INSTITUTE of
HYDROLOGY

Predicting the Effects of Acid Deposition on Water Quality

by

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First Report on Contract
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TABLE OF CONTENTS

PREFACE

This report describes research completed in the first six months of a contract (ENV-829 UK(H)) between the Commission of the European Communities (CEC) and the Natural Environment Research Council (NERC), entitled 'Predicting the Effects of Acid Rain on Water Quality'. The research has been carried out at the Institute of Hydrology (H), a component body of NERC.

1. INTRODUCTION

In recent years significant changes in stream acidity have been observed in Scandinavian and British catchments and these changes have been attributed to acid deposition. Research has been conducted on a wide range of processes affecting stream acidity and there is now a need to study the integrated process behaviour at the catchment scale. Studies at the Institute of Hydrology and elsewhere have shown that mathematical models of catchment hydrology can be developed given a suitable data base. Hydrological models are an essential requirement of any water quality study since it is necessary to provide information on water movement and the associated residence times before chemical process equations can be applied to predict water quality.

Fundamental to any catchment modelling study is the need for adequate data on hydrological and chemical variables together with information on soil characteristics and soil-water interactions.

2. EXPERIMENTAL STUDIES

As part of the CEC - NERC contract the Institute of Hydrology is establishing a catchment study in the Cairngorm region of Scotland in collaboration with DAFS (Department of Agriculture and Fisheries for Scotland) and the Macaulay Institute. IH would be responsible for providing stream gauging, rainfall stations, a weather station, snow surveys, sampling and continuous water quality monitoring. IH would also be responsible for the subsequent data management, analysis and interpretation. DAFS would be responsible for all chemical and biological analysis, with the exception of snowmelt chemistry, which would be undertaken by IH. The Macaulay Institute would be responsible for soil-surveys and soil-water chemistry. Details of the initial survey work on this catchment are given in Appendix 1.

In addition to the Cairngorm catchment study, the Institute of Hydrology is already associated with several major catchment studies including the Balquhidder project (South East Scotland), the Loch Dee project (South West Scotland), the Llynn Brianne project (South Wales) and the Plynlimon Catchment Study (Mid-Wales). All of these will provide valuable information on different catchment geology and soils, different land uses (particularly forestry) and different management practices, with specific application to the control of acidity in UK catchments. Additional studies on pH measurement have shown the difficulties involved in obtaining reliable data for modelling purposes (see Appendix 2). Thus a wide range of process information will be available with which to develop hydrological and chemical models and assess the effects of long term and short term management changes.

3 MODELLING STUDIES

3.1 Objectives

The hydrological and chemical data collected from the catchment studies forms the basis of a comprehensive modelling research programme by IH. The objectives of this aspect of the study are as follows:-

(i) to provide a comprehensive framework with which to assess the sensitivity of hydrological and chemical processes controlling catchment acidity;

(ii) to assist in the planning of field and laboratory experiments;

(iii) to aid in the interpretation and analysis of field data;

(iv) to investigate the short-term dynamic response or catchment behaviour and assess the impact of 'acid shocks' on the aquatic environment;

(v) to assess the long-term acidification problem and the possibilities of remedial management action.

3.2 Background

The research programme draws heavily on the wide range of experience available at IH in hydrological and chemical modelling.

Hydrological models have been developed and applied to a spectrum of catchments from small upland basins of a few hectares in area to major multi-tributary river systems of many thousands of hectares in area. Models of varying time scales are available and of varying spatial complexity so that many aspects of hydrological phenomena may be investigated. For example the IHDM (Institute of Hydrology Distributed Model - Morris, 1980) is a physics-based model which allows the detailed movement of water to be followed through vegetation, snow, soil, overland and in stream channels. It is therefore an ideal base for the investigation of short term events. A second distributed model (TOPMODEL - Beven et al, 1983, 84) makes some simplifying assumptions but also provides spatial patterns of soil moisture levels and runoff production. The model requires less computational effort and is therefore better suited to long period simulations. Further system models of catchment hydrology and recursive methods of time series analysis are available at IH and have been applied to model catchment hydrology (Whitehead et al, 1979).

In terms of modelling water quality (chemical hydrology) IH has undertaken research for the UK department of the Environment, the European Commission and the Anglian and Thames Water Authorities. Modelling studies have included oxygen balances in rivers, nitrate studies, the movement and distribution of heavy metals, dispersion studies and the modelling of algal growth processes (Whitehead et al, 1981, 1984, Whitehead, 1980). As in the case of hydrological models, model complexity can vary considerably from simple time series models to detailed reaction kinetic models incorporating dispersion and mixing processes. That such models can be applied to catchment acidification has been demonstrated by Christophersen et al (1982, 1984) and Cosby et al (1985) at the University of Virginia; IH has developed strong collaborative links with both these modelling groups. Both chemical models developed by these researchers are available at IH for application to UK catchment studies. In addition, we have recently applied recursive time series approach to catchment data from Norway, Scotland and Wales and developed models of the dominant processes controlling stream acidity (Whitehead et al, 1984 - see Appendix 3). Further process models have been developed by Morris et al, 1984 (see Appendix 4) on the pollution of snowmelt in a Cairngorns catchment study in Scotland.

Thus a sophisticated suite of modelling techniques ~~are~~ is available at IH and these will be further developed and enhanced during the project.

3.3 Modelling strategy and application

It is proposed to adopt a modular approach to modelling so that the most appropriate hydrological and chemical models are applied to any particular catchment. With the wide variety of catchment land use, geology, hydrology and chemistry a single universal model is unlikely to be applicable. Rather a spectrum of models will be required for application to different catchments.

Hydrological and chemical models will be applied to catchment data and modified as necessary to incorporate relevant processes. Chemical and hydrological processes will be reviewed and mixing processes investigated to ensure that the correct combination of chemical reactions, mixing and dispersion is incorporated. Sensitivity analysis will be performed to assess parameter uncertainty and this information will be used to refine field and laboratory experiments.

The models will be used to assess both short term and long term changes in stream acidity. For example long term records of past acidity can be reconstructed by paleo-ecological studies (Batt~~e~~arbee, 1984) and the models can be tested against these observed changes given information on acid deposition levels. Such long term simulations could be used to assess the effects of future acid deposition scenarios. However such analysis should be undertaken as part of a stochastic simulation exercise to provide information on confidence levels.

Short term on dynamic responses of catchments are particularly important for predicting the effect on fisheries or water resources. The models will provide valuable information on dynamic changes which can be linked to the DAFFS fisheries studies and river authority water resource concerns.

Finally the aspect of land use and management practice will be extensively studied using information from the Loch Dee, Plynlimon, Brianne and Balquhidder catchment studies. Effects of land use change and the possibility of managing catchments to minimise stream acidity will be fully explored using the models.

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APPENDIX 1

THE PROJECT CATCHMENT STUDY

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. Introduction

This report is concerned with the detailed catchment study commissioned the CEC and the Royal Society Surface Water Acidification Project WAP). Three research institutes will take part in the study. These are e Fresh Water Fisheries Laboratory, Pitlochry (FFL); The Macaulay stitute for Soil Science, Aberdeen (M) and the Institute of Hydrology, llingford (IH). The aims of the catchment study may be summarised efly as follows:-

1. To study processes controlling the chemistry of surface waters in an area sensitive to the effects of acid deposition.
2. To study the effect of acidification and especially of acid episodes in surface waters on aquatic biota.
3. To provide a complete and reliable set of data which may be used to test and develop hydro-chemical models. These models will allow the effects of future acid deposition to be predicted and the long term consequences of acid deposition in the area to be assessed.

2. Research Programme

The research programs of the three Institutes have been designed to cover the whole range of processes in the catchment. The work to be done by each Institute has not yet been completely finalised but the broad outlines are as follows

(i) Precipitation and chemical inputs (IH)

Rainfall will be measured at five sites at hourly intervals. The sites will be chosen to cover a range of altitudes and aspects so that a distributed rainfall input to the catchment may be established. At the same sites, samples of rain for chemical analysis will be collected at weekly intervals and over rain storm episodes using automatic samplers. Snow inputs will be measured at ten sites using snow stakes and measurements of the attentuation of natural X-ray radiation. Fresh snow samples will be collected for chemical analysis at regular weekly intervals and after major snow storms. As well as the regular monitoring of inputs experiments will be undertaken to investigate the spatial variability of rain and fresh snow chemistry and the rates of solid particle deposition.

(ii) Processes within the snowpack (IH)

Regular measurements of vertical profiles of density, grain size, temperature, water content and snow chemistry will be made. These will allow the processes of redistribution of pollutants within the snowpack as it matures to be studied. The meltwater released at the base of the snowpack will be collected by automatic samplers so that the quantity and quality of the water input to the soil during snowmelt will be monitored. This is important since preferential elution of impurities from snow can be a major cause of acid episodes in stream water. The spatial distribution of meltwater inputs over the catchment will be established using a network of five melt gauges set into the soil surface near the raingauges and recording at hourly intervals.

(iii) Evaporation and evapotranspiration (IH)

Hourly measurements of solar and net radiation, humdity, wind speed and direction and air temperature will be made using an Automatic Weather Station situated in the centre of the catchment. These data will be used to estimate evaporation and evapotranspiration over the catchment on a routine basis. Short-term process experiments will also be undertaken to look in detail at evapotranspiration from heather and evaporation from snow using a small weighing lysimeter.

(iv) Soil processes (M)

A full field survey will be made of the distribution of soils within the catchment. Physical properties and chemical behaviour of the soils will be investigated in the laboratory. At several sites within the catchment field lysimeters will be used to monitor the quantity and quality of water flowing in the various soil horizons and over the surface of the ground. These sites will be as far as possible the same as those used for collecting meteorological data and the process experiments described in sections (ii) and (iii). The water content of the soil will be monitored, if possible on a weekly basis, using a neutron probe.

(v) Streamflow (FFL, IH)

In order to achieve the required accuracy in measurements of stream flow from the catchment ($< 10\%$) it will be necessary to build a gauging structure at the catchment outlet. This structure will be rated by dilution gauging throughout the four years of the research programme. A small weir may also be installed within the catchment if a suitable site is available. The stream chemistry will be monitored on a regular twice-weekly basis and samples will also be taken at hourly intervals during acid episodes. Electrical conductivity, stream temperature, stream flow and pH will be recorded at 20 minute intervals. Dissolved organic material and suspended solids will also be measured.

(vi) Aquatic biota (FFL)

Fish population studies will be undertaken with specific reference to the effect of the intensity and duration of episodic chemical fluctuations on egg survival.

3. Criteria for the choice of catchment

The scientific criteria for the choice of catchment have been established by discussions between the SWAP management committee and the three research organisations involved in the study. They may be summarised as follows:-

(i) The catchment should be in the Upper Spey region

This region has been identified by the FFL as one in which important fisheries are vulnerable to episodic chemical fluctuations. Because of the particular character of the acid inputs, hydrology and geochemistry of the region, streams are at a transitional stage of acidification where background levels are not so high that fish have disappeared (as in the Loch Aard region) but peaks of acidity are high enough to produce toxic effects especially during more sensitive stages of the life cycle.

(ii) The catchment should have thin soils on a slowly-weathering bedrock

These are favourable conditions for the production of acid episodes in the catchment stream; this criterion ensures that the catchment represents the most sensitive areas of the transitional Upper Spey region.

(iii) The catchment should have an area of about 10 km^2

The preferred area of the catchment is defined by a number of factors. Episodic events decrease in importance as catchment size increases, so there is an upper limit of around 25 km^2 on the preferred area. On the other hand fish do not reach very small, high-level mountain streams, so there is a lower limit of about 5 km^2 on catchment size. The maximum size for a research catchment which is to be intensively monitored and surveyed is about 10 km^2. For greater areas costs become prohibitive.

(iv) There should be a good gauging site

In order to measure water and pollutant outputs from the catchment accurately, it is necessary to have a site where as much as possible of the output leaves the catchment in the stream rather than through the soil. This means that the stream must flow over bed-rock and through rock banks. Furthermore, the approach to the gauging site should be as straight as possible, and not too steep. Otherwise any gauging structure installed in the stream will not act as it has been designed to do and a large amount of dilution gauging will be required to establish the relation between stage and discharge (the rating curve). There should be no possibility of bypassing of the structure at high flows.

(v) The catchment should not be forested

Previous research has shown that afforestation has a marked effect on the hydrological and hydrochemical behaviour of a catchment. Work will continue on this problem in the Loch Aard region but as far as the Upper Spey is concerned the aim is to investigate the effects of acid deposition on the area in its natural state. Remnants of the ancient natural forest in the catchment would be acceptable but there should be no areas planted with trees if possible.

(vi) There should be good access

In practice this means that the gauging site should be accessible by Landrover or similar vehicle at all times of the year, except perhaps during very heavy snow storms when main roads in the area are closed. This is important because this will be the main point at which water samples (up to 2 kg of water per sample for trace metal analysis) will be collected. Ease of access within the catchment is desirable but not essential.

4. Survey of Potential Sites

Background information to assist the search for a suitable catchment in the Upper Spey region has kindly been provided by the Elgin office of the North East River Purification Board. On 22nd August 1983 water samples were taken from 55 streams in the region. Since this was after a period of prolonged drought the chemistry of the samples reflects the chemistry of baseflow in each catchment. The baseflow or "background" levels of alkalinity, pH and eletrical conductivity (which is a measure of total dissolved load) for the 15 catchments for which these values were lowest are shown in Table 1. Catchments which were chosen for regular monitoring are starred. Chemical data for these catchments are available from NERPB at monthly intervals. Clearly a granite bedrock with no till or peat produces the lowest values of alkalinity, pH and conductivity in base flow. The first few catchments in Table 1 were therefore regarded as good potential candidates for the SWAP experimental site. Indeed the Allt Ruadh and Allt Fhearnagan were recommended by the FFL who had already been studying these catchments. The NCC office in Aviemore also suggested that the Allt na Cuhaige at Lagg (624932) might be suitable. Two other catchments, the Allt a'Mharcaidh (881045) and Allt Chriocaidh (853098) were identified as possible sites from topographical and geological maps.

The results of a survey of these catchments made in January 1985 are summarised in Table 2. All were examined for possible gauging sites except the Beanaidh Bheag which was not accessible at the time. For each of the scientific critera identified in the previous section a mark of

1 meets the criterion well

2 just meets the criterion

3 fails to meet the criterion

has been assigned. Where there is no gauging site (ie a mark of "3" in column 4) the access is also given a mark of 3. Otherwise the marks are independent. Clearly the only catchment which meets all the criteria well is the Allt a'Mharcaidh. This catchment (area 10 km^2) is a tributary the R. Feshie. The bedrock is granite and soils are very thin with rock exposed in most of the highest areas. There is a small area of ancient forest near the catchment outlet but otherwise the vegetation is heather and mountain tundra. There is an excellent gauging site 100 m from the end of a Forestry Commission road which is accessible even in deep snow conditions. The pH of baseflow in January 1985 was low, at 6.2. A preliminary study by FFL has located a spawning ground for trout and salmon just below the gauging site propsed by IH. All three Institutes working on the project are satisfied that the Allt a'Mharcaidh will be a suitable site.

We therefore recommend that the Allt a'Mharcaidh catchment should be chosen for the SWAP experimental catchment if access and planning permission can be obtained. Since the catchment lies in the Natural Nature Reserve full discussions must be held with the NCC and the local conservation groups.

