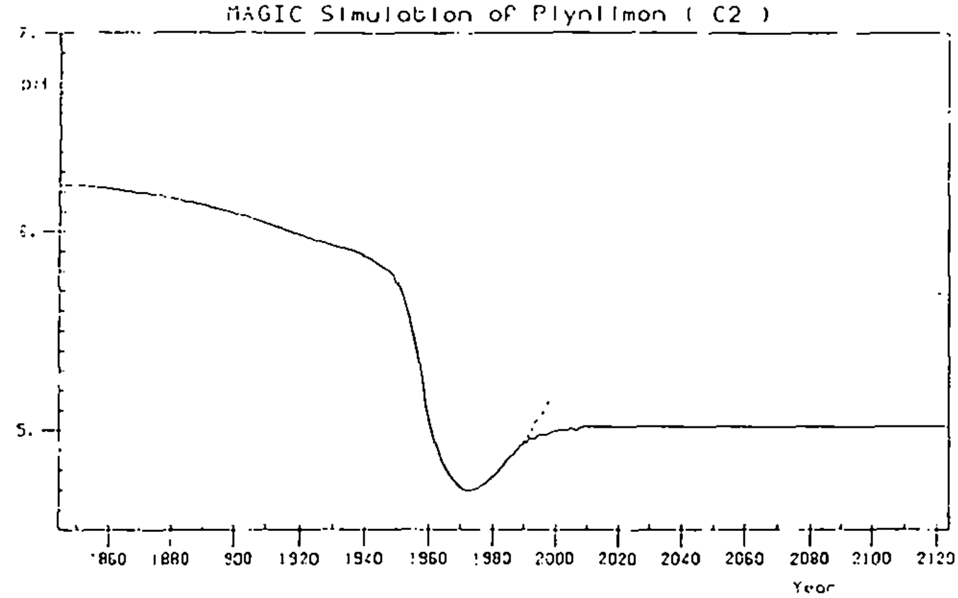
		Grassland stream	Forest stream
pH		5·3	4·8
Ca	μeq l^{-1}	54·9	61·0
Mg	μeq l^{-1}	57·5	73·9
Na	μeq l^{-1}	134·9	201·1
K	μeq l^{-1}	3·4	4·7
NH_4	μeq l^{-1}	0·1	0·1
SO_4	μeq l^{-1}	99·9	135·5
Cl	μeq l^{-1}	140·6	224·9
NO_3	μeq l^{-1}	5·0	7·0
Alkalinity	μeq l^{-1}	5·2	−26·8
Al (assuming Al^{3+})	μeq l^{-1}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

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

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

EFFECTS OF REDUCED DEPOSITION

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



e 6. Simulated pH in forest catchment assuming constant (– –) and reduced (···) future deposition

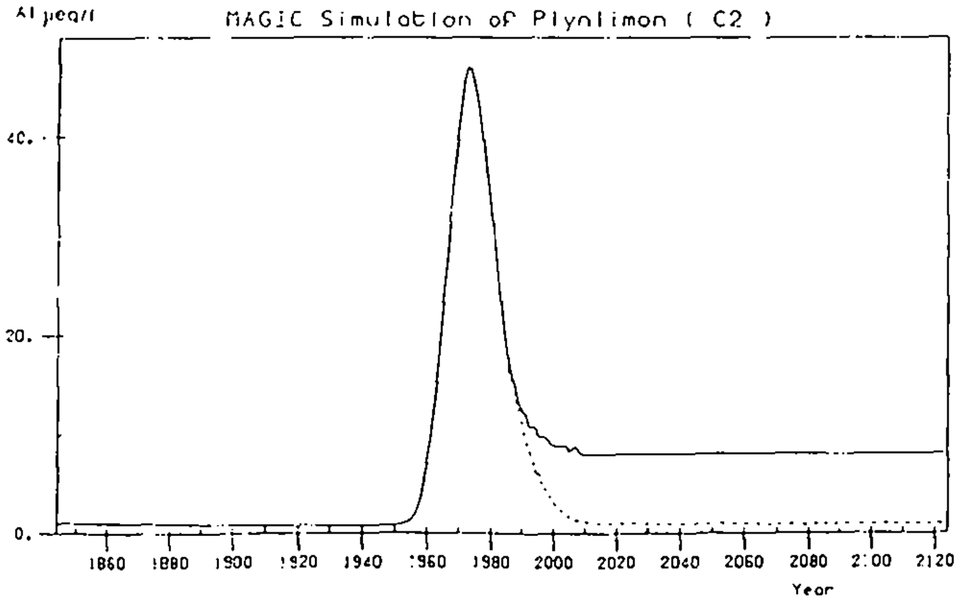


Figure 7. Simulated aluminium in forest catchment assuming constant (——) and reduced (···) future deposition levels

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

CONCLUSIONS

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

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SECTION 2

STREAM ACIDIFICATION IN SCOTLAND

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

Modelling the effect of acid deposition in upland Scotland

P. G. Whitehead and C. Neal

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

KEY WORDS: acidification, afforestation, catchments, models.

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

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

The hydrological and chemical data collected from the catchment studies form the basis of a comprehensive modelling research programme by The Institute of Hydrology. Recently there has been considerable use of mathematical models to describe the dominant interactions and processes operating in catchments and to simulate catchment behaviour. Steady state models have been used prescriptively to demonstrate the long term consequences of changes in the industrial emissions of SO_2 (Cosby *et al.* 1985a; Kamari *et al.* 1984). Correspondingly, dynamic models have been successfully applied descriptively to several catchments (Christophersen *et al.* 1982, 1984). For example, Christophersen *et al.* 1982 have developed a simple conceptual model that reproduces major trends in chemical and hydrological behaviour in Norwegian catchments. This model has been successfully extended (Seip *et al.* 1985) and applied descriptively to the Harp Lake catchment in Canada. The model has also been applied to two forested catchments in Sweden (Grip *et al.* 1985).

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

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

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

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

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

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

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

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

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

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

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

2. Applications of the 'Birkenes' models

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

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

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

and

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

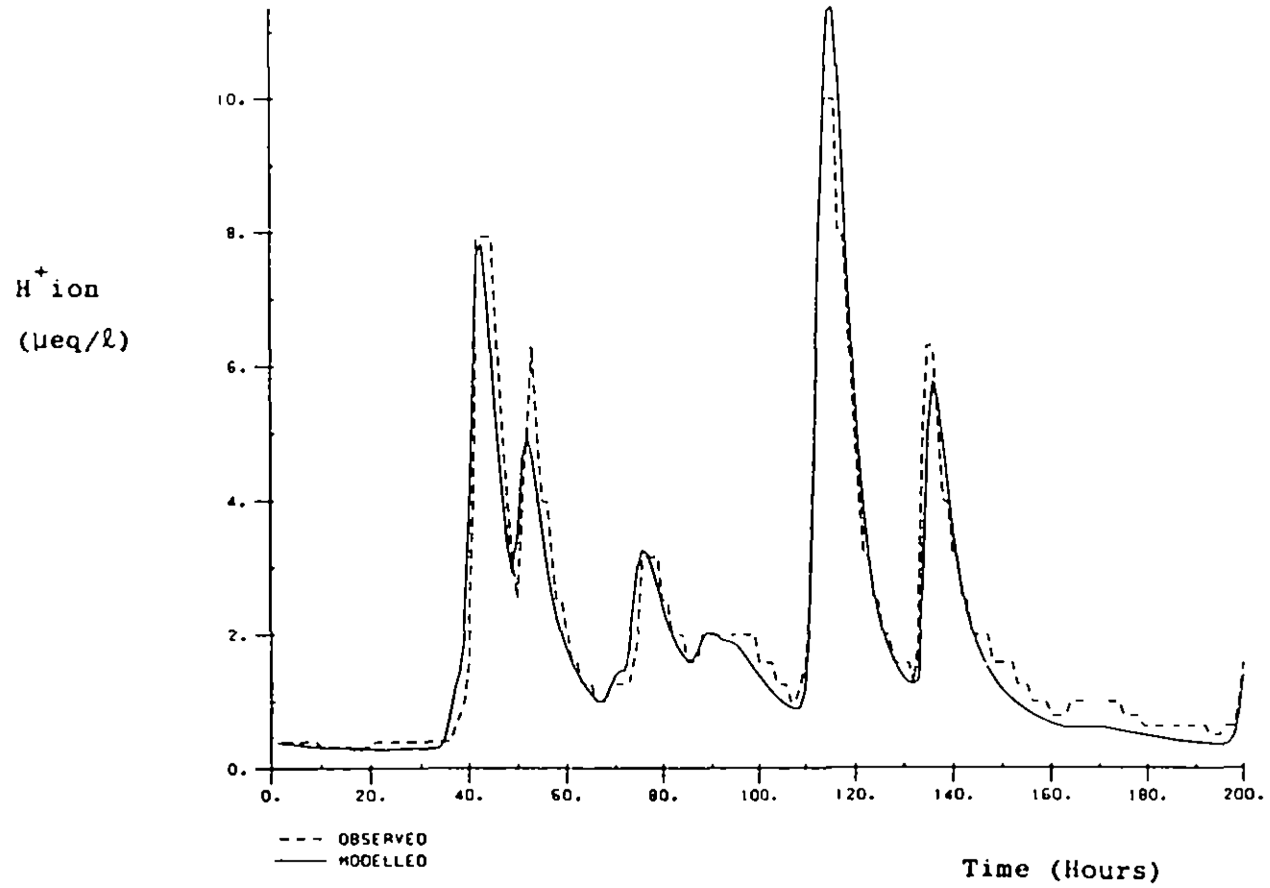
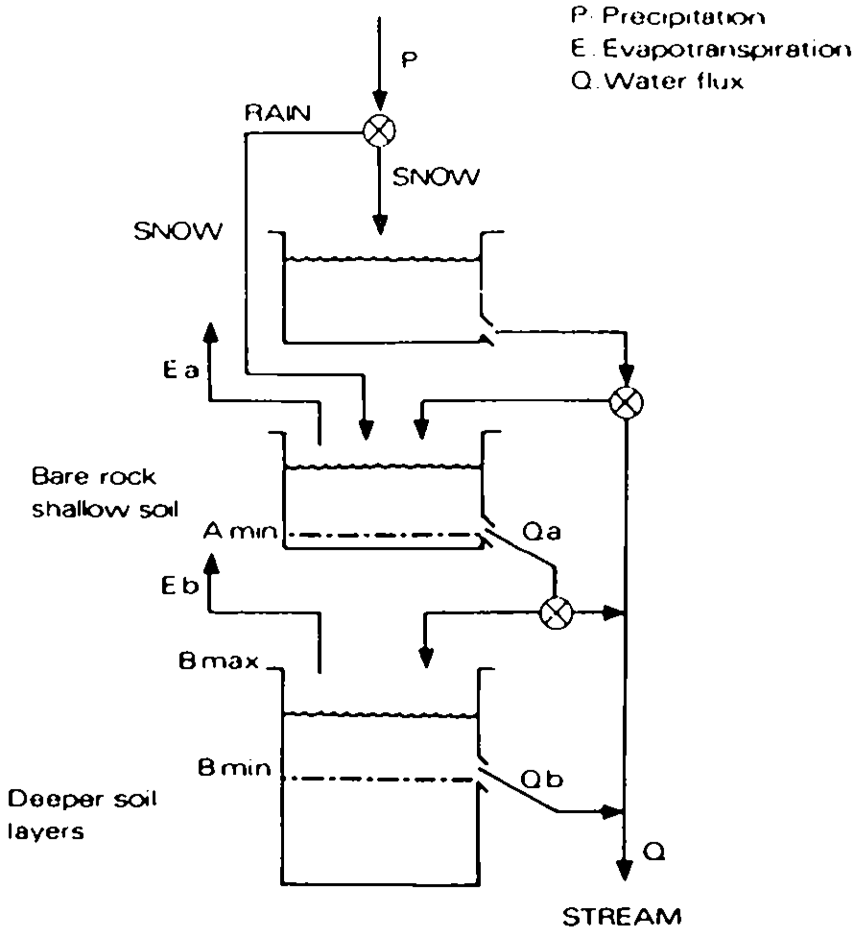


Figure 1 Simulated and observed H^+ ion in the White Laggan, Loch Dee, Scotland, based on the flow model.

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

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



Processes operating

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

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

3. Application of MAGIC to Loch Dee

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

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

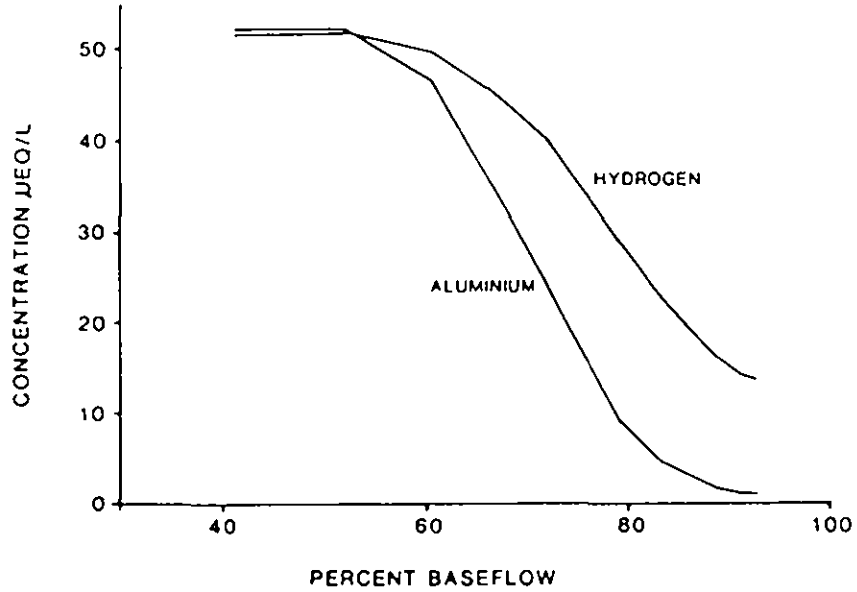


Figure 3 Maximum H^+ and Al^{3+} concentrations in the stream, showing variation over a range of baseflow conditions (Three Year Simulation 1977–1980).

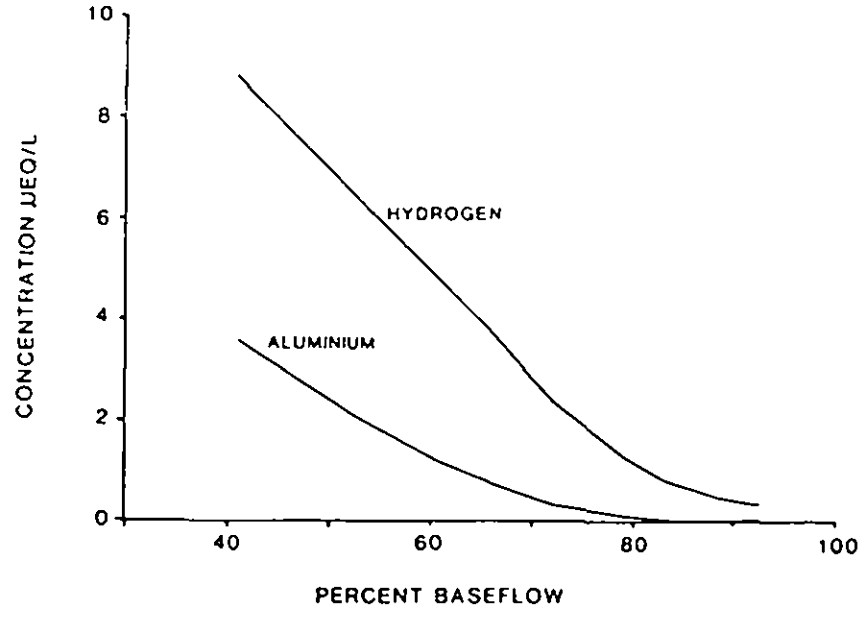


Figure 4 Mean H^+ and Al^{3+} concentration in the stream, showing variation over a range of baseflow conditions (Three Year Simulation 1977–1980).

4. Long-term acidification trends for Dargall Lane

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

5. Afforestation

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

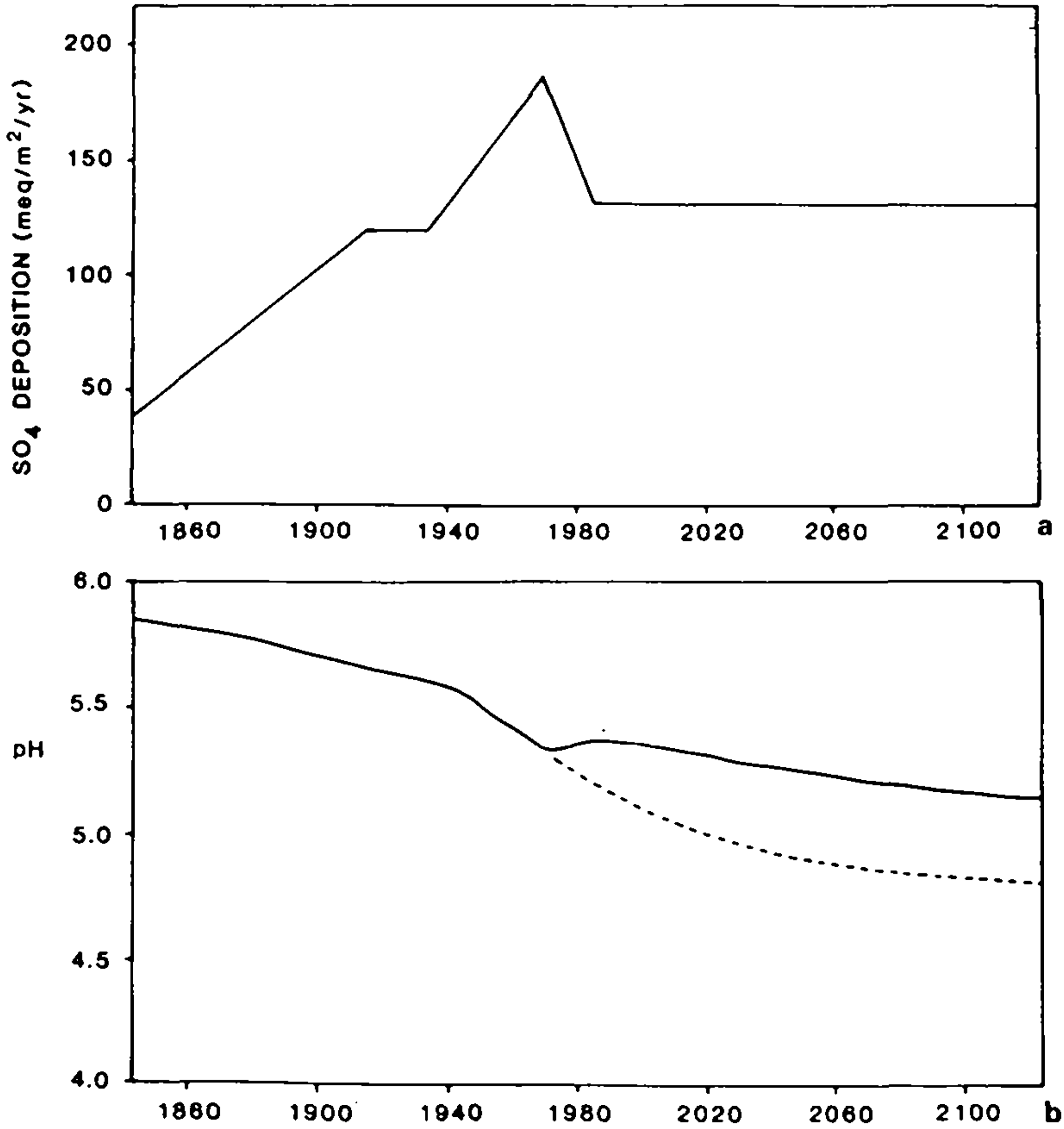


Figure 5 (a) Sulphate deposition history used as input for the MAGIC reconstruction of pH in the Dargall Lane moorland catchment. (b) Simulation of the pH of streamwater in the Dargall Lane moorland catchment assuming three sulphate deposition scenarios:—historical levels to 1984 and constant 1984 levels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

