Predicting the Effects of Acid Deposition on Water Quality

by

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PREFACE

This report describes research completed for the 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 (IH), a component body of NERC.

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SUMMARY AND CONCLUSIONS

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 has established 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 has been responsible for providing stream gauging, rainfall stations, a weather station, snow surveys, sampling and continuous water quality monitoring. IH has also been responsible for the subsequent data management, analysis and interpretation. DAFS has been responsible for all chemical and biological analysis, with the exception of snowmelt chemistry, which would be undertaken by IH. The Macaulay Institute have been 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 has been associated with several major catchment studies including the Loch Dee project (South West Scotland), the Llyn Brianne project (South Wales - see Appendix 2) and the Plynlimon Catchment Study (Mid-Wales). All of these have provided 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 upland catchments. Additional studies on pH measurement have shown the difficulties involved in obtaining reliable data for modelling purposes (see Appendix 3). Thus a wide range of process information is 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 Modelling strategy and application

A modular approach to modelling has been adopted at IH in which 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 have been applied to catchment data and modified as necessary to incorporate relevant processes. These processes have been reviewed and sensitivity analyses performed to assess parameter uncertainty and help refine field and laboratory experiments.

The models have been 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 and the models can be tested against these observed changes given information on acid deposition levels. Such long term simulations have been used to assess the effects of future acid deposition scenarios and preliminary results are presented in sections 1 and 2 of the report. The model has also been employed to investigate the effects of conifer afforestation and deforestation (see Section 2).

Short term on dynamic responses of catchments are particularly important for predicting the effect on fisheries or water resources. The models provide valuable information on dynamic changes occurring in catchments and a range of time series analyses and hydrochemical models have been applied to catchment datea collected during storm and snowmelt events (see Section 3, 4 and 5, and Appendix 2).

CONCLUSIONS

There have been a number of major conclusions from the study.

1. The acidification problem can be divided into two time scales in terms of catchment response.

Firstly, there is the short term response to storm events in snowmelt events in which pH falls rapidly over a few hours and high peak concentrations of aluminium occur. These 'shock' pulse affect stream biota and cause immediate damage.

Secondly, there is a very long term response which can take several years or decades when a catchment is responding to many years of atmospheric pollutant deposition. These long term responses are controlled by the buffering capacity of the catchment which is a function of several factors such as soil chemistry, soil depth, underlying geology, deposition rates, land use etc. Thus it is important to understand interactions occurring in catchments in order to predict how each catchment will respond.

It is important to realise that the short term response is largely dependent on the long term acidification state of the catchment so that those catchments with the least buffering capacity will generally exhibit the worst short term chemical response.

2. Models can be developed for predicting both short term and long term behaviour of catchments and can be used to provide management information on land use change and/or the effects of different emission strategies.

3. A primary factor controlling acidification is the hydrology in a catchment. Quite often surface waters are very acidic and base flow waters are well buffered so that the degree of mixing of these two principle types of water will control the final stream quality. The degree of mixing is determined by the hydrological pathways and a change to the hydrology of a catchment (eg. by afforestation) will have a major effect on the mixing process and hence acidity.

4. The effects of sea-salt on catchment acidity can be significant, but the effects of atmospheric pollutant deposition superimposed on the sea-salt effect can be far greater and cause a catchment to become very acidic.

5. The effects of conifer afforestation can be severe through two principal mechanisms. Firstly, a significant change in the hydrology occurs causing highly acidic surface waters to drain off rapidly. Secondly, there is an additional input of acidity to the catchment via the scavenging of dry particles and mist or 'occult' depositions. These can increase the acid loading to the system by up to 80 or 90 percent, thereby enhancing the rate of weathering and speeding up the acidification process.

6. Liming can be used to mitigate the acidification process but it is generally considered a short term effect in lakes or streams with high turnover (ie. low residence times) and would need to be repeated on a regular (annual) basis. Liming of land has a longer term effect but it is not necessarily practical to lime remote regions or upland catchments.

7. The models suggest that emission reductions of the order of 50 percent from present day levels have a significant effect on acidification, although the

effects will be long term. There appears to be a significant store of sulphate in many acidified catchments and this store could take years to deplete. On the other hand sensitive upland catchments may respond rapidly to these emission reductions.

8. The models need to be applied in a regional context to assess thoroughly the effects of emission reductions.

Section 1

A model of long term changes in catchment acidification

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[3]

A PRELIMINARY MODEL OF LONG-TERM CHANGES IN STREAM ACIDITY IN SOUTHWESTERN SCOTLAND

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ABSTRACT

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A modelling study has been undertaken to investigate long-term changes in stream acidity in Dargall Lane, a sub-catchment of Loch Dee, in Galloway, southwestern Scotland. The model, which includes sea salt effects, is based on the assumption that surface water chemistry is determined by reactions taking place in the soils and rocks within a catchment. Stream chemistry data are used to calibrate the model and the model reproduces the declining pH levels of recent years as indicated by paleoecological analysis. Stream acidity trends are investigated assuming two scenarios for future deposition. Assuming deposition rates are maintained in the future at 1984 levels, the model indicates that stream pH is likely to continue to decline below presently measured values. A 50% reduction in deposition rates would likely result in an increase in the pH of the stream, although the pH will not return to estimated preacidification levels.

INTRODUCTION

There is both empirical and theoretical evidence that surface waters are acidified by atmospheric deposition of sulphur (Beamish and Harvey, 1972; Gjessing et al., 1976; Schofield, 1976; Wright, 1976; Thompson et al., 1980; NAS, 1984). Although the "sensitivity" of regions to potential damage by acidic deposition can be defined on a relative scale (Galloway and Cowling, 1978; Hendry et al., 1980) a generally acceptable approach to the difficult problem of forecasting water quality changes under different scenarios of atmospheric deposition has not been identified. At present there are two basic methods for projecting future water chemistry for sensitive areas. The first is an empirical approach whereby extrapolations from present conditions are made using conceptual and statistical relationships among rainfall chemistry, soil chemical processes and surface water quality (e.g., Henriksen, 1979, 1980; Church and Galloway, 1984). The second method utilizes mechanistic, process-oriented numerical models of hydrology and

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geochemistry to make the quantitative linkage between deposition and water quality (e.g., Christophersen et al., 1982; Schnoor et al., 1983; Goldstein et al., 1984; Cosby et al., 1985a, b; Rustad et al., 1986). A critical question in any attempt to project future water quality for a catchment is how quickly and to what extent the physical/chemical characteristics of the catchment control water quality response to changes in atmospheric deposition. This question is best addressed through the second method, the use of process-based dynamic simulation models of long-term catchment responses.

Recent research has increasingly focused attention on certain chemical processes in the soils of catchments as likely keys to the responses of surface water quality to acidic deposition (NAS, 1984). These processes include: (1) anion retention by soils; (2) cation exchange by soils; (3) solubility and mobilization of aluminium; (4) weathering of minerals as a source of base cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}); and (5) dissociation of carbonic acid (resulting from elevated partial pressure of CO_2 in soils) with subsequent exchange of the hydrogen ions for base cations.

The interactions of these processes are non-linear and the catchment scale water quality effects they produce in response to acidic deposition can occur over several years (or decades) in natural systems. Direct observations of the catchment scale effects will, in most cases, require the acquisition of lengthy and costly time series of water quality measurements. Manipulating whole systems to observe catchment scale effects will be even more difficult and expensive. In the meantime, we are faced with the problem of understanding the implications (for forecasting long-term whole catchment responses) of what has been learned from the many studies of these individual processes. If mathematical representations of these processes are included in numerical models of catchment responses, their implied effects on the magnitude and timing of catchment surface water acidification can be examined in a series of speculative simulation exercises (e.g., Hornberger and Cosby, 1985).

We present here a preliminary calibration of a quantitative model for the Dargall Lane sub-catchment of Loch Dee in Scotland. The model is based on mathematical representations of those processes (outlined above) which are currently thought to be the primary catchment controls on acidification. Because the model is based on the assumption that surface water chemistry is determined by reactions taking place in the soils and rocks within a catchment, the model is named MAGIC (Model Acidification of Groundwater In Catchments).

The MAGIC model as applied to Dargall Lane in this study is conceptually very simple with regards to spatial heterogeneity in the catchment. As implemented, the model contains three compartments (Fig. 1) which are assumed to be internally homogeneous. This assumption implies that vertical stratification of soils in the catchment is unimportant or, equivalently, that all water reaching the stream contacts and has its chemical quality determined by a single layer within the soil column. While this assumption is probably overly restrictive in a model intended to reproduce short-term (i.e.

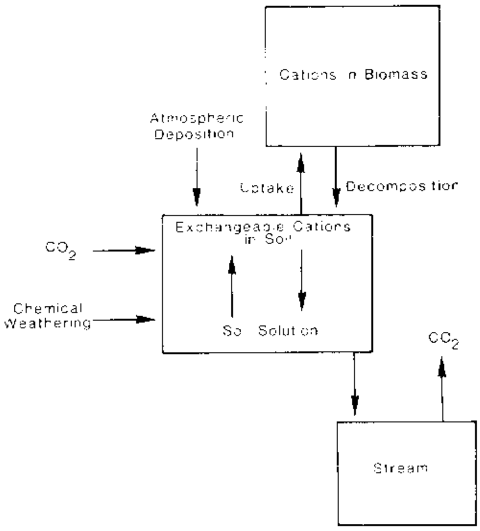

Fig. 1. Schematic view of MAGIC (Model for Acidification of Groundwater in Catchments, Cosby et al., 1985a, b) as applied to Dargall Lane. MAGIC is comprised of two parts-fluxes to and from the soil and a series of chemical equilibria between soil and soil solution.

daily to weekly) water quality responses, the purpose of this modelling exercise is to estimate long-term (i.e. decades) changes in annual average water quality. Viewed at this scale, many of the short-term dynamic water quality changes arising from spatial heterogeneity of soil chemical and hydrological processes "disappear" into the much slower long-term "chronic" changes of water quality which are most likely determined by single bulk properties of the whole catchment. Such lumped parameter models are common in rainfall runoff modelling (e.g., Beven and Kirkby, 1979; Hornberger et al., 1985) and in chemical models of lakes and oceans (e.g., Lerman 1971; Imboden and Lerman, 1978). Lumped hydrochemical models of surface water quality responses have also been successfully applied to whole catchments (e.g., Schnoor et al., 1983; Cosby et al., 1985a). The use of lumped hydrochemical models for long-term water quality reconstructions is less common, although, in cases where historical water quality can be inferred (e.g., Wright et al., 1986), the models were capable of reproducing the important historical water quality changes.

The objectives of this modelling study are threefold:

(1) To evaluate the suitability of a hydrochemical model containing soil ion exchange reactions when applied to a catchment receiving large amounts of sea salt deposition.

(2) To examine the extent to which soil processes may have controlled surface water quality in southwest Scotland in response to increases in acidic deposition over the last century.

(3) To estimate likely future water quality responses to assumed scenarios of future deposition (given that the soils might be the primary controls on surface water quality responses). To these ends, the model we present has the simple spatial structure illustrated in Fig. 1. Our current enquiry concerns the role soils may play in the acidification response of surface waters. We have chosen Dargall Lane as a study site because the land use practices there have not much changed over the period of interest. The changes in fluxes between the soils and the terrestrial biota (Fig. 1) are therefore minor compared to the changes in fluxes from the atmosphere through the soil to the stream. The model presented below contains only reactions expected from the mineral fraction of the soil. The role of biological transformations (except for uptake of NO_3^- and NH_4^+) and reactions involving organic compounds are ignored. The implicit assumption is that these reactions have proceeded unchanged despite the increase in deposition and therefore have produced no effect on the changes in surface water quality. To this extent, the present model must be considered preliminary. Future work will examine these assumptions.

CONCEPTUAL BASIS OF THE MODEL

The most serious effects of acidic deposition on catchment surface water quality are thought to be decreased pH and alkalinity and increased base cation and aluminium concentrations. In keeping with an aggregated approach to modelling whole catchments, we postulated that 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. Christophersen et al. (1984) describe a model based on similar chemical equilibrium reactions. This conceptual approach is attractive in that a wide range of observed catchment responses can be theoretically produced by a rather simple system of soil reactions. MAGIC has its roots in the Reuss-Johnson conceptual system, but has been expanded from their simple two-component (Ca-Al) system to include other important cations (and anions) in catchment soil and surface waters.

MAGIC assumes that atmospheric deposition, mineral weathering and exchange processes in the soil and soil water are responsible for the observed surface water chemistry in a catchment (Fig. 1). Alkalinity is generated in the soil water by the formation of bicarbonate from dissolved CO_2 and water:

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

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

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

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:

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

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 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 (eqn. 3) and the Al^{3+} concentration in the water entering the stream channel 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 (e.g. the reverse of reaction 2). These aluminium precipitation reactions retard the increase of streamwater pH as the CO_2 degasses, resulting in lower streamwater pH for the case where exchangeable cations are less available.

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

$$ALK = (HCO_3^-) - (H^+) - 3(Al^{3+}) \tag{4}$$

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.

If anions derived from atmospheric deposition are accompanied by H^+ (i.e. acidic deposition) the excess H^+ will initially displace base cations from the soil exchange sites. As the base saturation (amount of exchangeable base cations on the soil) declines, aluminium and hydrogen ion become increasingly important in maintaining the ionic charge balance. The water delivered to the stream becomes more acidic as the acidic deposition persists.

On the other hand, if anions derived from atmospheric deposition are accompanied by a base cation (i.e. deposition of neutral salts such as sea salt), the catchment soils produce a different response. At the onset of the neutral salt deposition, the water flowing through the soil has a higher concentration of base cations than previous flow-through. This causes a shift in the equilibrium conditions of the soil (the reverse of reaction 3) and aluminium ions are initially displaced from the soil until a new equilibrium with the higher concentrations of base cations is established. Higher aluminium concentrations in soil water produce lower soil and streamwater alkalinity and pH (as discussed above). As the new equilibrium is established, the initial mass action displacement of Al^{3+} declines and the soil and streamwater alkalinity and pH rise again. This temporary depression of pH and alkalinity on addition of neutral salts to catchment soils is known as the "salt effect" (e.g. Reuss, 1980). It is important to note that the salt effect is only temporary and, once the new equilibrium conditions have been established in the soil, continued addition of neutral salts (unlike continued addition of an acid) does not produce a progressive decline in pH or alkalinity of the soil and streamwater.

Deposition of large amounts of sea salt has occurred historically in the Dargall Lane subcatchment (Table 1). It is expected that the soils at Dargall Lane have achieved an equilibrium with this sea salt flux at some point in the distant past. One of the objectives of the present study is to examine the expected effects of more recent additions of acidic deposition to soils historically receiving large amounts of neutral salt deposition.

TABLE 1

Chemical characteristics of precipitation, streamwater and soils in Dargal Lane subcatchment. Values in A and B are volume weighted annual averages for 1981. Values in C are from regional soil surveys

	Ca	Mg	Na	K	NH_4	SO_4	Cl	NO_3
A Bulk precipitation: pH = 4.6								
meq m^{-3}	16	19	83	6	28	48	94	19
B Streamwater: pH = 5.1; alkalinity = 7 meq m^{-3}								
meq m^{-3}	52	58	137	12	1	79	158	19
C Soil: pH = 4.7—5.0; base saturation = 5—10%; cation exchange capacity $\simeq$ 100 meq kg^{-1}								

THE LOCH DEE STUDY AND SITE DESCRIPTION

This modelling study was undertaken as part of the Loch Dee Project in Galloway, southwestern Scotland. The Loch Dee Project (1985) was initiated in 1979 by the Solway River Purification Board with the support of the Forestry Commission and the Department of Agriculture and Fisheries for Scotland (Freshwater Fisheries Laboratory). The project is intended to examine the combined and individual effects of acid deposition and afforestation on surface water quality with particular emphasis on evaluation of the Loch's potential as a trout fishery (Burns et al., 1984). The Loch Dee Catchment ($15.6\,\mathrm{km}^2$) lies in the Galloway Hills of Scotland west of Dumfries. It consists of three subcatchments, Dargall Lane, Green Burn and White Laggan Burn. The relief in the catchment is from 225 to 716 m. Nearly two-thirds of the catchment is above 305 m (Burns et al., 1984). The catchment is underlain by Ordovician and Silurian greywackes and shales and intrusive granites of the Old Red Sandstone Age. Soils in the catchment include peaty podzols and peaty gleys with basin and valley peats in the lowest areas at the edge of the Loch (Bown et al., 1982).

The White Laggan Burn and Green Burn subcatchments have been planted with Sitka Spruce and Lodgepole Pine and have been treated with P-K fertilizers and limestone (see Burns et al., 1984, for details). The Dargall Lane subcatchment is treeless, has not been manipulated and is used as a control for the project. We will confine our attention to Dargall Lane in this study.

The Loch Dee area has a mean annual rainfall (1941—1970) of 2.2 m. The data presented by Burns et al. (1984) and unpublished data from the Loch Dee project indicate that 80—90% of rainfall volume appears as runoff in White Laggan Burn, the only gauged subcatchment prior to 1983. Burns et al. (1984) have presented volume weighted annual average chemical data for precipitation and Dargall Lane streamflow for 1981 (Table 1A and B). These data are based on stream and bulk precipitation samples taken on a weekly basis. Soil chemistry in the Green Burn is currently being investigated as part of the Loch Dee study (Grieve, 1985). Soil chemical characteristics in Dargall Lane have been estimated for this study (Table 1C) by using analyses of peaty podzols and peaty gleys in other catchments in southwestern Scotland (Mitchell and Jarvis, 1956; Bown, 1973). Average soil depth in Dargall Lane subcatchment is approximately one metre.

EQUATIONS AND PARAMETERS REPRESENTING THE SOIL PROCESSES AT DARGALL LANE

Complete details of the model structure and the method of implementation are given by Cosby et al. (1984, 1985a, b). For this analysis we will be concerned mainly with those inputs or parameters related to the five soil chemical processes listed in the introduction.

The model calculates the concentrations of four strong acid anions in both soil and streamwater (SO_4^{2-}, Cl^-, NO_3^- and F^-). Chloride, nitrate and fluoride ions are assumed not to have an adsorbed phase at Dargall Lane. Sulphate, however, does have an adsorbed phase and the relationship between adsorbed sulphate (E_s, meq kg^{-1}) and the concentration of dissolved sulphate [(SO_4^{2-}), meq m^{-3}] in soil water at Dargall Lane is assumed to follow a Langmuir isotherm (Hasan et al., 1970; Cuoto et al., 1979; Singh, 1984):

$$E_s = E_{mx} \frac{(SO_4^{2-})}{C + (SO_4^{2-})} \tag{5}$$

where E_{mx} is the maximum adsorption capacity of the soils (meq kg^{-1}) and C is the half saturation concentration (meq m^{-3}). Sulphate adsorption parameters used in the model for Dargall Lane are:

$$E_{mx} = 0.1\,\text{meq kg}^{-1}; \qquad C = 150\,\text{meq m}^{-3}$$

These values are characteristic of podzolic soils with a low sulphate adsorption capacity (Singh, 1984).