Table 1 N.E.R.P.B. August 1983 'Acid Rain' Survey

Catchment	N.G.R.	Altitude/m	Area/km²	Rock	Alkalinity mg/l	pH	Conductivity μ S cm^{-1} at 25°C
Beanaidh Bheag	NH926029	470	8	Granite	5	6.20	22
*Allt Ruadh	NH859010	270	13	Granite	7	6.50	31
R. Nethy at Bynack Stable	NJ022105	440	17	(4 Moinian Association (13 Granite	9	6.50	35
*Allt Fhearnagan	NN851971	310	10	Granite/Till	9	6.55	34
*Allt Gabhiach	NN850953	350	7	(2 Granite (5 Monian Association	10	6.60	40
Caol Gleann	NJ151065	460	7	Granite Lime rich patches	10	6.70	38
Allt Dubh	NH867117	370	3	Granite/Till/Peat	12	6.35	49
Allt Madagain	NN649985	380	11	Pelitic Gneiss + Schist/Peat	13	6.65	42
Allt an t'Slugain Dhuibh	NH955201	320	7	Granite/Till/Peat	14	6.55	48
Allt Feith a'Mhoraire	NN468960	340	8	Granite/?Till(Part Forest)	14	6.75	46
Shesgnan Burn	NN433943	350	6	Granite/?Till	15	6.60	39
*Allt Coire Chaoil	NN847934	360	6	Moinian Association/Till	15	6.75	46
Allt Coire A'Bhein	NN514946	300	7	Moinian Association/?Till	15	6.90	42
Allt Coire Bhanain	NN433940	350	6	Granite/?Till (part forest)	16	6.60	40
R. Feshie	NN911881	470	31	(27 Moinian (Association/ (Diorite/Peat (4 Granite	16	6.80	44

Table 2 Potential Sites for SWAP Catchment Study

Catchment	Scores for the criteria defined in section 3					
Allt a' Mharcaidh	1	1	1	1	1	1
Bearnaidh Bheag	1	1	2	?	1	3
Allt Ruadh	1	1	1	3	1	3
R. Nethy at Bynack Stable	1	1	2	2	1	1
Allt Fhearnagan	1	2	1	2	1	2
Allt na Cuhaige	1	2	2	3	2	3
Allt Chriocaidh	1	2	2	2	1	3
Allt an t'Slugain Dhuibh	1	2	1	3	1	3

APPENDIX 2

FIELD AND LABORATORY MEASUREMENT OF PH IN LOW CONDUCTIVITY NATURAL WATERS

Field and Laboratory measurement of pH in low conductivity natural waters

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Introduction

The accurate measurement of pH is fundamental to most environmental and hydrogeological studies. Many mineral and ion exchange equilibria are controlled by acidity levels and establishment of saturation indices requires accuracies to within 0.1 pH units. Correspondingly, in studies of the impact of acidic deposition, accurate pH measurement of rainfall, surface runoff and unsaturated zone/ground water it is essential to establish the proton sources and sinks in the various hydrological pathways. Measurement of pH both in the field and laboratory almost universally involves electrode systems based on silver - silver chloride and calomel cells; these devices although convenient, inexpensive and portable are in many instances not sufficiently accurate for low conductivity waters such as rainfall and many upland streams. Numerous studies for biological and inorganic systems as well as inter laboratory comparisons have demonstrated this problem (Illingworth, 1981; Tyree, 1981; Mason, 1984, Covington et al, in press); hydrogen ion concentration discrepancies of up to an order of magnitude are observed even under laboratory conditions. Such inaccuracies will be exacerbated in the more testing environment of field measurement. Improved electrodes based on a free diffusion liquid junction and flowing sample are being designed (Covington et al, 1983, in press), however, these are not readily available and may not be suitable for field use.

A description of the sources of these errors is given and suggestions are made for pragmatic solutions to the problems encountered. It is concluded that a fresh approach to field and laboratory measurement of the pH of low conductivity waters is urgently needed.

Magnitude and Sources of Error

Laboratory and field studies have shown at least 4 major sources of error with pH measurement using Ag/Ag Cl and calomel electrodes. These studies have employed commonly used electrodes from various manufacturers to provide a limited, but representative, selection. The different types of error are described below, detailed results are described elsewhere in report form (Neal and Thomas in press)

(1) Different pH responses are obtained when different electrodes are used on low conductivity stream waters and dilute sulphuric acid solutions (even when ionic strength, buffers (KCℓ) are added). These differences show that while consistent results can be obtained by different workers using the same electrode (i.e. precision is high), major differences occur when different electrodes are used (i.e. accuracy is low). For example the pH of an upland stream water (Afon Hore) of low conductivity varied by up to 0.6 units, a 4 fold difference in hydrogen ion concentration, according to which of 6 electrodes were used. Correspondingly for a 10^{-4} N sulphuric acid solution the pH varied by 0.8 units, a 6 fold difference in hydrogen ion concentration (for 11 electrodes). Such variations are usually considered related to differences in the liquid junctions of the various electrodes used (Illingworth, 1981) although the glass electrode also does not behave "ideally" (Covington et al, in press); all the electrodes were calibrated satisfactorily using standard NBS buffers; i.e. the Nernst response (electrode efficiency) lay between 95 and 100% and results were independent of the meters used and the analysts.

(2) The electrode response time varied according to the particular electrode used and its storage history. For example stable readings were achieved more slowly, for most of the electrodes tested, when the electrode was transferred from buffer to low conductivity waters. Transferring subsequently from low conductivity to other low conductivity waters, decreased the time to achieve a stable value. Stable readings, in several cases, took over 1 hour to achieve when the previous solution was a buffer although in some cases reaction times were of the order of minutes. Errors incurred due to unstable readings could amount to 0.6 pH. This effect probably relates to contamination/ diffusion in the electrode's porous plug (liquid junction).

(3) Differences in temperature between sample, buffer and electrode introduced discrepancies of up to 0.7 pH for a temperature range 6 to 16°C even after temperature compensation although response

varied according to the individual low conductivity water analysed. For example, Afon Hore stream water at field temperature (9°C) gave a pH of 4.9, at 6°C this value was reduced to 4.4 and at 16°C it was increased to 5.1, the electrodes and buffers being at 16°C in the first instance. Analogous discrepancies were observed in the field as the electrode cooled to the temperature of the stream. One possible source of these differences is the slow precipitation or solution of KCl in the reference electrode.

(4) Errors associated with stirring the sample during pH measurement can give systematic errors of up to 0.5 pH with the stirred values being lower. This phenomenon is commonly assumed to be associated with streaming potential and has been described previously (Bates, 1973). While adding an ionic strength buffer (0.02 N KCl) stabilised the readings, the large inter-electrode variations in values remained.

Discussion

Given these results, informal comments made by other workers at several meetings, the results of Illingworth (1981) and interlaboratory studies (Tyree, 1981; Mason, 1984), major problems exist in pH measurement of low conductivity waters. For example, the typical pH measurement errors observed (0.5 pH) would make correlation of fish mortality, from laboratory studies, to lake acidity (Record et al, 1982; Mason, 1984; Howells et al. 1984) very difficult. The great variation in the techniques of pH measurement and in the equipment used by the various laboratories casts doubts upon the accuracy of the quoted pH values in the literature notwithstanding the precision of the various sets of data. This is of profound importance to the establishment of multinational/multidisciplinary studies planned for the near future on acidic deposition, as well as to the interpretation of historical data on acidity.

In the absence of a definitive solution to the problem several possible pragmatic alternatives can enhance the reproducibility of measurement. These include (i) the introduction of new electrodes (Covington et al, 1983) for laboratory use which avoid the liquid junction potential problem, (ii) new calibration solutions more representative of the samples under investigation (Galloway and Cosby, 1979), (iii) the addition of an inert electrolyte to increase the conductivity of the samples near to that of the electrode filling solution (Whitfield, 1971), to reduce the stirring effect (iv) pH measurement should be made under isothermal conditions with buffer solutions, electrodes used and waters collected being at field temperature, (v) where several groups measure acidity for the same project/location a thorough intercomparison under working conditions is required, (vi) the standard approach to acceptance of an electrode, ie the gradient of the Nernst Slope, is inappropriate and should be changed to include measurements of dilute mineral acids of known pH. This final alternative should also be incorporated into manufacturer's electrode specification.

Whatever the intermediate solution adopted, the introduction of a universally applied standardised method using electrodes which have been shown to provide reproducible results is imperative.

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APPENDIX 3

A TIME SERIES APPROACH TO MODELLING STREAM ACIDITY

1. INTRODUCTION

In recent years acid rain has had significant effects on water quality in North American, Scandinavian and European rivers, lakes and reservoirs. Extensive research has been conducted on individual processes affecting acidity (e.g. interception, rock weathering, soil chemistry) and there is now a need to study the integrated process behaviour at the catchment scale. Studies in the USA and Norway have shown that descriptive mathematical models can be developed successfully given a suitable data base. Such models provide an understanding of the interactions between chemical and hydrological processes and in the future may allow realistic predictions to be made of the long term acidity of catchments, the possible effects of land use change and the short term acute effects such as acidity associated with snowmelt.

2. MODELLING PROCEDURES

Physical, chemical and biological components all affect the behaviour of catchment runoff water quality and it is not surprising that a wide range of models have been developed to predict stream acidity. A summary of the approaches that may be used in such circumstances is given in Figure 1 which shows the two ingredients necessary for a suitable model. Firstly, a knowledge of the theoretical behaviour is required so that the correct principles can be incorporated. Secondly experimental or field data are required to calibrate and validate the models. Models vary according to the degree to which theoretical information is included and the extent to which data are used to derive or estimate model parameters.

A conventional approach is to use physical, chemical and biological theories to derive partial differential equation descriptions of the system under investigation. These models are likely to be non-linear and although they represent the best information available on the system behaviour they are certainly not perfect representations. For example the heterogeneous nature of a catchment both chemically and hydrologically defies precise mathematical representation, or the constantly changing shape of a river bed cannot be reproduced precisely in a mathematical form. Moreover, the solution of partial differential equations is particularly difficult requiring finite difference or finite element approximations. Such approximations may introduce numerical dispersion unless extreme care is taken and thus even computer solutions may

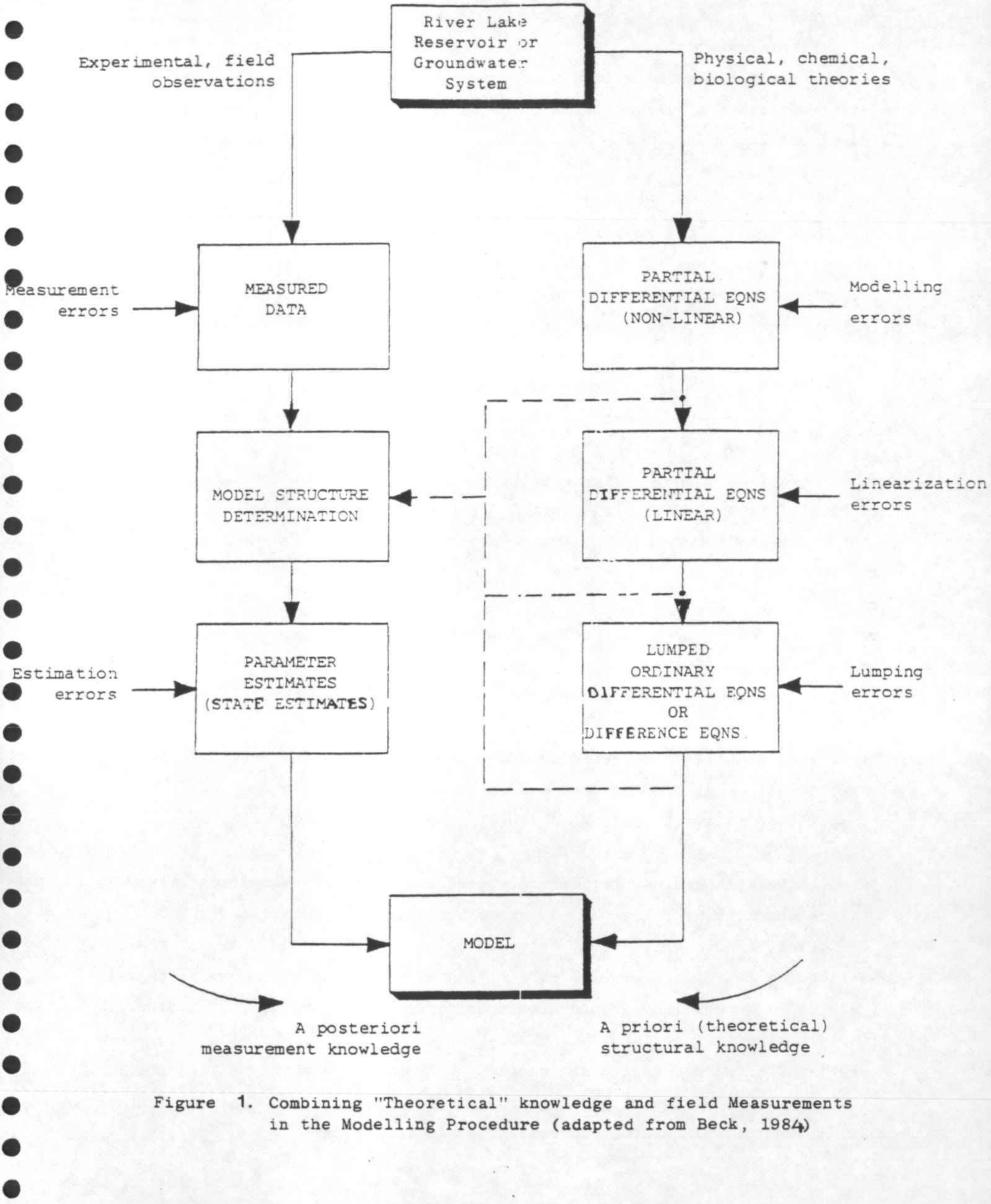


Figure 1. Combining "Theoretical" knowledge and field Measurements in the Modelling Procedure (adapted from Beck, 1984)

not accurately portray the behaviour represented by the model equations. Nevertheless some of the most advanced modelling research has resulted in partial differential equation descriptions (Lam and Simons 1982) and these may become available as modelling packages. Users not familiar with the difficulties of numerical integration techniques may however be mislead by the model results.

An approach which avoids solution problems of this type is to linearize the equations. This approach produces sensible solutions provided the system is not changing rapidly or has not moved away from the linearization range (when linearization errors become large). Another simplified approach is to develop ordinary differential equation models (Christophersen et. al., 1982 and Cosby et. al., 1984). In order to use these approaches, assumptions are made to lump system characteristics or parameters. Thus a catchment may be segmented into compartments and soil characteristics are assumed to apply uniformly over a compartment. The advantage of this approach is that the model equations can be solved with relative ease and the model parameters determined by calibration against field data. The disadvantage is that errors may be introduced by the lumping of system characteristics. However, provided care is taken this simplified modelling approach is often very productive.

The other source of information required for model development is experimental or field data with which to calibrate and validate models. Sampling errors and laboratory analysis errors are common (Whitehead et. al., 1981, UNESCO report, 1978) and these should always be considered in any modelling study. Thus expending considerable computation effort in solving partial differential equations may be totally inappropriate if there is insufficient accurate data to calibrate the model.

Recently there has been research conducted on the estimation of model parameters from hydrological and water quality field data (Beck and Young, 1976, Whitehead, 1979, 1980, Whitehead et. al., 1979, 1981, 1984). These estimation techniques provide an efficient means of analysing water quality data and although lumped parameter models are generally used in combination with these techniques, the joint approach represents an efficient procedure, drawing the maximum degree of information from the data whilst incorporating theoretical knowledge of process behaviour. It is the application of these estimation techniques that is considered in this paper.

3. TIME SERIES MODELLING TECHNIQUES

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.