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

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

6. Atmospheric acidic oxide inputs

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

7. Deforestation

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

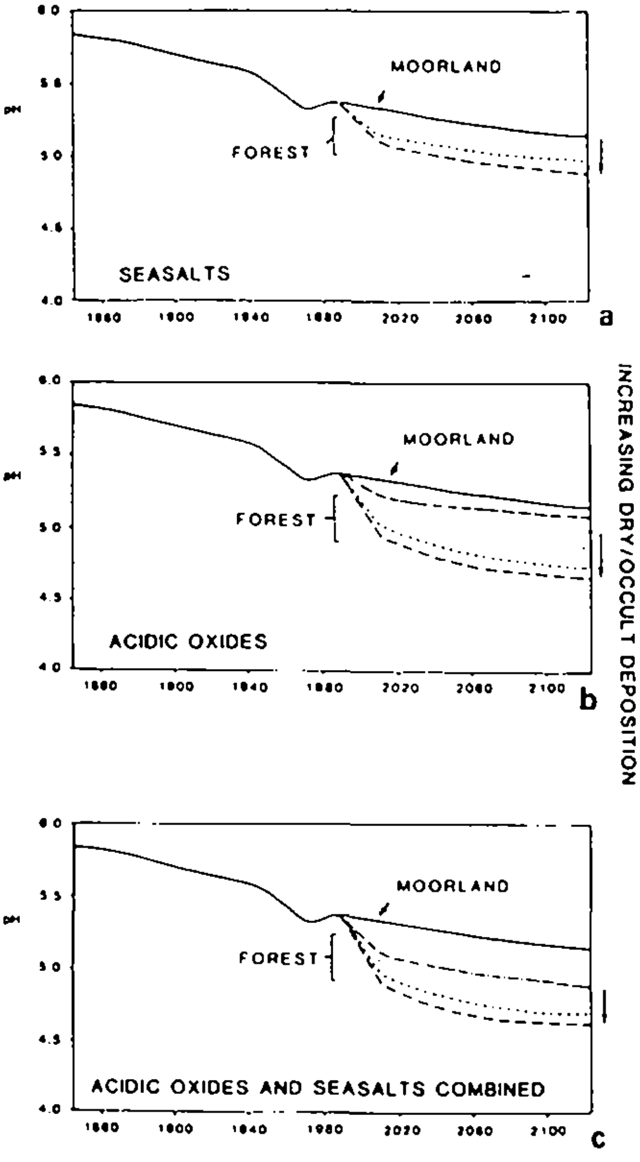


Figure 6 (a) Simulation of the pH of the streamwater from the Dargall Lane catchment, comparing: the moorland catchment response assuming Figure 5(a) deposition rates (——), the effect of 14% additional evaporation following afforestation (. . .), the effect of 14% additional afforestation in 1985 (-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

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

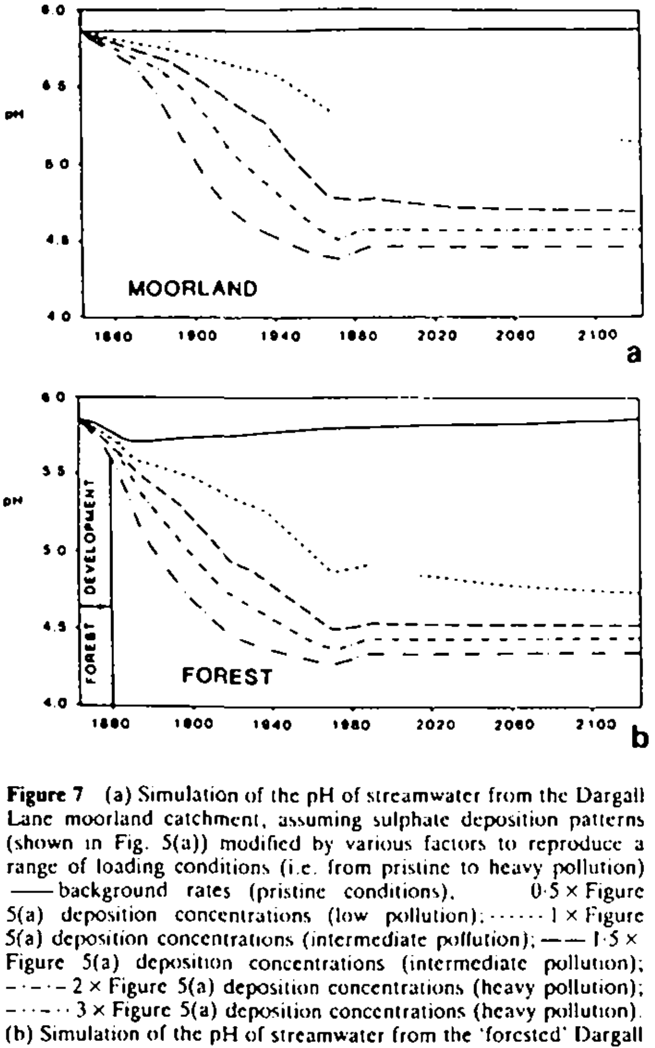


Figure 7 (a) Simulation of the pH of streamwater from the Dargall Lane moorland catchment, assuming sulphate deposition patterns (shown in Fig. 5(a)) modified by various factors to reproduce a range of loading conditions (i.e. from pristine to heavy pollution) —— background rates (pristine conditions),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

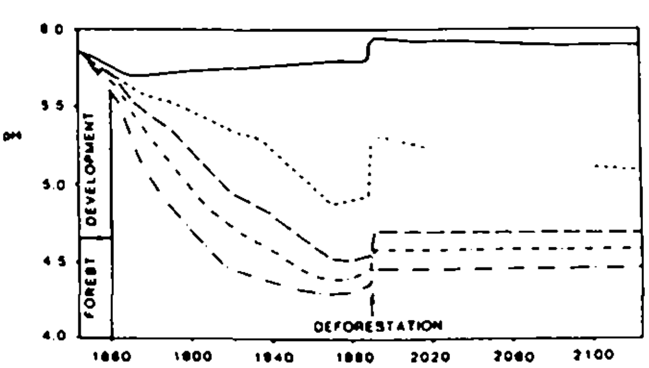


Figure 8 Simulation of the pH of streamwater for the Dargall Lane catchment, assuming afforestation from 1844 and deforestation in 1990; see caption to Figure 7(a) for key.

8. Implications

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

9. Conclusions

The model techniques applied at the Institute of Hydrology have proved to be particularly useful, yielding information on the catchment responses, processes and possible future behaviour. On the hydrological side, time series techniques, lumped and distributed hydrological models are available. In the case of chemical processes, time series techniques can be applied, but the principal models available at the Institute of Hydrology are the BIRKENES and MAGIC models. Modifications such as the introduction of sea salt will be necessary in the case of the BIRKENES model before application to the Loch Dee and Plynlimon catchments is possible. Also, it may be necessary to reassess the dominant equilibria used in the model; for example, is aluminium controlled by Al(OH), Al(OH)SO or by $Al(OH)_{1-x}$, Si_xO_2. We hope to develop a modified and combined BIRKENES and MAGIC chemistry and couple this with the distributed models to provide an additional tool with which to investigate catchment behaviour.

10. Acknowledgements

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

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

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

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

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

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

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

1. Introduction

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

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

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

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

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

2. Methods and Materials

2.1. STUDY SITE

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

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

2.2. METHODOLOGY

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

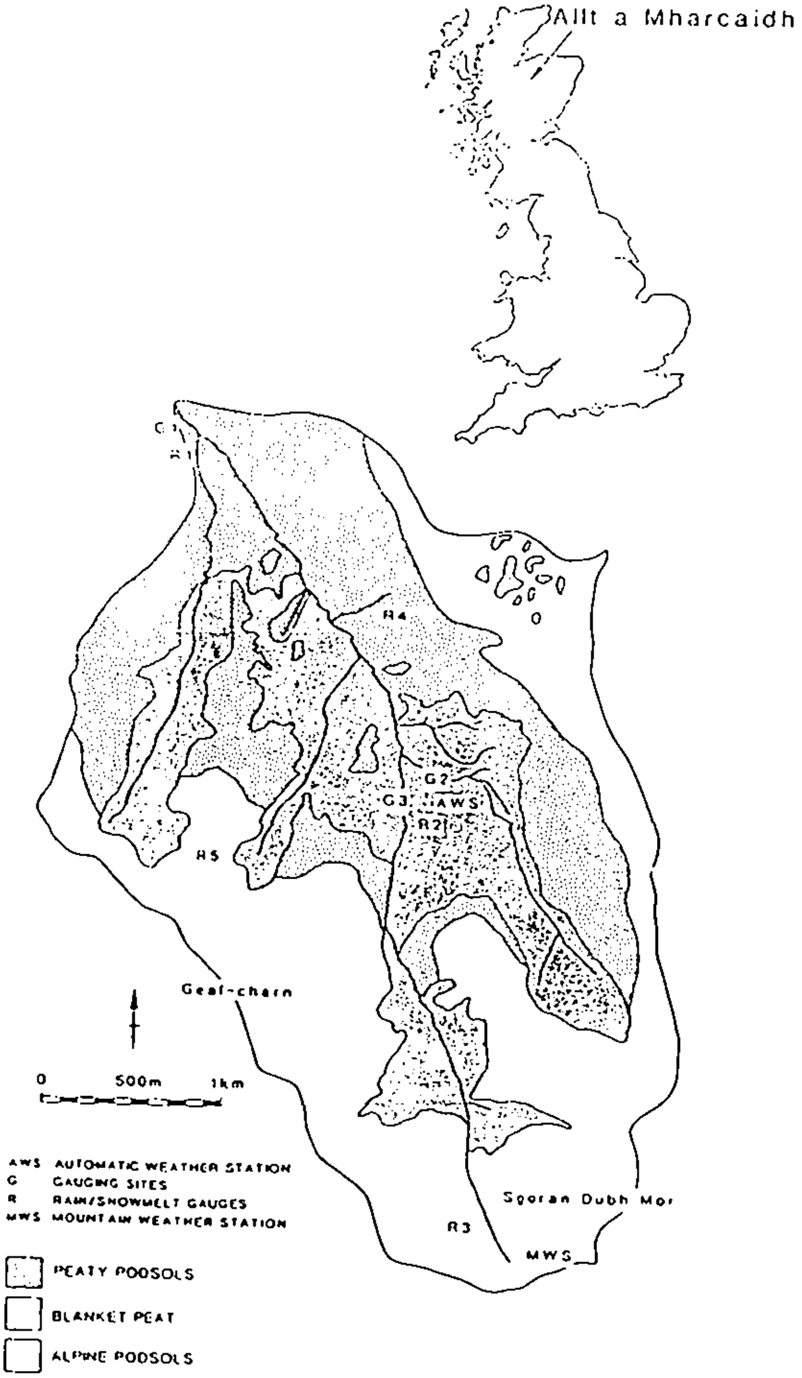

Fig. 1. Distribution of soil types and location of rain samplers (R1–5) and gauging stations (G1–3)

TABLE I

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

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

* Estimated, not measured – see Section 3.2.

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

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

TABLE II

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

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

TABLE III

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

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

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

2.3. MAGIC MODEL

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

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

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

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

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

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

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

Dynamic simulation of stream and soil water chemistry is achieved by coupling the equilibria concepts (Equations (1) to (3) with dynamic mass budgets for each base cation and strong acid anion in the soil model. Sulphate has an adsorbed phase in the soil and the relationship between adsorbed phase (E_s, meq kg^{-1}) and concentration of dissolved sulphate (SO_4^{2-}, meq m^{-3}) in soil water is assumed to be described by a Langmuir isotherm (Singh, 1984) of the form;

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

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

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

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

2.4. APPLICATION TO ALLT A MHARCAIDH

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

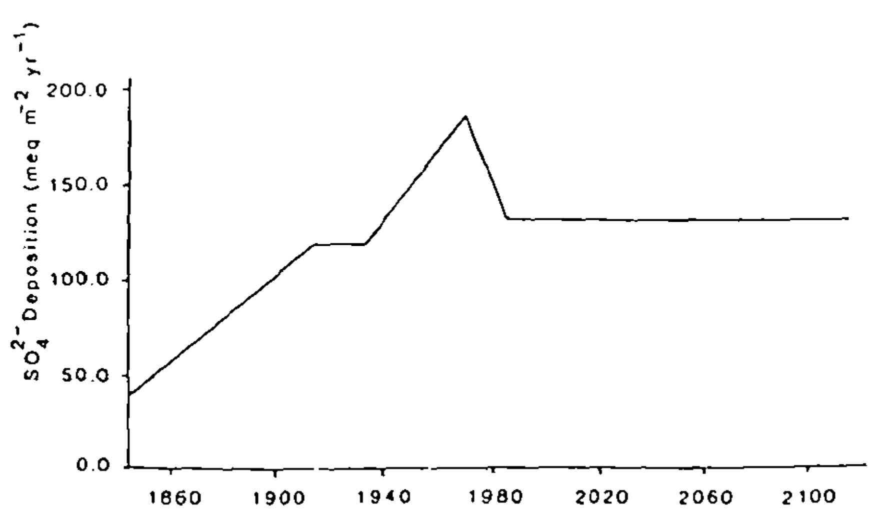

Fig. 2. Sulphate deposition pattern 1845–2125 assuming constant deposition since 1985

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

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

TABLE III

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

	Organic	Mineral	Mean
W CA (meq m^{-2} yr^{-1})	24.7 (0.8)	22.7 (7.0)	23.3
W Mg (meq m^{-2} yr^{-1})	5.7 (0.9)	4.5 (8.0)	4.6
W Na (meq m^{-2} yr^{-1})	20.6 (3.5)	17.9 (30.8)	17.1
W K (meq m^{-2} yr^{-1})	2.7 (2.9)	1.0 (26.1)	0.8
S CA	−0.33	1.94	2.7
S Mg	−0.17	2.57	1.49
S Na	−0.23	0.25	−0.21
S K	0.39	2.22	−0.32
p^{CO_2} (atm)	2.0	2.0	2.0
E_{mx} (meq kg^{-1})	0	9	14.4

3. Results

3.1. CATCHMENTS RESPONSE

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

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

3.2. SULPHATE ADSORPTION CHARACTERISTICS

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

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

3.3. ASSESSMENT OF WEATHERING RATES

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

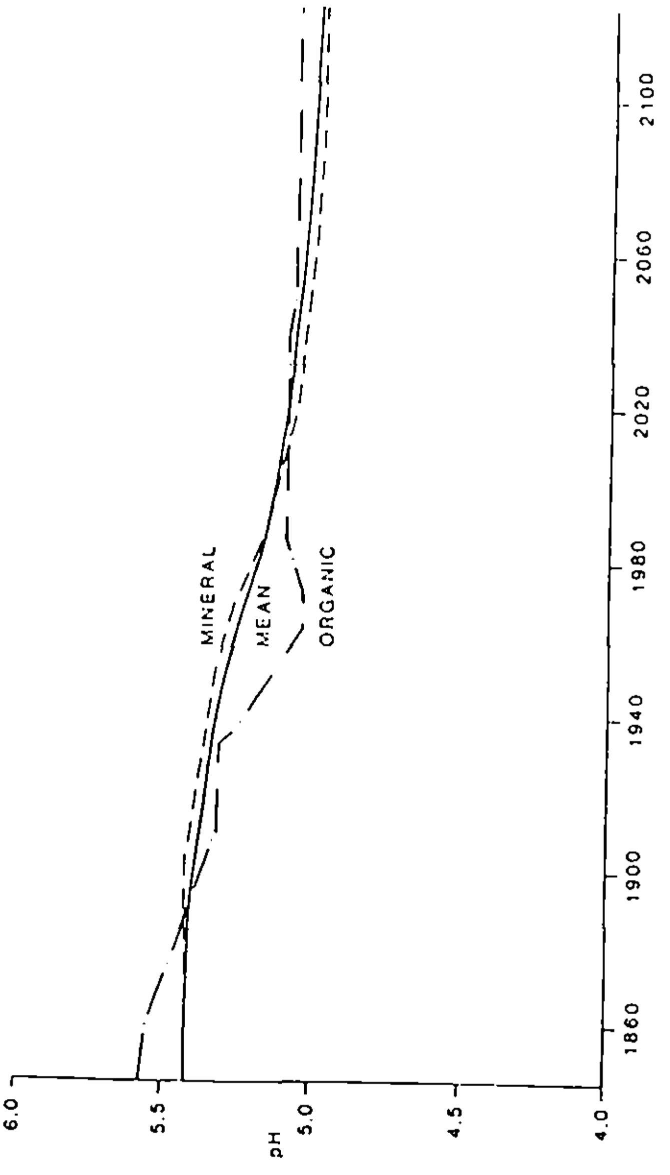
pH
6.0
5.5
5.0
4.5
4.0
1860
1900
1940
1980
2020
2060
2100
MINERAL
MEAN
ORGANIC

Fig. 3a.

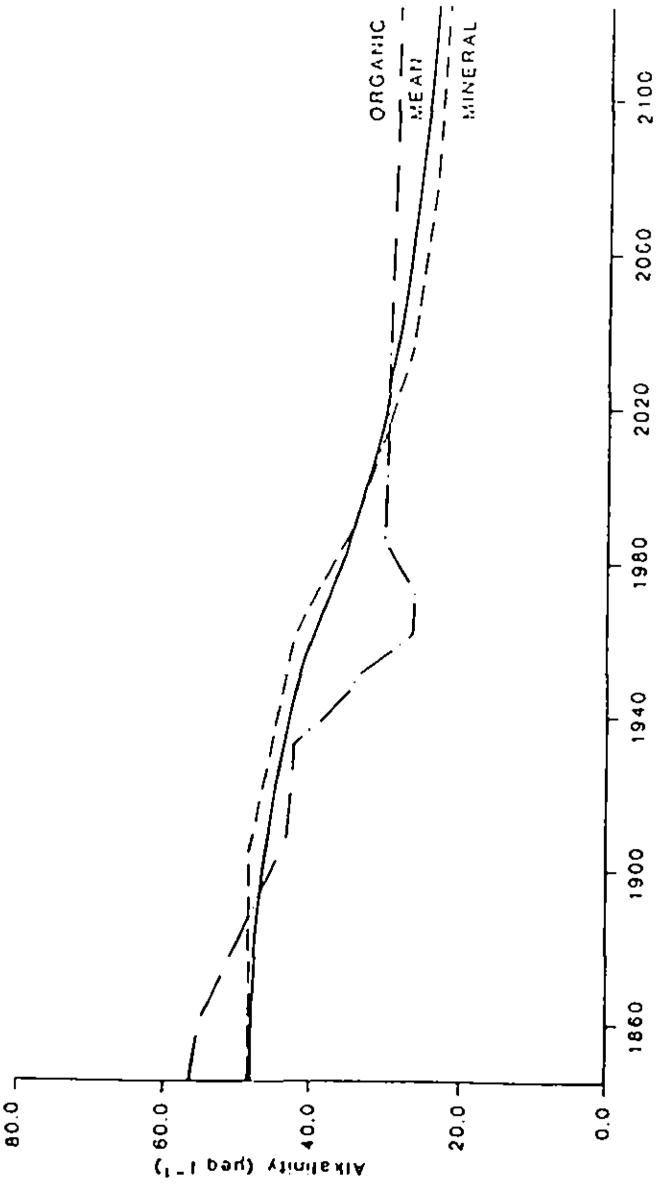
ORGANIC
MEAN
MINERAL
80.0
60.0
40.0
20.0
0.0
Alkalinity (μeq l⁻¹)
1860
1900
1940
1980
2020
2060
2100

Fig 3b.