The model calculates the concentration of Al^{3+} in soil water assuming dissolution of a solid phase of $Al(OH)_3$ (eqn. 2). The equilibrium expression for this reaction is:

$$K_{Al} = \frac{\{Al^{3+}\}}{\{H^+\}^3} \tag{6}$$

where the accolades indicate aqueous activities. Several forms of $Al(OH)_3$ may be present in the catchment at different locations. The value of K_{Al} selected for a particular catchment will be some effective lumped value characteristic of the entire catchment. For Dargall Lane the value of K_{Al} was set to $10^{9.0}$, typical of a range of crystalline forms of gibbsite (e.g., Cosby et al., 1985a). Several aqueous complexation reactions of Al^{3+} (hydration reactions and formation of dissolved complexes with F^- and SO_4^{2-}) are included in the model (see Cosby et al., 1985a, b). These reactions are temperature dependent and appropriate corrections for temperature and ionic strength are made in the model.

Bicarbonate ion concentrations (eqns. 1 and 4) in soil water are calculated using the familiar relationships between the partial pressure of CO_2 and hydrogen ion activity in the soil water:

$$\{HCO_3^-\} = K_C \frac{P_{CO_2}}{\{H^+\}} \tag{7}$$

where the combined constant K_C is known for a given temperature (Stumm and Morgan, 1970) and P_{CO_2} is the partial pressure of CO_2 in soil water (atm). P_{CO_2} must be an effective partial pressure for all catchment soils. As such, it is not clear that a value of P_{CO_2} measured directly at some single point in the catchment is representative of the catchment as a whole. We thus consider P_{CO_2} a parameter whose value must be ascertained for each catchment by an appropriate calibration procedure. CO_2 partial pressure was set to 0.02 atm for the soils of Dargall Lane. This is approximately sixty times atmospheric P_{CO_2}.

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

$$S_{AlBC} = \frac{\{BC^{2+}\}^3\ E_{Al}^2}{\{Al^{3+}\}^2\ E_{BC}^3} \qquad \text{or} \qquad S_{AlBC} = \frac{\{BC^{+}\}^3\ E_{Al}}{\{Al^{3+}\}\ E_{BC}^3} \tag{8}$$

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

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

where CEC is the cation exchange capacity of the soil (meq kg^{-1}). The base saturation (BS) of the soil is then the sum of the exchangeable fractions of base cations:

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

If the aluminium-base cation exchange equations in the model (eqn. 8) are combined with the aluminium solubility equation (eqn. 6), the results are equations that are Gaines-Thomas expressions for hydrogen ion-base cation exchanges. That is, even though we have chosen to represent the exchange processes using equations based explicitly on aluminium-base cation interactions, the formulation is mathematically equivalent to exchange equations based on hydrogen ion-base cation interactions. The equivalence holds as long as the hydrogen ion to aluminium ratio is constant due to the assumed presence of a soluble aluminium solid phase.

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. Cation exchange capacity for Dargall Lane soils was set to 100 meq kg^{-1}. This value is typical of the mineral horizons of many peaty podzols and peaty gleys in south-western Scotland (Bown et al., 1982). Values for the selectivity coefficients were predetermined in the model from base cation weathering inputs (see below) and the initial base saturation of the soil used in the simulations.

The values of the selectivity coefficients used for Dargall Lane in this study are:

$$S_{\mathrm{AlCa}} = 10^{2.49}; S_{\mathrm{AlMg}} = 10^{2.91}; S_{\mathrm{AlK}} = 10^{-3.92}; S_{\mathrm{AlNa}} = 10^{-0.22}$$

The model assumes that there is a long-term net input of base cations from mineral weathering. Weathering rates, and the degree to which the weathering changes as soil conditions change, are extremely difficult to determine (NAS, 1984). The weathering rates of base cations are treated as lumped, constant imputs to the model. Weathering rates and initial base saturation conditions were selected by a trial and adjustment procedure such that simulated water quality variables matched measured water quality variables in 1981 (Table 2).

Atmospheric deposition of base cations and strong acid anions used for the simulations was calculated using measured concentrations of each ion in precipitation (Table 1) and the annual average precipitation volume. Sulphate deposition in excess of sea salt inputs was increased by a constant

TABLE 2

Model output of variable values at different points in the simulation, and a comparison with measured values at Dargal Lane in 1981

		Model output	Model output	Dargal Lane measured	Model output constant deposition	Model output 50% reduction of the deposition
Year		1844	1981	1981	2001	2001
Streamwater						
meq m^{-3}	H	1	4	8	4	3
	Ca	26	51	52	46	38
	Mg	48	62	58	56	48
	Na	136	140	137	140	133
	K	8	13	12	13	12
	NH_4	0	0	1	0	0
	SO_4	17	80	79	72	47
	NO_3	4	18	19	17	10
	Cl	159	159	158	159	159
	Alk	39	8	7	8	14
	pH	5.85	5.38	5.10	5.36	5.49
	Σ^+	220	271	268	261	235
	Σ^-	220	271	263	261	235
Soils						
% BS		11	7.5	5—10[a]	7.1	7.3
pH		5.1	4.9	4.7—5.0[a]	4.9	4.9

[a] Estimated from soil survey data for similar soils in southwestern Scotland (Mitchell and Jarvis, 1956; Bown et al., 1982).

factor (1.4) to account for aerosol and dry deposition of anthropogenically derived sulphur. A basic assumption of the modelling exercise was that the catchment was in steady state with constant background levels of deposition prior to 1844. A 140 yr deposition history was estimated for Dargall Lane based on historic sulphur dioxide emissions records. The emissions data used were those for the United Kingdom compiled by the Warren Spring Laboratory (1983). The deposition trajectory for Dargall Lane was assumed to have an identical shape to the regional emission data. The trajectory for each ion that increased in concentration between 1844 and 1981 was assumed to follow the same trajectory. Background (1844) deposition inputs to the model were calculated from the sea salt fraction of current deposition at Dargall Lane. The background deposition of sea salt calculated in this manner from bulk precipitation measurements was increased by a factor of 1.4 to account for aerosol and sea spray inputs to the catchment.

Two scenarios are used for projecting future water quality in Dargall Lane. The first scenario assumes continued deposition at current (1984) rates for the next 140 yrs. The second scenario assumes a 50% reduction of the deposition in excess of sea salts. The reduction is assumed to occur uniformly over 20 yrs (1984—2004) followed by 120 yrs of deposition at the reduced level.

RESULTS

The historical reconstruction of water quality at Dargall Lane indicates that the catchment surface waters have lost approximately 80% of their alkalinity (Fig. 2a and Table 2). Streamwater pH is higher than soil water pH but has decreased more rapidly in recent years, (Fig. 2d). The decline in pH follows closely the patterns of pH change determined by Batterbee et al. (1985) and Flower and Batterbee (1983) from paleoecological studies in southwestern Scotland. For instance, Flower and Batterbee (1983) estimate that the pH of nearby Loch Grannoch has declined by 0.5 of a unit in recent years. A very similar rate of decline, from 5.85 to 5.38 (Fig. 2a) has been estimated by MAGIC for Dargall Lane over the same period. Concentrations of strong acid anions (principally sulphate) have responded very rapidly to changes in atmospheric deposition but base cation concentrations have responded more slowly (Fig. 2b). Base saturation of the soil has declined by more than 30% from a preacidification value of 0.110 to a 1981 value of 0.075 (see Fig. 2c). Even though deposition decreased and pH rose slightly during the last 14 yrs of the historical reconstruction (Fig. 2a), the base saturation of the soil continued to decline during this period as base cations were leached from the soils (Fig. 2c).

Simulations of future responses of Dargall Lane water quality are based on the preceding historical reconstruction. Continued deposition at current levels (Fig. 3) results in further deterioration of the water quality in Dargall

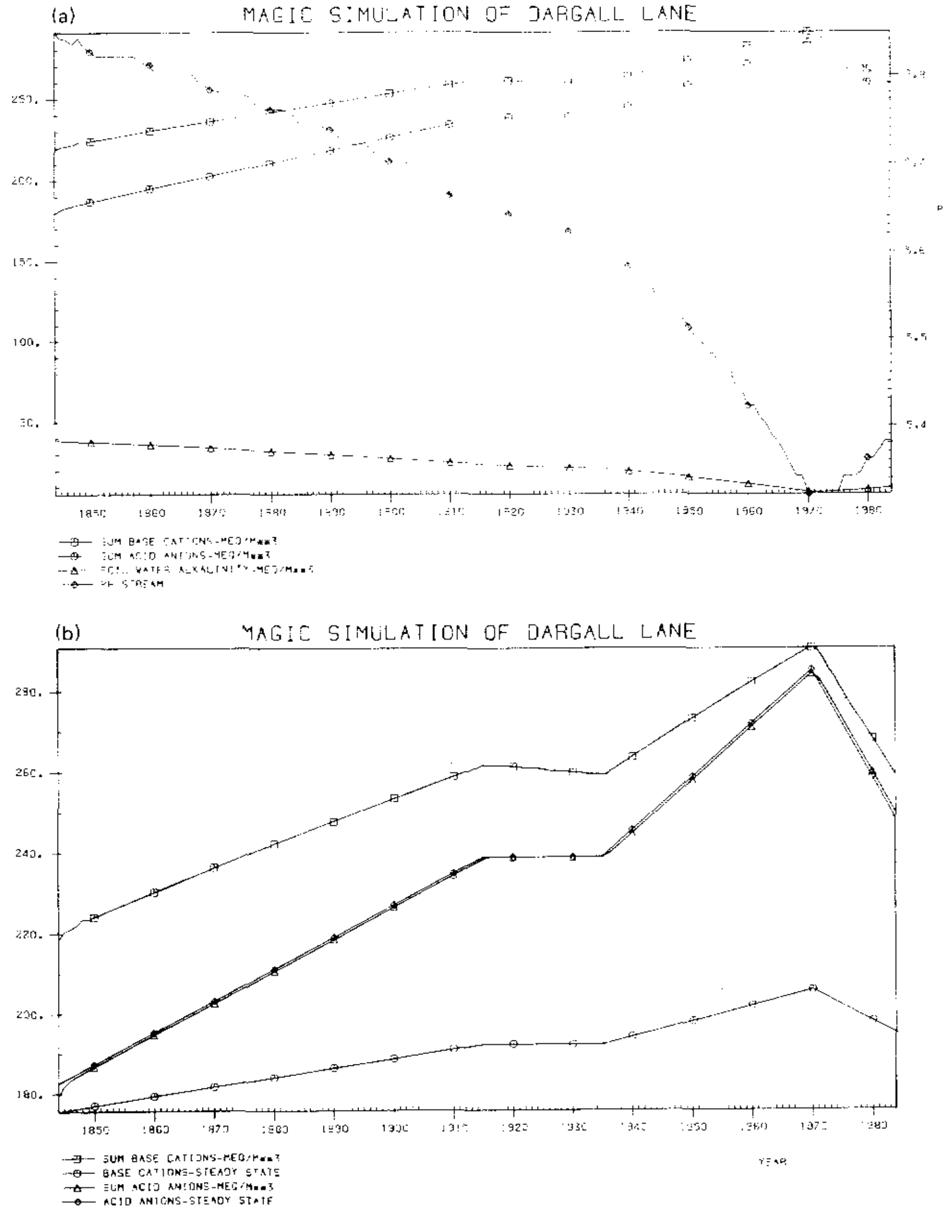

Fig. 2a, b. Simulations of Dargall Lane for the period 1844—1984.

Lane. Despite the slight recovery resulting from the deposition decrease (1970—1984), and the subsequent slight rise in streamwater pH, continued deposition in the future at 1984 levels produces further declines in soil base saturation (Fig. 3c) and the improvement in streamwater pH is soon lost (Fig. 3d).

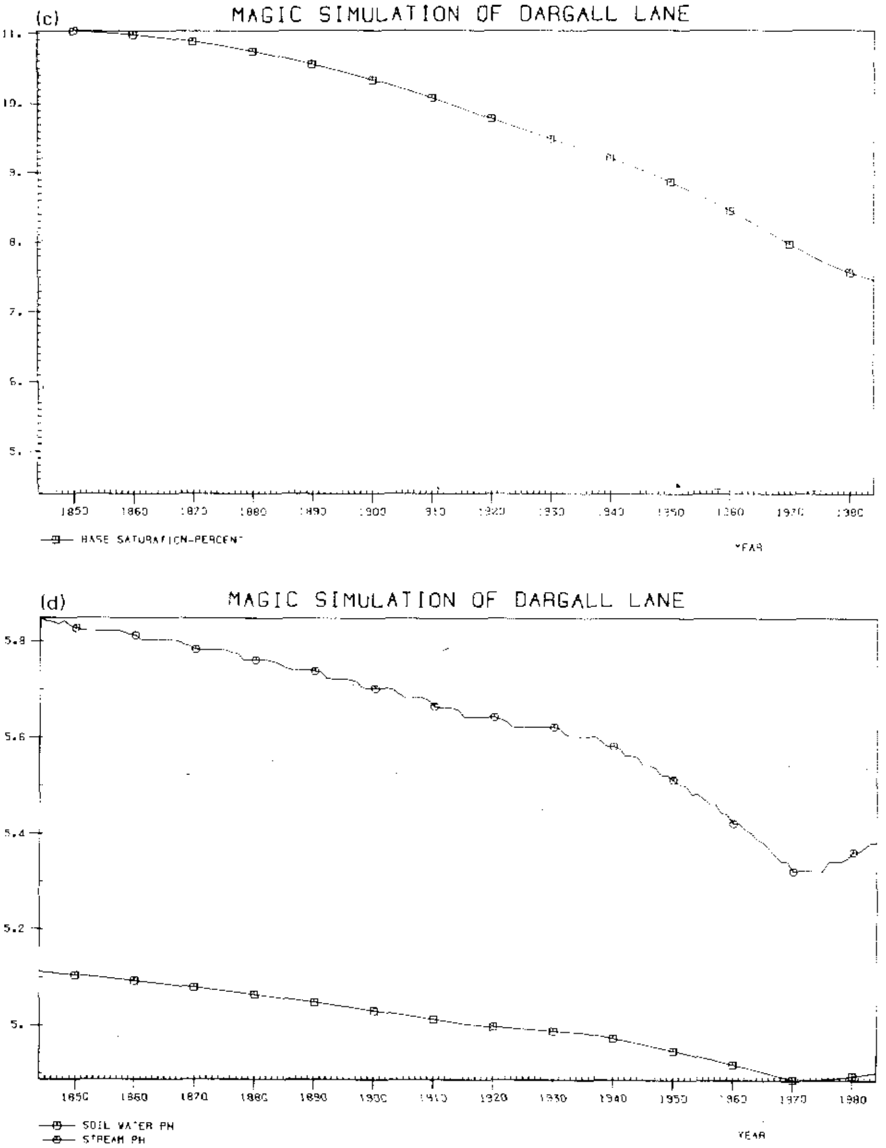

Fig. 2c. Simulation of base saturation-percentage for Dargall Lane soils for the period 1844—1984. d. Simulation of soil water and stream pH in Dargall Lane for the period 1844—1984.

A reduction by 50% of deposition over a 20 yr period (1984—2084), on the other hand, results in a slight improvement of water quality followed by reasonably steady conditions at the lower level of deposition (Fig. 4). By reducing the acid input to the system, the leaching of base cations is slowed

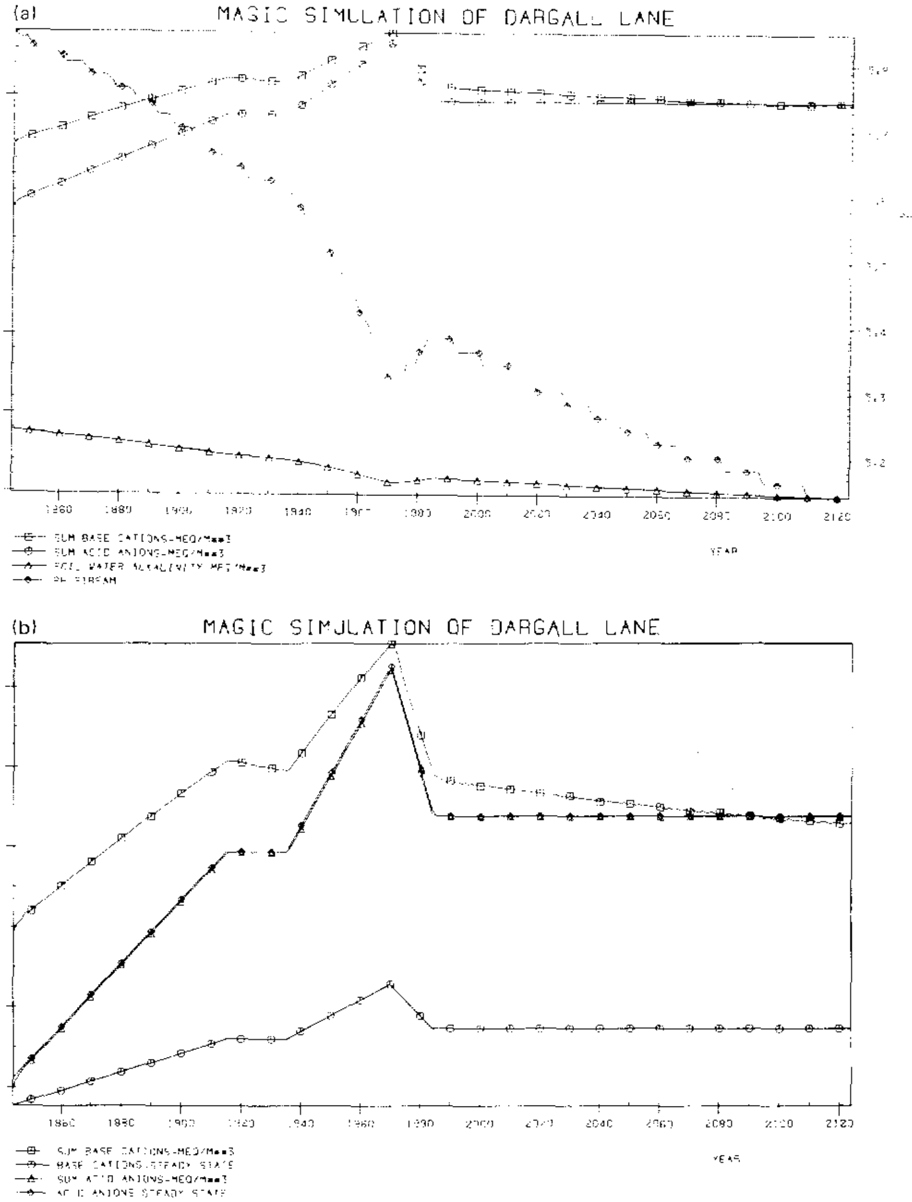

Fig. 3a, b. Simulations for the period 1844—2124 assuming 1984 deposition rates.

and the decline in base saturation is also slowed (Fig. 4c). The combination of lower deposition and stable base saturation produces streamwater pH values that are higher and steadier (Fig. 4d) than in the case of no reduction. Note, however, that even a reduction of 50% does not return the water