The single-input single-output black-box model as shown in Figure 2, is specified by a linear stochastic difference equation of the form:

$$y_k = [B(z^{-1})/A(z^{-1})]u_k + [D(z^{-1})/C(z^{-1})]e_k \qquad (1)$$

where u_k and y_k represent the input (flow) and output (hydrogen ions) time series at time k; z^{-1} is a backward shift operator, $(x_k z^{-1} = x_{k-1})$; e_k is a zero mean serially uncorrelated sequence of random variables with variance σ^2 (discrete white noise), i.e. $E(e_k) = 0$, and:

$$E(e_k e_k) = \sigma^2 \delta_{jk} \text{ with } \delta_{jk} = \begin{cases} 1, & j = k \\ 0, & j = k \end{cases} \qquad (2)$$

e_k is also assumed independent of the deterministic input. In addition, A, B, C and D are polynomials in z^{-1} of order n, i.e.:

$$\begin{aligned} A(z^{-1}) &= 1 + a_1 z^{-1} + a_2 z^{-2} + \ldots + a_n z^{-n} \\ B(z^{-1}) &= b_0 + b_1 z^{-1} + b_2 z^{-2} + \ldots + b_n z^{-n} \\ C(z^{-1}) &= 1 + c_1 z^{-1} + c_2 z^{-2} + \ldots + c_n z^{-n} \\ D(z^{-1}) &= 1 + d_1 z^{-1} + d_2 z^{-2} + \ldots + d_n z^{-n} \end{aligned} \qquad (3)$$

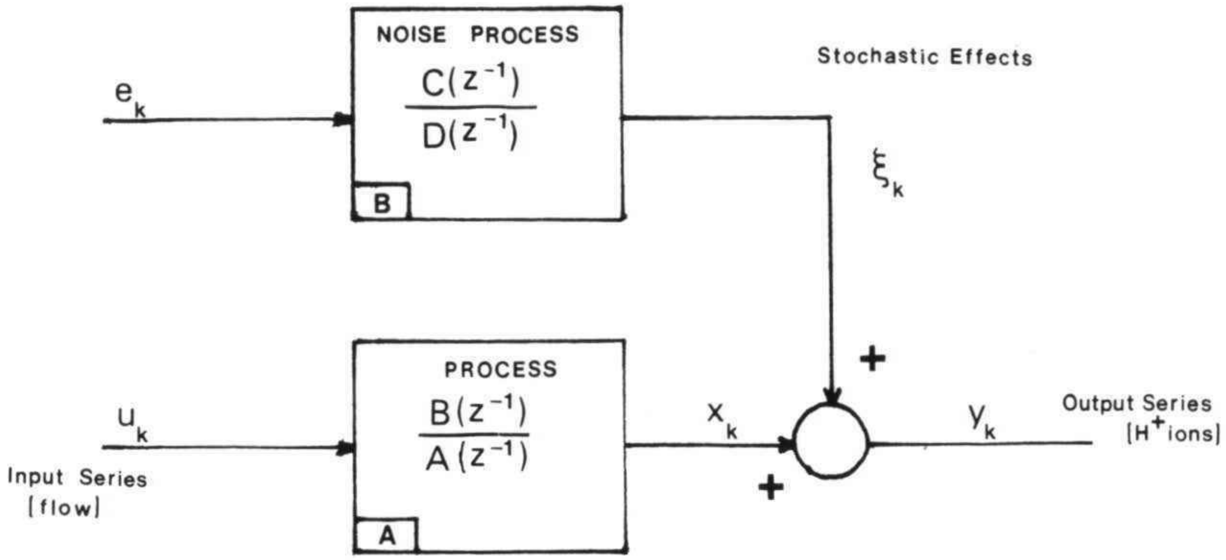


Fig 2. Input-Output time-series model

Eq.1 constitutes therefore a model of the deterministic and stochastic aspects of the system in which the past history of the input - output data provides some degree of model structure.

There are several techniques for estimating model parameters; for example Box and Jenkins (1970) utilised an optimization procedure. In the present approach, the parameters characterising the deterministic or process time-series model, a and b, are estimated using a recursive instrumental variable approximate maximum likelihood (recursive IVAML) procedure in which the parameter estimates are updated a sample at a time while working serially through the data (Young et. al., 1971).

The instrumental variable (IV) procedure for estimating the unknown parameters a and b requires that the system equation is first written in the following alternative vector form:

$$y_k = \underline{z}_k^T\underline{a} + \eta_k \qquad (4)$$

where

$$\underline{z}_k^T = (-y_{k-1}, \ldots, -y_{k-n}, u_k, \ldots, u_{k-n})$$

$$\underline{a}^T = (a_1, \ldots, a_n, b_0, \ldots, b_n) \qquad (5)$$

$$n_k = a_1\xi_{k-1} + \ldots + a_n\xi_{k-n} + \xi_k$$

The IV estimate $\hat{a}_k$ of a at the kth instant is then given by the recursive IV algorithm:

$$\hat{a}_k = \hat{a}_{k-1} - \hat{P}_{k-1}\,\hat{x}_k\,[z_k^T\hat{P}_{k-1}\,\hat{x}_k + 1]^{-1}\,\{z_k^T\,\hat{a}_{k-1} - y_k\}$$

$$\hat{P}_k = \hat{P}_{k-1} - \hat{P}_{k-1}\,\hat{x}_k[z_k^T\hat{P}_{k-1}\hat{x}_k + 1]^{-1}\,z_k^T\,\hat{P}_{k-1} \qquad (6)$$

where $\hat{x}_k^T = (-\hat{x}_{k-1}, \ldots, -\hat{x}_{k-n}, u_k, \ldots, u_{k-n})$ is a vector of instrumental variables generated by the "auxiliary" model:

$$\hat{A}(z^{-1})x_k = \hat{B}(z^{-1})u_k \qquad (7)$$

where

$$\begin{aligned} \hat{A}(z^{-1}) &= 1 + \hat{a}_1 z^{-1} + \ldots + \hat{a}_n z^{-n} \\ \hat{B}(z^{-1}) &= \hat{b}_0 + \hat{b}_1 z^{-1} + \ldots + \hat{b}_n z^{-n} \end{aligned} \qquad (8)$$

The choice of the a priori estimates required by the auxiliary model can be based upon either physical knowledge of the system obtained from prior identification studies, or from the biased least-squares estimates obtained in an initial estimation run. As the estimation improves the auxiliary model is updated in order to enhance the quality of the IV vector and so improve the statistical efficiency of the estimates. This updating can be carried out in one of two ways. Firstly the recursive estimates can be used as the basis for continuous updating of the auxiliary model parameters. Secondly an off-line iterative procedure can be used in which there are repeated runs through the block of data with the auxiliary-model estimates updated only after each run is finished. This iterative procedure is considered complete when further iteration yields negligible change in the estimates. Both approaches are described in detail elsewhere (Young et. al., 1971; Young, 1974) but, not surprisingly, experience has shown that the iterative method is able to "refine" the estimates and yield superior estimation performance, particularly in applications where there is a relative paucity of data.

While the iterative scheme provides final "refined" estimates it is the recursive aspects of the algorithm which are of particular importance during the model identification stage. Here an additional degree of flexibility is required to allow explicitly for the estimation of possible parametric change over the observational interval.

The recursive IVAML algorithm has been incorporated into a time series analysis computer program package (Shellswell, and Young 1973; Mutch and Whitehead, 1976; Venn and Day, 1977), and has been applied to the modelling of water quality data for several systems (Whitehead and O'Connell, 1984).

The time series techniques have been extended to estimate multi-variable systems (Young and Whitehead, 1977; Jakeman and Young, 1979) and applied to water quality problems. Such models are relevant in this study because of the complexity of catchment chemistry and hydrological behaviour.

The model has the following discrete time state-space representation of a multi-variable (multi-input multi-output), linear dynamic system:

$$x_k = Ax_{k-1} + Bu_k \qquad (9)$$

where $x_k = (x_{1,k}x_{2,k}\cdot\cdot x_{n,k})^T$ is an n-dimensional vector of state variables that characterise the system at the kth instant of time. $u_k = (u_{1,k}u_{2,k}\cdots u_{m,k})^T$ is an m-dimensional vector of deterministic input variables, also sampled at the kth time instant, while A and B are, respectively, n x n and n x m matrices with elements:

$$a_{ij}\ (i,\ j = 1,2,\ \ldots,\ n) \text{ and } b_{ij}(i = 1,2,\ \ldots,\ n; j = 1,2,\ \ldots,\ m)$$

As in the case of the single input - single output case a recursive I.V. algorithm may be used to estimate the model parameters (Young and Whitehead, 1977, Jakeman and Young, 1979).

4. CATCHMENTS STUDIES

The data used in the present modelling studies have been obtained from three principal catchment areas, Loch Dee in South West Scotland, Birkenes catchment in Southern Norway, and Plynlimon in Mid Wales.

Loch Dee

Loch Dee has a remote setting in the Galloway Hills in South West Scotland (see Figure 3). The catchment is made up of three sub-basins: the Dargall Lane to the west, the White Laggan Burn with its tributary the Black Laggan towards

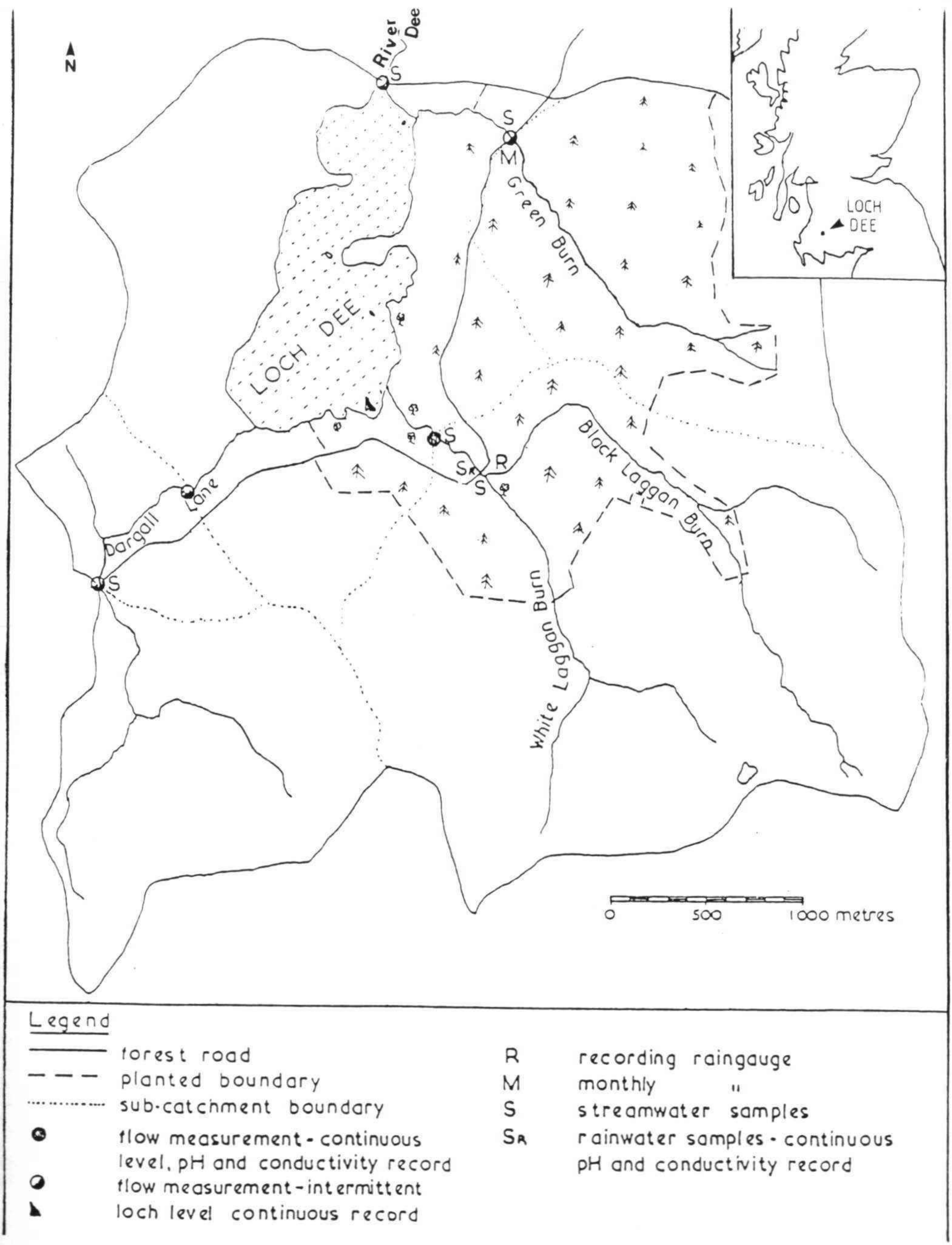


Fig3. LOCH DEE CATCHMENT

the south, and the Green Burn entering from the south east. The outflow at the north east end of the loch is the source of the River Dee and up to this point the catchment has an area of 15.6 km^2 of which the loch surface itself occupies 1.0 km^2. 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 (1000 ft). Geologically the area comprises two distinct rock types: Ordovician greywackes/shales and granites of Old Red Sandstone Age (Loch Dee Report, 1982).

The climate in this region is cool and wet. Annual rainfall averages 2200 mm and monthly falls of less than 25 mm are rare. Night frosts are common throughout the year. Based on a daily mean temperature threshold value of 6°C the growing season varies between 220 days at the loch side to 150 on the high ground where little growth can be expected before the end of May.

Birkenes

The southern area of Norway is severely affected by acid precipitation, acidification of surface waters and loss of fish population. In the Birkenes catchment (Figure 4) precipitation and runoff flow and chemistry have been measured in detail since 1972 with the aim of describing and quantifying the chemistry of acidified waters (Christophersen et. al., 1982, 1984).

Birkenes lies at 200 - 300 m above sea level about 15 km north of Kristiansand, near the southernmost tip of Norway. The 0.41 km^2 catchment is semi-circular in shape and drained by two first-order streams that combine to form a second-order stream 150 m above the catchment outflow weir. Relief is up to 100 m over 600 m distance with granitic outcrops on the ridge tops and moraine or peat deposits in the low lying areas. The vegetation is characterized by mixed coniferous forest, and about half the catchment has a soil depth less than 20 cm.

Plynlimon

The Plynlimon study area lies in mid-Wales, (Figure 5), and consists of two sub-catchments, the upper Wye catchment and the upper Severn catchment. The Wye catchment is used for sheep grazing and the Severn catchment has been extensively forested with spruce and larch from 1930 onwards. These two

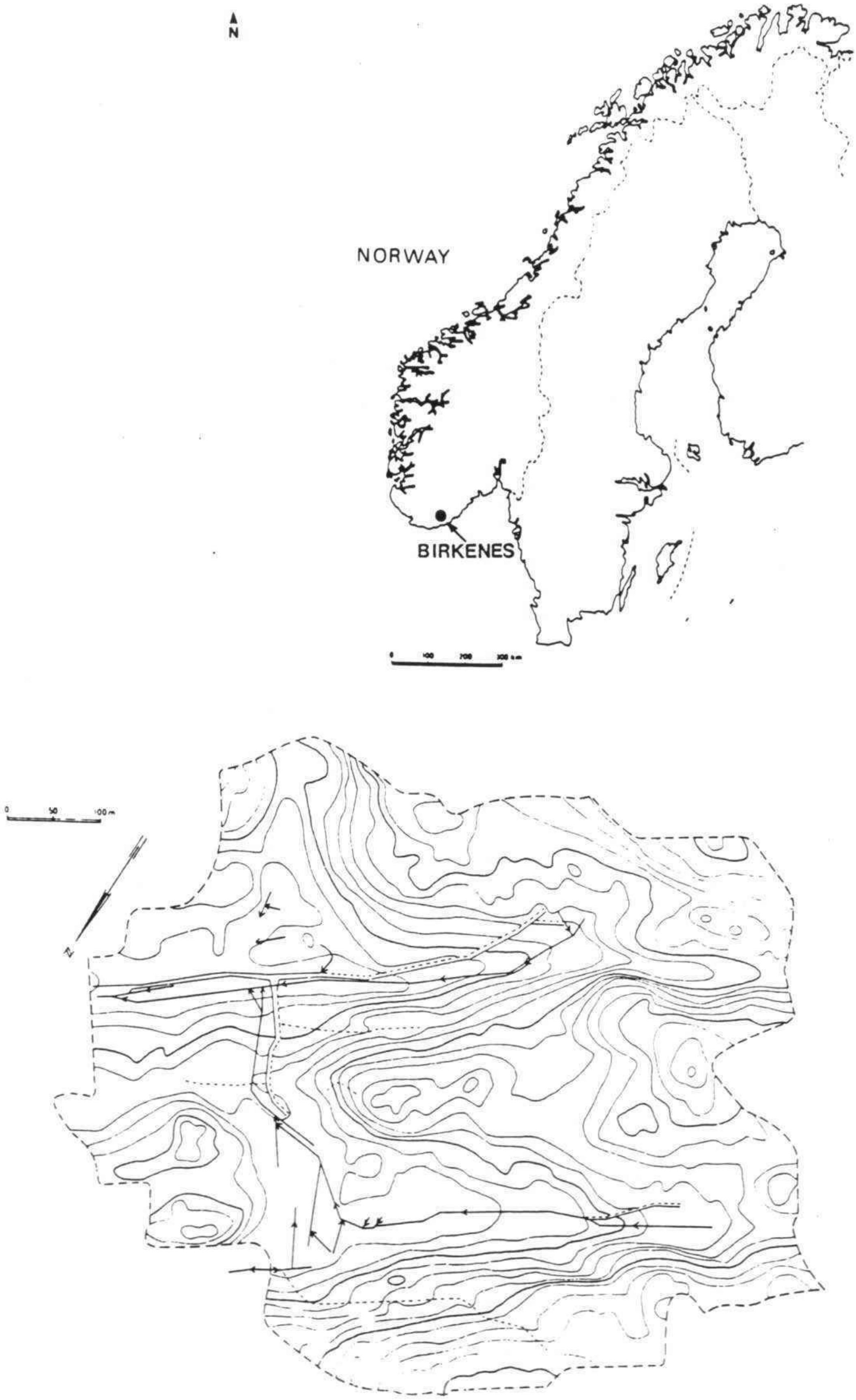


Fig 4. Birkenes Catchment, Norway.