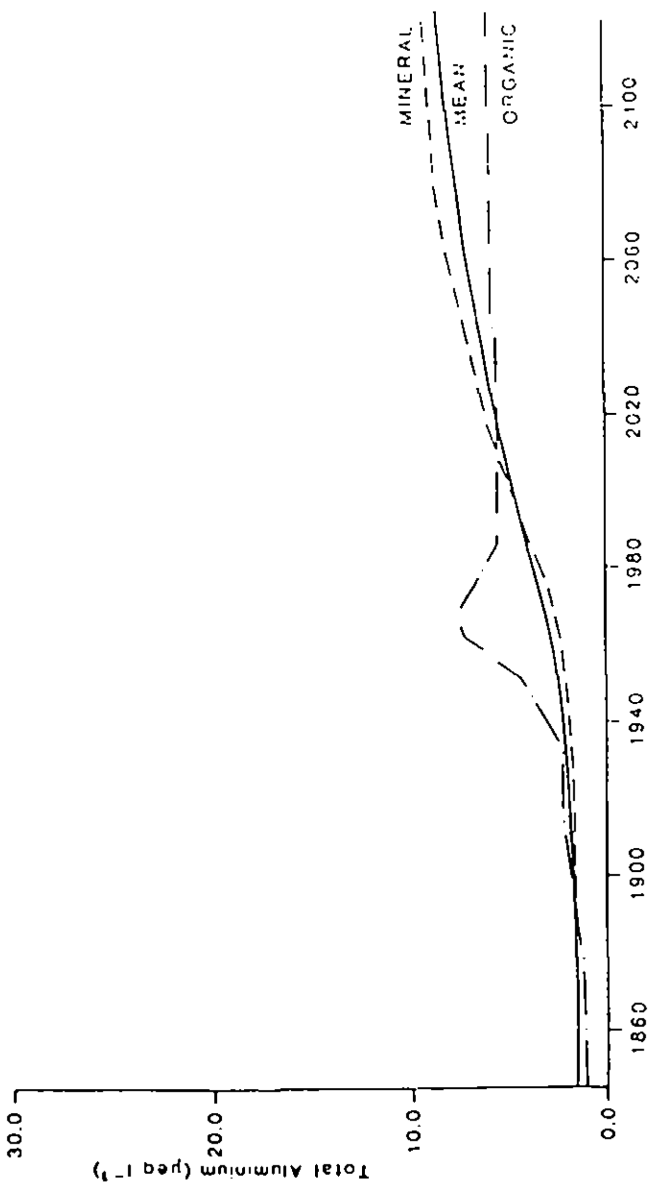
MINERAL
MEAN
ORGANIC
Total Aluminium ($\mu eq\ l^{-1}$)
0.0
10.0
20.0
30.0
1860
1900
1940
1980
2020
2060
2100

Fig. 3c.

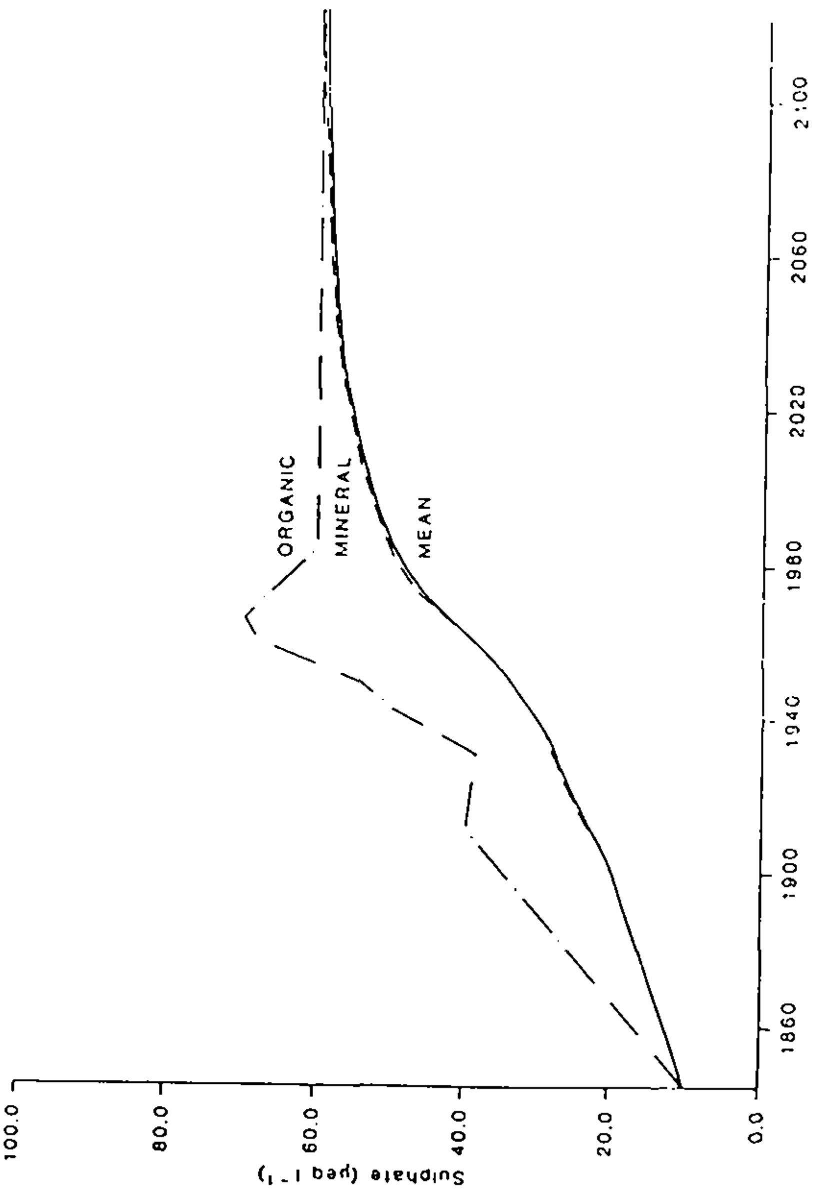
ORGANIC
MINERAL
MEAN
100.0
80.0
60.0
40.0
20.0
0.0
Sulphate (μeq l⁻¹)
1860
1900
1940
1980
2020
2060
2100

Fig. 3d.

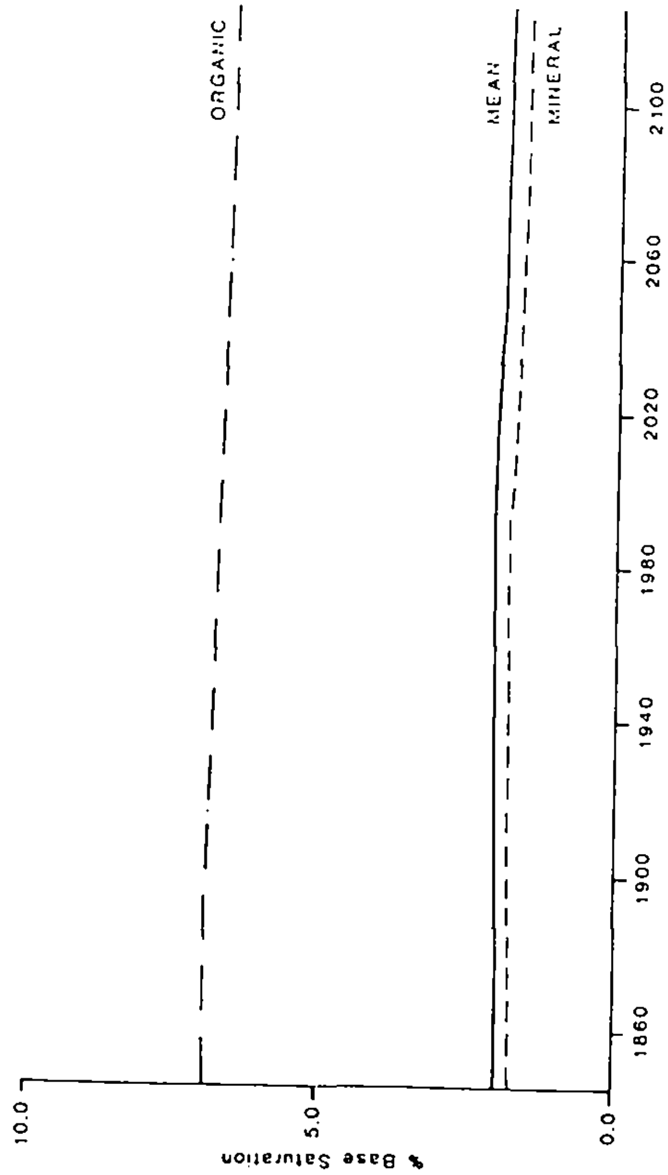

Fig. 3e.

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

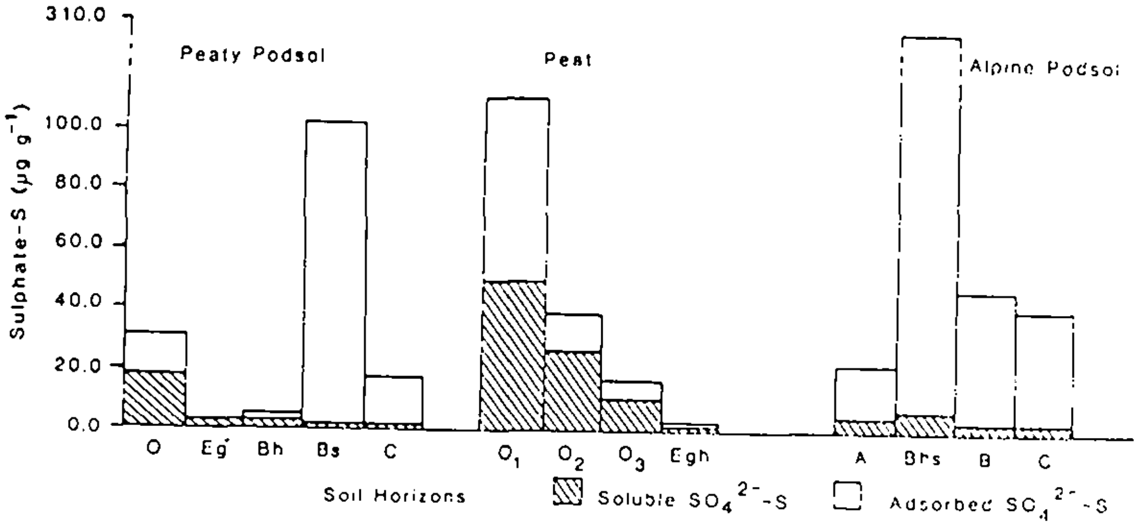

Fig. 4. Levels of soluble and adsorbed sulphate in Allt a Mharcaidh soils.

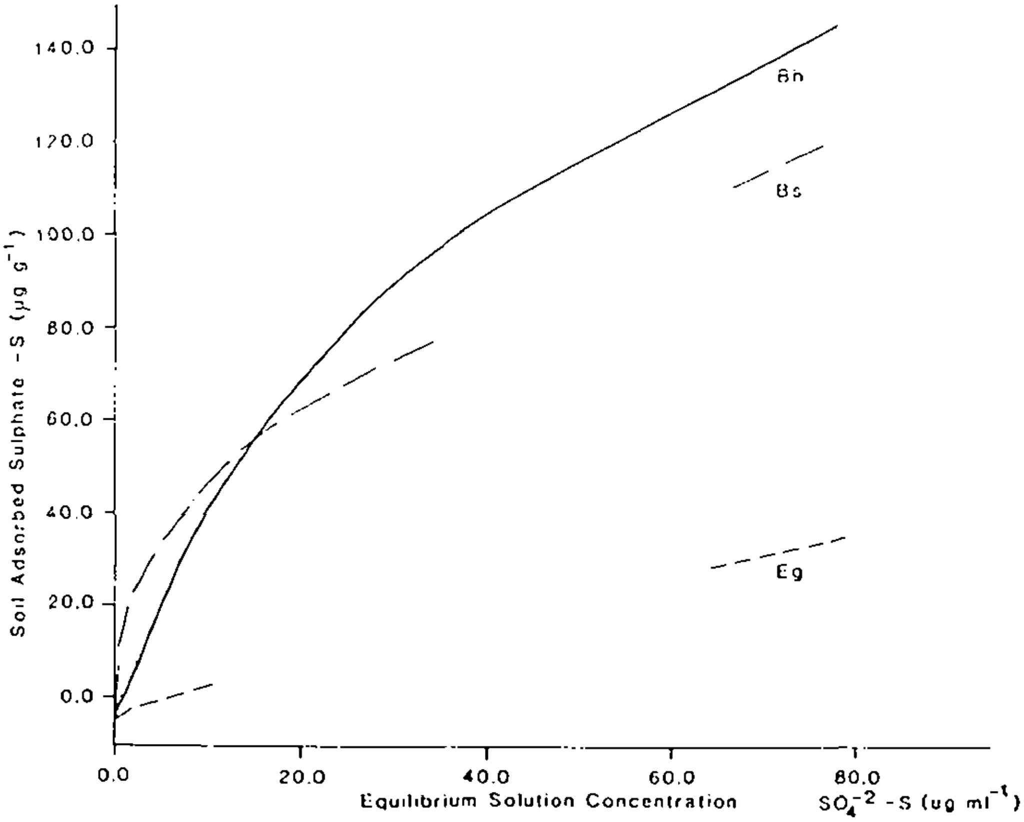

Fig. 5. Sulphate adsorption isotherms of the four horizons of the peaty podsol profile.

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

4. Discussion

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

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

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

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

Acknowledgments

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

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SECTION 3

REGIONAL MODELS OF ACIDIFICATION

A Regional Model of Acidification in Wales

Musgrove[1], T. J., Whitehead[1], P. G., Cosby[2], B. J.

[1] Institute of Hydrology, Wallingford, Oxon, UK.
[2] Department of Environmental Science, University of Virginia, Charlottesville, Virginia, USA.

ABSTRACT

A regional model of stream water quality in Wales is presented which reconstructs the historical trend for acidification and predicts the effect of several pollutant deposition reduction policies. The chemical model used to predict surface water chemistry from deposition chemistry, via the soil is the MAGIC model. The regional methodology used is a two stage coupling of Monte Carlo simulations with a calibration procedure designed to produce a coarse fit to the joint distribution of the key stream water quality variables. The regional model is based on data from the Welsh Water Authority Survey of 1983-1984 in which streams and lakes were sampled on a weekly basis for the period of a year. The modelling results reveal a significant decline in water quality across the region since industrialisation. The model predicts that 40% of the streams and lakes within the region have suffered a decline in mean yearly pH of greater than 0.5. Future predictions indicate that a 30% reduction in deposition would halve the present rate of acidification and maintain present day stream quality levels. Reductions of the order of 60% are required to ensure a significant recovery in most sites.

Introduction

Industrial complexes and power plants have historically been sources for chemical by-products expelled as waste gases. These may take the role of pollutants when borne by wind to environmentally sensitive areas. The pollutants may be brought to the ground by dissolving in rainfall or may be caught on the leaves and branches of tall vegetation. Passage through the catchment may be fast, along near surface routes, or slow, through the soil, where important chemical interaction takes place between soil matrix and soil water. Prolonged contact with polluted water may induce a gradual acidification of the soil with concomitant acidification of any streams or lakes draining the catchment. The effect may be of devastating ecological consequence, including loss of fish and other aquatic species.

There is a need to identify the acid sensitive areas in order to assess the potential environmental damage and to investigate methods to halt or reverse the trend in affected areas. Two methods in particular have been highlighted as important candidates for relieving the impact of acidification. The first is a reduction in the emission of pollutants and the second is addition of a neutralizing agent to targetted sensitive sites. The prescription of the most effective remedy requires assessment of the different management strategies proposed in terms of financial and environmental costs. An important link in the chain of cause and effect from emission to ecological impact is the transmission of acidity from deposition to the stream and lake waters. This focuses upon the chemical status of soil matrix and soil water which greatly affect stream water quality. The soil accumulates changes induced by the proximity of pollutant through time. This heightens the importance of the historical trends for emission and depositon, which must be incorporated into any estimation of the rate and magnitude of acidification and the likely recovery. The complexity of the problem allows accurate evaluation of management strategies to be achieved only through the use of mathematical models. These must represent the key processes believed to influence the long term acidification of the soil and must be applicable for long term regional analyses. An example of a model which incorporates emissions, transport, soil and lake acidification and forest impact is the RAINS model (Alcamo et al., 1987). This sulphur based model also includes a cost analysis submodel to provide a complete control strategy evaluation tool. A second example is the Model of Acidification of Groundwater in Catchments (MAGIC), which looks at the surface and soil waters from acid deposition to stream emergence. This soil based model represents five processes of major importance to soil acidification and is sufficiently adaptable to be useful for long term prediction on either a site or a regional basis. It is driven by acid deposition trends since the industrial revolution and may be used for evaluating the effect of proposed future deposition scenarios. The results of the MAGIC model have been used to drive biological models of trout density and survival and interverbrate species and floral community absence or presence (Ormerod et al., 1988). When linked to a model relating emissions and depositions the MAGIC model may clearly play an important role as a link in an overall control strategy evaluation exercise. This present study uses the MAGIC model to make a regional simulation of the acid sensitive areas within Wales and to make a preliminary assessment of the ability of the region to recover. Evidence for acidification in Wales has accrued from many investigations including studies of fisheries, forest and moorland soils, geology and hydrochemistry. There are two main sites for hydrochemical investigation in Wales, namely Plynlimon (see Hornung et al., 1986; Neal et al., 1986) and Llyn Brianne (Stoner et al., 1984). These have shown some effects of acidification. In 1984 the Welsh Water Authority attempted to investigate the extent of the acidification throughout Wales through a year long survey of streams and rivers in a subregion of Wales. The subregion was selected from a knowledge of geology, soil type, and land use from which the region of greatest acid susceptibility was deduced. Rainfall and stream water quality were investigated across the region. The results indicate that a section of the streams monitored are becoming acidified in terms of the chemical indicators: aluminium, alkalinity and pH. An earlier modelling study of the Welsh region was undertaken by Musgrove et al. (1988) who attempted to simulate the marginal distributions of the yearly means of the important chemical variables across the region.

The present study uses a refined method that produces simulations which are consistent with the covariance structure of the important chemical variables. This method was developed by Hornberger et al. (as yet unpublished) who applied it to a survey of Norwegian lakes. A refinement is also made to the aluminium submodel that enables a good match of simulated to observed chemistry for aluminium in Wales. This is important since aluminium exerts a strong influence on aquatic biological species and is one of the key indicators of acidification in streams.

Description of survey region

Between October 1983 and September 1984 the Welsh Water Authority undertook a regional survey of streams and rivers within an area of Wales believed to be sensitive to acid deposition. One hundred and twenty streams were sampled on a weekly basis, with sixteen of them being sampled at more than one point. The locations of the sampling points are shown in Fig. 1. During the same period rainfall quality was monitored at forty-four sites throughout Wales. The mean yearly rainfall concentrations are summarised in Table 1. A breakdown of the results by region shows the most acidic rain-falls in the uplands of mid and North Wales (Donald, 1988). The east of Wales is seen to receive the highest concentrations of the acid pollutants, sulphate and nitrate. It also receives high levels of ammonia and calcium, which partially buffer the rainfall. Meanm pH at each of the sites varied from 4.4 to 5.0.