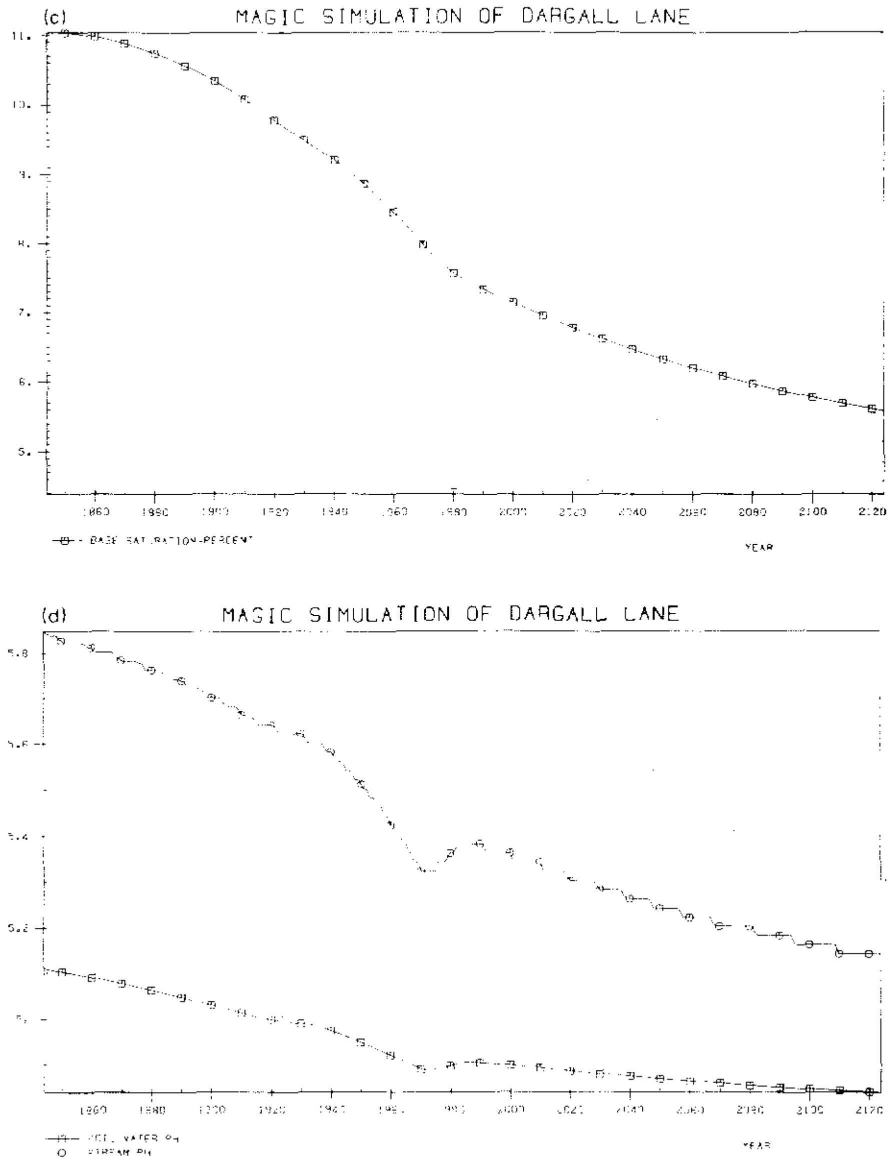

Fig. 3c. Simulation for the period 1844—2124 assuming 1984 deposition rates. d. Simulation for the period 1844—2124 assuming 1984 deposition rates showing long-term decline in soil water and stream pH.

quality to preacidification levels (Fig. 2). In fact, once the deposition reduction is complete, no further improvement in stream quality is forecast. At this new state with 50% reduced deposition, the catchment waters still have less than 50% of their original alkalinity.

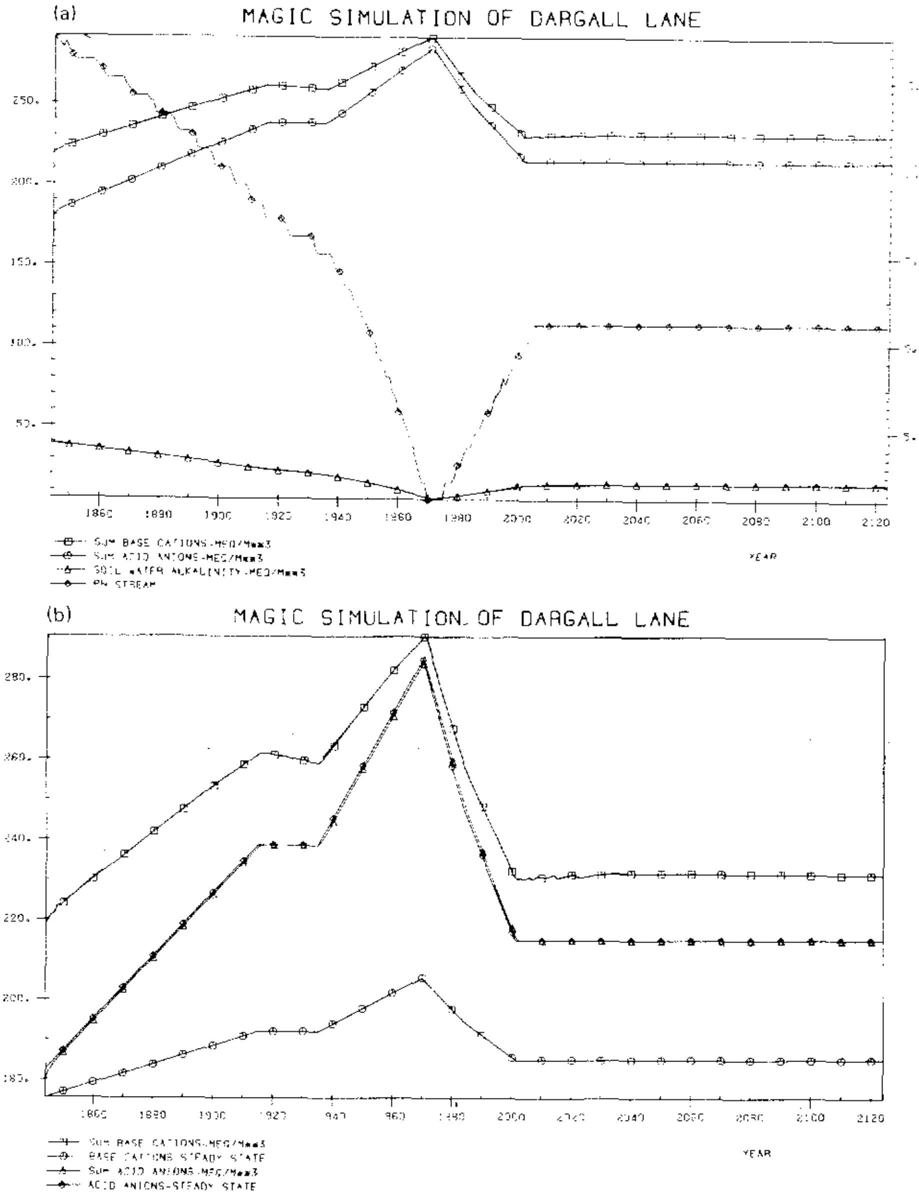

Fig. 4a, b. Simulation of Dargall Lane for the period 1844—2124 assuming 50% reduction in deposition rates.

DISCUSSION AND CONCLUSIONS

Application of this model of acid deposition effects based on soil ion exchange processes to a catchment receiving large amounts of neutral salt

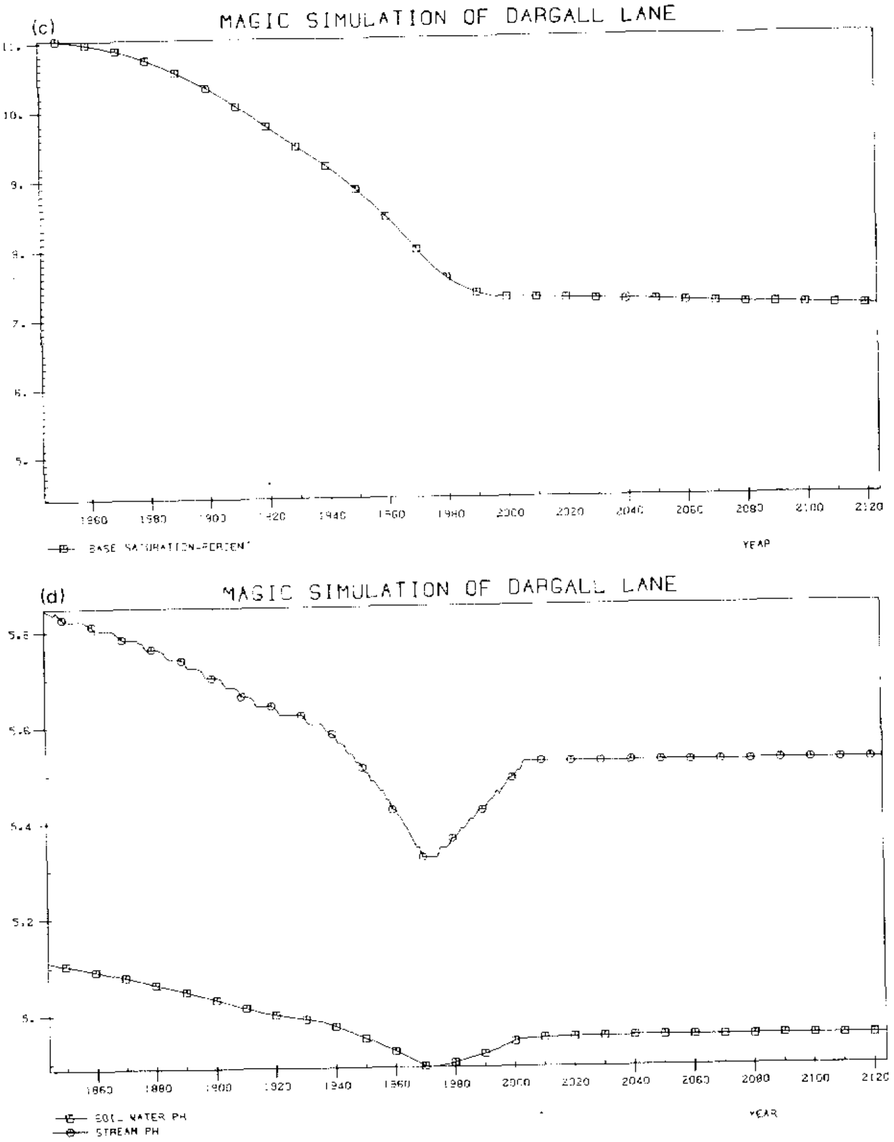

Fig. 4c. Simulation of Dargall Lane for the period 1844–2124 assuming 50% reduction in deposition rates. d. Simulation of Dargall Lane for the period 1844–2124 assuming 50% reduction in deposition rates showing levelling off of soil water and stream pH.

(sea salt) presents no difficulty. Earlier attempts at modelling catchments in areas subject to sea salt deposition tended to ignore sea salt inputs and treat only the inputs of strong acids (H_2SO_4 and NO_3, e.g., Christophersen et al., 1982). This exercise indicates that sea salts can be explicitly treated and equations involving exchange of all cations can be included. The conceptual approach of Reuss (1980, 1983) and Christophersen et al. (1984) is robust and the practice of "subtracting" sea salts from model atmospheric inputs is not necessary.

The accuracy of the model results, however, cannot be directly addressed except to say that the values produced by the model for the 1981 streamwater quality variables are consistent with the measurements available. This application of the model to Dargall Lane demonstrates a major problem inherent in all efforts to model acid deposition effects; lack of data needed for rigorous identification of model structures and the estimation of parameter values. Our understanding and conceptualizations of soil and surface water acidification by atmospheric deposition are continually improving as the results of process level field and laboratory experiments become available. It is natural that we try to incorporate these results into quantitative models of the acidification response of whole catchments. Unfortunately, the models we construct quickly become more complex than the available data will support. This is particularly true in models of long-term response such as the one presented here. The problem is two-fold. First, catchment surface water acidification is controlled by catchment soils and complex, process-oriented models of acidification thus contain soil and soil water variables that are infrequently (if ever) measured in the field. Without measurements of the internal state variables, the models cannot be sufficiently constrained and unique calibrations of the models are not possible. Second, models of long-term responses can, strictly speaking, only be calibrated and verified using long time series of data from natural systems. Such extended records exist for very few catchments. Simulation exercises such as this one in which response times are on the order of decades suggest that even the longest data records may be inadequate.

Despite these limitations, there is much that can be learned from the process of constructing and testing acidification models. Even though traditional tests of models against observations on real systems may not be possible, we can conduct simulation experiments in which alternate model structures (or parameter values) are compared to each other. In many cases, the act of designing the alternate structures can result in identification of gaps in our knowledge. In other instances, the simulations may reveal unsuspected or inconsistent behaviour implicit in the model assumptions that would lead us to reformulate or reintegrate the various components we are considering, to adopt new structures or even to delete components that have no demonstrable effect on the variables of interest. Speculative simulation exercises may also indicate new or different data that can be brought to bear on the problem.

It is difficult at this stage to reach any firm conclusions with regard to the problem of acid deposition in the UK. However there is increasing evidence that streams draining upland catchments in the UK with little buffering capacity are acidic (Harriman and Morrison, 1981; Stoner et al., 1984) and the paleoecology work of Batterbee et al. (1985) suggests that the levels of acidity have increased in recent years. The results presented here support these conclusions and give an indication of future catchment acidity. Despite a 25% reduction in the UK emission levels since 1970 a continuing decline in streamwater pH is predicted if further reductions in deposition are not achieved. This is because the weathering rate of base cations in catchment soils is not large enough to buffer the atmospherically derived acidity and the cation exchange capacity of the soils is only a finite resource for buffering purposes. A further reduction of 50% from present-day deposition levels is required even to maintain current pH levels at Dargall Lane. Clearly this has serious implications for the management of upland water resources, forest and fisheries.

Management practices such as those discussed by Whitehead et al. (this volume) may alleviate the problems to some extent but it does appear that there has been a basic underlying change in upland stream chemistry which will continue in the future.

ACKNOWLEDGEMENTS

The authors are particularly grateful to the Solway River Purification Board for providing data from the Loch Dee study and to the EEC for funding the modelling research. The views expressed represent those of the authors. We thank Hans Martin Seip, George Hornberger and Dave Kinniburgh for their helpful comments. This analysis was accomplished while one of the authors (BJC) was visiting the Department of Environmental Science, University of Lancaster, Lancaster, England. We gratefully acknowledge the support of Professor P.C. Young and his staff. The research was accomplished with the help of grants from the National Science Foundation (#CEE-8215914).

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Section 2

Modelling the effects of acidic deposition and conifer afforestation

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[3]

MODELLING THE EFFECTS OF ACIDIC DEPOSITION AND CONIFER AFFORESTATION ON STREAM ACIDITY IN THE BRITISH UPLANDS

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ABSTRACT

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

Predictions of streamwater acidification using the MAGIC model, for the British upland regions sensitive to acidic deposition are presented. They provide examples of how both acidic deposition and conifer afforestation can increase streamwater acidity. Long term trends are predicted. Model simulations demonstrate the relative effects of sea salt and acidic oxide inputs. The study highlights the need for regional surveys of chemical and hydrological catchment characteristics and the need for applications of the models at a regional scale.

INTRODUCTION

Acid soils overlying massive base-poor bedrock occupy much of the British uplands. These soils, varying from peats, peaty gleys, peaty podzols, podzols to rankers, are not only acidic but also most are a potential source of environmentally toxic aluminium. Consequently, much of the British uplands are both acidic and acid-sensitive. Stream acidification with concomitant loss of fisheries is being observed, probably on a large scale throughout the British uplands. For example, Flower and Batterbee (1983) and Batterbee et al. (1985) have shown that pH has decreased in several lochs in southwest Scotland and Harriman and Morrison (1981), Stoner et al. (1984), Harriman and Wells (1985) and Gee and Stoner (1984) report declining fish populations and in some cases disappearance of fish from lakes and streams in Scotland and Wales. These declines are associated with waters that are both acidic and have anomalously high aluminium concentrations compared with most natural waters, and which drain both moorland and conifer afforested catchments. The reason for the decline in streamwater quality remains uncertain. However, the two principal causes are believed to be acid deposition and conifer afforestation. As the U.K. debate on stream acidification progresses the relative importance of these two factors may well develop in a manner similar to that which has occurred in

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other countries where both factors have been attributed as the principal causes of stream acidification (Rosenqvist, 1980; Seip, 1980; Christophersen et al., 1982; Krug and Frink, 1983; Havas et al., 1984). Establishment of the relative importance of these two factors is essential for assessing different U.K. management strategies given that for the uplands: (1) they are extensively afforested (Binns, 1985; Davis and Solbe, 1984); (2) there is considerable economic pressure to increase conifer afforestation (the U.K. produces only 12% of its timber requirements); (3) soil cover is predominantly acidic and highly susceptible to acid deposition; (4) acid deposition levels are as high as in other countries which are believed to suffer from the effects of acidic deposition (Overrein et al., 1981; Barrett et al., 1983).

Many multidisciplinary studies have been initiated within the last five years to identify the causes of stream acidification and fish decline. They demonstrate the seriousness with which the UK considers the problems of stream acidification. Such studies have included work in the Galloway Region of South West Scotland (Burns et al., 1984), Wales (Roberts et *al*., 1983; Reynolds et al., 1983; Hornung et al., 1985; Neal et al., 1986; Llyn Brianne study, 1986) and Central Scotland (Mason and Seip, 1985); collaborating bodies include the Solway River Purification Board, D.A.F.S. Freshwater Fisheries Laboratory, Forestry Commission, Department of the Environment, Institute of Hydrology, Institute of Terrestrial Ecology, the Macaulay Institute, a team from the Imperial College, the Royal Society and the Scandinavian Academies of Science.

Given the scale of these U.K. studies and the fact that both acidic deposition and upland afforestation are extensive and variable on a regional scale there is a great opportunity to determine some of the major effects of atmospheric pollutants and conifer afforestation. Knowledge gained would also be important with regard to the European debate on the effects of acidic deposition.