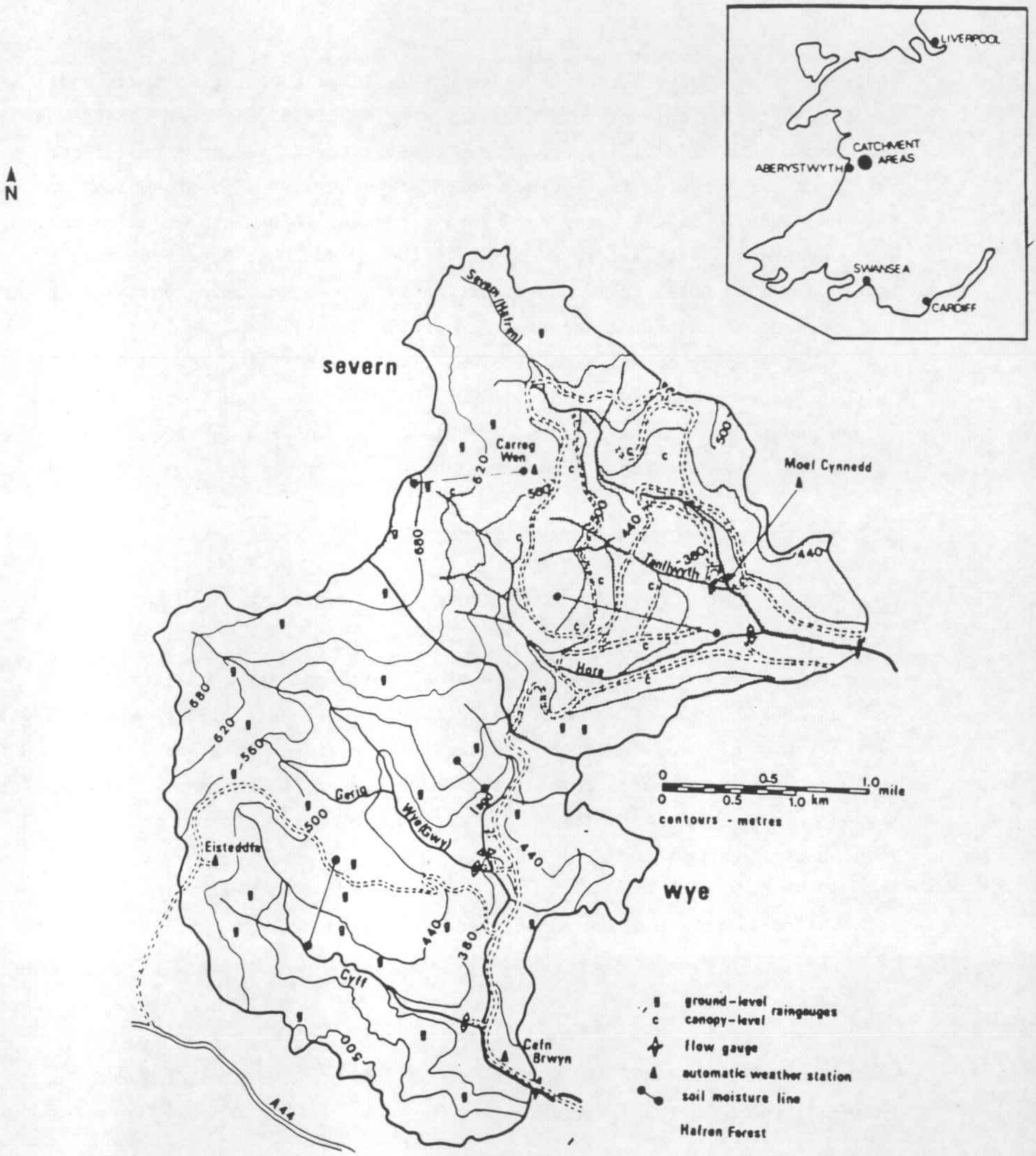


Fig 5. The Severn and Wye Experimental Catchments, Plynlimon.

different land uses provide the basis for an ideal comparative study and detailed hydrological and water quality data has been collected for the past ten years. The wide variety of stream acidity for different parts of the catchment is reflected in Figure 6 which shows how the pH varies with land use (Newson, 1984). In the forested Severn catchment (Afor Hore and Afon Hafren) storm events generate acidic runoff. In the grassed Wye catchment acidity levels are much more stable and higher in value due to liming of the land and the presence of calcium carbonate rich sediments derived from lead mining. However, this part of Wales is also subject to significant loads of deposited sulphur (Barrett and Irwin, 1984) in which 30% of the load is of non-marine origin and it is to assess and model this aspect and the interaction with the forest that we are primarily concerned here.

5. TIME SERIES ANALYSIS OF CATCHMENT DATA

Loch Dee

In Loch Dee an extensive record of hydrological water quality data has been collected over a five year period (Loch Dee Project, 1982, Langan, 1984). Our 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 (Langan, 1984).

The model fitted is an autoregressive moving average type of the form

$$x_k = -a_1 x_{k-1} + b_0 u_k \tag{10}$$

where x_k is the hydrogen ion concentration ($\mu eq\, l^{-1}$) and u_k is the flow ($m^3 sec^{-1}$) in the stream at time k.

The parameters a_1 and b_0 were estimated using the time series algorithm referred to previously and applied to 200 **hourly** observations of pH and flow. The parameters were estimated to be;

$a_1 = -0.680$

$b_0 = 0.659$

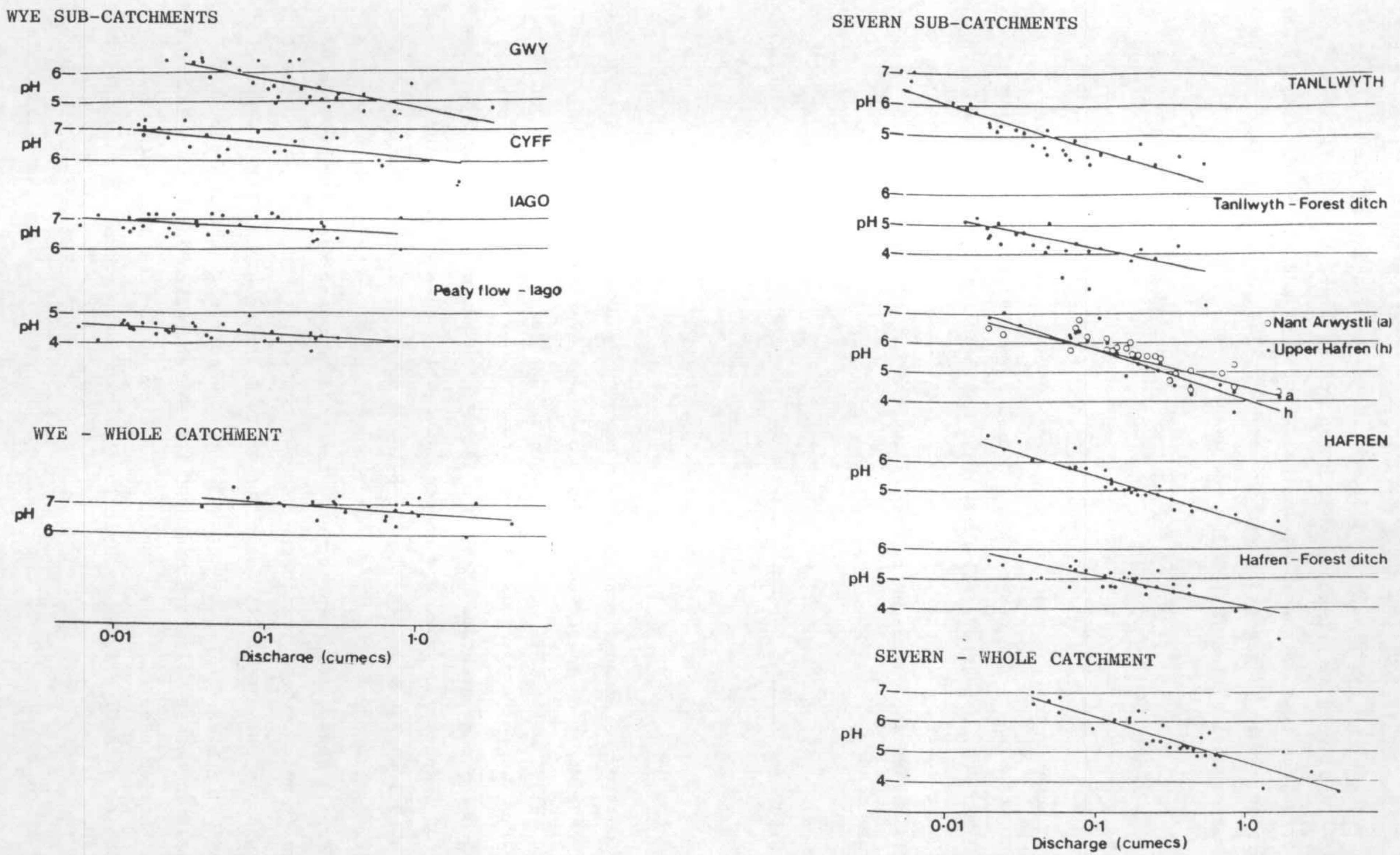


Fig.6 pH-flow relationships in the Severn and Wye Catchments (from Newson, 1984).

and Figure 7 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; data is currently being collected for this purpose. The model suggests that there is a mean response time (T) of 2.6 hrs where

$$T = -\frac{1}{\ln(-a_1)} \tag{11}$$

In other words the mean response time between flow and hydrogen concentration is of the order of 2.6 hours, a very short period of time. (N.B. This does not necessarily mean that the mean residence time is on such a short time scale; it merely reflects the fast response time between output flow and hydrogen ion concentration). The gain of the system can be determined as

$$\text{Gain} = \frac{b_o}{1 + a_1} = \frac{0.659}{1 - 0.68} \tag{12}$$

$$= 2.06$$

In other words an increase of 1 $m^3 sec^{-1}$ (or cumec) in flow is associated with aconcentration increase of 2.06 μeq ℓ^{-1} of hydrogen ions in the stream water. Thus using this model and assuming buffering reactions do not affect the relationship, a major storm of 50 cumecs would be required to increase the hydrogen ion concentration above 100 μeq ℓ^{-1} (ie below a pH of 4). However flows of 5 cumecs and more are common, suggesting that hydrogen ion concentrations above 10 μeq ℓ^{-1} (ie below a pH of 5) will be frequent.

From a management point of view the model demonstrates that even a very simple dynamic representation can be used to predict hydrogen ion concentration and supports the view that, for the relatively homogeneous White Laggan catchment, a simple hydrological model should suffice. (N.B. Although the good correlation between flow and hydrogen ion concentration has been obtained this should not be used to imply causality. It cannot be deduced that stream acidity is directly caused by hydrological processes rather than by pollutant inputs.)

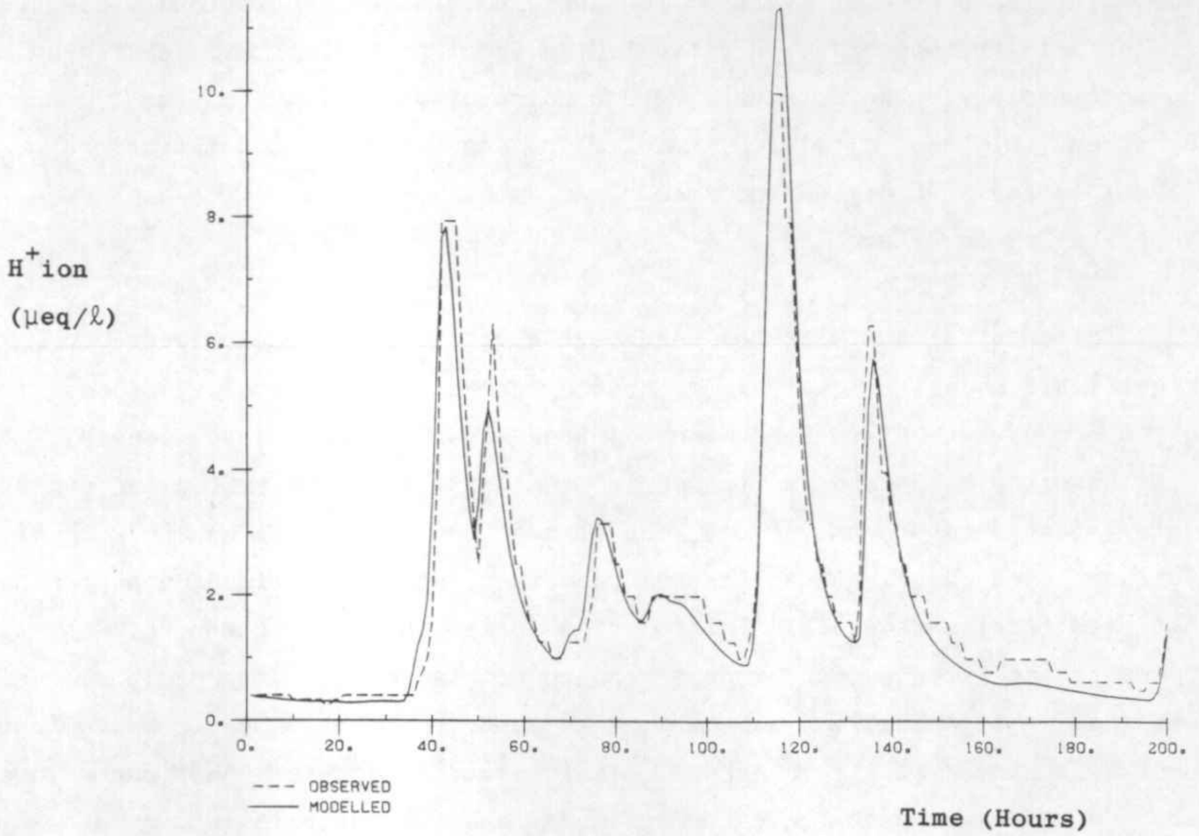


Fig.7. Simulated and Observed H^+ ion in the White Laggan, Loch Dee, Scotland, based on the Flow model.

Birkenes

In the case of Birkenes the aim of the modelling from a management viewpoint is to predict hydrogen ion and aluminium concentrations since these are of primary importance in establishing the impact of stream acidity on aquatic ecology. The data used here consist of **daily** flow (m^3 sec^{-1}) and hydrogen, sulphate, aluminium, calcium and magnesium ion concentrations (μeq ℓ^{-1}) for a 90 day period from
September to November, 1974.

The data for the Birkenes Catchment have already been subjected to significant modelling analysis. Christophersen et. al. (1982, 1984) developed a two compartment hydrochemical model based on the mobile anion concept. Early work has also been done on time series analysis of precipitation and runoff data (Skööppa and Mohn, 1975). The current analysis draws on the work of Christophesen et al. but again uses the times series optimization approach to estimate model parameters. Initial time series analysis showed that the flow peaks in the Birkenes Catchment introduce highly non-linear behaviour. In order to achieve stable parameter values these peaks have been removed in our analysis using a simple threshold. It is assumed therefore that peak flows above 7 mm/day by-pass the catchment model and take no part in the water quality reactions; hydrogen ion concentration is therefore a function of the remaining flow moving through different flow pathways. This reflects the observation that hydrogen ion release is limited on high flow.