The study is underlain by rocks of the Cambrian, Ordovician and Silurian Series. In the upland areas the soils are thin and base-poor. The combination of slowly weathering rocks and thin, poor soils gives the region its vulnerability to acid deposition. Prolonged acid deposition may induce a leaching of the base cations from the soil, reducing the buffering ability and allowing the surface waters to become acidic. The study area lies mainly in the region of high rainfall acidity and is consequently of prime interest in the investigation of acidification in Wales.

The mean yearly results are presented in Table 2. The pH of streams varies across the region from 4.2 to 7.3 with a mean of 5.6. The very high maximum level for calcium of 862 μeq/l and the maximum magnesium concentration of 393 μeq/l were both measured at the site on the Isle of Anglesey where there is a large industrial source. At this site, the alkalinity is also a maximum for the region at 1104 μeq/l. The mean annual sodium and chloride levels are strongly correlated. A linear regression model of sodium on chloride in the surface water predicts a slope of .69 and an intercept of 34 μeq/l with an R-squared value of .93. Sea salt concentrations are high, reflecting the near coastal location for most of the region. The area is mountainous and rainfall is high with a large orographic input. The predominant weather pattern sweeps air from the Atlantic Ocean and the Irish Sea, which lie to the west of Wales. The high mean sulphate concentration in the streams includes a large component in excess of marine origin sulphate. The presence of the sulphate in the streams is balanced by base cations in the well buffered catchments and by hydrogen and aluminium in the more acidic sites. This leaching of aluminium into the streams is environmentally damaging and of prime interest in the study of acidification. The partial pressures of the carbon dioxide in the streams have been deduced for the streams using the equilibrium relation given by the following equation:

$$\frac{\{H^+\}\ \{HCO_3^-\}}{\{CO_2(aq)\}} = K_{CO2} \qquad \text{Eq. 1}$$

CO_2 is the partial pressure of carbon dioxide present in the stream.

K_{CO2} is an equilibrium constant.

This equation is used by the MAGIC model to determine stream bicarbonate concentrations, with CO_2 as a parameter for the model. The median value for CO_2 in the streams is 4 times the atmospheric partial pressure of carbon dioxide. This value was used in the model with the soil CO_2 partial pressure set equal to ten times the stream value.

Description of the Chemical Model

The Model of Acidification of Groundwater In Catchments (MAGIC) was used to simulate the region. MAGIC is a dynamic model of soil and stream chemistry in catchments. Developed by Cosby et al. (1985a--and b) MAGIC simulates long term acidification in soils by incorporating several key soil processes in a lumped parameter representation. The catchment may be represented by one or two 'boxes' of homogeneous soil conditions. In each box the soil characteristics are set to mean values in either topsoil, subsoil or the soil as a whole, depending upon the model structure used. A mixing tank collects the water draining the soil thus acting as a stream. Hydrologic partitioning is catered for in the two-box version of MAGIC and in the single box case an effective rainfall amount is assumed to pass through the box and into the stream. An overall equilibrium within the soil is assumed, incorporating the effects of five major soil processes believed to be important in the acidification of catchments. The cation exchange process allows mutual regulation of base cations. The model uses the Gaines-Thomas equilibrium relationship (Gaines and Thomas, 1953) to formulate the representation of this process. This is particularly suitable for long term modelling as it allows the form of the exchange relationships to vary with individual cation content in the soil. Thus cation depletion, one of the features of acidification in soils, may be effectively modelled. A second process allowed for in MAGIC is the dissolution of carbon dioxide under high partial pressure in the soil to produce bicarbonate (c.f. equation 1). This may generate alkalinity to buffer the acidity in the soil. Upon emerging into the stream however, the soil water releases a large part of its carbon dioxide content, thereby consuming alkalinity in the stream. The role of carbon dioxide in the system is one of resisting acidification and promoting recovery when acidic stress is relieved. Sulphate adsorption on the soil is a third process represented in MAGIC. A simple equilibrium model is used, incorporating the Langmuir isotherm. This process affects the timing of acidification and recovery and may also affect the extent of degradation. The fourth soil process in MAGIC is weathering of base cations. This is usually incorporated by specifying the weathering to occur at a constant rate throughout time. This term introduces a source of cations to aid soil recovery and also to partially counter the trend in acidification to remove base cations from their cation exchange sites on the soil. The final process represented is that of aluminium mobilisation. In the soil this is represented by an equilibrium with an assumed phase of Gibbsite.

Under acidic conditions aluminium may be released by the soil to help provide the cation content required to balance the net charge on the anions filtering through the soil. The soil water emerges into the stream where the chemical balance is further altered as a result of carbon dioxide degassing. This affects the hydrogen and aluminium concentrations which adjust to maintain an ionic balance. In the stream the aluminium is usually represented by an equilibrium with a phase of Gibbsite. For the Welsh regional data Neal et al (1988) show that the aluminium levels are better predicted when either allowing precipitation of aluminium in the stream only when saturation occurs or by disallowing aluminium precipitation in the stream. The latter submodel is used in the present simulations. In the MAGIC model allowance is made for the effects of temperature and ionic strength on the equilibria and also for complexation of aluminium in soil and in stream. The equilibrium constants are mainly taken from relevant literature. The Gaines-Thomas equilibrium expressions require either the base cation fractions or their selectivities to be specified prior to calculating the initial equilibrium levels. The change in equilibrium level is computed thereafter at each time step by tracking the predicted change in base fractions with time. Initial conditions are usually taken for the year 1844, this being a representative year prior to industrialisation and its concomitant emission of pollutants. The catchment is assumed to be in its pristine condition at this time. The soil and stream water concentrations are calculated using a specified background level of precipitation concentration to feed the model. These concentrations may be set equal to the measured sea salt contribution in current precipitation concentrations. The weathering rates are specified and the model proceeds. Mass and flux balances are kept for all key anions and cations and are used in the dynamic submodel section (Cosby et al., 1985a, b). Acidification in the model catchment is driven by the trend of acid anion deposition. The shape of this trend line for the UK is taken from the Warren Springs Laboratory report of 1983 which presents a reconstruction of the chronological variation in sulphate emissions. The magnitude of the trend for each pollutant is found by scaling this trend line and by constraining it to pass through both the 1844 background level and the 1984 measured concentration. The hydrologic partitioning is assumed to be constant through time.

Regional Application of the MAGIC model

The MAGIC model may be adapted for modelling on a regional basis by the simple introduction of Monte Carlo techniques. The idea is to assimilate regional variability into the model. From one site to the next and within each site there will be different weathering rates for base cations, different soil depths and porosity, different rainfall, cation exchange capacities and exchangeable base fractions on cation exchange sites. There will also be different chemical inputs from precipitation. In the model these entities are each represented by a model parameter. For any one site there is a combination of parameter values that will correspond with the lumped equivalent that in theory could be measured on site. In practice the spot measurement of some of the model parameters and the calculation of a lumped average for the catchment is extremely difficult. As a result the model parameters are calibrated to produce a parameter set that yields a close fit to the observed streamwater quality data. The values for each parameter in the calibration exercise are restricted to ranges within which the site values are expected to lie. Across a region the range within which a parameter may lie includes the variability from site to site and is thus larger than the range for any one site. Monte Carlo analysis allows the parameter to vary across a wide range. The essence of the technique is to run the model repeatedly until sufficient information is obtained. For each run some of the model parameters take a value randomly drawn from previously defined population distributions. These distributions may be of any type but are usually uniform, triangular or normal. A different distribution may be used for each parameter, if required. The idea is to combine the simulations for each run and to calibrate the model from the ensemble.

The calibrated set of model runs will have a distribution of parameters that it is hoped would adequately match the distributions of the observed equivalents were they available. Any knowledge of the likely covariation of parameters may be built into the Monte Carlo stage by specifing joint distributions for the varying parameters. For example, if there existed correlations between rainfall and elevation and between depth of soil and elevation, then a relation between rainfall and soil depth may be deduced. Usually little is known of the parameter covariation and they are assumed to be independent. For regional analysis with the MAGIC model the aim is to use the Monte Carlo technique to match the distributions of surface water chemistry across the region. The Monte Carlo runs provide many simulations which, if the parameter ranges are sufficiently wide, should span the range of observed chemistry. These simulations are employed in a calibration procedure to discard simulations with predictions that are not witnessed within the region and to tighten the model fit. Three calibration techniques have been employed in previous analyses using MAGIC. The first is a trial and error iterative estimation of the a priori parameter distributions. A few hundred runs are performed and the predicted marginal chemical distributions are compared with the observed. Some simulations are discarded to provide an approximate best fit and the a posteriori parameter distributions of the accepted simulations are used as a priori distributions in a second Monte Carlo phase. This process is repeated two or three times before performing a large final set of runs, to provide smoother predicted distributions. This technique has been employed by Cosby et al. (1988) who looked at the

Norwegian Lake Survey of 1974. A second technique requires the collection of a large pool of simulations which are resampled to match the observed joint distributions. Each of the axes of the response variables are divided into classes and an observed relative frequency is calculated for each bin formed in multivariate space. Simulations falling within each bin are randomly resampled to reproduce the overall relative frequency structure. Several different sets of resampled simulations may be assimilated and compared in order to look at the uncertainty of the procedure. This type of analysis was performed by Hornberger et al. (1988) who also looked at the Norwegian Lake Survey of 1974. The third calibration technique uses the same initial procedure as the second. That is a large pool of simulations is assimilated and a relative frequency count is made on the observed discrete joint distributions. This third technique then forms the overall relative frequency count of all the simulations and compares simulated to observed. Weights are assigned to each simulation to provide a weighted relative frequency count that is identical to the observed. Weights are calculated for each bin as the ratio of relative frequency count for observed to that for simulated. All simulations lying within the bin are attributed to the bin weighting. Simulations lying in bins where there are no observations have a weight of zero. Observations lying in bins where there are no simulations cannot be matched. By altering the axis class interval or by transforming any one variate the bin structure may be adjusted. Each strategy will have a different relative frequency structure. With large bins the overall fit of simulated to observed is coarse and with small bins the number of simulations required to cover each bin is large and the number of unmatched observations increases. Alternative strategies are compared to find the one with the best combination of matched observations and the precision of fit. Hornberger, Cosby & Wright (as yet unpublished) present an analysis of the Norwegian Lake data using this approach. The third calibration technique is the one employed in this present analysis.

Application to Wales

MAGIC has been applied to several individual sites within the study region (Whitehead et al., 1987a, b). The calibrated set of parameters formed the basis of the parameters that were assumed to be constant across the region. The one box version of MAGIC was chosen to run the analysis. Twelve parameters were subject to Monte Carlo uncertainty (Table 3). These were assumed to encapsulate the greatest variability across the region. Qp is the mean precipitation volume per year assumed to fall uniformly across the region. During each run Qp is held constant throughout the timescale of simulation. This parameter couples with a specified depth and porosity to enable the soil pore water volume to be calculated. Variability in the parameter Qp thus incorporates variability in soil depth and porosity to some extent. The hydrologic yield is fixed and is set to 0.85 for Wales. Thus 15% of the rainfall is assumed to evaporate. The 1984 rainfall concentrations of Cl and excess NO_3 and SO_4 were set for each model run by randomly sampling pre-set distributions. Within the model chloride is assumed to be conservative allowing the a priori chloride rainfall concentration distribution to be calculated from knowledge of the stream chloride concentration distribution and the yield. The sea salt contribution toward precipitation concentrations is determined by multiplying the Cl concentration in rainfall by the respective sea salt ratios. Background precipitation in 1844 was set equal to the present day sea salt concentrations.

The trend of excess sulphate and nitrate deposition through time is scaled by the SO_4 and NO_3 parameters. The shape of the trend is taken to be equal to the overall mean emission curve for the UK reported by Warren Springs Laboratory (1983). The true shape of the trend line for Wales may deviate from the overall trend line but has not been reported and is hitherto unknown. It may be possible to set the pollutant deposition time trend from that for industrial soot particles deposition. These are determined as part of the procedure in the reconstruction of pH changes in Lakes from the diatom contênt of a lake bed core (Batterbee et al. 1988). These analyses have been performed at several sites in Wales and Scotland and the work may eventually allow a breakdown of the mean emission trend into regional deposition trends. The scaling ensures that the magnitude of the predictions is reasonable. The time trend in the remaining chemical concentrations in precipitation is determined by using the present day excess concentrations over sea salt to scale the trend line. The present day rainfall concentrations used are shown in Table 1. These concentrations are the same for each model run. Nitrate in the soil is assumed to be taken up by plants. The model allows an uptake rate to be specified with time. Apart from this and the concentrating effect of evaporation, nitrate is assumed to pass straight through to the stream. The model uptake rate for Wales was set to 45%. CEC is the cation exchange capacity within the soil. A wide variation in CEC was allowed for in the Monte Carlo simulations reflecting the high variability of on site measurements. Each soil horizon within the catchment may have a different CEC value and the lumped model parameter must allow for uncertainty by specifying a wide range in value. WECA, WEMg and WEK are the weathering rates of calcium, magnesium and potassium respectively. The sodium weathering rate was set to zero and the soil and stream sodium was set directly from the sodium to chloride regression line mentioned earlier.

ENA, EMG, ECA and EK are the fractions of the cation exchange sites occupied by sodium, magnesium, calcium and potassium in 1844. These are required to initialise the problem and the ranges specified are deduced from knowledge of present day fractions and knowledge of the trend for base cation fractions to decrease under acidification. The total cation exchange capacity within the soil is held constant during each run.

The carbon dioxide partial pressure in the soil and stream was set to 40 and 4 times the atmospheric partial pressure respectively. The stream value was set from the observations of bicarbonate and hydrogen. These settings were held constant for each run. The value of the aluminium equilibrium constant was set at log $(a_{Al}/a_{H^+}^3)$ = 8.55. As mentioned previously the aluminium submodel for the stream was 'turned off', with the stream levels remaining the same as the soil levels. This allowed a fair fit to the data at the same time as eliminating one parameter. An interpretation of the submodel is that there is no net aluminium precipitation in the stream on a mean yearly basis. Other hypotheses that could have been used include: allowing precipitation only when saturation of aluminium occurs in the stream; having a different phase of aluminium in each site; having a depletable finite store of aluminium encompassing a range of solubilities in the pristine state as the catchment acidifies the more soluble phases are flushed from the soil; ion exchange of aluminium in the soil, with a finite store; using a two box version of MAGIC, with a mixing box at soil carbon dioxide partial pressure before release into the stream; and fitting an empirical curve to the data which is assumed constant through time. Each of the alternatives need to be examined before concrete aluminium predictions may be made. The soil sulphate adsorption within the model was set from the single site analysis of Welsh catchments by Whitehead et al. (1988). The Langmuir isotherm was set with a half saturation constant of 150 meq/m^3.

The model was run 2,000 times drawing the parameters from uniform distributions whose maxima and minima are given in Table 3. The results from these runs were used in the calibration phase of the analysis.

Six streamwater variables were used to calibrate the model, with the remainder acting as free variables whose closeness of fit could be used as a criterion for evaluating the model performance. The six variables were selected for their importance both in terms of their magnitude and variability in the observed data and in terms of their influence on the biological species in the stream. Calcium and magnesium determine the stream water hardness, nitrate, sulphate and chloride provide the acid anion content in the stream. The stream sodium was deduced from chloride and their regression line detailed earlier. Alkalinity is related to pH and to aluminium in the model such that given a value of alkalinity, the pH and aluminium are also known. The 'binning' procedure for forming the relative frequency structure for observed and simulated entailed setting a maximum and a minimum limit for accepting simulations. The range formed on each axis was divided linearly to form the bins. The number of divisions on each axis was allowed to vary to form alternative calibration strategies. By taking many divisions the number of observations matched decreases as the bin size diminishes. By taking few divisions the model fit becomes coarse. The strategy that was accepted finally is shown in Table 4.

Calcium, sulphate, alkalinity and chloride were each apportioned five divisions, magnesium had two and nitrate three. Increasing the number of divisions for magnesium or nitrate greatly reduced the number of observations that was able to be simulated. A coarser fit to these variables was accepted. An alternative would have been to run the model further to see whether the gaps in the mismatch could be filled. The total number of individual bins that had one or more observations in them was 74. Of these 19 had no matching simulation. The observations lying in these 19 bins were thus unable to be represented in the regional simulation along with the observations at the extreme unacidic end of the distributions, which were precluded by the maximum cut offs used in forming the bins. In total 35 of the observations could not be matched. These were mostly unacidified catchments apart from the three with the lowest pH values. These 3 observations had alkalinities given by -35, -90 and -100 μeq/l whereas the model predicts alkalinities, for the corresponding pH values, of less than -200 μeq/l. The observations in the tail ends of the distributions could have been forced into bins by transforming the data using logarithmic or power term transforms. In total 252 of the original 2000 simulations were accepted by the calibrated filter. Weights were given to each of the 252 simulations, as described previously, thus forcing the relative frequency of simulated to observed, using the bins, to be identical.

Results

The parameters that led to the 252 successful simulations are presented in Table 3. It is evident that these successful parameters span the complete range allowed for in the Monte Carlo analysis. A comparison of observed and simulated chemistry is presented in Tables 5 and 6. Good fits of mean value are obtained for each of the four variables that were assigned five axis divisions in the calibration procedure (ca, SO_4, alkalinity and Cl). A good fit is also achieved for magnesium despite only allowing for two divisions in the calibration phase. The closeness of the fit to the remaining variables is very good considering that they were set as free variables and did not take part in the calibration procedure (excepting NO_3). The lowest alkalinity of the accepted runs was -127 µeq/l. This is despite setting the bin minimum to -250 µeq/l (Table 4). The lowest alkalinity bin thus collected no matched observations and simulations and the effective number of alkalinity bins used is 4. The fit of simulated to observed distributions is thus expected to be slightly worse as a result. None of the other calibration variables had 'redundant' bins. Figure 2 shows the observed and simulated marginal distributions for Cl, alkalinity, SO_4 and Ca. The matches are good on the whole although some fine structure is unable to be reproduced. Exact matches would require more Monte Carlo runs and a finer bin structure in the calibration procedure. The simulated distributions incorporate the simulated weightings. Table 6 presents the observed and simulated correlation structure. The process of weighting the simulations from the joint relative frequency distributions allows a coarse match to the joint distributions. The table shows a close fit for most correlations, with the majority of simulated correlations being within .1 and most of the remainder within .2. The worst overall fit is for k, which is one of the variables that was not used in the calibration procedure. The mean value of k is 14 µeq/l (Table 5). This is small compared with the other three base cations and the consequences of a poor fit to the correlation of k with the remaining variables are slight. The very high simulated correlations for alkalinity with Al and pH reflect the strong model relationship. The fact that the observed correlations are also high indicate that these relationships are good approximations for this Welsh region. The overall regional simulation is thus seen to be quite good for the 95 more acidic catchments that the model is able to simulate. The extent of acidification of the region since pre-industrial times can be seen by comparing the present day stream chemistry with the stream chemistry predicted by the model in calculating the background conditions of 1844. The model predicted changes in mean chemistry from 1844 to 1984 as follows: the mean pH dropped from 6.4 to 5.6; mean alkalinity has declined from 63 to 3 µeq/l, and the mean sum of acid anions (Cl + SO_4 + NO_3) has more than doubled from 278 to 584 µeq/l. Breaking down the pH changes reveals that 40 of the catchments have a simulated pH drop less than .5, 37 catchments show a pH drop between .5 and 1.5 and 18 catchments show a drop in pH greater than 1.5 units. The number of catchments represented in any particular chemical class is determined by summing the weights of all the simulations falling within that class. Figure 3 shows the regional weighted marginal distributions in 1844 and 1984 simulated for alkalinity, calcium, sulphate and hydrogen. Also shown are the model predictions for equilibrium with a pollutant deposition loading that is 70% of its present level. The model may take up to 10 years from the end of the deposition reduction period to arrive at its final equilibrium. The precise number of years taken is dependent upon the rapidity of the change and the strength of sulphate adsorption in soils across the region. With high sulphate adsorption the recovery process may be delayed. The alkalinity across the region is seen to slightly deteriorate further under a 30% reduction in deposition. Calcium shows a slight return toward the 1844 conditions whereas the hydrogen remains more or less the same: The large change in sulphate from 1844 to 1984 reflects the enormity of pollutant loading since industrialization.