To illustrate the importance of both acidic deposition and conifer afforestation a modelling study has been undertaken to investigate long-term changes in stream acidity in Dargall Lane, a moorland sub-catchment of Loch Dee, in Galloway, southwest Scotland. The model used, MAGIC, (Model of Acidification of Groundwater In Catchment) which includes sea salt effects, is based on the assumption that surface water chemistry is determined by reactions taking place in the soils and rocks within a catchment (Fig. 1). The processes described by the model include anion retention by the soils, cation exchange by soils, solubility ($Al(OH)_3$) and mobilisation of aluminium, weathering of minerals as a source of base cations, dissociation of carbonic acid with subsequent exchange of hydrogen ions for base cations, and degassing of CO_2 in the streams (Cosby et al., 1984, 1985a, b, 1986a, b; Wright et al., 1986). Stream chemistry data for Dargall Lane are used to calibrate the model and details of catchment characteristics, model structure and the application to Dargall Lane are described elsewhere (Cosby et al., 1986b). While the model represents a simple lumped description of the catchment, the appropriateness of the model has been

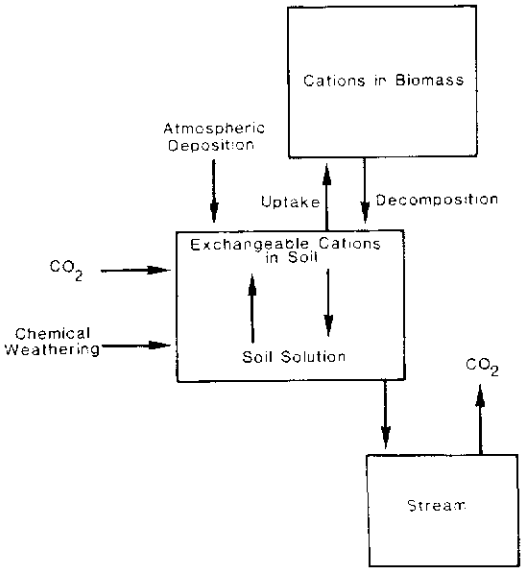


Fig. 1. The magic model.

in part validated in that it is able to reconstruct the same declining pH levels of recent years obtained by paleoecological analysis not only for the U.K. (Batterbee et al., 1985; Cosby et al., 1986b) but also for Scandinavia and the USA (Wright et al., 1986). These results have been obtained using acidic oxide (SO_x, NO_x) deposition rates following the pattern of industrial emissions.

No account has been taken of the role of organic acids in buffering streamwater pH, and consequently here the model is primarily being used for catchments where strong acids are the major acidifier. Various factors, such as soil depth, soil chemistry, rainfall chemistry and bedrock type, affect catchment and hence streamwater acidity. Thus different catchments will respond to land use change and acidic oxide inputs in different ways, as the MAGIC model predicts. For example with thin soils, consumption of base cations will be much more rapid and consequently acidification will take place earlier. Examples of different catchment responses are illustrated by the field work of Batterbee et al. (1985) and the modelling exercises of Cosby and co-workers (Cosby et al., 1985a, b, 1986a, b). Other factors such as climate or agricultural changes have yet to be explored within a modelling context. Also, the MAGIC model gives annual flow weighted averages whereas during storm events there will be significant fluctuations around this mean. Dynamic models have been developed and applied to hydrology (Christophersen et al., 1982; Whitehead et al., 1986a, b; Reynolds et al., 1986) and a dynamic version of MAGIC is currently under development.

Several chemical, biological and hydrological processes control streamwater 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 some aspects of afforestation and deforestation, dry and occult deposition and variations in acidic oxide loading.

LONG-TERM ACIDIFICATION TRENDS FOR THE MOORLAND DARGALL LANE

Fig. 2 shows a simulation of long-term *acidity* for the Dargall Lane moorland catchment. The sulphate deposition history (Barrett et al., 1983) is shown in Fig. 2a and this 'drives' the MAGIC model. The historical simulation of pH shown in Fig. 2b 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 (Batterbee et al., 1985; Flowers and Batterbee, 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 streamwater acidity given different future deposition levels. For Dargall Lane moorland 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 linearly by 50% from 1984 levels (between 1985 and 2000) the results indicate that further streamwater acidity will be averted and pH rises to 1950 levels (Fig. 2b). Further details of the application of this model are given elsewhere (Cosby et al., 1986b). Note an increase in streamwater pH about 1980; this follows a significant drop in sulphur emissions during the 1970s. Evidence is emerging for this recovery based on diatom records although chemical evidence is inconclusive to date. Note also that a more rapid decline in streamwater pH is predicted if there had been no reductions in emissions since 1970. Regarding the effects of reduced emissions the size of the adsorbed organic and inorganic sulphur stored in the soil will be a major factor in controlling recovery rates. If this store is large, recovery in streamwater pH could be extremely slow.

AFFORESTATION EFFECTS

Afforested systems are more complex to model than moorland systems because of the introduction of the forest perturbs a moorland ecosystem which in itself is difficult to 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 (Fowler, 1984; Unsworth and Crossley, 1986; Fowler et al., 1986) and evapotranspiration will increase the concen-

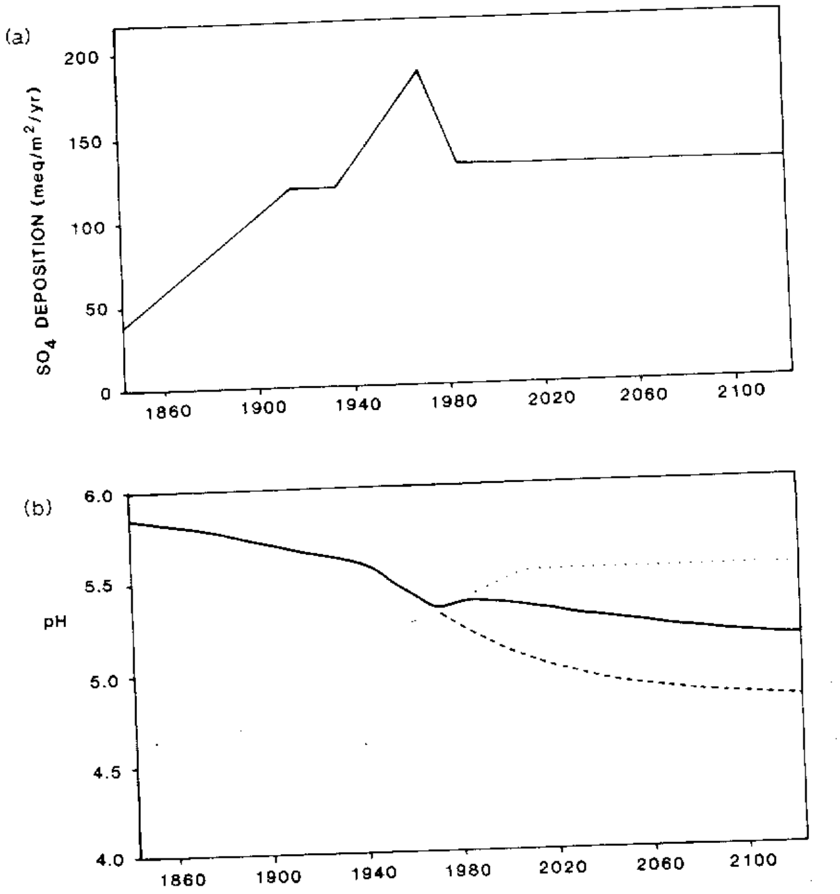


Fig. 2. a. Sulphate deposition history used as input for the MAGIC reconstruction of pH in the Dargall Lane moorland catchment.
b. Simulation of the pH of streamwater in the Dargall Lane moorland catchment assuming three sulphate deposition scenarios.
——— = Historical levels to 1984 and constant 1984 levels thereafter (see 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.

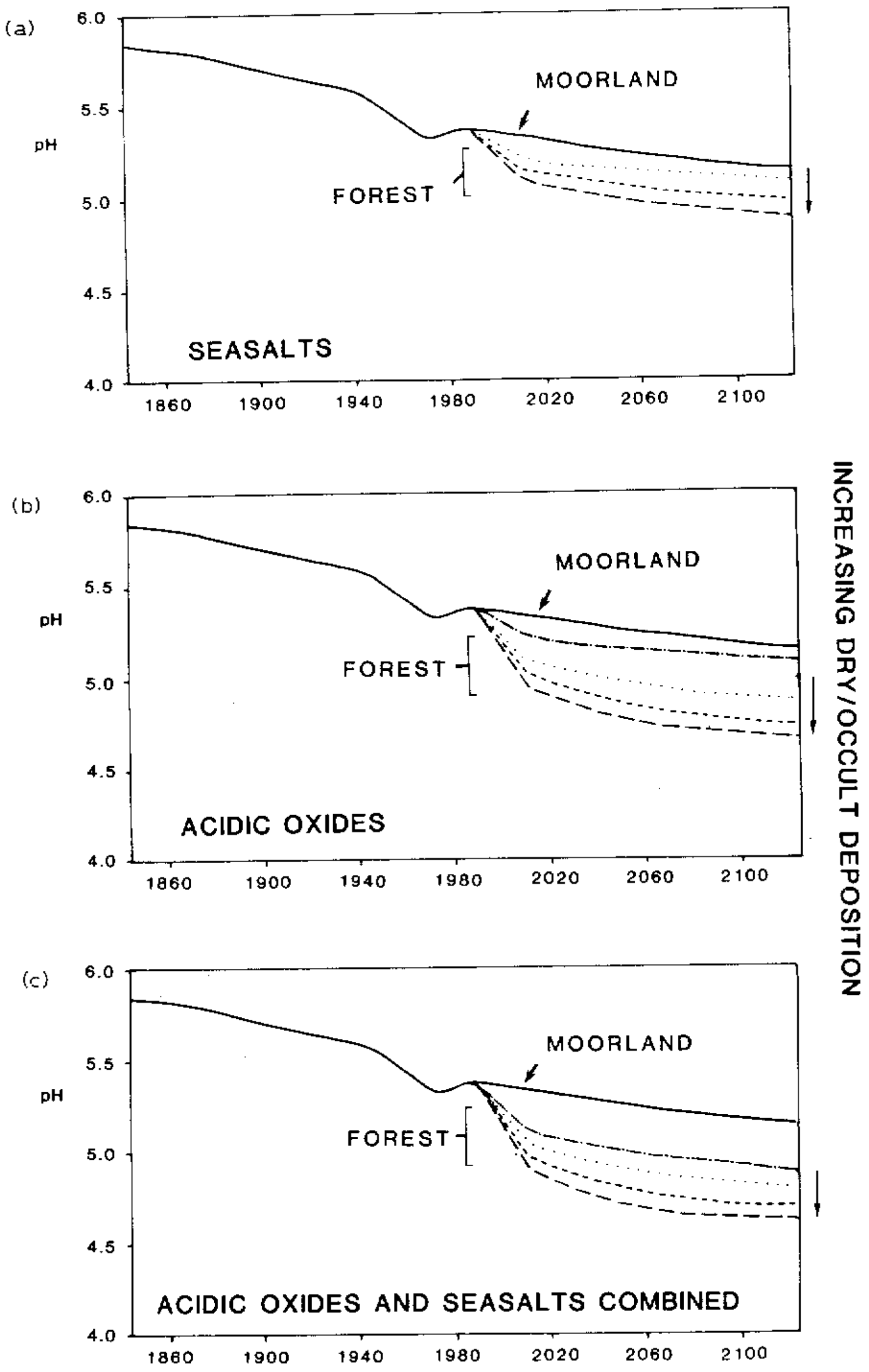
tration of dissolved components entering the stream. The magnitude of these different effects varies considerably; for example evapotranspiration from forests in the British uplands is typically of the order of 30% of the precipitation which is almost twice the figure for moorland estimated as 16%. This will have the consequence that the total anion concentrations within the stream and soil waters increase by 14% following afforestation (Law, 1956, 1957; Calder, 1979; Calder and Newson, 1979). The forest will also increase anion and cation loading due to the enhanced filtering effect of the trees on air and occult sources. By occult deposition we refer to deposition of wind-driven particles and droplets that are not captured/detected in standard open collector raingauges, e.g., low cloud and mist. [Several forest catchment studies have shown that chloride concentrations are higher in streamwaters than in the corresponding rainfall or grassland streams. Such a difference results from dry and occult deposition assuming that chloride is derived from a maritime source and not from leaching from the catchment bedrock. Such increases are typically of the order of 30%; N.B. sometimes Cl inputs do not match Na inputs, and consequently not all Cl inputs come from a maritime source. However, such pollutant Cl inputs are only likely close to major sources of HCl.] The filtering effects will apply both to marine and pollutant aerosol components. Altering the hydrological pathways can also have a major effect on streamwater 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 whilst the bedrock, if silicate or carbonate bearing, provides proton consumption by weathering reactions (Neal et al., 1986; Whitehead et al., 1986b; Reynolds et al., 1986). 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 40 years. It should also be noted that many biological, chemical and hydrologic factors may also be important. For example, 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. Consequently the results presented here must be viewed as highlighting the importance of dry and occult deposition processes.

Of critical importance is the relative and absolute contribution of marine and pollutant inputs from dry and occult deposition. Fig. 3a shows the effect of increasing evapotranspiration from 16 to 30% over the forest growth period with varying levels of marine, pollutant and marine plus pollutant inputs.

Fig. 3. a. Simulation of the pH of the streamwater from the Dargall Lane catchment comparing the moorland catchment response assuming the Fig. 2a deposition rates (———), the effect of 14% additional evaporation following afforestation (······), the effect of 14% additional evaporation plus 15% additional input of natural seasalts following afforestation in 1985 (– – – –), and the effect of 14% additional evaporation plus 30% additional input of natural seasalts 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).


(a)
6.0
5.5
pH
5.0
4.5
4.0
MOORLAND
FOREST
SEASALTS
1860
1900
1940
1980
2020
2060
2100
(b)
6.0
5.5
pH
5.0
4.5
4.0
MOORLAND
FOREST
ACIDIC OXIDES
1860
1900
1940
1980
2020
2060
2100
(c)
6.0
5.5
pH
5.0
4.5
4.0
MOORLAND
FOREST
ACIDIC OXIDES AND SEASALTS COMBINED
1860
1900
1940
1980
2020
2060
2100
INCREASING DRY/OCCULT DEPOSITION

Increasing either marine or pollutant components (Fig. 3, b and c) 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% has a similar effect but the changes are much smaller. The important features of these results are the enhanced sea salt and acidic oxide inputs from increased scavenging by the trees resulting in a marked reduction in pH levels and the additive effect when both processes are combined. These reductions are much greater than the effect of evapotranspiration.

ATMOSPHERIC ACIDIC OXIDE EFFECTS

An important factor in determining stream acidity in the upland U.K. is the amount of acidic oxide deposition; rates of deposition (non marine wet deposition and dry deposition) can vary from 0.5 to over 6 $g\,m^{-2}\,yr^{-1}$ of S and from 0.1 to over 0.5 $g\,m^{-2}\,y^{-1}$ of N (Barrett et al., 1983; Overrein et al., 1981). Fig. 4 shows the effects of such variations for both moorland and forested catchments; the highest levels correspond to areas with high atmospheric acidic oxide rates (3 times the historic and 1984 deposition levels observed in the Southern Uplands of Scotland). For the forest simulations it has been assumed that a conifer forest has been introduced onto the Dargall Lane moorland in 1844. With increasing atmospheric acidic oxide pollution, the decline in stream pH is accelerated, the changes occur much earlier, and the final pH of the streamwater is lower.

DEFORESTATION EFFECTS

Whilst afforestation increases stream acidity, as shown both by the model predictions and field evidence (Harriman et al., 1985), then deforestation will result in a reduction in streamwater acidity. Fig. 5 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 pH recovery following deforestation at the intermediate deposition levels is greater than that at the higher levels. However, in terms of H^+ concentrations the greatest recovery occurs under the highest deposition loadings. This is because base saturation has not been completely depleted, and the reduced deposition following deforestation can be buffered by the available cations. Note that afforestation following tree harvesting will negate the improvement in streamwater acidity. At deforestation, several factors not included in the model will become particularly important (e.g. increased NO_3^- in the streamwater, changes in acidity/base saturation, accumulation/breakdown of humus, and logging practice).

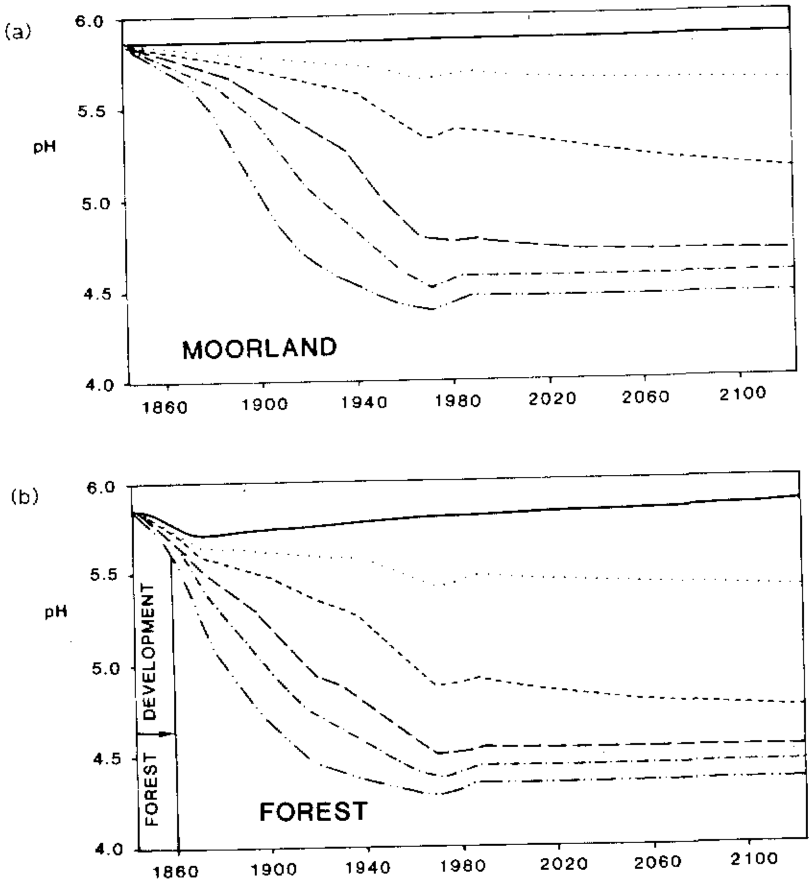


Fig. 4. a. Simulation of the pH of streamwater from the Dargall Lane moorland catchment assuming sulphate deposition patterns (shown in Fig. 2a) modified by various factors to reproduce a range of loading conditions (i.e. from pristine to heavy pollution).

b. Simulation of the pH streamwater from the 'forested' Dargall Lane catchment assuming afforestation from 1844 onwards and sulphate deposition patterns (see Fig. 2a) multiplied by various factors to reproduce a range of loading conditions from pristine to heavy pollution.