As in the case of Loch Dee a time series model of the form of equation (10) was fitted to the data initially. The response (Figure 8) indicates that again the model output follows the observed hydrogen ion concentration although the model fit is generally not as good as the Loch Dee model with only 64.9% of variance being explained by the model. Of particular interest is that the model does not reproduce the first flush of hydrogen ions following the first storm event. This is reflected in the parameter estimates for b which shows a significant rise in this period (see Figure 9), and consequently it is necessary to modify the model to incorporate the sulphate component. Figure 10 shows the effect of including sulphate in the model. The estimate equation in this case is;

$$x_k = 0.45 \; x_{k-1} + 2.62 \; u_{1,k} + 0.045 \; u_{2,k}$$

where $u_{1,k}$ and $u_{2,k}$ refer to flow and sulphate respectively at time k. The effect of including sulphate is now to reproduce the flushing effect. However, the recession part of the response is still inadequately modelled.

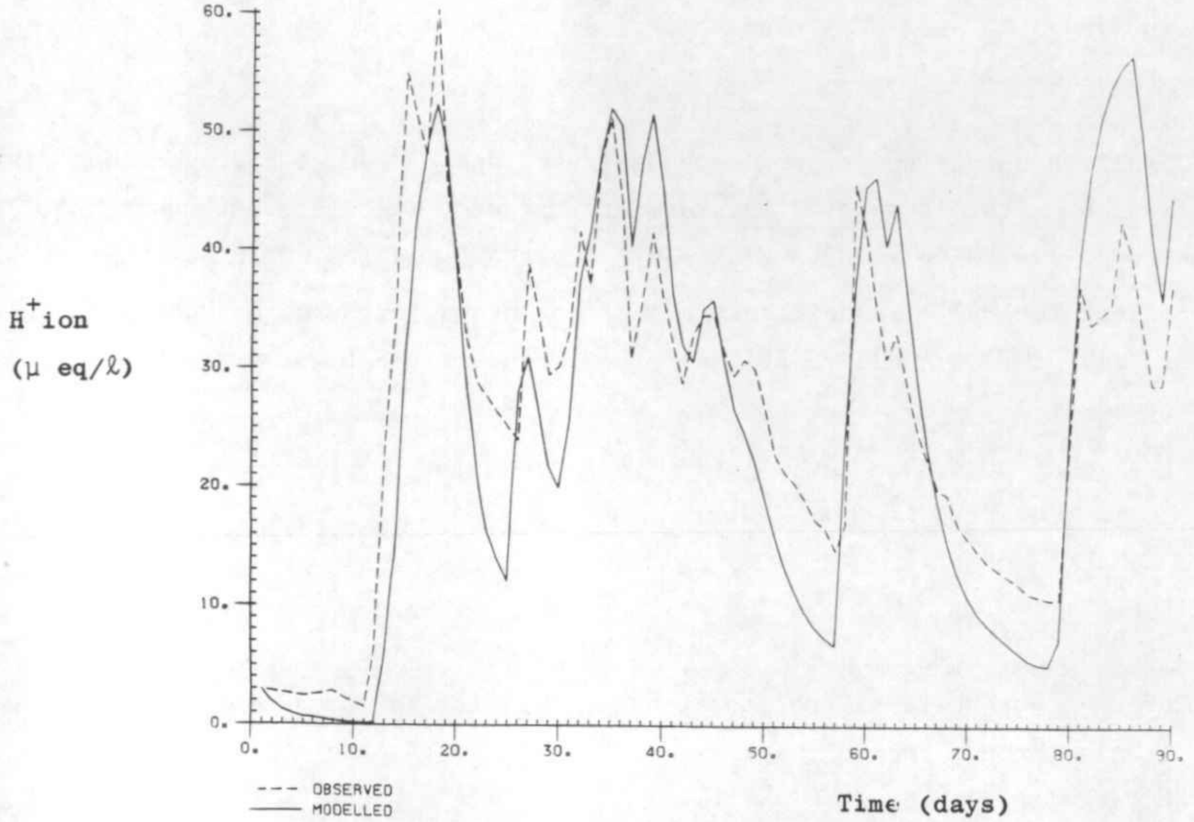


Fig.8. Simulated and Observed H$^+$ion in the Birkenes Catchment, Norway, based on the Flow model.

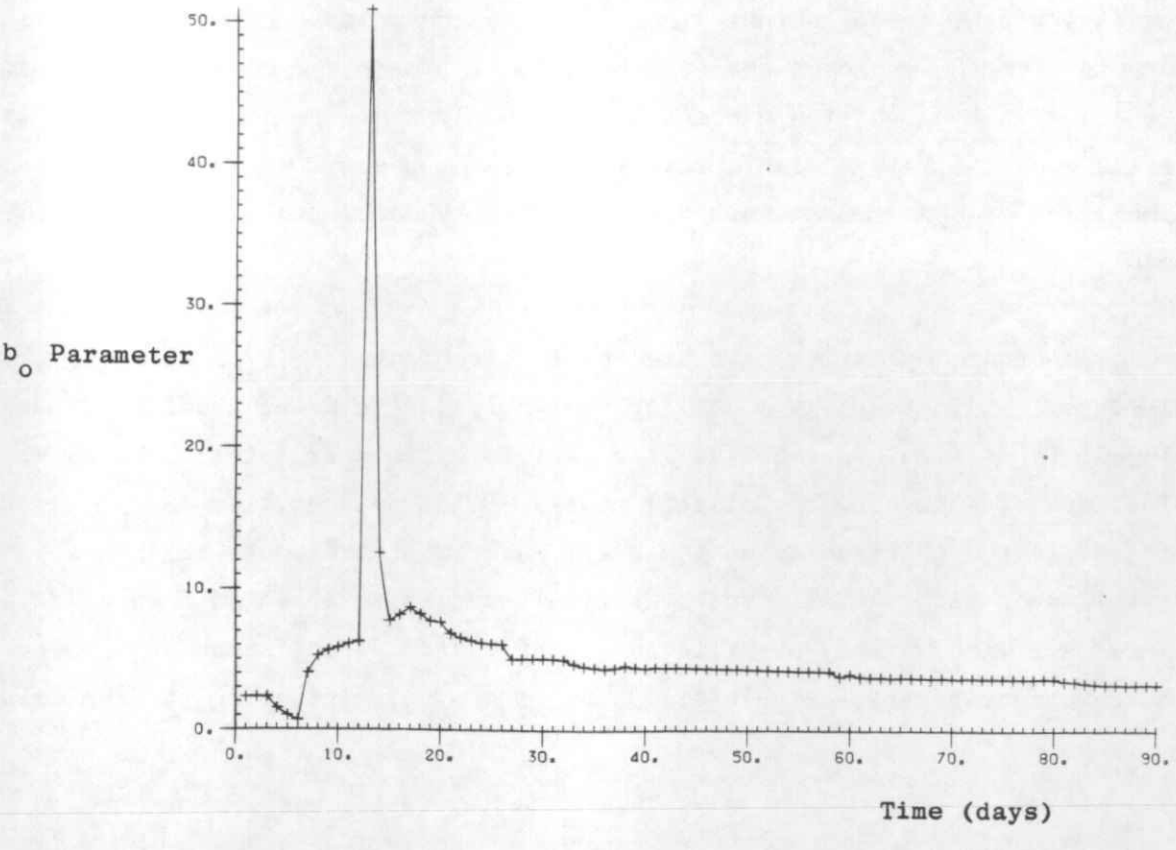


Fig.9. b_o Parameter from the Flow model.

This is possibly due to ion exchange reactions, in which hydrogen ions displace divalent metal ions (M^{2+}) on sediment surfaces, which are not taken into account i.e. $NIC_M + 2H^+ \rightleftharpoons NIC_H + M^{2+}$ where NIC_M is the notional interfacial content for M^{2+} of a soil particle - analogous to the term 'adsorbed' (cf Neal et. al., 1982). This relationship can be described by an exchange constant where

$$K = \frac{NIC_H \left[M^{2+}\right]}{NIC_M \left[H^+\right]^2}. \qquad (14)$$

For the case where the cation exchange capacity is large compared with the flux of ions through the soil system $\sqrt{[M^{2+}]} \propto [H]$. Incorporating this factor into the model gave

$$x_k = 0.38\, x_{k-1} + 2.38\, u_{1,k} + 0.13\, u_{2,k} - 1.12\, u_{3,k} \qquad (15)$$

where $u_3 = \sqrt{M^{2+}}$ and the model response is now close to the observed hydrogen ion concentration (see Figure 11). The estimated coefficient on $\sqrt{M^{2+}}$ is - 1.12 suggesting that hydrogen ions are removed by the release of Ca and Mg and this fits in with the expected chemical behaviour. The observed model now predicts the observed hydrogen ion concentration closely and consequently the time series model, albeit a simple representation of the system, gives an adequate simulation of system behaviour with 92.4% of the variance explained by the model.

The other key variable to predict in catchment acidity studies is aluminium. Unfortunately modelling the variation in water chemistry of this element is difficult due to the wide variety of complex species (hydroxy, fluoride, organic etc. cf Driscoll et.al. 1984; Seip et.al., 1984) present in the pH range of most natural waters. For example the pH relationship with the Al^{3+} and hydroxy Al species is shown in Figure 12. Also, there is a wide variety of silicate and hydroxide parent/secondary minerals in the catchment capable of releasing aluminium or precipitating it from solution.

However assuming aluminium solution, precipitation can be described for time series modelling purposes by general reactions of the type

$$3H^+ + \text{Solid}_1 \rightleftharpoons \text{Solid}_2 + Al^{3+} + xH_2O \pm SiO_2$$

$$3H^+ + \text{Solid}_1 \rightleftharpoons Al^{3+} + xH_2O \pm SiO_2 \qquad (16)$$

where silica concentrations are buffered in solution, eg by quartz solubility, an equilibrium equation can be derived such that

$Al(OH)_3 + 3H^+ \rightarrow Al^{3+} + 3H_2O$

$$K = \frac{[Al^{3+}]}{[H^+]^3} \quad (= 10^{8.1}) \quad \text{(cf Christophersen et. al., 1984 for gibbsite solubility)} \qquad (17)$$

Given that aluminium is complexed in natural waters,

$$\text{Total Aluminium} = Al^{3+} + Al(OH)^{2+} + Al(OH)_2^{+} + Al(OH)_4^{-} + \Sigma Al_x$$

where ΣAl_x is the sum of the non hydroxy aluminium complexes (in the case presented here this is mainly for organo and fluoride-aluminium complexes). Also since the chemical and thermodynamic data available is very limited, as a first approximation, ΣAl_x is taken as independent of pH and aluminium concentration. Thus

$$\text{Total aluminium} - \Sigma Al_x = Al^{3+}\left\{1 + \frac{k_1}{[H^+]} + \frac{k_2}{[H^+]^2} + \frac{k_3}{[H^+]^4}\right\} \qquad (18)$$

where k_1, k_2, k_3 are equilibrium constants for the reactions

Gibbsite [illegible] $Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$

$$Al^{3+} + H_2O \rightleftharpoons Al(OH)^{2+} + 2H^+ \qquad \text{so } k_1 = \frac{[Al(OH)^{2+}][}{[H^+]}$$

$$Al^{3+} + 2H_2O \rightleftharpoons Al(OH)_2^{+} + 2H^+ \qquad (19)$$

$$Al^{3+} + 4H_2O \rightleftharpoons Al(OH)_4^{-} + 4H^+$$

Rearranging the above equations and incorporating values for k_1, k_2, k_3 provided by Truesdell and Jones (1974) gives

15.76 ?

$$(\text{Total Aluminium} - \Sigma Al_x) = b_o \{10^{-18}[H^+]^3 + 10^{-17}[H^+]^2 + 10^{-15\ 76}[H^+] + 10^{-16\ 1}[H^+]^{-1}\}$$

$$= b_o\, f[H^+]$$

16.1 ?

where hydrogen ion concentrations are given in μeq l^{-1}.

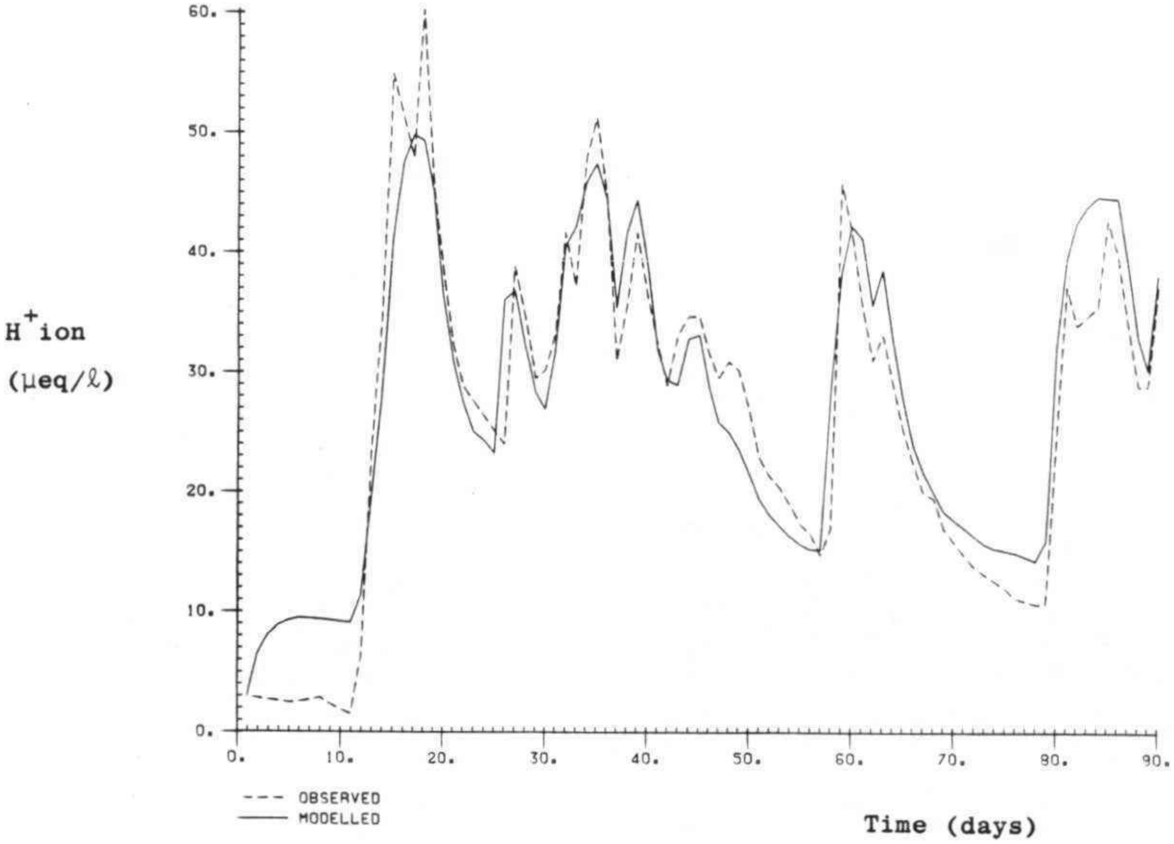


Fig.10. Simulated and Observed H^+ion in the Birkenes Catchment, Norway, based on the Flow and Sulphate model.