The accepted model parameters were fed back into the model in an attempt to assess the ability of the region to recover from acidification. Several future deposition scenarios were used and the final equilibrium stream water quality variables were saved. Figure 4 shows the effect of reduction in pollutant deposition on both alkalinity and pH. The future forecasts are compared with the present day. The figure indicates that a reduction of 30% in pollutant deposition is required to halt acidification in Wales and that reductions greater than this may start to reverse the acidification in most sites. All sites show a recovery of at least .2 in pH under a 70% reduction scenario. Table 7 shows the results for 30%, 50% and 70% reduction in deposition, these reflecting scenarios that are currently believed to be achievable. Overall, by decreasing deposition of pollutants it is seen that the alkalinity and pH will rise whereas the base cation concentrations will fall. This decline in base cation concentration in the stream is due to the decline in acid anion pollutants. Less cations are required to make an ionic charge balance and so less cations are removed from the soil. Thus deposition reductions may lead to a recovery in the base cation fraction on the soil cation exchange sites leading to a recovery in stream acidity.

Discussion and Conclusions

A regional model of a part of Wales, believed to be sensitive to acid deposition, has been presented. The model has been used to predict the extent of acidification through the region and has enabled a dose-effect type of relationship, for reducing the deposition of acid pollutants, to be predicted. The model has been tested against present day joint distributions of water chemistry. The simulated range of pH decline across the region is compatible with that reported by Batterbee et al. (1988), who looked at the evidence for acidification of several lakes, in the same study region, using diatom analysis. The observed present day chemistry is fitted well by the model providing confidence for predictions and reconstructions. Assuming the catchments across the region to be broadly similar in response to acidification, the present day chemistry may represent the response of any one site through time. The idea is that all of the catchments will be at a different stage of acidification. Some will have been poorly buffered from the start and will be highly acidified whereas others will have been buffered to a greater extent. Collectively they may allow a substitution of space for time in the interpretation of the sampling variable. If this is the case then predictions using the same relationships may be assumed to be reasonable. Another indirect way of testing the model is to use the predictions to feed biological models of fish density, survival and floral and macroinvertebrate speciation. The result of this two stage modelling may be compard with biological evidence for trends in acidification. For example there may be anecdotal evidence of fish loss from streams and lakes which may allow the timing of keystones in acidification to be pinpointed. Ormerod et al. (1984) use the results of this present analysis to feed such biological models. The timing of acidification has not been presented as the key to the time trend is the deposition sequence of pollutants since 1844. The model uses reported mean emissions for the UK in that period to predict the deposition trend line. This may or may not accurately portray the actual trend line felt in Wales. Further evidence is required and this may come from the record of historical deposition of carbonaceous soot particles in lakes. These are assumed to originate in coal burning, which is also one of the processes that emits pollutants into the atmosphere. The model has been used to indicate possible future trends for acidification in Welsh catchments. It must be remembered that reductions in deposition were used in the analysis. To see how these relate to reductions in emissions a model of atmospheric pollutant transport must be used and applied to Wales. Several models of this type have been devised and it is envisaged that the model link from emission to deposition to stream water quality and its biological consequence is a real possibility.

TABLE 1. Rainfall at fifty sites in wales 1983/84

	N	Mean	Median	Standard Deviation	Minimum	Maximum
		4.7	4.7	0.56	4.4	5.0
		47.7	41.0	38.6	9.9	102.2
Mg		42.6	33.4	43.8	17.4	177.8
Na		137.0	124.5	171.2	62.5	510.9
K		8.6	7.3	5.4	4.7	21.8
SO_4		118.7	110.8	34.3	52.0	217.1
Cl		176.1	162.1	192.5	96.8	525.0
HCO_3		51.3	38.7	49.9	22.9	114.9

(all units μeq/l, except for pH)

TABLE 2. Mean yearly stream chemistry over 130 sampling sites in Wales

	Mean	Standard Deviation	Minimum	Maximum
pH	5.6	0.7	4.2	7.3
Ca	130.9	91.7	40.4	862.3
Mg	111.5	113.4	44.4	393.2
Na	220.1	62.0	149.1	640.0
K	13.4	9.8	5.4	89.0
SO_4	153.7	64.4	49.1	507.4
Cl	267.4	86.2	167.0	918.0
HCO_3	75.5	87.3	0.7	604.1
H	1.9	3.4	0.05	24.0
Alk	30.6	125.4	- 206.9	1103.9
PCO_2	7.25	7.6	1.0	51.2
$A\ell_T$	6.3	4.3	0.7	24.3

(Units are in μeq/L except for Al (μmol/L), pH and PCO_2 ($PCO_2 \times 10^{-3.5}$ is the partial pressure of carbon dioxide in the stream in atmospheres).)

TABLE 3. Ranges for the parameters used in the Monte-Carlo simulations for Wales. The parameters are defined in the text.

		MONTE CARLO RANGES		ACCEPTED SIMULATIONS			
		a priori		a posteriori			
				Weighted			
Parameter	Units	Min	Max	Mean	S.D.*	Min	Max
OP	cm	120.0	230.0	177.3	29.5	122.4	229.8
Cℓ	μeq/L	167.0	400.0	243.4	34.0	175.8	379.2
SO_4	μeq/L	20.0	225.0	79.7	34.9	20.3	211.0
NO_3	μeq/L	2.4	140.0	46.5	22.0	4.1	125.7
CEC	meq/m^{-2}	10.0	300.0	148.7	87.0	10.0	299.4
WE CA	meq/m^{-2}/yr^{-1}	0.5	150.0	83.5	38.0	1.1	149.9
WE MG	meq/m^{-2}/yr^{-1}	0.5	50.0	21.3	13.9	0.9	49.9
WE-K	meq/m^{-2}/yr^{-1}	0.5	10.0	5.3	2.7	0.5	9.9
ECa		0.5	20.0	11.1	5.3	0.6	19.9
ENa		0.5	5.0	2.8	1.3	0.5	0.5
EK		0.5	5.0	2.7	1.2	0.5	0.5
EMg		0.5	20.0	9.2	5.9	0.5	19.9

(The a priori distributions are all rectangular. •S.D. stands for Standard Deviation).

TABLE 4 Calibration procedure: bin selection for final calibration

Variable	Minimum (μeq/l)	Maximum (μeq/l)	Number of axis divisions
Ca	40	230	
Mg	40	160	
SO_4	50	300	
Alkalinity	-250	160	
Cl	160	400	
NO_3	0	60	

Total acceptance simulations:	252
Total observations matched:	95
Number of occupied bins:	74

TABLE 5 Comparison of simulated and observed stream chemistry (observed in brackets)

Variable	Mean	Min.	Max.
pH	5.6 (5.6)	4.5 (4.2)	6.5 (6.6)
Ca	105 (106)	42 (40)	202 (208)
Mg	87 (86)	40 (44)	160 (135)
Na	206 (202)	152 (149)	295 (289)
K	14 (11)	4.6 (5.4)	38 (35)
SO_4	138 (138)	52 (49)	284 (277)
CL	246 (244)	176 (167)	379 (365)
Alkalinity	2.8 (2.9)	-127 (-141)	89 (90)
Total Aℓ	0.16 (0.18)	.01 (.02)	0.96 (0.67)
NO_3	25 (20)	2.3 (7.1)	60 (60)

Units are μeq/l except for aluminium (mg/l) and pH.
Total Aℓ is total inorganic labile aluminium.

TABLE 6 Simulated and observed correlation matrices

a) Simulated, using weighted correlation:

	Cl	SO_4	Na	K	Mg	Ca	pH	Total Al	Alk	NO_3
Cl		[illegible]		.1	.3	.3	[illegible]		.1	.3
SO_4				.2	.4	.5	.2		.2	.1
Na				.1	.3	.3	.1		.0	.3
K					.0	.0	.2	.0	.1	.0
Mg								[illegible]		
Ca				.0	.5					
pH				.2	.5					
Total Al				.0	-.5	.4	.8			
Alkalinity			.0	.1	.5	.6	[illegible]			
NO_3	.3	.1	.3	.0	.1	.3	-.1	.2	.2	

b) Observed:

	Cl	SO_4	Na	K	Mg	Ca	pH	Total Al	Alk	NO_3
Cl					.3				.2	
SO_4				.2	.5				.3	
Na				.2	.5			.0	.0	
K					[illegible]			.2	.5	
Mg								[illegible]		
Ca				.5	.6					
pH				.4	.5					
Total Al			.0	.2	-.3					
Alkalinity			.0	.5	.5					
NO_3	.3	[illegible]	.5	.2	.4	.5	[illegible]	[illegible]	.0	

TABLE 7 Stream concentrations in equilibrium with reduced depositions.

a) Effect of a 70% reduction in deposition

Variable	Mean	Standard Deviation	Minimum	Maximum
pH	6.0	0.3	4.7	6.9
Ca µeq/L	72.1	17.7	14.3	150.8
Mg µeq/L	64.6	7.8	39.6	99.8
Na µeq/L	201.7	16.0	152.6	293.5
SO_4 µeq/L	62.6	7.4	33.9	105.1
Cl µeq/L	246.4	23.0	175.8	379.3
Alk µeq/L	28.8	18.7	- 60.2	118.2
Aℓ mg/L	.06	.03	.006	0.41

b) Effect of a 50% reduction in deposition

Variable	Mean	Standard Deviation	Minimum	Maximum
pH	5.7	0.3	4.5	6.5
Ca µeq/L	77.1	18.0	16.8	151.6
Mg µeq/L	67.7	8.3	40.2	102.2
Na µeq/L	202.6	16.0	152.8	293.8
SO_4 µeq/L	83.8	11.4	38.8	155.7
Cl µeq/L	246.4	23.0	175.8	379.2
Alk µeq/L	12.3	20.9	92.3	92.9
Aℓ mg/L	.09	.06	.009	.63

TABLE 7 continued

c) Effect of a 30% reduction in deposition

Variable	Mean	Standard Deviation	Minimum	Maximum
pH	5.4	0.4	4.5	6.5
Ca µeq/L	80.7	18.8	17.1	154.3
Mg µeq/L	69.6	9.1	40.2	117.6
Na µeq/L	203.2	16.0	152.8	294.2
SO_4 µeq/L	104.8	15.5	43.7	203.6
Cl µeq/L	246.4	23.0	175.8	379.2
Alk µeq/L	6.8	25.7	-125.7	82.3
Aℓ mg/L	17	.10	.01	.90

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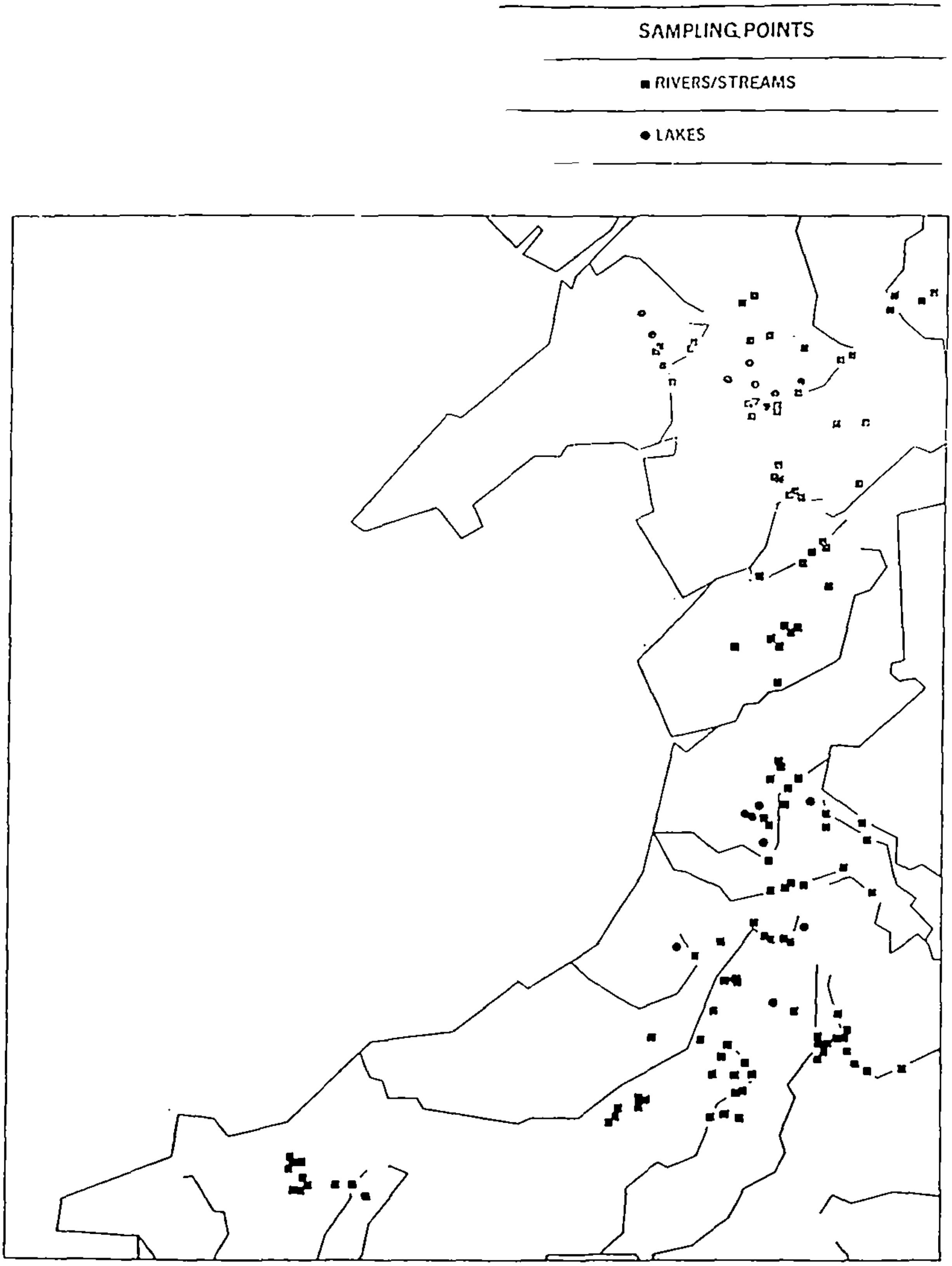
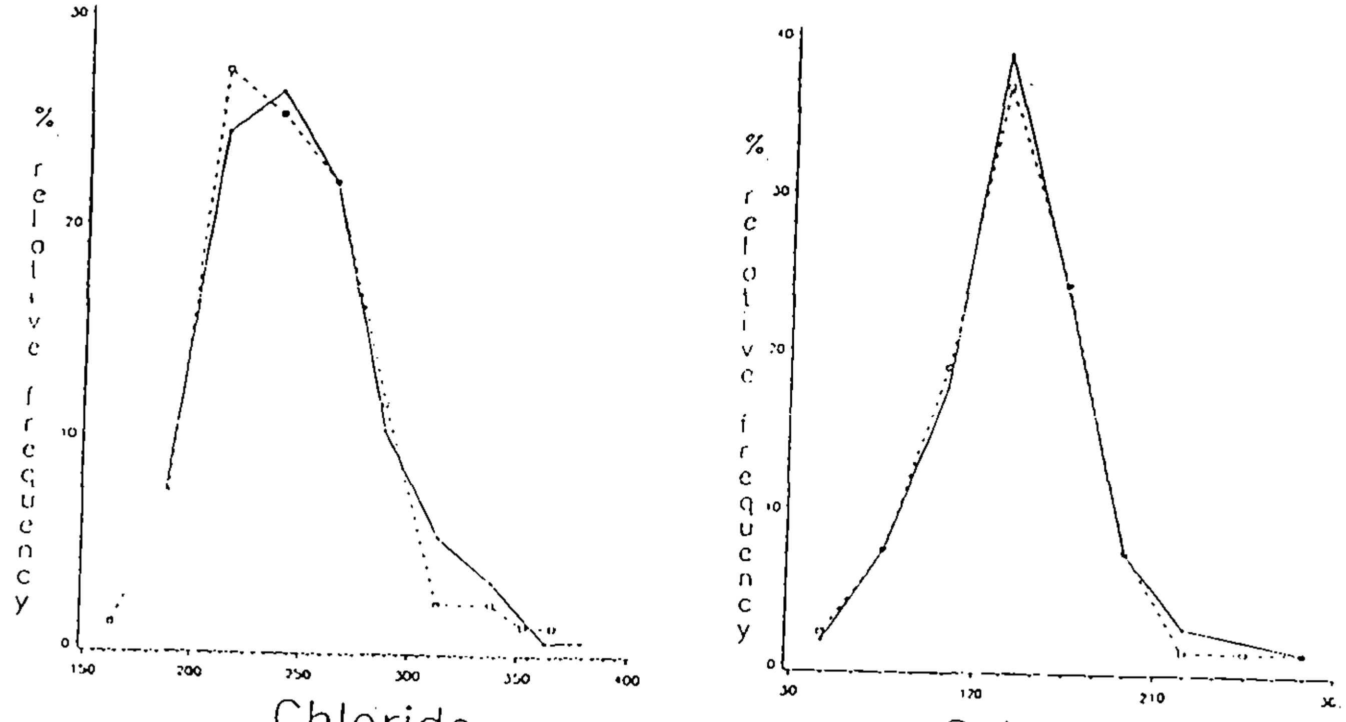