—— Background rates(pristine conditions)
······ 0.5 × Fig. 2a deposition concentrations(low pollution)
– – – – 1 × Fig. 2a deposition concentrations } intermediate pollution
–—— 1.5 × Fig. 2a deposition concentrations }
– ·–·– 2 × Fig. 2a deposition concentrations } heavy pollution
–·····–··– 3 × Fig. 2a deposition concentrations }

IMPLICATIONS

The modelling enables preliminary assessment to be made of some 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

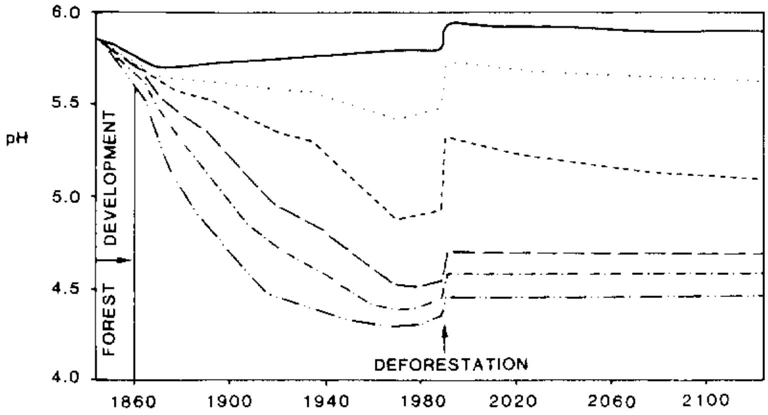


Fig. 5. Simulation of the pH of streamwater for the Dargall Lane catchment assuming afforestation from 1844 and deforestation in 1990. Deposition patterns as described in Fig. 4.

example, the above simulation suggests that for present acidic oxide loadings significant streamwater acidification can occur, irrespective of other complicating processes. The model also suggests that reductions or increases in acidic oxide loadings can significantly change the acidity of streamwater in upland areas similar to Dargall Lane. The model predictions are similar to observations of stream acidity found in Southern Scandinavia and add weight to the conclusion that such pollutant inputs can be a major source of stream acidification in those countries as well. How important this acidification process is on a regional basis in the upland U.K. cannot be gauged immediately from the present study because many unresolved factors remain, as mentioned above. However, much of the British uplands have soils which are susceptible to acidic inputs; it is therefore reasonable to assume that the modelling exercise could be applied on a regional scale. If the above results are representative of sensitive upland areas then reductions in present acidic depositions of the order of 50% are required to prevent further increase in stream acidity for moorlands; afforested catchments require greater reductions. N.B. The relationship between deposition and emissions is not necessarily linear, emission levels may need more substantial reductions. The study points to the need for further regional analysis of soil and streamwater 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 and modelling studies. 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 (Whitehead et al., 1986b).

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Section 3

Modelling the effects of hydrological changes on stream water acidity

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[3]

MODELLING THE EFFECTS OF HYDROLOGICAL CHANGES ON STREAM WATER ACIDITY

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ABSTRACT

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A mathematical model describing the hydrology and chemical reactions associated with soil and groundwater compartments in a catchment is used to assess the effects of hydrological changes on stream water acidity. By altering the percolation equation in the model the proportion of baseflow to surface soil flow is altered. This radically affects the stream chemistry and it is shown that increasing baseflow can significantly improve stream quality, reducing acidity and lowering aluminium levels. It is proposed that catchment experiments are established to investigate methods of altering the hydrology to take advantage of the buffering capacity of baseflow waters.

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 UK 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., 1984) and the Freshwater Fisheries Laboratory (Loch Ard Study; Harriman and 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 and Morrison, 1981; Gee and Stoner, 1984) have reported elevated acidity and aluminium levels in upland streams draining afforested (conifer) catchments in the UK. Moreover in many of these areas and particularly forested catchments fisheries have deteriorated and restocking programmes have been unsuccessful.

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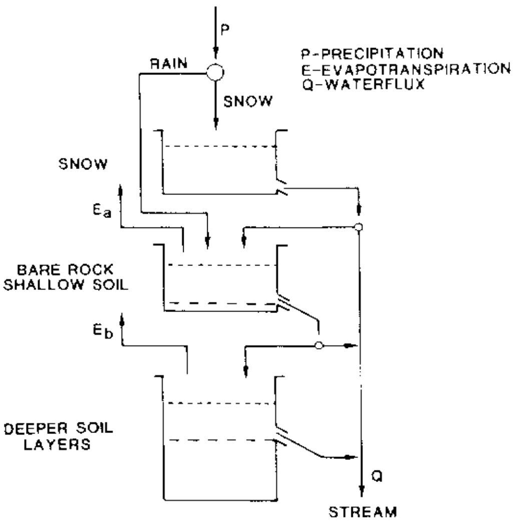

Processes operating

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

Fig. 1. Hydrological model used for Harp Lake catchment and main processes operating.

One major advance in this area has been the development of mathematical models to describe the dominant interactions and processes operating and to simulate catchment behaviour. Recently 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., 1985 a,b, this volume; Kämäri et al., 1985). Correspondingly, dynamic models have been successfully applied descriptively to several catchments (Christophersen et al., 1982, 1984; Whitehead et al., 1986). For example, Christophersen et al. (1982, 1984) 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; Rustad et al., 1986) 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).

Several workers have identified the importance of baseflow processes in buffering stream water acidity (Ramberg, 1981; Sharp et al., 1984; Kinniburgh and Edmunds, 1984; Puhe and Ulrich, 1985). In this paper the extended model applied to the Harp Lake catchment, has been used prescriptively to investigate the buffering potential and the effects of hydrological changes on stream water acidity. This work is presented to open discussion on the potential of using hydrological techniques to improve stream water quality particularly in areas where land use change may enhance the effects of acid deposition and acid soil formation such as upland afforested catchments.

MODELLING APPROACH

The model used here has been described in detail elsewhere (Seip et al., 1985; Rustad et al., 1986) and hence only the salient features are given here. The three-compartment model shown in Fig. 1 represents chemical and hydrological processes operating in snow cover, near-surface soils and groundwater. The figure shows the flow pathways and the dominant chemical processes in each compartment. Flow movement between the soil and groundwater compartments is restricted by a "percolation" equation as follows:

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

and:

$$A_{\mathrm{SIG}} = 1.33P - 0.33P(B/B_{\min})^3 \qquad \text{for} \qquad B < B_{\min}$$

where B refers to the groundwater compartment water level and $B_{\min}$ and $B_{\max}$ refer to minimum and maximum water levels, respectively. The parameter P can be considered as a percolation parameter so that increasing P increases the fraction of flow, A_{SIG}, routed to the lower 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.

This model has been calibrated and validated using several years data for the forested Harp Lake catchment in Canada (catchment area 1.4 km^2; bedrock geology is amphibolite, schist and gneiss; overlying soils are sandy loams of less than 1 m thickness; thin soils and rock ridges account for 33% of the catchment; tree types are sugar maple, beech, birch and aspen). Here the model and the data have been employed to evaluate the effects of changing

TABLE 1

Flow and chemistry simulation results for 1977—80: Percolation parameter 0.1 (52.3% baseflow)

	Flow ($m^3 s^{-1}$)	H^+ ($\mu eq\ l^{-1}$)	Al^{3+} ($\mu eq\ l^{-1}$)
Soil compartment			
mean	0.75	49.78	46.71
st. dev.	2.05	1.48	4.06
maximum	24.98	52.19	53.70
Groundwater compartment			
mean	0.82	2.32	0.0183
st. dev.	1.65	1.79	0.0644
maximum	11.47	12.38	0.7165
Stream			
mean	1.57	6.59	2.118
st. dev.	3.36	11.55	5.978
maximum	30.71	51.68	52.14

TABLE 2

Flow and chemistry simulation results for 1977—80: Percolation parameter 0.6 (88.5% baseflow)

	Flow ($m^3 s^{-1}$)	H^+ ($\mu eq\ l^{-1}$)	Al^{3+} ($\mu eq\ l^{-1}$)
Soil compartment			
mean	0.16	49.78	46.71
st. dev.	0.49	1.48	4.06
maximum	7.11	52.19	53.70
Groundwater compartment			
mean	1.23	1.69	0.0048
st. dev.	2.26	1.04	0.0143
maximum	18.48	7.58	0.1650
Stream			
mean	1.39	0.46	0.0095
st. dev.	2.71	1.43	0.0939
maximum	24.59	16.15	1.59

baseflow contribution via the percolation equation. Also since acidic deposition is relatively low for the Harp Lake area, additional model runs have been undertaken to simulate an area subject to significant stream water acidity by increasing wet and dry sulphur by a factor of 3 (from 2 to 6 g S m^{-2} yr^{-1}).

TABLE 3

Flow and chemistry simulation results for the rainfall period 28/7/77—17/12/77: Percolation parameter 0.1 (42.2% baseflow)

	Flow ($m^3 s^{-1}$)	H^+ ($\mu eq\ l^{-1}$)	Al^{3+} ($\mu eq\ l^{-1}$)
Soil compartment			
mean	1.27	51.12	50.48
st. dev.	2.17	0.65	1.94
maximum	11.28	52.19	53.70
Groundwater compartment			
mean	0.92	3.16	0.0242
st. dev.	1.14	1.77	0.0376
maximum	4.03	7.47	0.1573
Stream			
mean	2.18	16.56	6.369
st. dev.	3.07	15.29	9.302
maximum	11.75	51.68	52.14

TABLE 4

Flow and chemistry simulation results for the rainfall period 28/7/77—17/12/77: Percolation parameter 0.6 (89.5% baseflow)

	Flow ($m^3 s^{-1}$)	H^+ ($\mu eq\ l^{-1}$)	Al^{3+} ($\mu eq\ l^{-1}$)
Soil compartment			
mean	0.18	51.12	50.48
st. dev.	0.29	0.65	1.94
maximum	1.30	52.19	53.70
Groundwater compartment			
mean	1.28	2.09	0.0042
st. dev.	1.47	0.55	0.0033
maximum	6.04	3.65	0.0183
Stream			
mean	1.43	0.65	0.0008
st. dev.	1.71	0.68	0.0038
maximum	7.23	4.46	0.0335

RESULTS AND DISCUSSION

The percolation parameter, set to 0.75 for Harp Lake by Seip et al. (1985), was varied between 0.075 and 0.9 to assess the sensitivity of flows and chemistry to changes in percolation and hence baseflow.

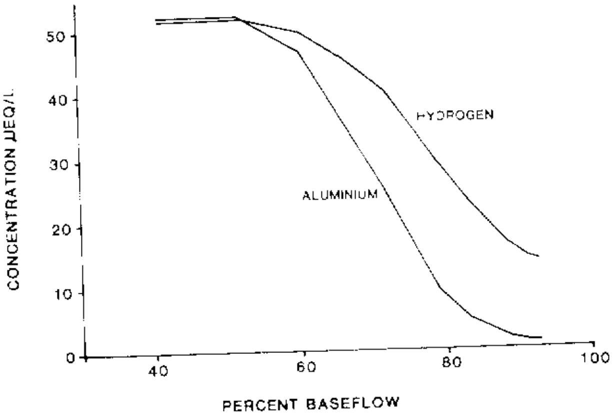

Fig. 2. Maximum H^+ and Al^{3+} concentrations in the stream showing variation over a range of baseflow conditions (three-yr simulation 1977–1980).

Tables 1 and 2 give summary statistics for flow, H^+ and Al^{3+} concentrations given low deposition rates (i.e. those used in the Harp Lake Study — Seip et al., 1985). The simulation period is 1977–80 and results are given for the outputs from the soil and groundwater compartments and the stream. Table 1 shows the results given a percolation parameter of 0.1 and Table 2 for a percolation parameter of 0.6; these runs correspond to baseflow contributions of 52.3 and 88.5%, respectively. In general there is little change in the concentrations of H^+ and Al^{3+} for the soil and groundwater compartments with changes in the percolation parameter since in the short-term the ion exchange and solubility controls are computed largely independent of flow. However the concentrations in the stream do change significantly with changes in the percolation parameter. For example maximum H^+ concentrations decrease from 51.68 to 16.15 μeq l^{-1}. Similarly maximum Al^{3+} concentrations decrease from 52.14 to 1.59 μeq l^{-1}. These changes are due to the reduction in the upper soil zone flows reaching the stream and the corresponding increase in flow from the lower soil horizon and bedrock. In this particular case average baseflow increases from 52.3 to 88.5% of the streamflow and average soil flow reduces from 47.7 to 11.5%. Thus changes in percolation and hence baseflow can have a significant effect on H^+ ion and Al^{3+} concentrations.

The peak values of H^+ ion and Al^{3+} concentrations in the stream waters are dominated by the snowmelt events in Harp Lake with snowmelt providing a major source of stream water acidity. However even mean stream water levels show reductions of 93% in the case of H^+ and 99.6% for Al^{3+} just by changing the proportion of baseflow. Mean levels are biased by the summer/dry season flows when the stream chemistry is dominated by nonacidic baseflow. Thus the effects can be even more significant if a rainfall rather than a snowmelt period is considered. Tables 3 and 4 show flows and concentrations during the rainfall period (28/9/77–17/12/77). Peak Al^{3+}

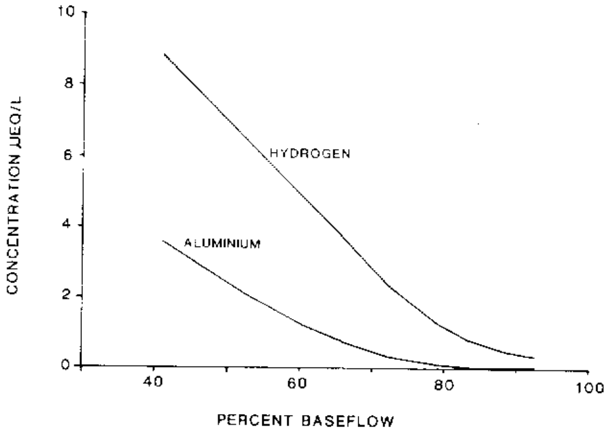

Fig. 3. Mean H^+ and Al^{3+} concentrations in the stream showing variation over a range of baseflow conditions (three-yr simulation 1977—1980).

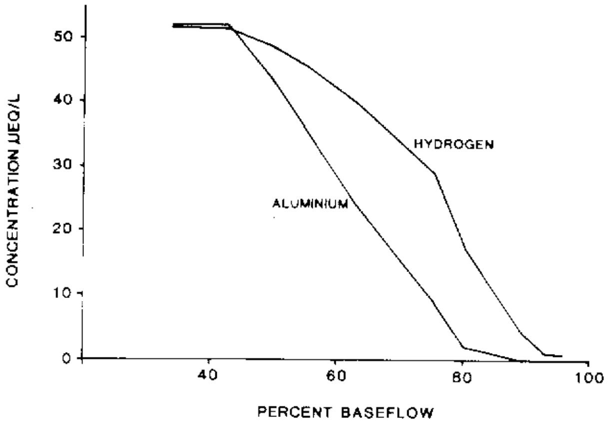

Fig. 4. Maximum H^+ and Al^{3+} concentrations in the stream showing variation over a range of baseflow conditions (simulation over rainfall period 28/7/77—17/12/77).

concentrations fall by 99.9% and peak H^+ ion concentrations fall by 91.4%. Mean concentrations over the period fall by 99.9 and 96.1% for Al^{3+} and H^+ ion concentrations, respectively.

The changes in stream water concentrations for H^+ ion and Al^{3+} to changes in the baseflow contribution to stream water is non linear. This is illustrated in Figs. 2, 3, 4 and 5 which show H^+ and Al^{3+} maximums and means over a range of baseflow conditions for both the long- and short-term data sets: All concentration values fall as the percolation parameter increases; the rate of decrease varying from one variable to another. In general increases in baseflow results in significant reductions in H^+ ion and Al concentrations. Studies by Seip and Rustad (1984) show a similar non-linear behaviour when

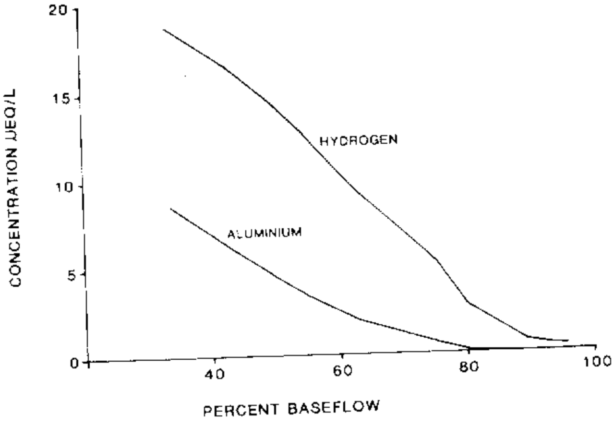

Fig. 5. Mean H^+ and Al^{3+} concentrations in the stream showing variation over a range of baseflow conditions (simulation over rainfall period 28/7/77—17/12/77).

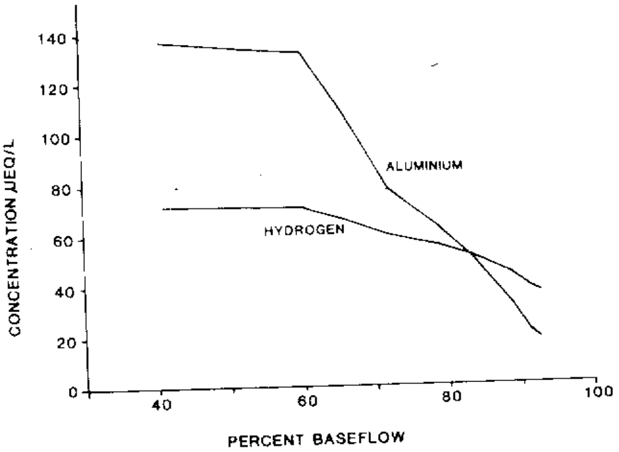

Fig. 6. Maximum H^+ and Al^{3+} concentrations in the stream showing variation over a range of baseflow conditions (three-yr simulation 1977—1980 assuming deposition increased to $6\,g\,S\,m^{-2}\,yr^{-1}$).

upper and lower soil horizon waters are mixed. Note, however, that the model assumes aluminium solubility controls with gibbsite and this may require modification as further information on aluminium chemistry becomes available.

Finally, the model runs have been repeated assuming an increased acid deposition rate of $6\,g\,S\,m^{-2}\,yr^{-1}$, a factor of three times the Harp Lake values. This higher rate is more representative of the values obtained in central Britain and central Europe. The effect of this change is illustrated in Figs. 6, 7, 8 and 9 which show the curves for the H^+ ion and Al^{3+} stream water concentrations; increased H^+ ion and Al^{3+} concentration maximums

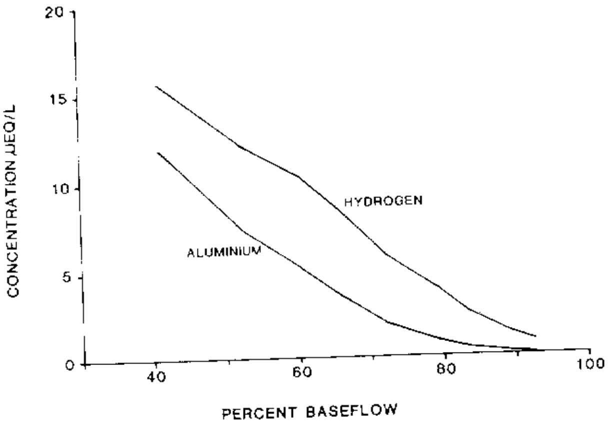

Fig. 7. Mean H^+ and Al^{3+} concentrations in the stream showing variation over a range of baseflow conditions (three-yr simulation 1977—1980 assuming deposition increased to 6 g S m^{-2} yr^{-1}).