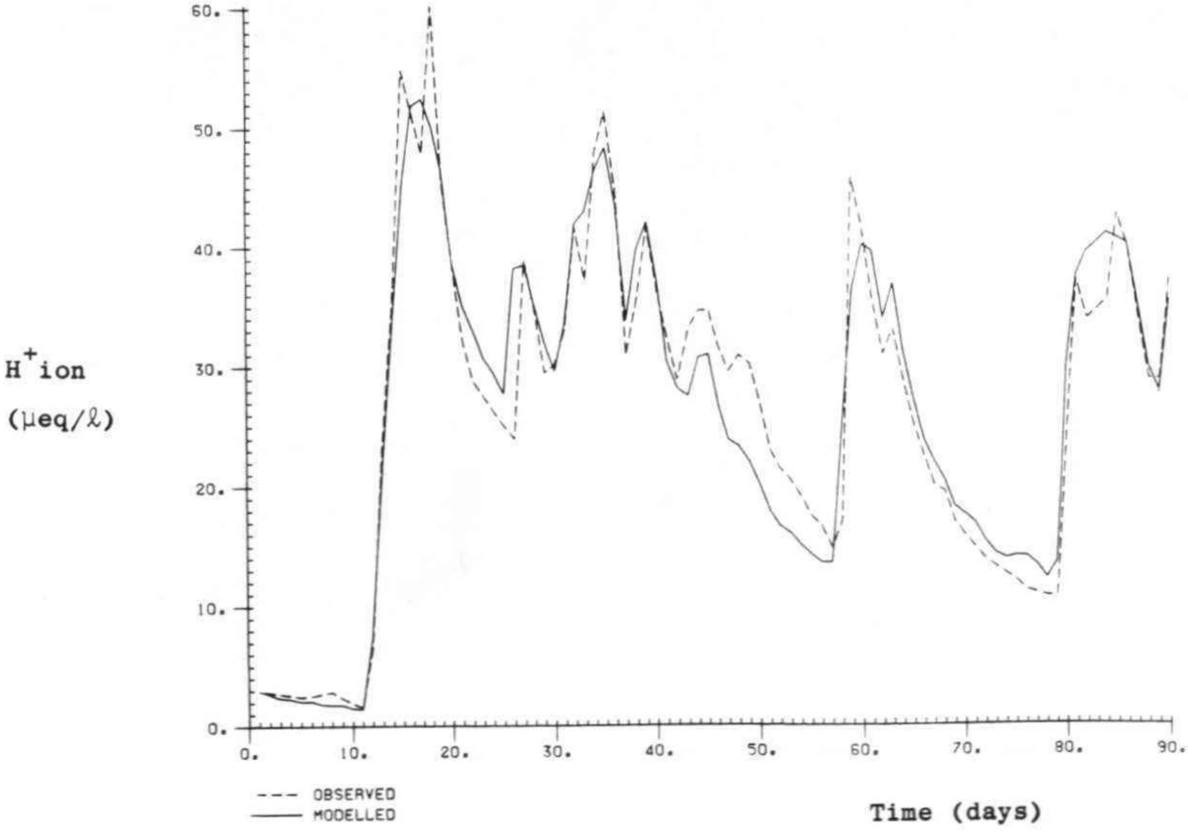
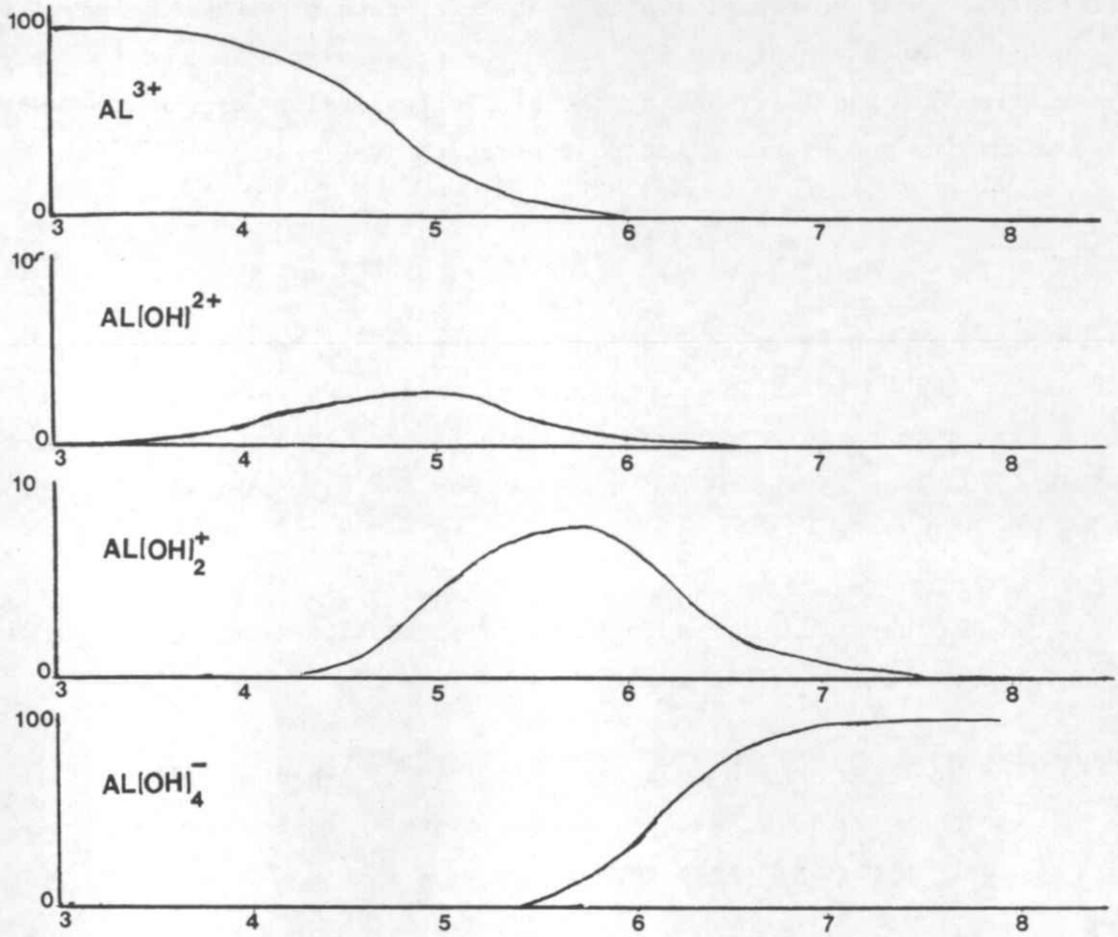


Fig.11. Simulated and Observed H^+ion in the Birkenes Catchment, Norway, based on the Flow, Sulphate and $\sqrt{M^{2+}}$



[Data of Truesdell and Jones, activities of ion taken as unity]

Fig.12. Aluminium-pH speciation relationships.

If this equilibrium relationship holds we would expect a plot of aluminium against hydrogen ion concentration to be curvi-linear (actually a cubic relationship). However the plot of the observed data shows a straight line relationship as shown in Figure 13. From the regression line the intercept on the y axis is 29.6 μeq l^{-1}. Taking the simple regression line as the model between aluminium and hydrogen ion concentration ie

$$(\text{Total Al} - 29.6) = 1.03\left[H^{+}\right] \qquad (20)$$

the simulation of aluminium, as shown in Figure 14, is particularly satisfactory with 83.5% of the variance explained. Why this linear relationship is so satisfactory when the equilibrium theory predicts a cubic relationship between aluminium and hydrogen ion concentration can be explained by three possible factors.

(a) some other aluminium solubility relationships are operating such that the stoichiometric relationship is less than three;

(b) The above assumptions of constant silica, organic carbon or fluoride is an oversimplification (variations in concentration of at least an order of magnitude are required);

(c) mixing of chemically distinct water from different compartments in the catchment is masking the equilibrium relationships for individual compartments. Thus it is necessary to move to a process based model (eg. Christophersen et. al., 1982) in order to adequately differentiate between chemical and hydrological factors.

Although equation 20 could be rewritten in the form

Total aluminium = Al^{3+} {..........}, where the term in brackets includes expressions for aluminium fluoride and carbon complexes, a cubic type relationship between total aluminium on hydrogen ion concentration would be observed; hence the above explanations would still be valid.

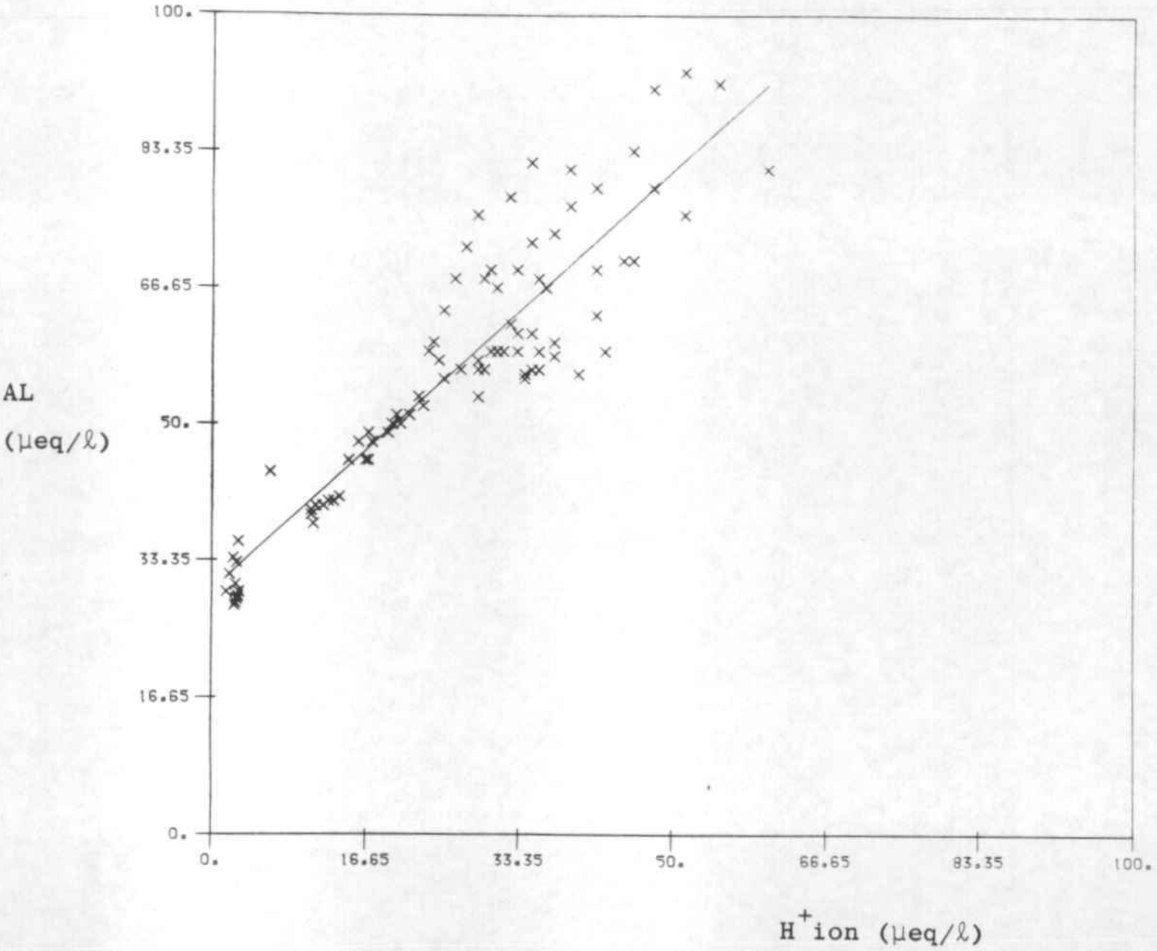


Fig.13 Scatter diagram of AL versus H^+ ion for the Birkenes Catchment, Norway

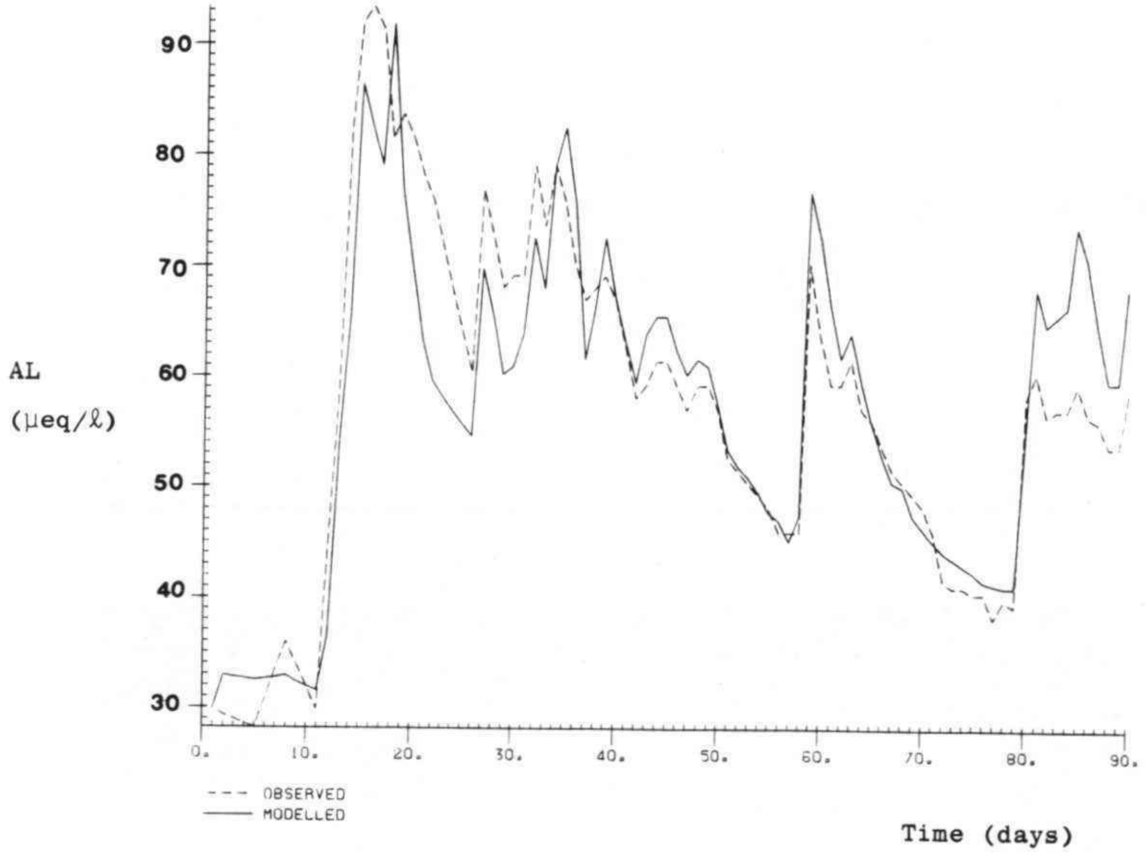


Fig.14. Simulated and Observed AL in the Birkenes Catchment, Norway, based on the H^+ion model.

Plynlimon

The data from Plynlimon consists of **weekly** flow, sulphate aluminium and hydrogen ion data for the Afon Hore and Afon Hafren catchments over a 45 week period summer 1983 - spring 1984. The same approach of relating flow to hydrogen ion concentration has been followed although, because catchment response is much faster than the weekly sampling rate, only the b_0 parameter need be estimated. Model equations were estimated as follows;

Afon Hafren $x_k = 1.75 \ u_{1,k}$

Afon Hore $x_k = 1.34 \ u_{1,k}$

where x_k is the hydrogen ion concentration (μ eql^{-1}) and $u_{1,k}$is the flow (cumecs) at time k.

The variances explained by the models are 65.4% and 66.8% respectively and this was improved slightly to 69.3% and 71.9% respectively by introducing sulphate into the model. The models in this case were estimated as;

Afon Hafren $x_k = 1.26 \ u_{1,k} + 0.09 \ u_{2,k}$

Afon Hore $x_k = 1.22 \ u_{1,k} + 0.026 \ u_{2,k}$

where $u_{2,k}$is the sulphate concentration (μ eql^{-1}).

Figures 15a and 15b show the model simulation for the two catchments and in both cases a reasonable prediction of hydrogen ion concentration is obtained. However the model simulations are not as good as for the Loch Dee or the Birkenes Catchments primarily because of the use of weekly data rather than hourly or daily data. This is emphasised by the values obtained around week 25 when peak hydrogen ion concentrations correspond with low flows following major storm events. Using the storm flow values the peak hydrogen ion concentrations were reproduced.