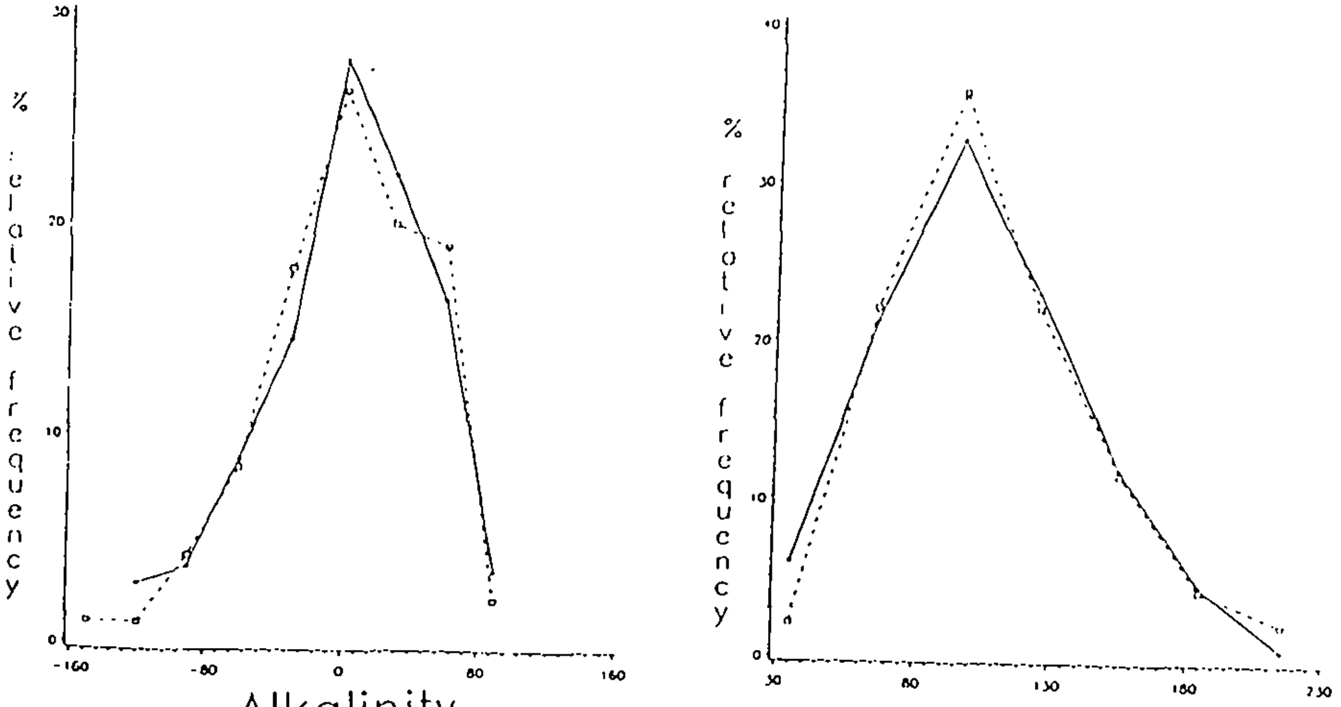
Figure 1

OBSERVED AND SIMULATED CHEMISTRY DISTRIBUTIONS



Chloride

Sulphate



Alkalinity

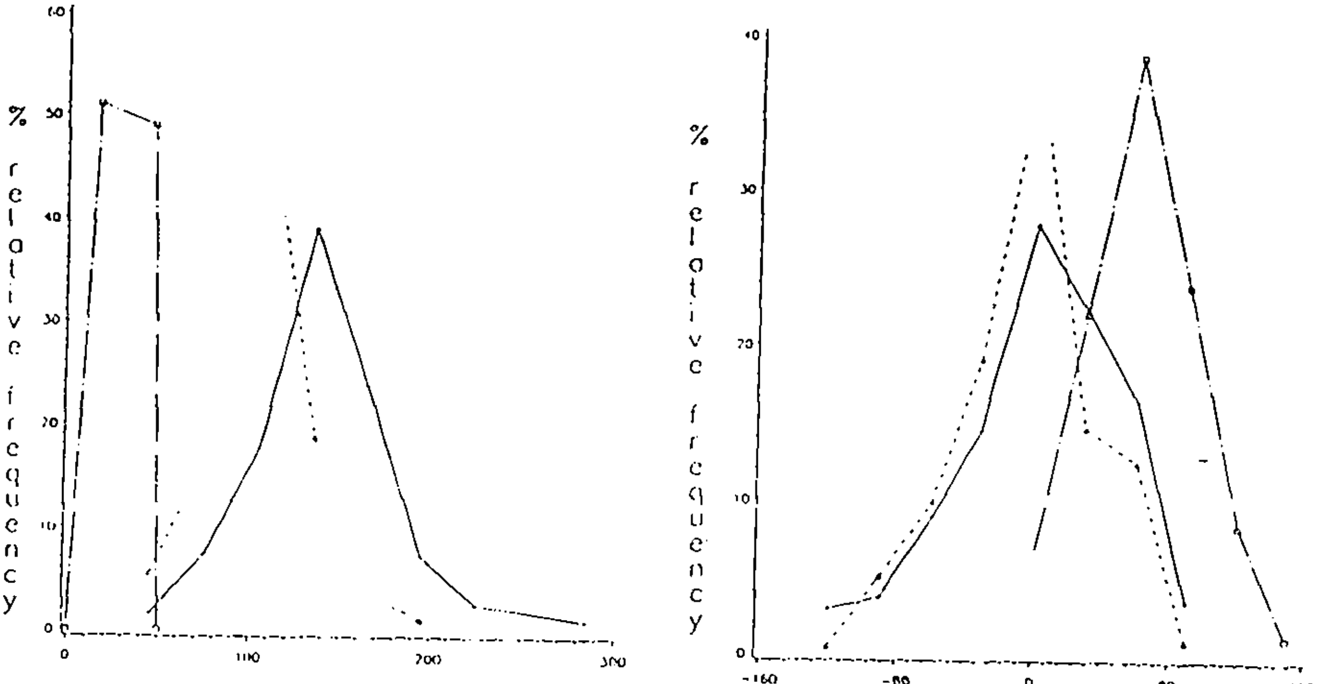
Calcium

Figure 2

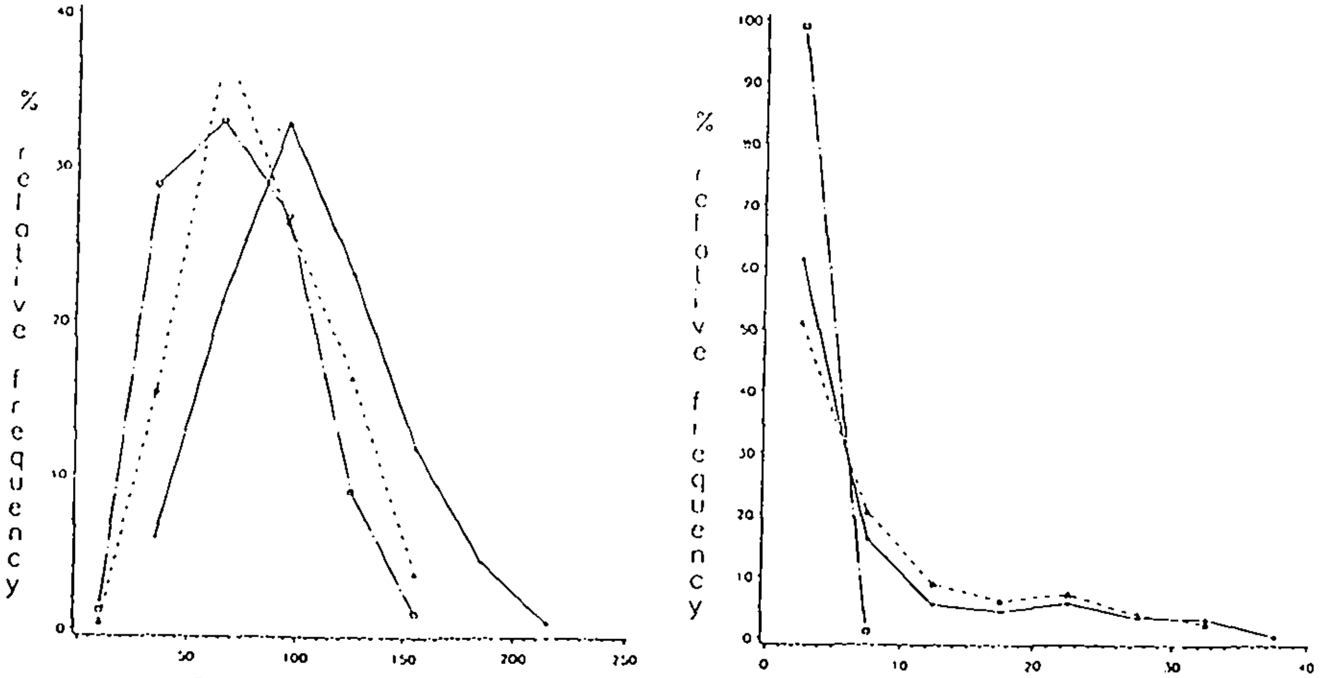
ALL UNITS .(UEQ/L)

□-□-□ 1984 observed +—+—+ 1984 simulate

AND THE FINAL EQUILIBRIUM UNDER A 30%
REDUCTION IN ACID DEPOSITION



Sulphate Alkalinity



Calcium Hydrogen

Figure 3 ALL UNITS (UEQ/L)

□—□—□ 1844 simulate
△—△—△ 2124 simulate
+—+—+ 1984 simulate

MAGIC PREDICTIONS FOR PH AND ALKALINITY : MEAN ,1 STANDARD DEVIATION,AND EXTREMA OF DISTRIBUTIONS UNDER A GIVEN % REDUCTION IN SULPHATE DEPOSITION

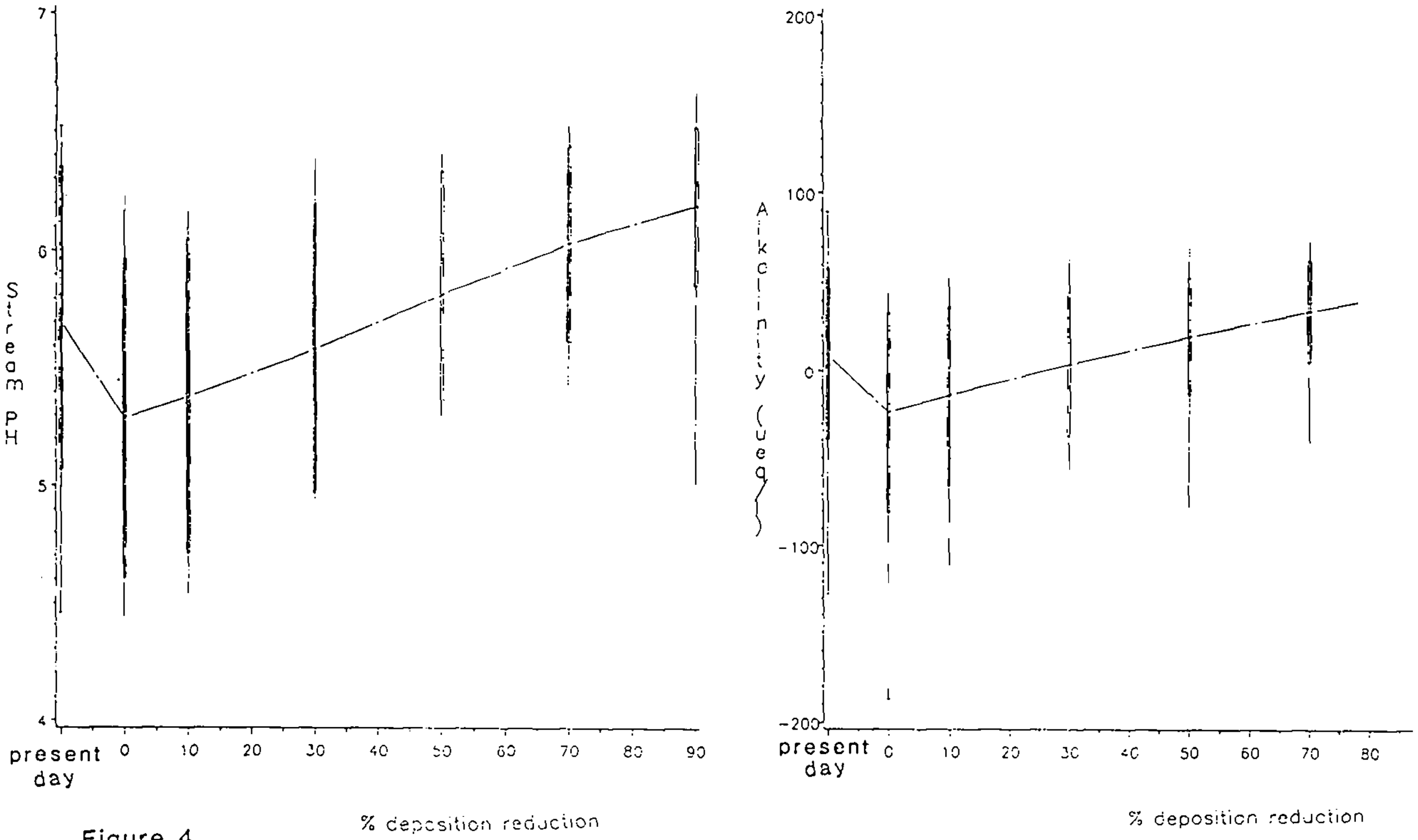


Figure 4

Regional modelling of acidity in the Galloway region in South West Scotland

Musgrove T.J.[1], Whitehead,P.G.[1] and Cosby, B.J.[2]

[1] Institute of Hydrology, Wallingford, Oxon, UK.
[2] Dept. of Environmental Sciences, University of Virginia ,U.S.A

ABSTRACT

Regional scale surface water characteristics of the Galloway area of south west Scotland are simulated using the MAGIC model of acidification of groundwater in catchments. Data from several studies within the area are pooled to provide a large, single data set for calibrating the model. The Monte Carlo technique is employed with the MAGIC model to produce a wide ranging model response encompassing the observed chemical features of the region. The simulation indicates that a substantial portion of the Galloway area has been significantly acidified during the past 140 years and that future sulphate deposition levels must be reduced significantly in order to achieve even partial recovery.

INTRODUCTION

The south west region of Scotland (Figure 1) is believed to be particularly vulnerable to the effects of acidic deposition, Wright and Henrikson (1979). Reports of long term changes in acidic status of lakes and streams combine with reports of a decline in fish populations to present a picture of concern to freshwater fisheries and environmentalists alike (Battarbee and Flower, 1986, Burns et al., 1984). Action to reverse the observed trends can only be effectively prescribed once the processes within the catchment soils that transform acidic precipitation into stream water pollution are understood. Practical experimentation in the laboratory and in the field can help to explain part of the story. The picture for soils, however, is obscured in the field by their heterogeneous nature, and in the laboratory by the inability to exactly reproduce field conditions. Mathematical models are very useful as an aid to undestanding the intrinsic processes in complex systems such as the soil-water chemical interaction through time and space. By using models, hypotheses may be tested by simulating processes and the results compared to their measured counterparts. Useful information may often be deduced irrespective of the outcome of the comparison.

In this study we use a well documented and extensively used model of groundwater in catchments (the MAGIC model) to perform a regional analysis of lakes and streams in South West Scotland. Instead of modelling each lake and stream separately we pool them all and model the overall probability density functions of water chemistry variables. We use the Monte Carlo technique to run the model 880 times, taking for each run a different set of parameters randomly sampled from specified distributions. The runs that enable us to match the observed distributions are investigated to determine the sensitivity of the model results to the individual parameters. The changes that have occured in the region as a result of increased deposition during the past 140 years are simulated and a possible future scenario of deposition is investigated.

ANALYSIS OF CHEMICAL DATA FOR THE GALLOWAY REGION

The Galloway Region of South West Scotland contains many lochs and streams that drain moorland, forest and pasture catchments. The bedrock consists mainly of lower palaeozoic rocks of Ordovician and Silurian systems with a few intrusions of Granite of the Old Red Sandstone era (Harriman et al., 1986). These catchments have only a thin covering of unconsolidated glacial till, often closely related to the nature of the underlying rocks (Greig, 1971). Many catchments in the region are covered by a blanket layer of peat of between 50 and 100 cm thickness. The southern part of the region is reported to have a higher calcite availability than the northern part. (Welsh et al., 1986, Edmunds and Kinniburgh, 1986). The mean yearly rainfall ranges from .8 to 2.4 metres with a mean of 2.0 metres. The concentrations of the major ions indicate three inportant sources: terrestrial input of Ca,Mg,Al,HCO_3 as products of weathering; atmospheric pollution input of H,NH_4,NO_3 and SO_4; and atmospheric input of seawater salts Na,Cl,Mg and SO_4 (Wright et al., 1980) The distribution of these ions varies spatially with a regional character. Concentration of all the major ions is higher nearer the coast to the south. Pollutant concentrations are higher as a result of the location of the sulphur emission areas to the south and the south east of Galloway. Weathering is highest in the more calcareous Silurian and Ordovician rocks to the south rather than the slowly weathering harder Granitic intrusions to the North. Sea salts are more evident nearer the coast. The pH of precipitation is 4.1 to 4.4 and contains a large excess sulphate proportion (Wright and Henrikson, 1979). The region as a whole is believed to be highly sensitive to acidic deposition and is therefore a useful area for scientific study.

Data sets from four separate investigations in Galloway were used in the study. Firstly, Edmunds and Kinniburgh (1986) sampled sites during the wet summer of 1985 as part of a larger survey of groundwaters throughout the United Kingdom. They took spot samples from springs, shallow wells, boreholes and river baseflow from a 20 km by 25 km area extending from Wigtown in the south to Loch Macaterick in the north and from the River Luce to the east to the Waters of Ken to the west. The study encountered the full range of Galloway bedrock but sampled few coastal sites. Secondly, Wright and Henrikson (1979) took spot samples from 72 lochs and 39 streams during the wet period in 19-26 April, 1979. The data was compared to an area of similar acidic susceptibility in Norway. The area of study was 70 km by 50 km and covered the entire Galloway region. These samples thus enveloped the complete spectrum of Galloway chemistry. Thirdly, Flower et al. (1987) looked at the water quality and diatom content of 34 Galloway lochs in November 1984 and again in July 1985. The study area once again encompassed the whole of Galloway. Finally, Harriman et al. (1986) sampled 22 lochs and 27 streams, looking at their chemistry and their fish populations. The region of study was limited mainly to the Granitic area between loch Dee and loch Doon in a 20 km by 15 km area.

A summary of each data set is presented in Table 1. It is seen that the highest mean pH levels were recorded by Flower et al (1985) in their July sample and by Edmunds and Kinniburgh (1986), for whom the shallow well and borehole samples show the more alkaline groundwater chemistry. The latter study also shows the highest base cation concentrations. The data from Harriman et al. (1986) shows low base concentrations indicative of the slowly weathering, acidic Granite region away from the coast and the emission sources. Of the major anions, SO_4 levels are more or less similar at approximately 158 meq/m3, but Cl is more variable ranging from 148 to 385 meq/m3.

The probability density distributions of corresponding chemicals within data sets are roughly triangular with a tail of varying length. The tail values affect the mean results in Table 1 by shifting them from their respective median values. This effect is greatest for the three data sets with a low number of samples. The distribution of pH has three peaks, at 4.5,6.1 and 7.1, for each of the studies except for that of Harriman et al. who sample the most acidic area and hence only show the lower two.

The data were pooled together to yield a large data set whose samples covered a variety of conditions produced by both spatial and temporal variation within the region. The samples were all taken within a five year period, and it was assumed that the pooled set could represent the mean state of the region during those five years. The time scale of the model is large compared to this and the errors introduced by such an approach were considered to be outweighed by the benefit of utilising all of the data to get a more accurate representation of region as a whole during that time. The overall mean results are presented in Table 1. Probability density functions showing the three peaked pH distribution and the long tailed "triangular" distribution for calcium, but also typical of each of the major ions, are shown in Figure 2.

A cluster analysis was performed on the data in an attempt to categorize groups of data linked by a common chemical make up. The minimum variance method of Ward was used to cluster the data (Ward, 1963) and the algorithms used were those available in the Statistical Analysis Systems computer package (SAS user guide, 1983). The clearest division of the data was obtained by forming six clusters. Two main clusters contained 322 and 74 of the total sample of 453 sets of measurements, and four minor clusters effectively accounted for the long tails of the distributions for the appropriate chemicals. Table 2 shows summaries of the two major clusters. Cluster 1 has a mean pH of 5.3 and includes all the low pH sites. Concentration of all major ions is low, e.g. mean Ca is 83 meq/m^3 and mean SO_4 is 120 meq/m^3. This is contrasted by Cluster 2 which has high values for ions (Ca is 412 meq/m^3 and SO_4 is 216 meq/m^3, see Figure 2, with a mean pH of 6.4. The differences may be interpreted by assuming that cluster 1 contains the more acidic sites on and around the Granitic regions to the north of the Galloway region, and that cluster 2 represents the area with Silurian and Ordovician bedrock near to the coast. Cluster 2 chemistry thus reveals the prevalance of higher deposition rate of sea salt and of atmospheric pollutant and also the higher source of weathered minerals. The main interest focuses upon cluster 1 as representing the most acid sensitive subdivision, and here only the simulation for cluster 1 is presented.