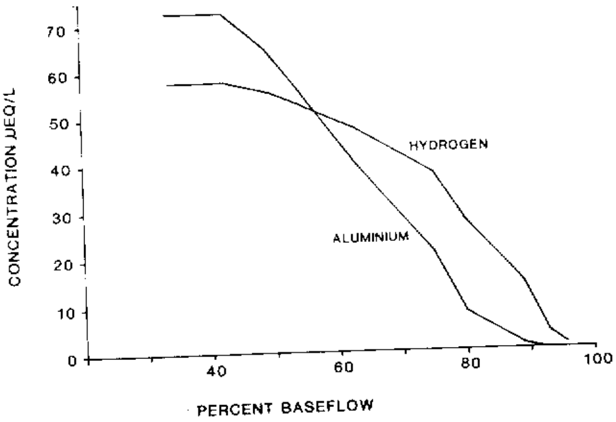

Fig. 8. Maximum H^+ and Al^{3+} concentrations in the stream showing variation over a range of baseflow conditions (simulation over rainfall period 28/7/77—17/12/77 assuming increased deposition of 6 g S m^{-2} yr^{-1}).

are obtained and the curves are shifted along the baseflow axis. In other words in catchments subject to increased acid deposition the effect of the baseflow contribution is even more important in determining streamflow chemistry. Thus a small increase in baseflow is likely to have a significant effect in reducing stream acidity and aluminium levels.

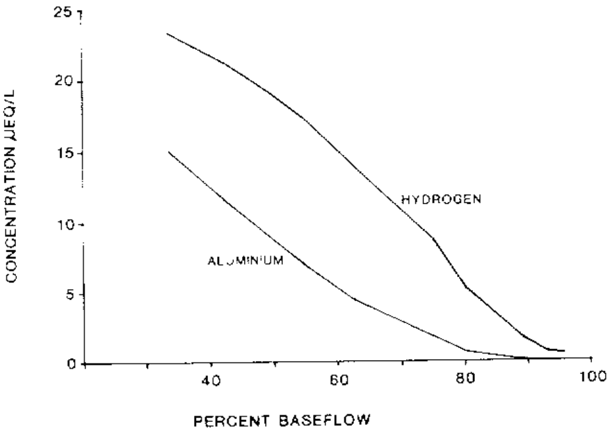

Fig. 9. Mean H^+ and Al^{3+} concentrations in the stream showing variation over a range of baseflow conditions (simulation over rainfall period 28/7/77—17/12/77 assuming increased deposition of $6\ g\ S\ m^{-2}\ yr^{-1}$).

CONCLUSIONS

The Harp Lake model has demonstrated the importance of baseflow contribution to controlling stream water acidity from conifer forest systems and has highlighted the value of mathematical modelling as a prescriptive tool. Clearly generalisations cannot be made regarding the effects of baseflow changes for catchments since acid buffering mechanisms will be strongly related to bedrock type, the nature of hydrological and chemical processes in the different soil horizons, the extent of mineralisation and land use; the latter three usually being poorly defined and not easily definable on a catchment scale. Nevertheless the results suggest the need for research on the physical means of controlling stream water quality in upland afforested catchments and also illustrates the sensitivity of predictions to changes in the parameters controlling percolation and hence baseflow. In general there is a need for further research into the sensitivity of the process models particularly in relation to parameter uncertainty.

Some of the drainage and cultivation techniques used in upland afforestation programmes in the UK have proved inappropriate, and are presently being reviewed and changed. Downslope ditches and land disturbance have led to the reduction of drinking water quality (colour, turbidity and taste) and increased costs of treatments to the water industry (Davis and Solbe, 1984; Richards, 1985). This water quality deterioration results from increased physical erosion which in turn has had a deleterious effect on the landscape (Newson, 1980; Robinson, 1980). Further the use of downslope drainage ditches has ensured that acidic, aluminium bearing, storm water from the upper soil organic horizons enters the stream directly. During high flow events the groundwater store (where acidic surface soil waters are neutralised by inorganic reactions) is bypassed (if percolation rates are low) and thus groundwater buffering controls are minimised. As mentioned in the introduction, this has had a deleterious effect on fish populations in afforested streams in upland UK. Consequently there is an urgent need to review and modify forestry practices in the uplands particularly since there is considerable economic pressure to increase conifer afforestation in the "economically marginal" upland regions; the UK produces only 9 to 12% of its timber requirements.

New forestry management practices are being investigated as part of several studies, supported by the Forestry Commission. The results presented here suggest that modifying the hydrological regime to increase percolation and hence baseflow could significantly improve stream water acidity and reduce aluminium levels. Regarding the techniques used to change the hydrological regime, these are not well established and will need to be site specific and cost effective. Schemes that might be/are being considered include contour or herring bone drainage, deep planting/ploughing to allow water penetration through the impermeable clay soil layer (while minimising erosion effects), planting without ploughing, planting of deep rooted trees (particularly near the stream channels), and the restriction of direct entry of drainage channels into the stream, and the drainage of "old" water from the catchment. These alternatives might not only improve stream acidity and aluminium levels but most would also reduce the problems of colour, turbidity, taste and erosion.

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Section 4

A time series approach to modelling stream acidification

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[3]

A TIME-SERIES APPROACH TO MODELLING STREAM ACIDITY

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ABSTRACT

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The techniques of time-series analysis are applied to field data from Norway, Scotland and Wales to model the response of stream acidity. Hourly, daily and weekly data for pH, flow, aluminium, sulphate, magnesium and calcium are used to identify model structures and estimate model parameters. The recursive time-series techniques are shown to be particularly useful for identifying physical and chemical changes and providing simple, robust models of streamwater chemistry. The dominant processes are identified using the time-series techniques which provide a systematic method of analysing hydrochemical data prior to the development of more complex physico-chemical models.

INTRODUCTION

In recent years acid deposition is believed to have 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, Norway and the UK have shown that descriptive mathematical models can be developed successfully given a suitable data base (Christophersen et al., 1982, 1984; Cosby et al., 1985, 1986). 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.

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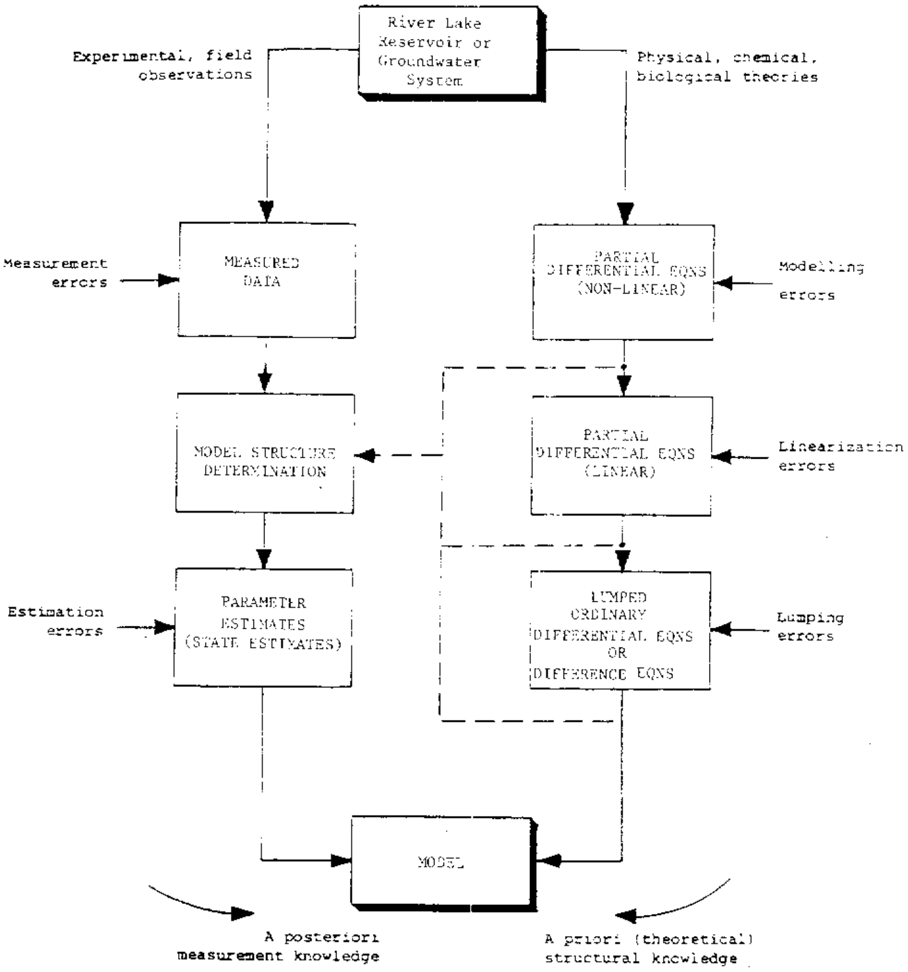

Fig. 1. Combining "theoretical" knowledge and field measurements in the modelling procedure (adapted from Beck, 1984).

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 Fig. 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.

One 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 while 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 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.

One simplification used by modellers to ease the computation burden is to linearize the equations. The 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). However numerical dispersion again causes problems because of the discretization of advective terms in linear partial differential equations. Another simplified approach is to develop ordinary differential equation models (Christophersen et al., 1982; Cosby et al., 1985). 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.

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; Whitehead and O'Connell, 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. The particular technique applied in this paper to model stream acidification is the recursive approach to time-series analysis. The emphasis

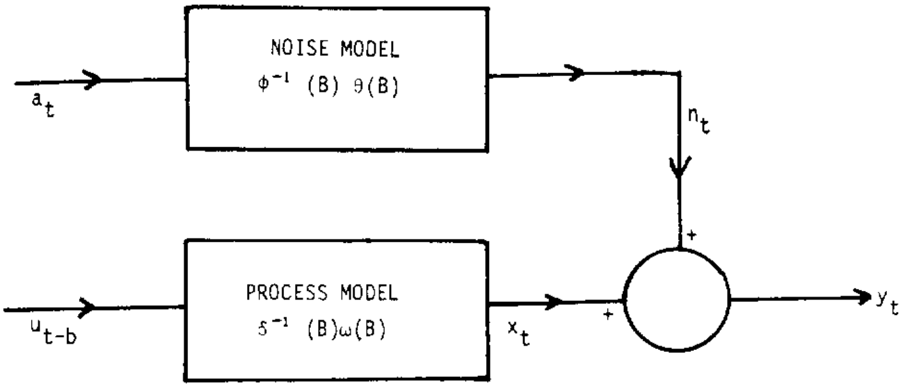

Fig. 2. Representation of a general transfer function with superimposed noise model.

in the current approach is to identify and represent dominant processes controlling system behaviour with the minimum number of parameters. This avoids the problems of over-parameterization in models of such ill-defined systems, as emphasised by Young (1978).

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.

It will be seen from Fig. 2 that the general single input—single output (SISO) model consists of two parts, a process model, and a noise model (Box and Jenkins, 1970). The observed output, y_t is taken to result from an observed input u_t, which causes most of the output variation and a stochastic input a_t, that accounts for random disturbances such as measurement noise. The output y_t is then given by the sum of the deterministic and stochastic components x_t and n_t, respectively, i.e.:

$$y_t = x_t + n_t \tag{1}$$

x_t is obtained from the transfer function model:

$$\delta(\mathbf{B})x_t = \omega(\mathbf{B})u_{t-b} \tag{2}$$

where:

$$\delta(\mathbf{B}) = 1 + \delta_1\mathbf{B} + \delta_2\mathbf{B}^2 + \ldots + \delta_r\mathbf{B}^r$$

and:

$$\omega(\mathbf{B}) = \omega_0 + \omega_1\mathbf{B} + \omega_2\mathbf{B}^2 + \ldots + \omega_s\mathbf{B}^s \tag{3}$$

B is the backward shift operator, i.e. $B^b x_t = x_{t-b}$. Thus, $b = 1$ gives a time delay of one sample instant between the input and the systems response to it, via its output, y_t.

The noise component at *time*, t, n_t, is generated by an ARMA model similar to eqn. (2) but in this paper the analysis is restricted to the transfer function model. This is because we are concerned with investigating the process behaviour and the relationships between variables associated with stream acidity and not with providing real time forecasting models.

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, δ_n and ω_n, are estimated using a recursive instrumental variable procedure in which the parameter estimates are updated a sample at a time while working serially through the data. The technique strongly resembles the Kalman filter and details of the estimation procedure are given by Young (1974) and Young et al. (1971).

The recursive I.V. 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 also been extended to estimate multivariable 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 multivariable model has the following discrete time state—space representation of a multi-input multi-output, linear dynamic system:

$$x_t = Px_{t-1} + Qu_t \tag{4}$$

where $\boldsymbol{x}_t = (x_{1,t}x_{2,t}\ldots\ x_{n,t})T$ is an n-dimensional vector of state variables that characterise the system at the kth instant of time. $\boldsymbol{u}_t = (u_{1,t}u_{2,t}\ldots u_{m,t})T$ is an m-dimensional vector of deterministic input variables, also sampled at every time instant, while $\boldsymbol{P}$ and $\boldsymbol{Q}$ are, respectively, $n \times n$ and $n \times m$ matrices with elements:

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

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).

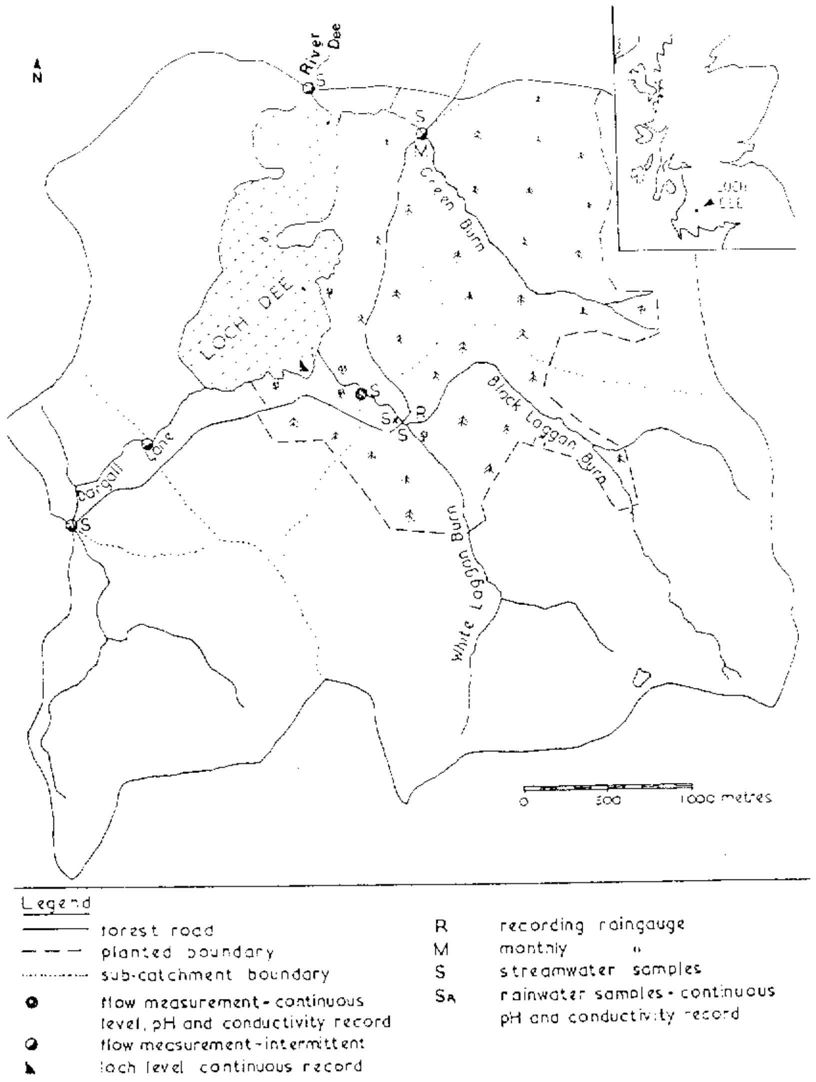

Fig. 3. Loch Dee catchment.

CATCHMENT STUDIES

The data used in the present modelling studies have been obtained from three principal catchment areas, Loch Dee in southwestern Scotland, Birkenes catchment in southern Norway, and Plynlimon in mid-Wales.

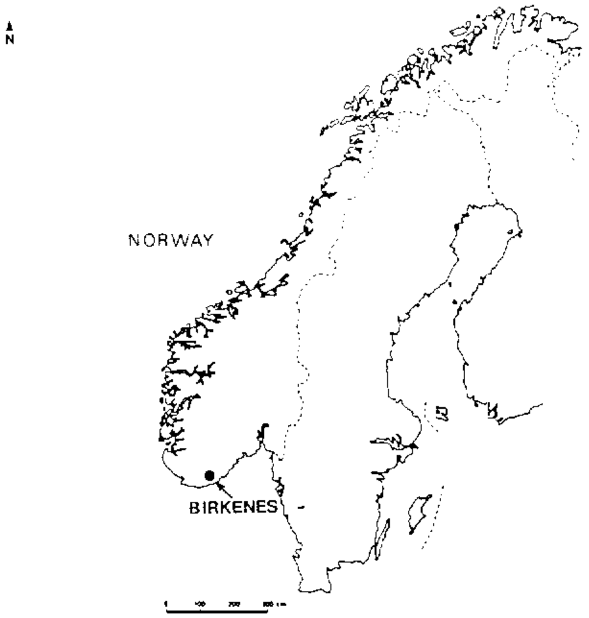

Fig. 4. Birkenes catchment, Norway.

Loch Dee

Loch Dee has a remote setting in the Galloway Hills in southwestern Scotland (see Fig. 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 the south, and the Green Burn entering from the southeast. The outflow at the northeast 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 (Burns et al., 1984).

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.

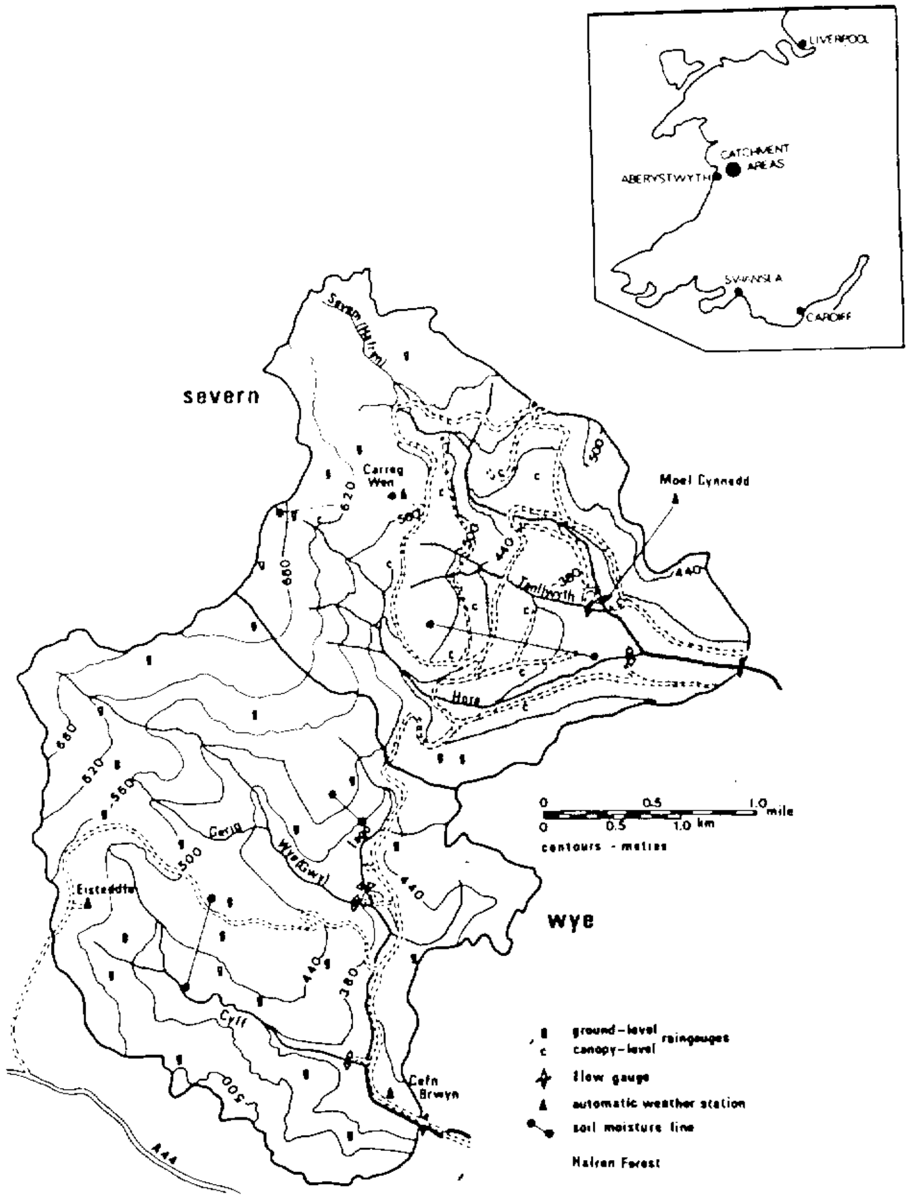

Fig. 5. The Severn and Wye experimental catchments, Plynlimon.