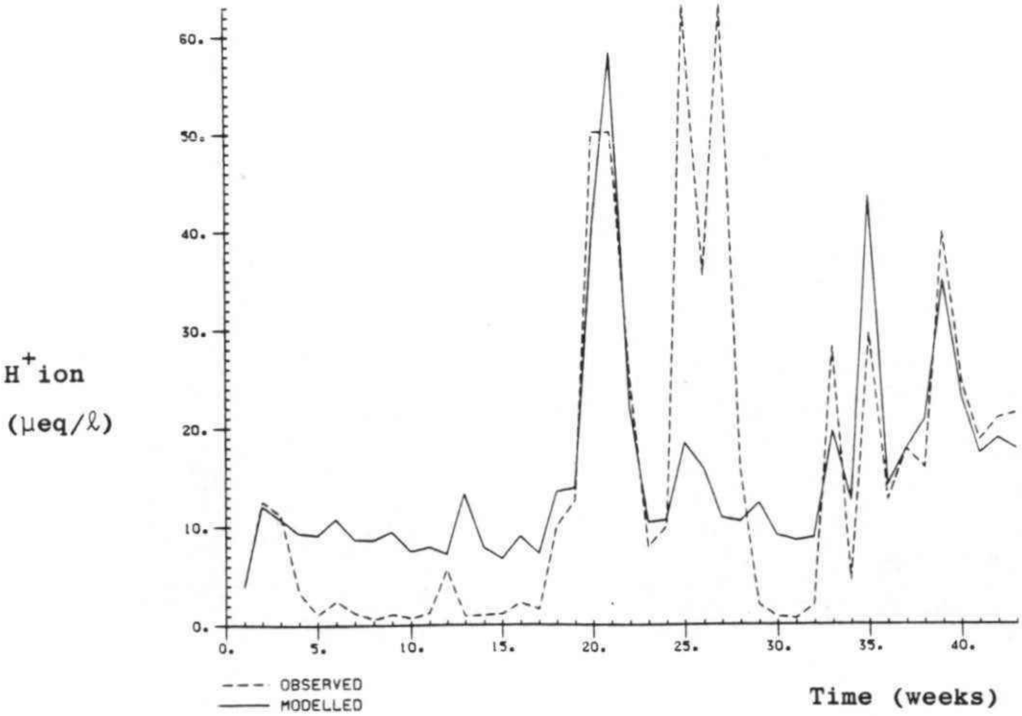


Fig.15a. Simulated and Observed H$^+$ion in the River Hafren, Plynlimon, UK, based on the Sulphate model.

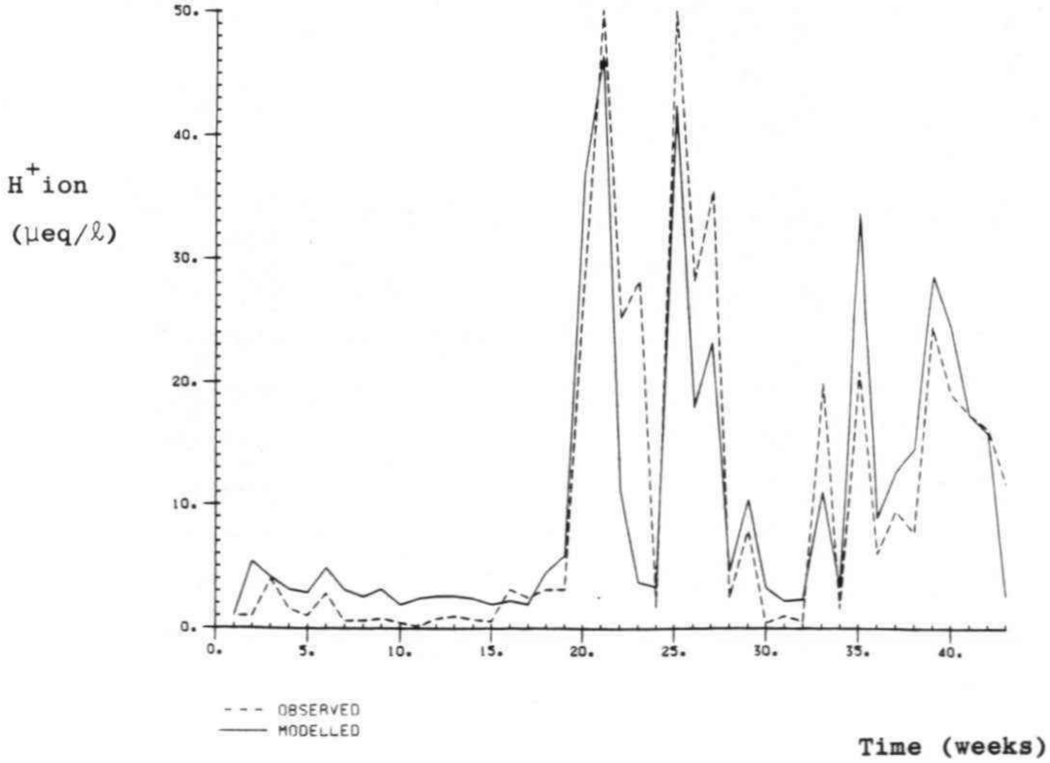


Fig.15b. Simulated and Observed H$^+$ion in the River Hore, Plynlimon, UK, based on the Sulphate model.

In the case of aluminium a scatter diagram of aluminium against hydrogen ion concentrations shows that the aluminium concentration intercept is much lower than Birkenes with a level of 8.6 μ eql^{-1} for the Afon Hafren and 8.8 μ eql^{-1} for the Afon Hore. Fitting a model between hydrogen ion concentration and aluminium gives the following relationships;

Afon Hafren $(x_k - 8.6) = 1.085\ u_{1,k}$

Afon Hore $(x_k - 8.8) = 1.338\ u_{1,k}$

where x_k is the aluminium concentration and $u_{1,k}$ is the hydrogen ion concentration, μ eql^{-1}.

The models explain 76% and 80% of the observed data respectively suggesting that even with weekly data the model is providing a reasonable simulation of streamwater chemistry. Figures 16a and 16b show the model simulations for the two catchments.

6. CONCLUSIONS

Firstly, successful characterisation of streamwater acidity and aluminium concentrations using relatively simple time series models can be achieved for a wide range of catchments and sampling frequencies. In contrast to conventional modelling approaches, model structure can be identified in a systematic manner and parameters estimated directed from observed streamflow and water chemistry data. Since parameters are obtained within a recursive framework the time variation in parameter estimates can be investigated. Such variations highlight process changes such as the flushing effect in the Birkenes Catchment.

The model results suggest that flow dominates the release of hydrogen ions for many catchments and emphasises the need for hydrogical modelling prior to detailed process model development. It is essential to know the residence times associated with different hydrological compartments in order to adequately predict water chemistry changes. Whilst flow and hydrogen ion concentrations are closely linked in the catchments studied this does not mean that this will always be so. For example a similar analysis of data from the Storgama Catchment in Norway (Christophersen et al., 1984) has shown that a

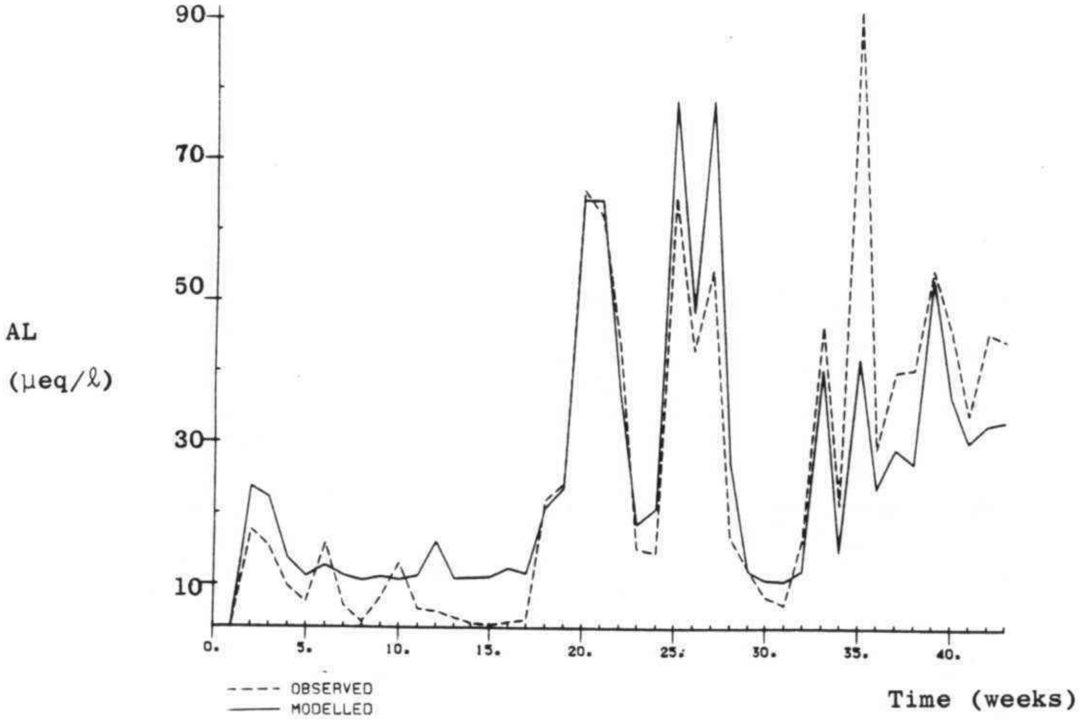


Fig.16a. Simulated and Observed Aluminium in the River Hafren, Plynlimon, UK, based on the H+ion model.

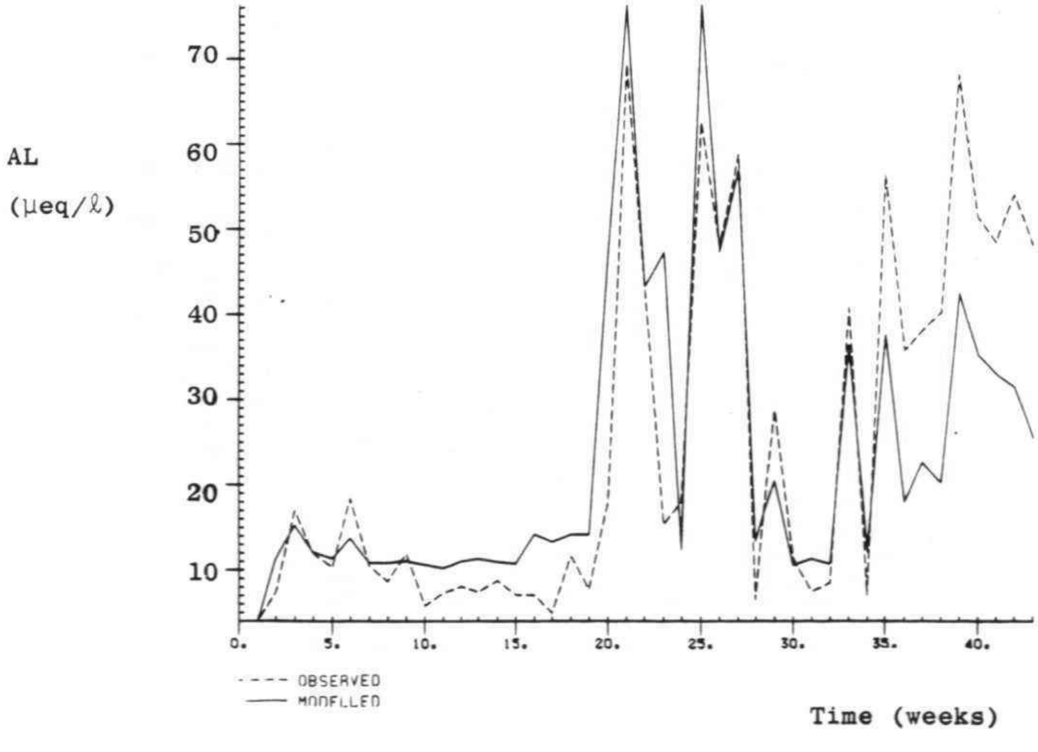


Fig.16b. Simulated and Observed Aluminium in the River Hore, Plynlimon, UK, based on the H+ion model.

simple flow - hydrogen ion relationship does not exist. The situation is further complicated by the snowmelt associated with the Storgama Catchment. Thus whilst time series analysis is extremely valuable early on in a modelling study it will not always be applicable.

A crucial factor in any modelling study is having data at a suitable sampling frequency. The time series models show that it is progressively more difficult to reproduce catchment behaviour as the sampling frequency increases relative to catchment response time. Thus sampling on a weekly basis in catchments that have a fast response, or in which antecedent conditions are important will produce poor time series models and make data interrogation difficult.

A common problem with modelling catchments is the extent to which hydrological complexity is required. Our analysis suggests that relatively simple hydrological descriptions will often suffice. Given typical errors of 10% on hydrological and chemical data it is unlikely that very detailed mechanistic models can be justified for management applications except in circumstances such as a highly heterogeneous catchment in which a particular zone or layer has a disproportionately significant effect on catchment quality. A time series analysis of the data will generally reveal any significant problems with the catchment and is recommended as an efficient means of analysing data prior to more complex modelling studies.

An extension of the 'black-box' time series analysis approach which provides a link to more complicated process models is the technique known as the extended Kalman filter (Jazwinski, 1970). This is currently being applied to the Birkenes data to provide further insight into aluminium speciation and is probably applicable to other aspects of modelling catchment acidity.

Additional catchments studies have been established recently by Stoner et al. (1984) and will provide additional data with which to test models.

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APPENDIX 4

PREFERENTIAL DISCHARGE OF POLLUTANTS DURING SNOWMELT IN SCOTLAND

A4

Introduction

Work in Scandinavia has shown that at the onset of spring snowmelt there can be a marked deterioration in the water quality of snow-fed streams (Skartveit and Gjessing,1979; Johannessen and others, 1980) caused by the preferential discharge of pollutants stored in the snow pack. This increase is associated with an increase in acidity which is known to have a serious effect on aquatic organisms; the spring snowmelt occurs at a time which is critical for the hatching stage of salmonid fish species (Johannessen and Henriksen, 1978). The level of acid precipitation in Scotland is comparable to that in Scandinavia (Fowler and others, 1982) so that there will be a similar amount of pollution in the snowpack. Since snow is an important part of the hydrological cycle in the upland parts of Britain a significant decrease in stream water quality could take place during snowmelt in this country. However, as we explain below, the different hydrological and meteorological conditions in Britain mean that it is impossible to predict a priori that this will occur. Hitherto there has been no direct evidence of a deterioration in water quality during snowmelt in Britain although fish kills at the time of snowmelt have been recorded in south Scotland (Newland, pers. comm.). This paper describes a three-fold increase in total dissolved load at the beginning of spring snowmelt in an upland stream in Scotland and shows that it is by far the most significant of the acute events occurring during the year.

When snow melts the first meltwater appearing at the bottom of the snow column contains much of the dissolved load of pollutants of the snow. This is because the impurities are concentrated on the surface of the ice grains and in the liquid water held between them and may thus be easily leached from the snow by the first meltwater which percolates through. The effect of this preferential discharge of impurities on the water quality of the catchment stream may be discussed in terms of a simple mixing model. Let f be the flow of water released from a snowpack of average concentration c_{av}. The concentration, c, of the meltwater will vary from a maximum value of $c_{max} > c_{av}$ at the onset of melt to values much less than c_{av} in the last stages. A component f_1 of the flow f travels rapidly over the underlying surface and through pipes and macropores to the stream and may be assumed to have the same concentration, c, as the metlwater. A second

f_1 may = 0 ?

component, f_2, travels more slowly through the soil and mixes with the soil water before reaching the stream. When f_1 reaches the stream the discharge will rise from the base flow value f_3 and the concentration will change from the base flow concentration, c_3, to $(f_1c + f_3c_3)/(f_1 + f_3)$. To simplify the discussion, suppose that f_1, f_3 and c_3 are constant in time. Then the maximum concentration in the stream will be $c_{peak} = (f_1\ c_{max} + f_3c_3)/(f_1 + f_3)$ and the relative magnitude of the concentration peak produced by the snowmelt will be

$$n = \frac{c_{peak}}{c_3} = 1 + [(\frac{c_{max}}{c_3} - 1)/(1 + f_3/f_1]$$

Clearly there will only be a marked peak with say $n \geq 3$ if both c_{max}/c_3 and f_1/f_3 are sufficiently large.

The magnitude of the base flow depends on the thickness and hydraulic conductivity of the organic and inorganic soils in the catchment and on the amount of water stored in them. Thus thin soils, impervious rock and long periods of no rain or snowmelt lead to low values of f_3. The magnitude of f_1 depends on the snowmelt rate and on the condition of the soil, which controls the partition of f into "fast" and "slow" snowmelt components.