TABLE 1 A SUMMARY OF DATA FROM EACH STUDY
(MINIMUM, MEAN, STANDARD DEVIATION, MAXIMUM)

all meq/m^3 except Al(mg/l)

Data set		pH	Al	Na	K	Ca	Mg	Cl	SO4	NO3
Kinniburgh & Edmunds (1986)	min	4.2	.01	96	0.	19	16.5	28.2	37.5	0.
	mean	5.8	.21	277	26.7	329	158	253	159	49.5
	std	.85	.21	153	65.3	38.7	171	192	112	125.5
	max	7.3	.8	1095	644	2136	1242	1291	1041	728
Wright & Henrikson (1980)	min	4.3	.01	101	1	6	21	37	47	0.
	mean	5.4	.19	210	19.8	174.5	107	233	163.8	35.5
	std	.92	.18	113	16.1	300	95	143	77	65
	max	7.6	1.1	761	176	1811	403	930	478	460
Harriman et al. (1986)	min	4.2	.01	100	3	15	34	100	88	1
	mean	5.2	.17	143	9	139	78	148.6	150.5	11.3
	std	.6	.1	29	2.3	92	31	32	36	6.6
	max	8.0	.62	257	13	1325	429	232	279	45
Flower et al. (1984)	min	4.4	.1	1748	4.6	14	38	90	54	.7
	mean	5.5	.21	286	13.4	134	121	385	161.5	17
	std	.9	.11	138	12	114	83	179	85	31
	max	7.0	.43	765	56.3	400	340	935	358	171
Flower et al. (1985)	min	4.5	.07	135	3.1	23	37	87	70.8	.7
	mean	6.0	.27	276	14.7	166.3	116	298	139	7.5
	std	1.3	.4	164	14.6	142	88	163	67	7.2
	max	7.2	.59	717	64	518	356	899	320.6	31.4
overall	mean	5.65	.21	248	21.5	248.6	132	250.4	158	37

TABLE 2 SUMMARY OF THE TWO MAJOR CLUSTERS

Variable	number	mean	standard deviation	minumum	maximum
CLUSTER 1 :					
Al	322	.312	.16	.01	1.05
Ca	322	82.9	52.9	6.0	339.3
Cl	322	189.8	80.1	28.2	541.5
SO4	322	120.3	42.7	37.4	341.5
pH	322	5.34	79	4.18	7.38
NO3	322	8.75	13.3	3.57	89.0
Mg	322	69.0	31.7	16.5	310.2
Na	322	184.7	60.2	1.0	404.3
K	322	8.6	11.4	2.6	130.5
CLUSTER 2:					
Al	74	172	.11	.01	.42
Ca	74	412.1	120.0	196.1	748.5
Cl	74	332.2	135.5	87.4	631.7
SO4	74	216.5	80.9	99.9	449.7
pH	74	6.4	.56	5.38	7.44
NO3	74	54.8	57.8	3.57	298.4
Mg	74	204.9	73.1	90.5	477.2
Na	74	361.3	110.2	169.6	776.1
K	74	31.6	30.4	2.5	181.6

DESCRIPTION OF MODELLING TECHNIQUES

The region was modelled using the Model of Acidification In Catchments (MAGIC), developed by Cosby et al. (1985a and b). This is a lumped parameter long term simulation model of soil and surface water quality. In the MAGIC model, five soil processes are identified as holding the key to understanding the acidification processes in soils. These are: formation of alkalinity in the soil from dissolution of carbon dioxide held at high partial pressure (Reuss and Johnson, 1985); mineral weathering of base cations as a source within the catchment; anion retention by the soil, e.g. sulphate adsorption; aluminium mobilisation and dissolution of aluminium minerals; and cation exchange by the soils. Dynamic variation in the catchment soil condition is included in the model by forming a mass balance for each of the major anions and cations (presented by Cosby et al. 1985b). Equilibrium is assumed for each time step with changes between time steps monitored by the ion flux budgets. The sulphate subsection of the model is investigated in detail by Cosby et al. (1986b). Initial conditions for the model are calculated by assuming an equilibrium with background chemistry prior to industrialisation in 1844. This background chemistry is calculated using the present sea salt rainfall contribution as the 1844 precipitation concentration, and by taking the weathering rates to be constant throughout the time period considered by the model. Deposition of SO_4, CL, NO_3 are specified as an input to the model. The trend of Sulphate deposition during the past 140 years is taken from findings of the Warren Springs laboratory in 1983. The effect of catchment flora is modelled as sink terms for the appropriate ions. Neal et al. (1986) and Whitehead et al. (1987) use this facility to simulate the effect of forest growth on stream acidity. The model has a simple component for the additional effect of organic chemistry, which has been applied by Lepisto et al. (1987) to simulate an organically rich catchment in eastern Finland. An analysis of the uncertainties inherent in the model is proffered by Hornberger et al (1986), whereas Musgrove et al. (1987) investigate the precision of the simulation results. Verification of the model has been attempted by comparing model simulations to palaeocological reconstructions of pH for sites in Norway, Scotland, Sweden and America (Wright et al., 1986). The use of the model for regional analysis is illustrated by the study of Cosby et al. (1987), who simulate the regional characteristics of the chemistry of 208 lakes in Norway.

For this study the model was set up for Monte Carlo analysis. In this technique, several arbitrary parameters are randomly selected from a prescribed parent distribution prior to running the model. This is repeated many times in order to build up a set of runs, each with a different set of parameter values. The statistical properties of the collection of runs are then analysed. Examples of this technique applied to water quality problems are presented in Whitehead and Young(1979),Spear and Hornberger (1980a and b) and Spear and Hornberger (1983). The twelve independent model parameters that were varied are: the mean annual precipitation, QP; the sulphate deposition rate for 1982, SO_4; the cation exchange capacity, CEC; the weathering rates of the base cations, WECA, WENA, WEMG, WEK; the $\log_{10}$ selectivity coefficients SALCA, SALMG, SALNA, SALK; and the thermodynamic equilibrium constant for the aluminium hydroxide dissolution, KAL.

The results of the present analysis were investigated using the generalised sensitivity approach of Spear and Hornberger (1980a and b). This method compares the simulations that accurately reproduced observed features of chemistry (the "behaviour criterion") with those that did not. It then investigates the merits of the hypothesis that the set of parameters giving rise to a successful simulation and the set of parameters failing to do so have the same parent distribution. This hypothesis is tested for each parameter individually assuming them to be independent. The force with which the hypothesis is rejected is strongest for those parameters to which the achievement of a successsful result is most sensitive. A pattern recognition technique based on the Fukunaga-Koontz transformation (Fukunaga and Koontz, 1970) is employed to determine any linear combinations of parameters that the model response is sensitive to. This technique has been previously applied to MAGIC by Hornberger et al. (1986) and Cosby et al. (1987).

MONTE CARLO RESULTS

Cosby et al (1986a) set up the MAGIC model to simulate one of the Loch Dee catchments. This catchment is located in the middle of the region described by cluster 1. For the present analysis we initially set up the model in the same way in order to simulate cluster 1. Table 2 indicates that for cluster 1 the effect of NO_3 is small. This is possibly due to a near equilibrium between the input sources to the catchments and the plant uptake sinks within the catchment. The uptake rate was set more or less to balance the source for this simulation. The ranges from which the parameters that were drawn in the Monte Carlo analysis are shown in table 3. The mode indicates the peak for the triangular distributions (a negative mode indicates that the distribution was rectangular). The specified ranges are wide in order to encompass the entire spread of parameter combinations that are able to reproduce cluster 1 chemistry. The extent of the range is limited, however, to those values that may be experienced in the field. The behaviour constraint was chosen such that a run was considered successful if its simulated chemistry for 1982 fell within the range of values between the appropriate 5 and 95 percentiles of the cluster 1 chemistry.

Of 880 runs, 530 were successful in reproducing the features of cluster 1 regional chemistry, and these are summarised in Table 3. Table 4 shows the behaviour constraint "windows" and a summary of the simulated chemistry. Figure 3 shows the observed and simulated probability density functions of the cluster for Cl, SO_4 and Ca. Good fits about the mean value are seen for Ca ,Cl and SO_4 and the shapes of the simulated distributions for these three variables are also good. The fits are worst at the tail ends, resulting from either specifying a too narrow range of parameter for the Monte Carlo analysis or from the sampling of the triangular distributions failing to pick up the extremes. The simulated distribution for pH is compared to the observed distribution in Figure 3. The simulation enabled the complete range of pH value, present in the region defined by cluster 1, to be reproduced. The bias towards reproducing the lower pH chemistry possibly lies with the model being set up to reproduce a poorly buffered, highly acidic catchment response. Whilst this is adequate for the majority of cluster 1 sites, it may be less good for the remainder. Alternatively, a better match may also have been achieved by selecting the parameters from more sophisticated distributions than the rather crude triangular ones that were used. By matching more closely of the uppermost part of the pH distribution, the upper tail end of the other distributions would also have been better matched.

TABLE 3 PARAMETER VARIATION FOR THE MONTE CARLO SIMULATION

	Range for Monte Carlo variation			successful simulations			
PARAMETER	MIN	MAX	MODE	MEAN	STD	MIN	MAX
QP	1.2	3.0	2.0	1.70	.50	1.2	3.0
SO4	50	220	150	121.5	32.4	52.2	184.1
CEC	40	250	120	178.5	119.9	40.0	229.
WECA	10	250	85	69.4	45.1	10.1	162.2
WEMG	0	50	25	13.4	8.9	6.5	39.4
WENA	0	50	25	10.3	6.93	.1	29.0
WEK	0	30	10	3.7	2.53	.1	10.5
SALCA	-1	5	3	2.08	1.28	-.7	4.8
SALMG	-1	5	3	1.87	1.24	-.9	4.7
SALNA	-3	3	0	.08	1.22	-2.9	2.9
SALK	-3	3	0	.03	1.28	-2.8	2.9
KAL	8	11	9.5	9.65	.6	8.1	10.9

(WECA, WEMG, WENA, WEK and SO4 have units of meq $m^{-2}year^{-1}$, QP is in metres depth over the catchment, CEC in meq/kg)

TABLE 4 SUMMARY OF BEHAVIOUR CRITERION WINDOWS AND THE SIMULATED CHEMISTRY THAT SATISFIED THE BEHAVIOUR CRITERION
FOR CLUSTER 1

	behaviour criterion windows		successful runs		
Variable	min	max	mean	min	max
pH	4.4	7.6	5.4	4.3	6.5
Ca meq/m^3	20	245	91.5	21.5	224
Mg " "	18	190	27	19	85
Na " "	10	330	196	11	372
K " "	3	35	12	3	34
SO4 "	40	245	115	39	242
NO3 '	9	25	16	9	22
Cl '	79	360	203	125	401

REGIONAL CHEMISTRY CHANGES OVER TIME

The historical changes in the distributions of values of the simulated chemicals were ascertained by saving the output for 1844 and 1982. The future deposition was modelled as a linear decrease to 30% of the 1982 level by the year 2001. This is merely one of many possible scenarios and is used only to illustrate the potential use of the model for regional prediction. The regional levels of chemical concentrations in 2060, under this deposition sequence,were also looked at. The results are shown in Figures 4 and 5.

For cluster 1, the MAGIC model shows a large drop in both pH and alkalinity over the past 140 years. The pH level falls by .8 pH unit and alkalinity falls by approximately 70 meq/m^3. This is in accord with the findings of Battarbee and Flower (1985), who report changes in pH level of up to 1.0 pH unit during the same period, for those lochs in the Granitic region of Galloway. A small recovery is seen during the future scenario. The small size of this recovery reflects the depletion in the soil of base cations (to between 2 and 5 % in 1982). The low rate of soil weathering in the region enable only a slow recovery rate. The sulphate distributions clearly show the shift in regional concentrations simulated as the result of industrialisation. The preindustrialised levels are between 0 and 38 meq/m^3, whereas the 1982 levels are much higher with values between 42 and 190 meq/m^3. The 2062 levels are reduced by about 30%, closely matching the decline in sulphate deposition. This confirms the status of the soil as having low sulphate adsorption capability. Aluminium is seen to increase in extent over the years, up to 36 meq/m^3 for the most acidic lakes. The majority of sites, however, show only a small increase. Of the base cations, Calcium levels are seen to rise only slightly, whereas magnesium levels show a much more substantial rise. The future scenario shows small decreases in these cations, as a result of the partial recovery of the soil.

SENSITIVITY ANALYSIS

The results of the generalised sensitivity analysis are presented in Table 5. This describes the difference between the distributions of parameters that give rise to a "behaviour" and those that do not. The Mann-Whitney statistic (M-W) indicates whether the distributions are significantly separated along the parameter axis, and the Kolmogorov-Smirnov statistic (K-S) gives the greatest separation of the two corresponding cumulative distribution functions. In both cases, a large number indicates a high significance and sensitivity of simulation to that parameter. The greatest sensitivity as indicated by these two statistics is seen for QP (M-W of 3.19) and for WECA (K-S of .219) respectively. Parameter SO_4, the 1982 deposition level, is high in both cases. WECA has a high value for the K-S statistic and a low value for M-W statistic. This indicates that one of the two distributions (behaviours or non-behaviours) is centrally placed within the domain of the other. The central distribution for WECA is the one for behaviours, showing a peaked, triangular distribution with a well defined band of acceptance. Thus, whilst the WECA parameter was outside the range 10 to 162 meq $m^{-2}yr^{-1}$, there was no chance of a successful simulation.

A method based on the Fukanaga-Koontz pattern recognition technique was used to look at the sensitivity with respect to linear combinations of the parameters. This analysis reveals two eigenvectors of high sensitivity. The first was more sensitive than any individual parameter, with M-W of 3.63 and K-S of .214. The weight of each component of the normalised eigenvector indicates the relative importance of that component in explaining the variance associated with it. In this way the most important components were SO_4, explaining 63% of the variance, and WECA, explaining 22%. The results indicate that the succes of the model in reproducing the regional characteristics for areas of high acid susceptibility is strongly dependent on the selection of values for the WECA, SO_4 and QP parameters (the weathering rate of calcium, the sulphate deposition rate in 1982 and the mean annual rainfall during the duration of the simulation).

TABLE 5 RESULTS OF THE GENERALISED SENSITIVITY ANALYSIS

	comparison of behaviours to non-behaviours	
parameter	Mann-Whitney z statistic	Kolmogorov-Smirnov d statistic
QP	3.19	.139
SO4	2.19	.204
CEC	1.59	.105
WECA	.76	.219
WEMG	.51	.045
WENA	.26	.052
WEK	.52	.065
SALCA	.26	.079
SALMG	1.21	.096
SALNA	.24	.042
SALK	1.08	.092
KAL	.01	.054

DISCUSSION

This analysis tends to confirm both the view that the Galloway region is susceptible to acidic deposition and the view that a significant change in soil conditions has occurred during the past 140 years. Falls in pH level of up to one pH unit have been discovered for the Galloway by Battarbee and Flower (1985) using the method of reconstrucion from study of diatom assemblage in the sediment of lochs. The simulation results show a drop in mean level of .8 pH unit. This is increased by the inability to match the highest portion of the 1982 pH distribution at the same time as matching its low end. This inability also spills into the simulated distribution for alkalinity, by cutting off the highest levels in the simulation. A fair view of the changes caused by the acidification processs can still be gleaned however, by noting that the lakes with higher alkalinity in 1982 are also those with the higher alkalinity in 1844. Hence the simulated results are valid for those lower alkalinity lakes that it represents well. The recovery under 30% deposition reduction in deposition is seen to be slight due to the depletion of base cation resource on the available cation exchange sites on the soil. In particular, alkalinity levels are seen to recover very little in the most highly acidified lakes.

Overall the simulation was successful using triangular distributions for the parameters in the Monte Carlo analysis. Better reproduction of the present day distributions could have been achieved using more complicated distributions to describe the parameters, noting that certain results in the behaviour criterion are more tuned in to particular parameters. For example, Calcium levels are strongly affected by its weathering rate and selectivity coefficient. The lack of available data for verification of the model calibration, however limits the usefulness of such a study. Without verification, fine points raised by such a simulation might be mere quirks of the model. The simulations obtained work only under the assumption that the model structure is valid and that its lumped representation of parameters is valid on a regional basis. This is a difficult assumption to prove and one is able only to look at the simulations and see whether the model appears to represent the region well. Given the assumption to be valid there are many uncertainties within the model itself that need to be borne in mind when interpreting the results or when using the model to project assumed deposition scenarios into the future. Uncertainties arise in measurement of both precipitation and stream chemistry as a result of both intrinsic uncertainty in the measuring technique and in the representative nature of the sampling plan used. In this study the results of five surveys are used, four of which are single sample surveys. The findings of each survey have been pooled to produce an observed chemistry that may average out, to a degree, any unrepresentative feature of any one survey. Each submodel within MAGIC also has an uncertainty to be associated with it. The true shape of the sulphate deposition trend curve, used to define the timing of precipitation pollutants, has been estimated and errors may seriously affect the timing of the onset of acidification. This aspect of the model has been investigated by Hornberger et al., 1986, who looked at the effect of uncertainty on a single site prediction using MAGIC. The aluminium submodel contains a cubic equilibrium between aluminium and hydrogen activities. Assuming an equilibrium model to be valid, there is uncertainty in the order of the relationship. A fit to observations at one point in time may be found for many different orders and the future predictions and past reconstructions may be very different for each one. Monte Carlo simulations are an excellent means of encountering the complete range of model response to uncertainty in parameters. The sensitivity of the model simulations to parameter value on a single site basis is presented by Musgrove et al., 1988, who use the Monte Carlo method to generate estimates of the uncertainty of model predition. The results for pH are in excellent accord with palaeocological pH reconstructions for the same site. On a regional basis, the model appears capable of simulating well the main bulk of the chemistry distribution but is less able to match the extreme values.

CONCLUSIONS

The MAGIC lumped parameter model of groundwater in catchments can be coupled with Monte Carlo trechniques to provide a useful method of simulating long term regional response to acidic deposition. The sensitivity of simulation to parameters in the model is seen to be dependent on the weathering rate of calcium, the level of deposition of sulphate and the mean annual rainfall for a region with low weathering rates and low sulphate adsorption. The response of the region to a future deposition scenario is gleaned from the model and after a prolonged period of deposition the ability of the region to recover from the historical deposition sequence is seen to decrease throughout the lifetime of the deposition sequence. Major future reductions in deposition are required to produce a significant recovery in the Galloway region of South West Scotland.

ACKNOWLEDGEMENTS

The authors are particularly grateful to the Solway River Purification Board for providing data from the Loch Dee study and to the British Scandinavian SWAP commitee and the commission of the European communities for providing research funding.