Birkenes

Birkenes lies at 200—300 m above sea level about 15 km north of Kristiansand, near the southernmost tip of Norway (Fig. 4). 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 200—300 m above sea level with granitic outcrops on the ridge tops and moraine and 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.

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

Plynlimon

The Plynlimon study area lies in mid-Wales (Fig. 5) and consists of two sub-catchments, the upper Wye catchment and 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 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. Newson (1984) has reported the wide range of pH obtained from different land use. In the forested Severn catchment (Afon Hore and Afon Hafren) storm events generate acidic runoff. In the grassed Wye catchment acidity levels are much more stable and pH values are higher 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.

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 (Burns et al., 1984; Langan, 1986). 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, 1986).

The hourly runoff and hydrogen ion concentration data was initially analysed using correlation and prewhitening techniques (Box and Jenkins, 1970). The cross-correlation of the prewhitened series suggested a first-order autoregressive model with a single moving average parameter; i.e. an equation of the form:

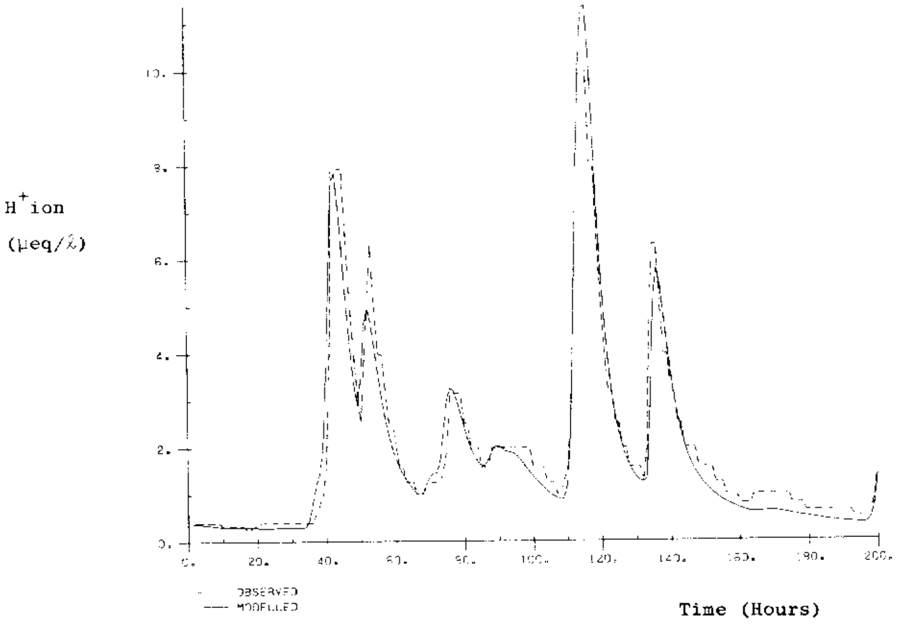

Fig. 6. Simulated and observed H^+ ion in the White Laggan, Loch Dee, Scotland, based on the flow model.

$$x_t = -\delta_1 x_{t-1} + \omega_0 u_t \tag{5}$$

where x_t is the hydrogen ion concentration (μeq l^{-1}) and u_t is the flow ($m^3\ s^{-1}$) in the stream at time t.

The parameters δ_1 and ω_0 were estimated using the time-series algorithm referred to previously and applied to 200 *hourly* observations of flow and hydrogen ion concentration. The parameters were estimated to be:

$\delta_1 = -0.680$ (standard error 0.012)

$\omega_0 = 0.659$ (standard error 0.022)

and Fig. 6 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 conducted split sample tests to data from all three subcatchments of Loch Dee and found that equally good results 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 h is obtained, reflecting the fast response time between output flow and hydrogen ion concentrations. The gain of the system can be determined as:

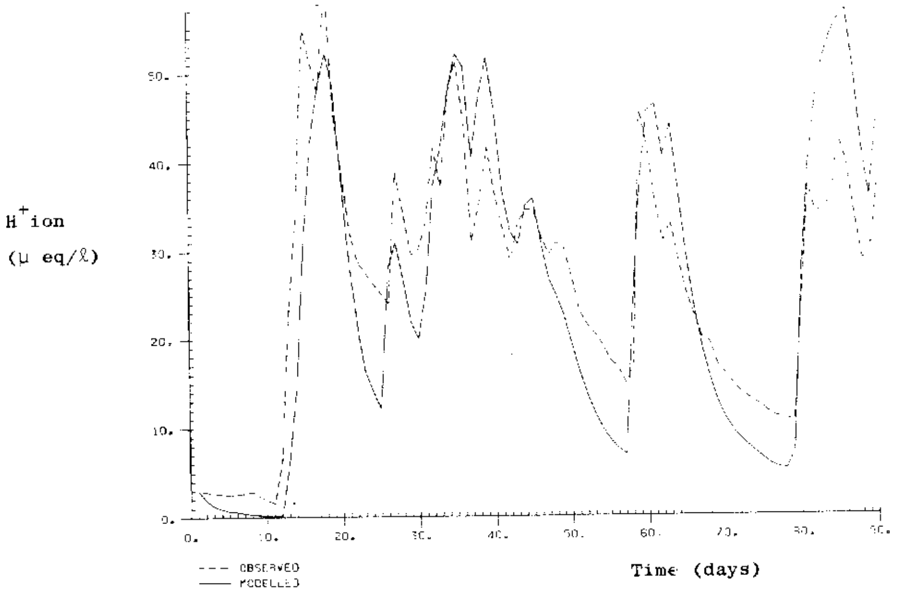

Fig. 7. Simulated and observed H^+ ion in the Birkenes catchment, Norway based on the flow model.

$$\text{Gain} = \frac{\omega_0}{1+\delta_1} = \frac{0.659}{1-0.68} = 2.06 \tag{6}$$

In other words an increase of $1\,\mathrm{m}^3\ \mathrm{s}^{-1}$ in flow is associated with a concentration increase of $2.06\,\mu\mathrm{eq\,l}^{-1}$ of hydrogen ions in the streamwater. Flows of $5\,\mathrm{m}^3\ \mathrm{s}^{-1}$ and more are common, suggesting that hydrogen ion concentrations above $10\,\mu\mathrm{eq\,l}^{-1}$ (i.e. below a pH of 5) will be frequent.

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. This should not be used to imply that stream acidity is directly caused by hydrological processes rather than by pollutant inputs. Acid deposition and flow through humus and mineral horizons in the soil give rise to stream water acidity. The hydrological processes provide the means of transfer of these acid waters into the stream (Whitehead et al., 1986).

Birkenes

The aim of the modelling in the Birkenes study is to predict daily hydrogen ion and aluminium concentrations since these are of primary importance in establishing the impact of stream acidity on aquatic ecology. The only unbroken and consistent set of daily data available consisted of *daily* flow ($\mathrm{m}^3\ \mathrm{s}^{-1}$) and hydrogen, sulphate, aluminium, calcium and magnesium ion concentrations ($\mu\mathrm{eq\,l}^{-1}$) for a 90 day period from September to November,

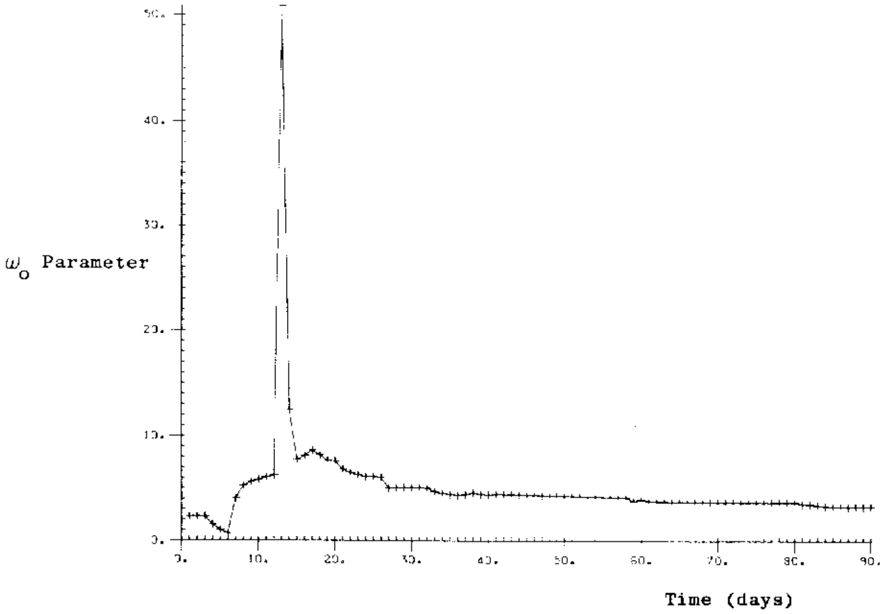

Fig. 8. ω_0 parameter from the flow model.

1974. (A much longer record of weekly data is available, Christophersen et al., 1982, 1984.)

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 undertaken on time-series analysis of precipitation and runoff data (Skroppa and Mohn, 1975). The current analysis draws on the work of Christophersen et al. (1982, 1984) but again uses the times series approach to estimate model parameters. Initial time series analysis showed that highly non-linear behaviour was associated with flow peaks in the Birkenes catchment and this prevented good estimation of model parameters. 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 per 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.

As in the case of Loch Dee a time-series model of the form of eqn. (5) was fitted to the data initially. The response (Fig. 7) 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

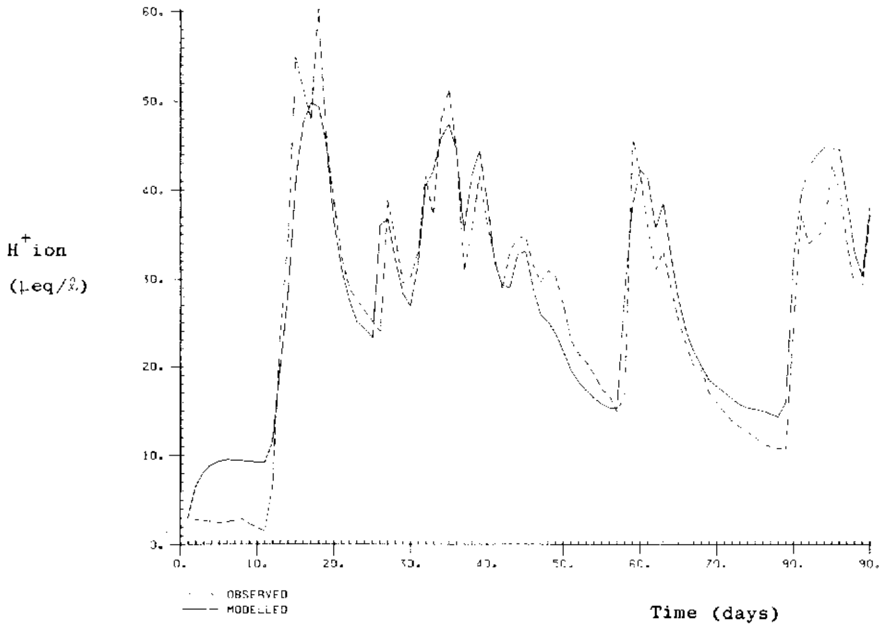

Fig. 9. Simulated and observed H$^+$ ion in the Birkenes catchment, Norway, based on the flow and sulphate model.

first storm event. This is reflected in the parameter estimates for ω_0 which shows a significant rise in this period (see Fig. 8), and consequently it is necessary to move to a multi-input, single output model of the form of eqn. (4) to incorporate the sulphate component. Figure 9 shows the effect of including sulphate in the model. The estimated equation in this case is:

$$x_t = 0.45\, x_{t-1} + 2.62\, u_{1,t} + 0.045\, u_{2,t} \tag{7}$$

where $u_{1,t}$ and $u_{2,t}$ refer to flow and sulphate respectively at time t. The effect of including sulphate is now to reproduce the flushing effect. However, the recession part of the response is still inadequately modelled. 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" (c.f. Neal et al., 1982). This relationship can be described by an exchange constant where:

$$K = \frac{NIC_H\,[M^{2+}]}{NIC_M\,[H^+]^2} \tag{8}$$

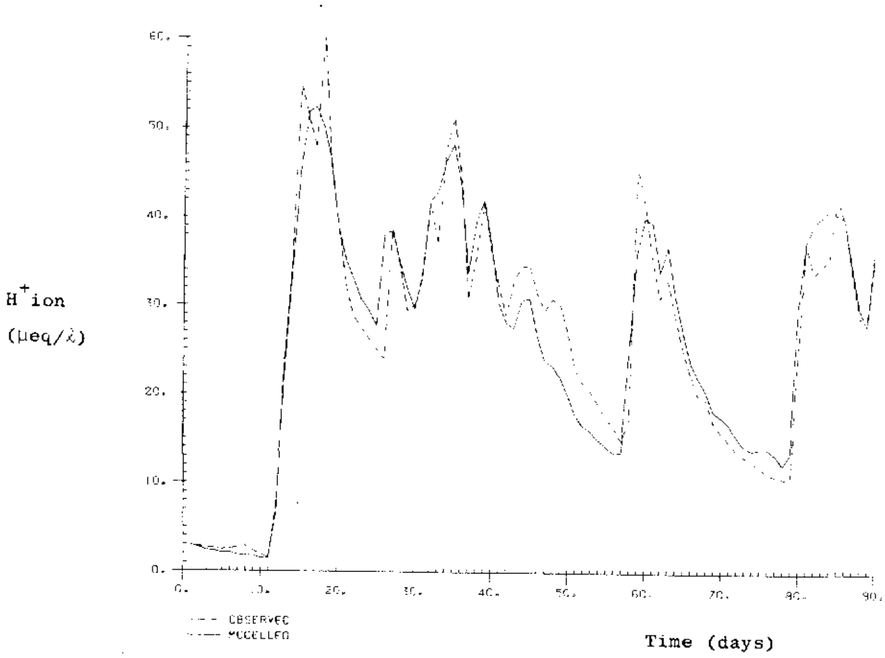

Fig. 10. Simulated and observed H^+ ion in the Birkenes catchment, Norway, based on the flow, sulphate and M^{2+}.

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:

$$x_t = 0.38\, x_{t-1} + 2.38\, u_{1,t} + 0.13\, u_{2,t} - 1.12\, u_{3,t} \tag{9}$$

where $u_3 = \sqrt{M^{2+}}$ and the model response is now close to the observed hydrogen ion concentration (see Fig. 10). 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. c.f. Driscoll et al., 1984; Seip et al., 1984) present in the pH range of most natural waters. For example the pH relationship with

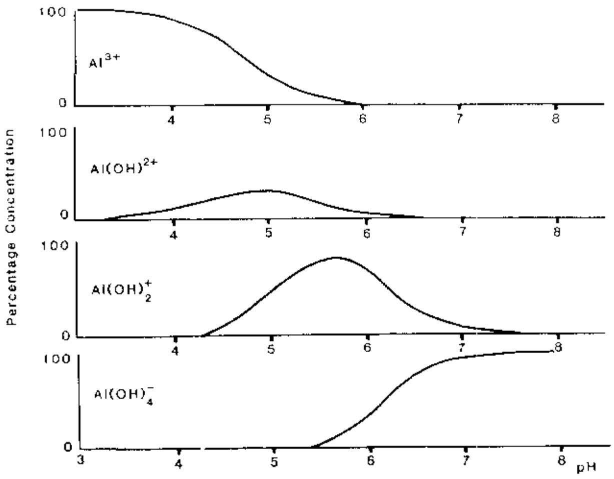

Fig. 11. Aluminium—pH speciation relationships (data of Truesdell and Jones, 1974; activities of ion taken as unity).

the Al^{3+} and hydroxy Al species is shown in Fig. 11. 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:

$$\left.\begin{array}{l} 3H^+ + Solid_1 \rightleftharpoons Solid_2 + Al^{3+} + xH_2O \pm SiO_2 \\ 3H^+ + Solid_1 \rightleftharpoons Al^{3+} + xH_2O \pm SiO_2 \end{array}\right| \qquad (10)$$

where silica concentrations are buffered in solution, e.g. by quartz solubility, and equilibrium equation can be derived such that:

$$K = \frac{[Al^{3+}]}{[H^+]^3} \qquad \text{(c.f. Christophersen et al., 1984 for gibbsite solubility)}$$

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 are very limited, as a first approximation, ΣAl_x is taken as independent of pH and aluminium concentration. Thus:

$$\text{Total aluminium} - \Sigma Al_x = Al^{3+} \left\{ 1 + \frac{k_1}{[H^+]} + \frac{k_2}{[H^+]^2} + \frac{k_3}{[H^+]^4} \right\} \qquad (11)$$

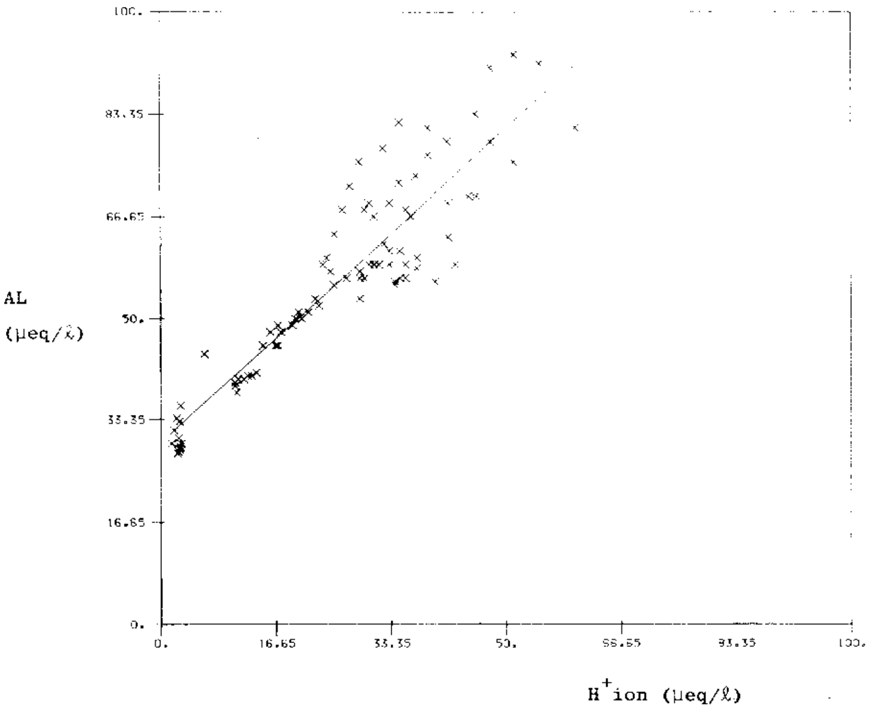

Fig. 12. Scatter diagram of Al versus H^+ ion for the Birkenes catchment, Norway.