The concentration of the base flow depends on the average concentration of the precipitation, $\bar{c}$, the residence time of water in the soil and the geochemical reactions occurring there. For a given input a thin organic soil on slowly-weathering impervious rock will produce the lowest values of base flow concentration, $c_3 \approx \bar{c}$. The value of c_{max} will always be several times that of c_{av} at the onset of melt because of preferential elution. However, c_{av} will decrease from $c_{av} = \bar{c}$ before the first melt episode of the season to values much less than this after the snow has been leached by several melting episodes. Hence c_{max} will also decrease from $c_{max} > \bar{c}$ to $c_{max} < \bar{c}$.

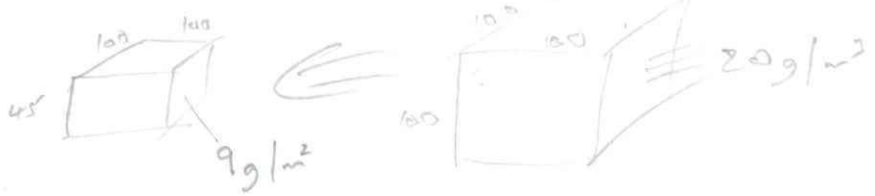
It is not suprising that peaks of pollution have been observed at the onset of the annual snowmelt flood in some Scandinavian streams. In these high mountain catchments the bulk of the snow accumulates during the winter at sub-zero temperatures and is melted during a short period in the spring. There is a large snowmelt flood $(f_1 >> f_3)$ and, since this is the first snowmelt episode, $c_{max} > \bar{c}$. The soils are thin, on a granite bedrock, so $c_3 \approx \bar{c}$. Thus $c_{max} > c_3$ and the two conditions for a marked pollution peak hold.

However, the pattern of snowmelt is different in Britain; it is usual for there to be several episodes of melting in a single winter, even in the highest areas. Snowmelt floods do occur but not every year and not necessarily during the first melt episode of the season. Therefore the pollutants may be released in several small, unimportant events with, say, $n \approx 1$, rather than in one major surge as in the Scandinavian case.

Results and Discussion

As part of an investigation of the acute effects of acid rain in British conditions, electrical conductivity, stage and stream temperature were measured at a gauging point 998 m above sea level in Ciste Mhearad, a corrie on the south-east side of Cairngorm Mountain. The catchment defined by this gauging point has an area of 0.4 km^2 and a median height of 1131 m. The soil consists of a thin organic mat overlying fairly coarse-grained pink granite composed of quartz and red feldspar with a little mica. The vegetation is sparse and typical of mountain tundra. The data were recorded at 20 minute intervals using an Institute of Hydrology solid state logger throughout the period 19 October 1982 to 17 August 1983. The stage measurements were converted to discharge using a calibration curve established by dilution gauging. The absolute error in discharge is $\cong 5.10^{-3}$ m^3 s^{-1}. The conductivity data were corrected to 25°C using the stream temperature measurements and are precise to ± 5%. An empirical relation between electrical conductivity at 25°C and total dissolved load was established for the stream. The relation is linear and gives total dissolved load values precise to ± 10%.

Figure 1 shows discharge and conductivity corrected to 25°C as a function of time during the first major snowmelt event of the year. Noise is present in the discharge record because the stage was measured in mid-stream, not in a stilling well. The average value of conductivity before the melt is 21 µS cm^{-1}. The peak in conductivity comes very quickly after the onset of melt with a maximum value of 63 µS cm^{-1}. The ratio of these two values, the maximum concentration factor, is $n = 3.0$. The second and third peaks in discharge are both larger than the first peak but produce far smaller peaks in conductivity. This is clear evidence of preferential discharge of pollutants at the onset of melt. The measurements of the pollutant levels in the snow before and after the melt support this.



At the onset of melt the average water equivalent of the snowpack was 22.5 cm, which is equivalent to an average snow depth over the catchment of 45 cm using the average snow density of 500 kg m^{-3}. Samples of snow taken before the melt had an average total dissolved load of 20 g m^{-3}, which is the same as the average total dissolved load of fresh snow samples. Thus the pollutant load in the snow per unit area before melt was ≅ 4.6 g m^{-2}. ? After the first melt episode, which lasted two days, 4.3% of the snow had melted but 7.8% of the load had been discharged to the stream. By the end of the third episode, after 24 days, 80% of the snow had melted and 86% of the load had been removed. Samples of snow taken at this time had a total dissolved load of 12 g m^{-3}, equivalent to an average pollutant load of ≅ 0.6 g m^{-2} for the average snow depth of 9 cm.

The maximum concentration factor $n = 3.0$ for the stream water is higher than the maximum value of 2 found by Johannessen and others (1977) for stream water in two catchments of similar area (0.98 km² and 0.56 km²) in Norway. However, since their water samples were taken daily this may be an underestimate of the true maximum. Since $f_3/f_1 = 0.2$ at the time of the concentration peak (Fig.1) equation (1) gives an estimate of $c_{max}/c_3 \approx 3.4$ Since $c_3 > c_{av}$ the maximum concentration factor for the meltwater c_{max}/c_{av} is certainly greater than 3.4. The range of values of c_{max}/c_{av} found for meltwater in field and laboratory experiments is 3 - 7 (Johannessen and others 1977; Johannessen and Henriksen,1978; Colbeck, 1981). Since equation (1) does not take any account of dispersion processes within the catchment it is likely that the meltwater had a maximum concentration factor towards the upper end of this range. The wide variation in the maximum concentration factor in the laboratory experiments may be attributed (i) to variation in the vertical distribution of the impurities in the snow with a higher factor occurring if the impurities are concentrated near the base of the column (Colbeck, 1981) and (ii) to variation in the type of impurities, since not all ions are leached from snow at the same rate. A high concentration factor in the first spring meltwater in Ciste Mhearad is quite possible since previous minor snowmelt episodes may have produced a higher concentration of impurities at the base of the snowpack.

Figure 2 shows the conductivity and discharge of the stream for the whole of the 10 month period. The range of the variables during each day is shown as a vertical line. There is a slow increase in the base level of conductivity during the autumn and winter when the discharge is very low and sustained by slow drainage of the soil and a decrease from March onwards when the streamflow is much larger and is fed by meltwater from leached snow. Small peaks are associated with autumn rain storms in November and minor snowmelt events during December and January. There is a small peak associated with the start of the second major snowmelt period in early May. Clearly the peak during the first snowmelt period in early March, which is shown in detail in Figure 1, is the most significant event in the year.

The minor snowmelt peaks during the winter illustrate how pollutants may be released in several unimportant surges in British conditions. Although $c_{av} \approx \bar{c}$ and the ratio c_{max}/c_3 is probably quite high the discharge record shows that $f_1/f_3 \lesssim 1$. Hence the maximum concentration factor n is only about 1.5 for these peaks. The effect of the slow snowmelt component f_2 can be seen in the slow rise in the base level of conductivity c_3 as the soil water gains pollutants from the snow.

The minor peaks in May illustrate the effect of snowmelt when c_{av} is low and c_3 high. Here the discharge record shows $f_1 \gg f_3$ but the ratio c_{max}/c_3 is too small for a large peak to be produced despite the fact that preferential elution still occurs. A high snowmelt discharge in June produces no peak at all in conductivity so by this time $c \approx c_3$.

For most of the year conditions in Ciste Mhearad may be taken as representative of these in areas of similar altitudes, vegetation and bedrock. The catchment faces southeast so melt rates will be a little higher than these in north facing areas. However, there is an unusually high rate of deposition of wind blown snow in this catchment. Snow persists later into the year than in most other areas of the Cairngorms. Thus the data from October to May may be taken as applicable to other areas, whereas the summer snowmelt in June and July is a special aspect of the hydrology of Ciste Mhearad.

The field data from Ciste Mhearad show that even under British weather conditions a three-fold increase in the level of pollution in a stream can occur during snowmelt. We have explained why this may not happen in every year or in every upland catchment. Nevertheless, aquatic organisms are clearly at risk at the onset of snowmelt in this country.

Acknowledgements

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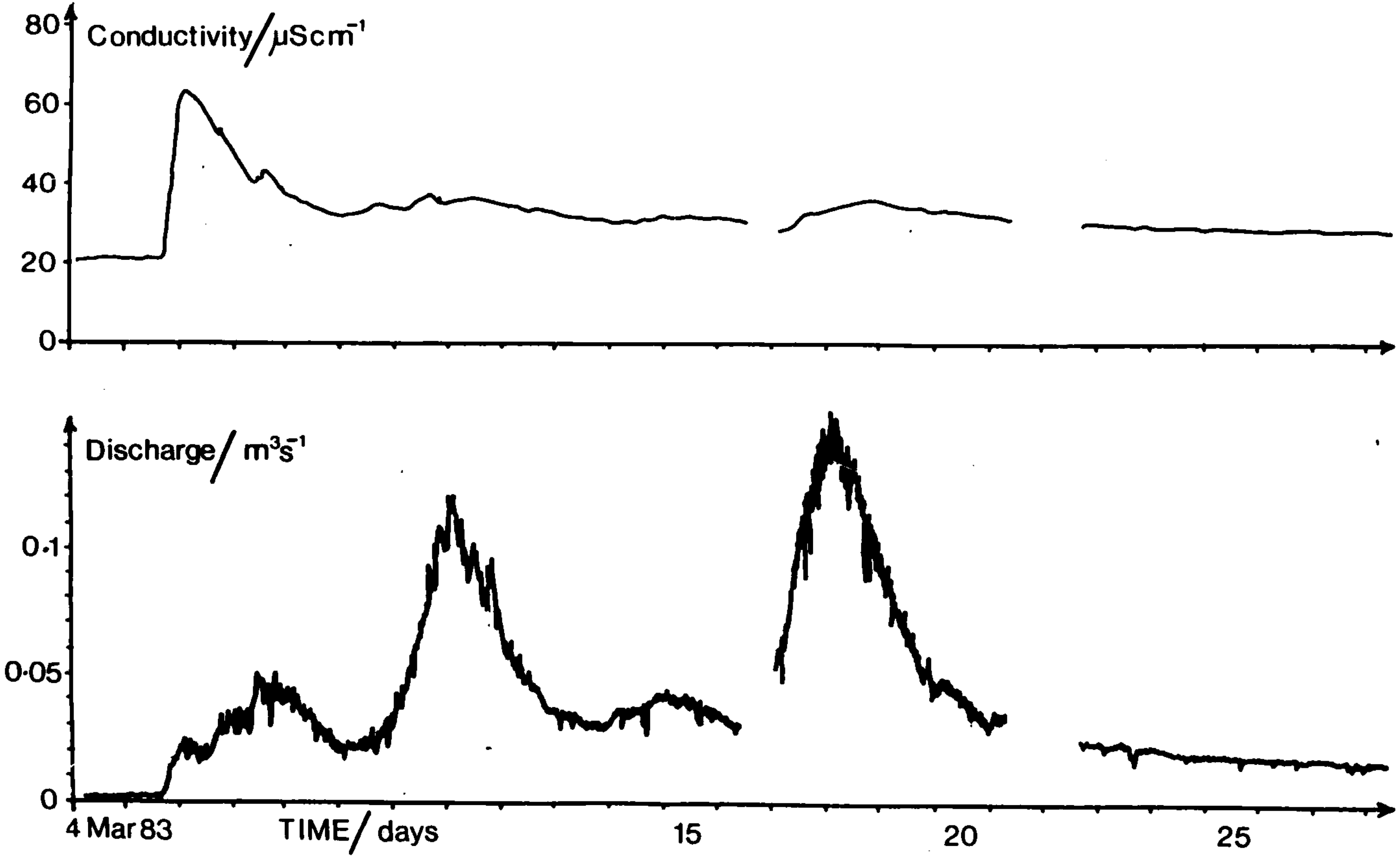
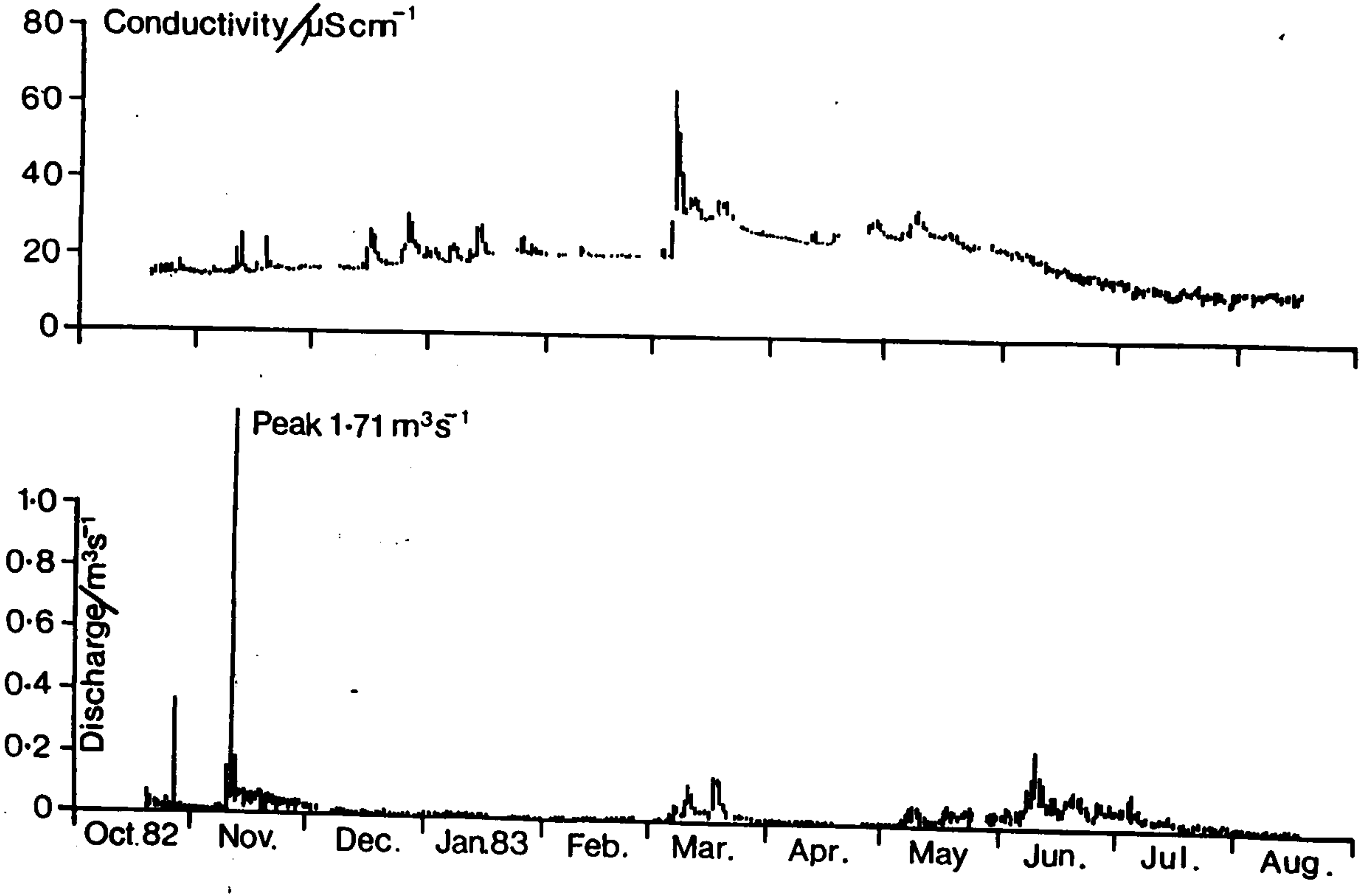
Legends for Figures

Figure 1	Conductivity and discharge during the first major snowmelt event.
Figure 2	Daily range of conductivity and discharge from October 1982 to August 1983.


80
60
40
20
0
Conductivity/µScm⁻¹
Discharge/ m³s⁻¹
0·1
0·05
0
4 Mar 83
TIME/ days
15
20
25


Conductivity/µScm^{-1}
80
60
40
20
0
Peak 1·71 m^{3}s^{-1}
Discharge/m^{3}s^{-1}
1·0
0·8
0·6
0·4
0·2
0
Oct.82
Nov.
Dec.
Jan.83
Feb.
Mar.
Apr.
May
Jun.
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