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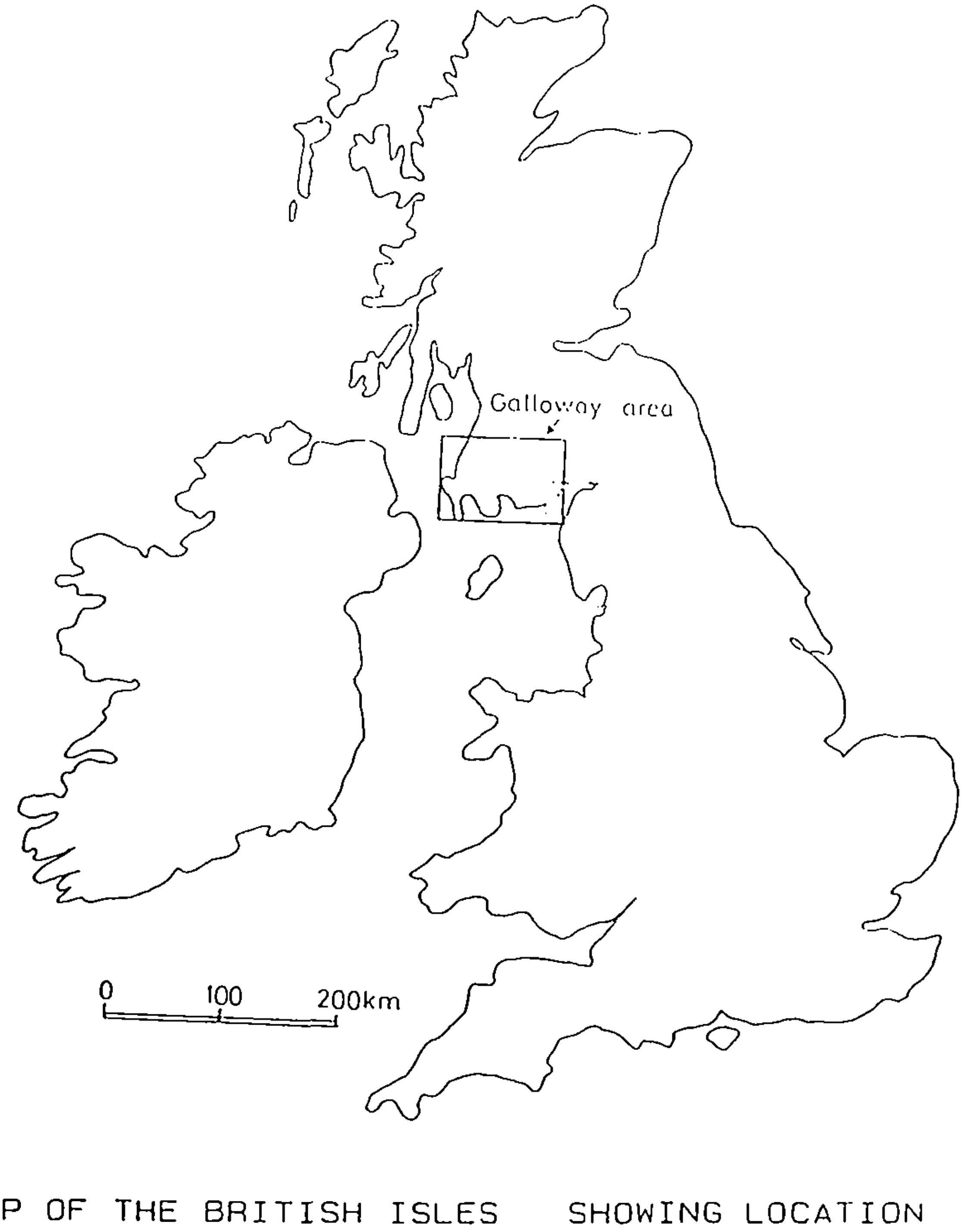


MAP OF THE BRITISH ISLES SHOWING LOCATION OF THE GALLOWAY AREA

FIGURE 1

Figure 2 Calcium and PH Distributions

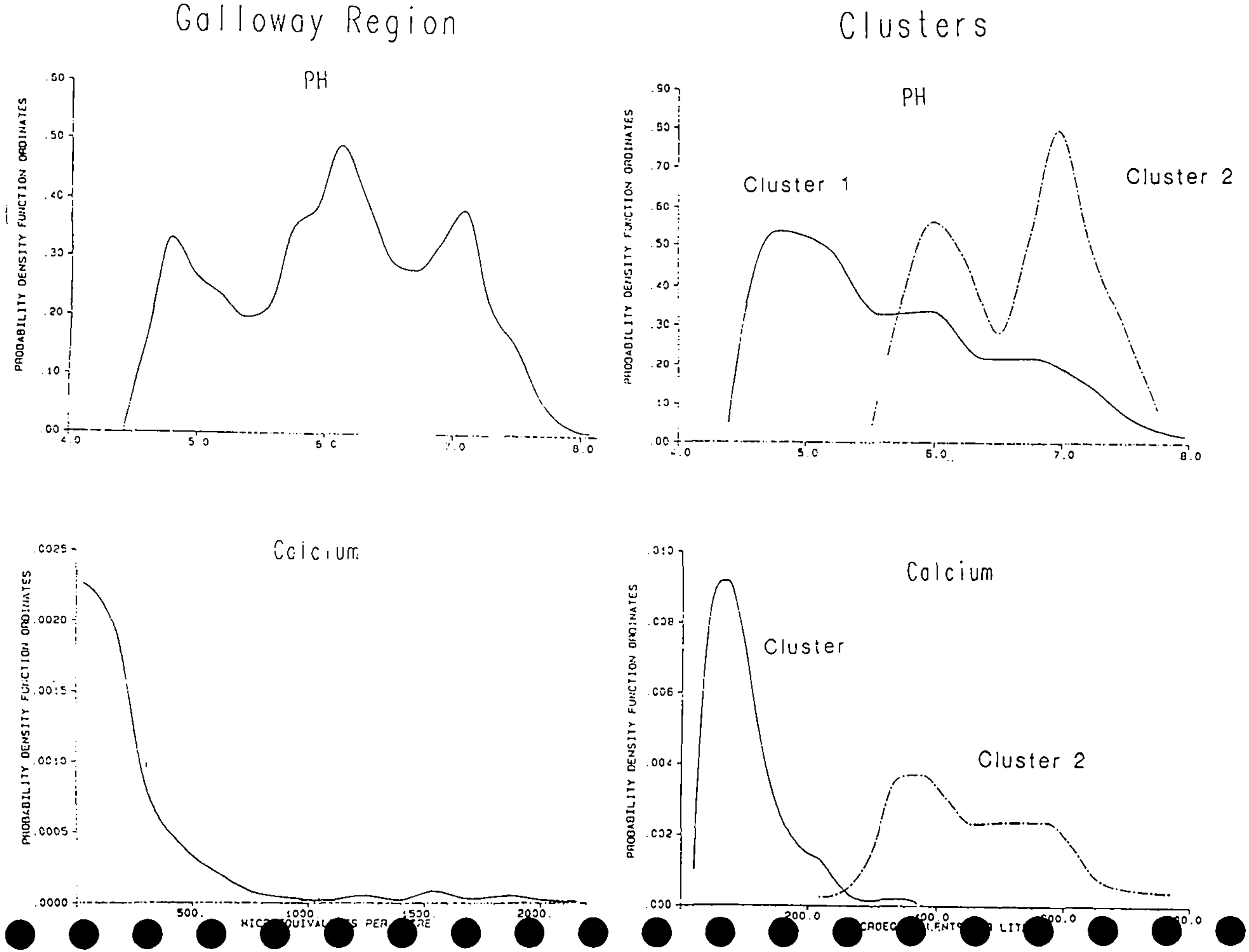


Figure 3 Cluster 1 Distributions
Simulated and Observed

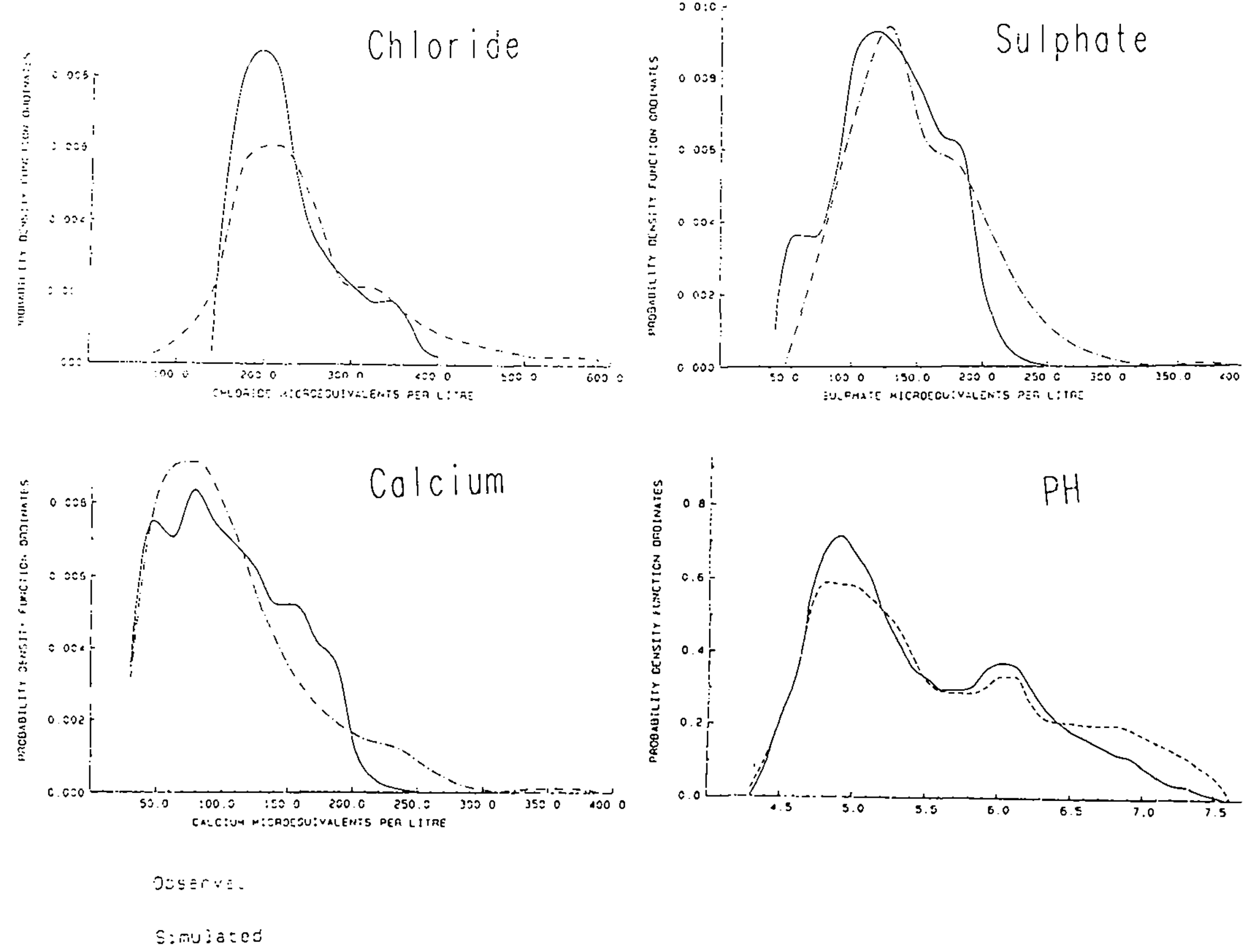
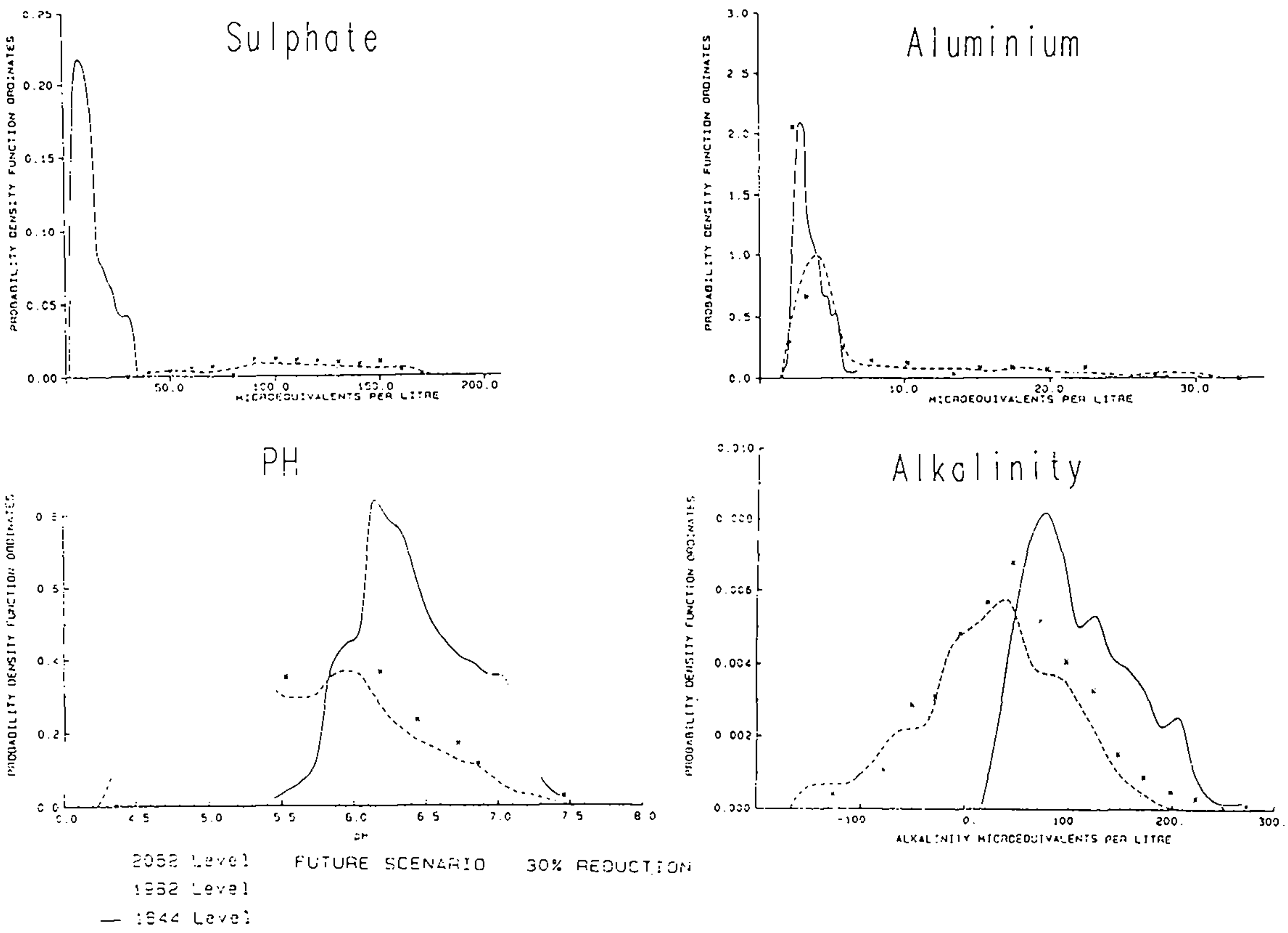


Figure 4 Cluster 1 Simulated Change Through Time



Cluster 1 Simulated Change Through Time

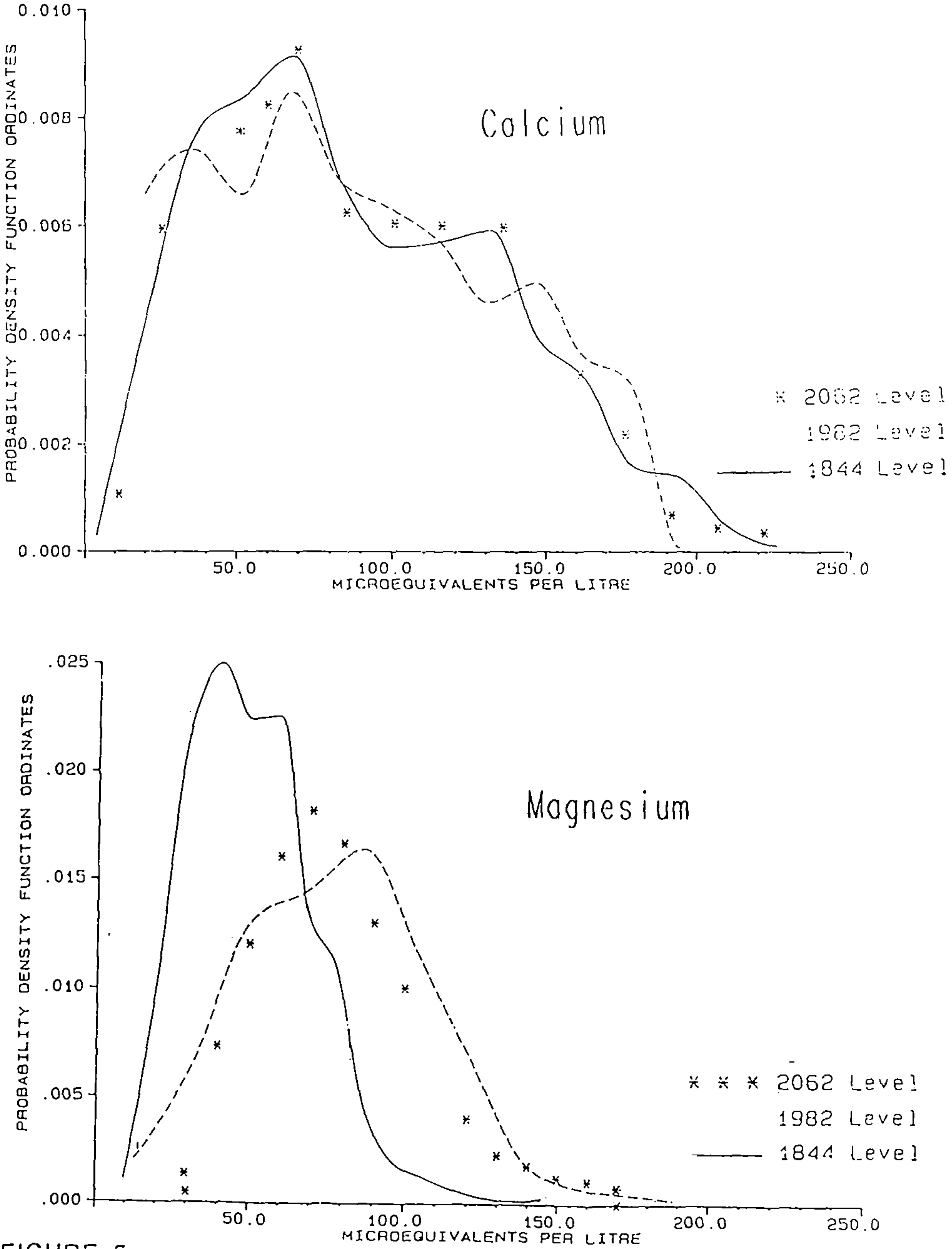


FIGURE 5

The demand for long-term scientific capabilities concerning the resources of the land and its freshwaters is rising sharply as the power of man to change his environment is growing, and with it the scale of his impact. Comprehensive research facilities (laboratories, field studies, computer modelling, instrumentation, remote sensing) are needed to provide solutions to the challenging problems of the modern world in its concern for appropriate and sympathetic management of the fragile systems of the land's surface.

The **Terrestrial and Freshwater Sciences** Directorate of the Natural Environment Research Council brings together an exceptionally wide range of appropriate disciplines (chemistry, biology, engineering, physics, geology, geography, mathematics and computer sciences) comprising one of the world's largest bodies of established environmental expertise. A staff of 550, largely graduate and professional, from four Institutes at eleven laboratories and field stations and two University units provide the specialised knowledge and experience to meet national and international needs in three major areas:

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Land Use and Natural Resources

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Ecology and Conservation