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

$$\left.\begin{array}{l} Al^{3+} + H_2O \rightleftharpoons Al(OH)^{2+} + 2H^+ \\ Al^{3+} + 2H_2O \rightleftharpoons Al(OH)_2^+ + 2H^+ \\ Al^{3+} + 4H_2O \rightleftharpoons Al(OH)_4^- + 4H^+ \end{array}\right| \quad (12)$$

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

$$(\text{Total aluminium} - \Sigma Al_x) = \omega_0 \{10^{-18}[H^+]^3 + 10^{-17}[H^+]^2 + 10^{-15.76}[H^+] + 10^{-16.1}[H^+]^{-1}\} = \omega_0 f[H^+]$$

where hydrogen ion concentrations are given in $\mu eq\, l^{-1}$.

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 Fig. 12. From the regression line the intercept on the y axis is $29.6\, \mu eq\, l^{-1}$ and the regression relationship is:

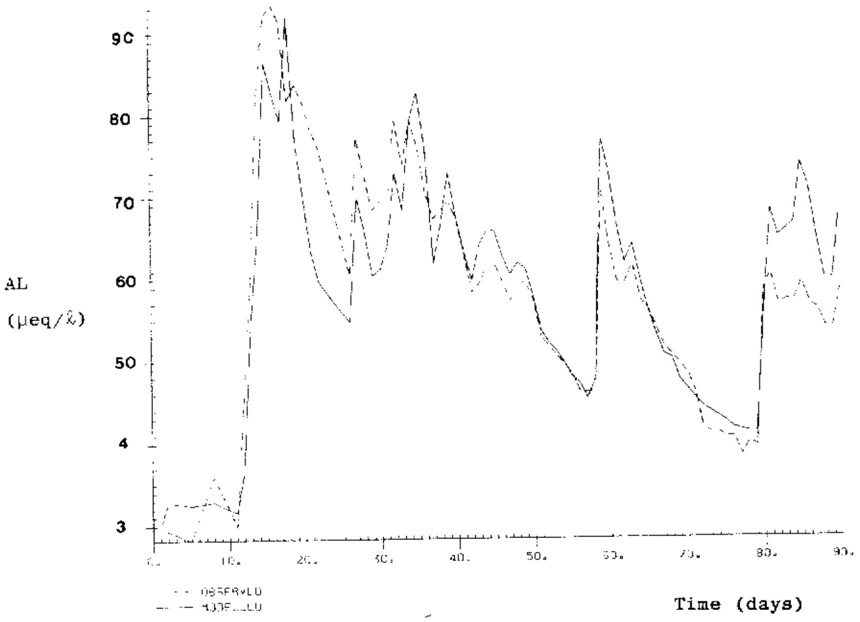

Fig. 13. Simulated and observed Al in the Birkenes catchment, Norway, based on the H^+ ion model.

$$(\text{Total Al} - 29.6) = 1.03\,[H^+] \qquad (R^2 = 0.83) \tag{13}$$

Using this relationship a simulation of aluminium, is shown in Fig. 13. 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 four possible factors:

(a) Some other aluminium solubility relationships are operating such that the stoichiometric relationship is less than three (for example Al and SO_4 are highly correlated and sorption/solubility controls involving Al-SO_4 surface complexes might be involved).

(b) The above assumptions of constant silica, organic carbon, fluoride and temperature are 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 (e.g. Christophersen et al., 1982) in order to adequately differentiate between chemical and hydrological factors.

(d) Kinetic rather than thermodynamic equilibrium processes are operating.

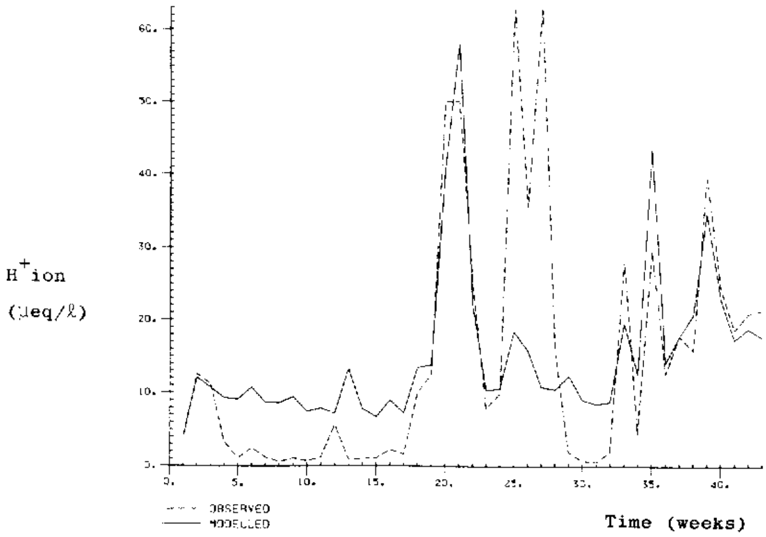

Fig. 14. (a) Simulated and observed H$^+$ ion in the river Hafren, Plynlimon, UK, based on the sulphate model.

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, the time-series model is reduced to a simple moving average model. Model equations were estimated as follows:

$$\text{Afon Hafren} \qquad x_t = 1.75\, u_{1,t}$$

$$\text{Afon Hore} \qquad x_t = 1.34\, u_{1,t} \tag{14}$$

where x_t is the hydrogen ion concentration ($\mu\text{eq}\,\text{l}^{-1}$) and $u_{1,t}$ is the flow ($\text{m}^3\,\text{s}^{-1}$) at time t.

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:

$$\text{Afon Hafren} \qquad x_t = 1.26\, u_{1,t} + 0.09\, u_{2,t} \tag{15}$$

$$\text{Afon Hore} \qquad x_t = 1.22\, u_{1,t} + 0.026\, u_{2,t} \tag{16}$$

where $u_{2,t}$ is the sulphate concentration ($\mu\text{eq}\,\text{l}^{-1}$).

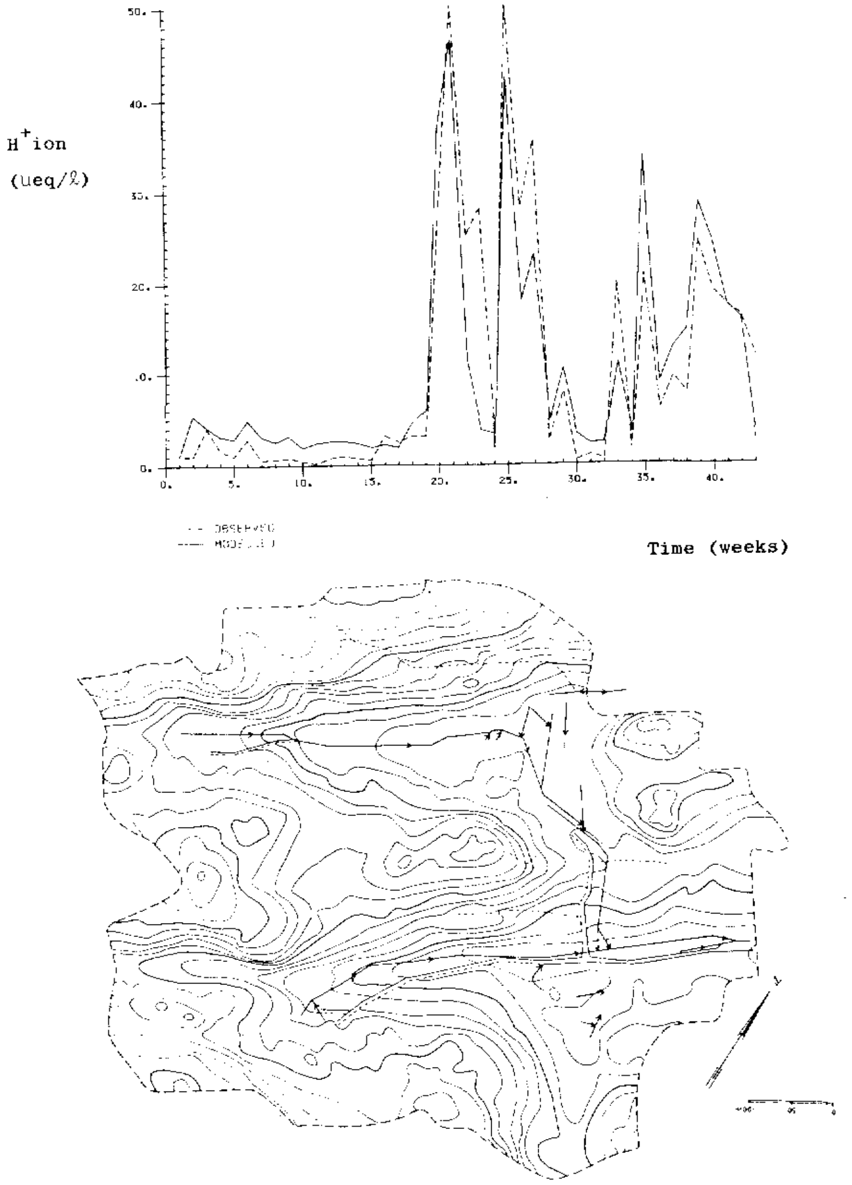

Fig. 14. (b) Simulated and observed H^+ ion in the river Hore, Plynlimon, UK, based on the sulphate model.

Figures 14a and b 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 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 for the Afon Hafren following major storm events. Using the storm flow values the peak hydrogen ion concentrations were reproduced.

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 $8.6\,\mu\mathrm{eq\,l^{-1}}$ for the Afon Hafren and $8.8\,\mu\mathrm{eq\,l^{-1}}$ for the Afon Hore. Fitting a regression model between hydrogen ion concentration and aluminium gives the following relationship:

$$\text{Afon Hafren} \qquad (x_t - 8.6) = 1.085\,u_{1,t} \qquad (r^2 = 0.75) \tag{17}$$

$$\text{Afon Hore} \qquad (x_t - 8.8) = 1.338\,u_{1,t} \qquad (r^2 = 0.62) \tag{18}$$

where x_t is the aluminium concentration and $u_{1,t}$ is the hydrogen ion concentration ($\mu\mathrm{eq\,l^{-1}}$).

Figures 15a and b show the aluminium simulations for the two catchments using these regression relationships.

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 parameters may be estimated directly 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 may highlight process changes such as the flushing effect in the Birkenes catchment.

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 simple flow—hydrogen ion relationship does not exist and that the situation is further complicated by the snowmelt processes. 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 decreases relative to catchment response time. Thus sampling on a weekly basis in

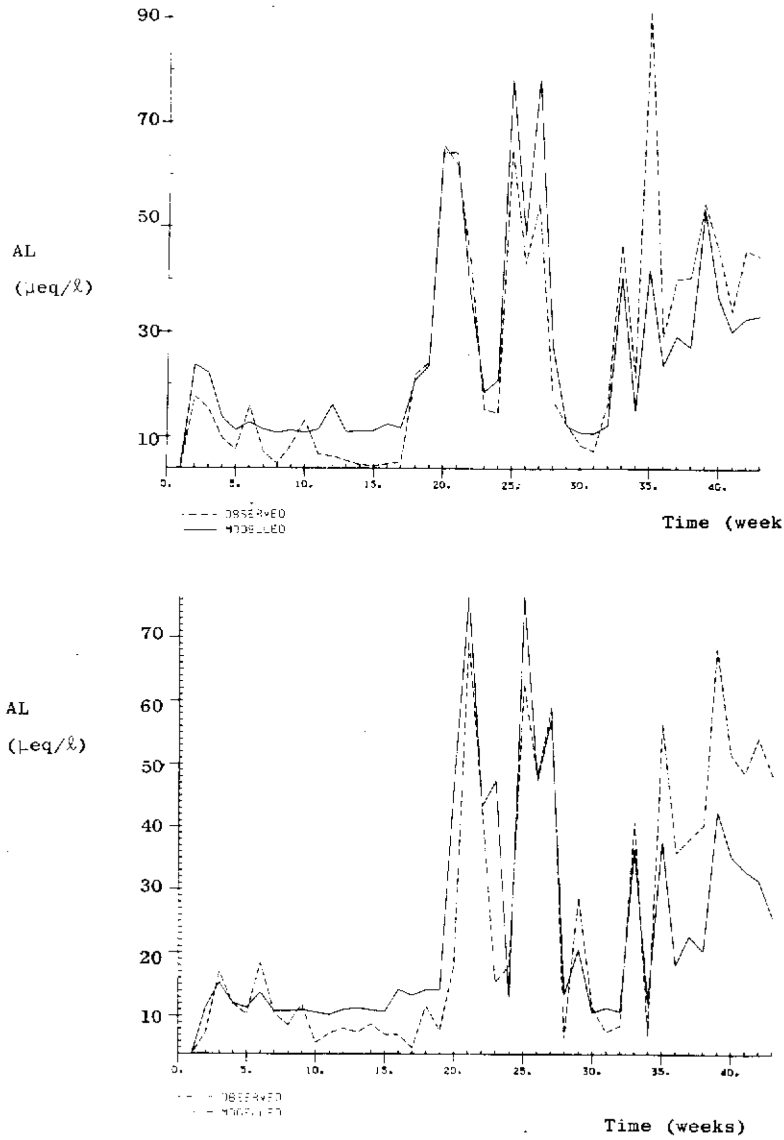

Fig. 15. (a) Simulated and observed aluminium in the river Hafren, Plynlimon, UK, based on the H^+ ion model. (b) Simulated and observed aluminium in the river Hore, Plynlimon, UK, based on the H^+ ion model.

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 hydrological models can be justified 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 difficulties associated with the catchment and is recommended as an efficient means of analysing data prior to more complex modelling studies.

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Section 5

Preferential discharge of pollutants during snowmelt

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 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 $(f_1 c + f_3 c_3)/(f_1 + f_3)$. 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 $c_{peak} = (f_1 c_{max} + f_3 c_3)/(f_1 + f_3)$ 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, $c_3 \simeq \bar{c}$. 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, $n \simeq 1$, 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 $\mu S\ cm^{-1}$. The peak in conductivity comes very quickly after the onset of melt with a maximum value of 63 $\mu S\ cm^{-1}$. 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 under-estimate 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 melt-water 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 $f_1 >> f_3$ 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

This paper appears with the permission of the Director of the Institute of Hydrology. We should like to thank M Porter, S J Edwards, W S Insell and R J Wyatt for their invaluable assistance in the field.

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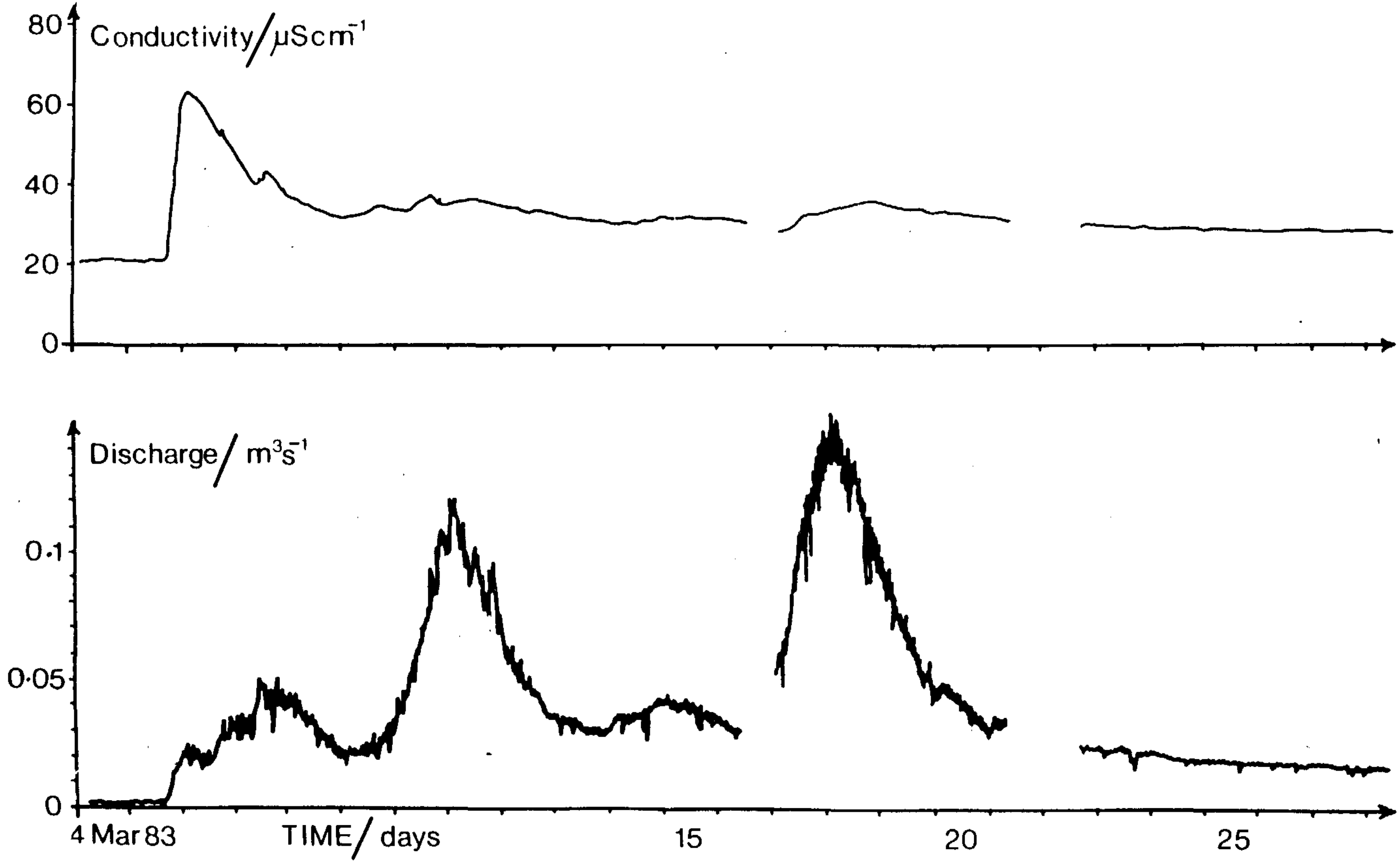
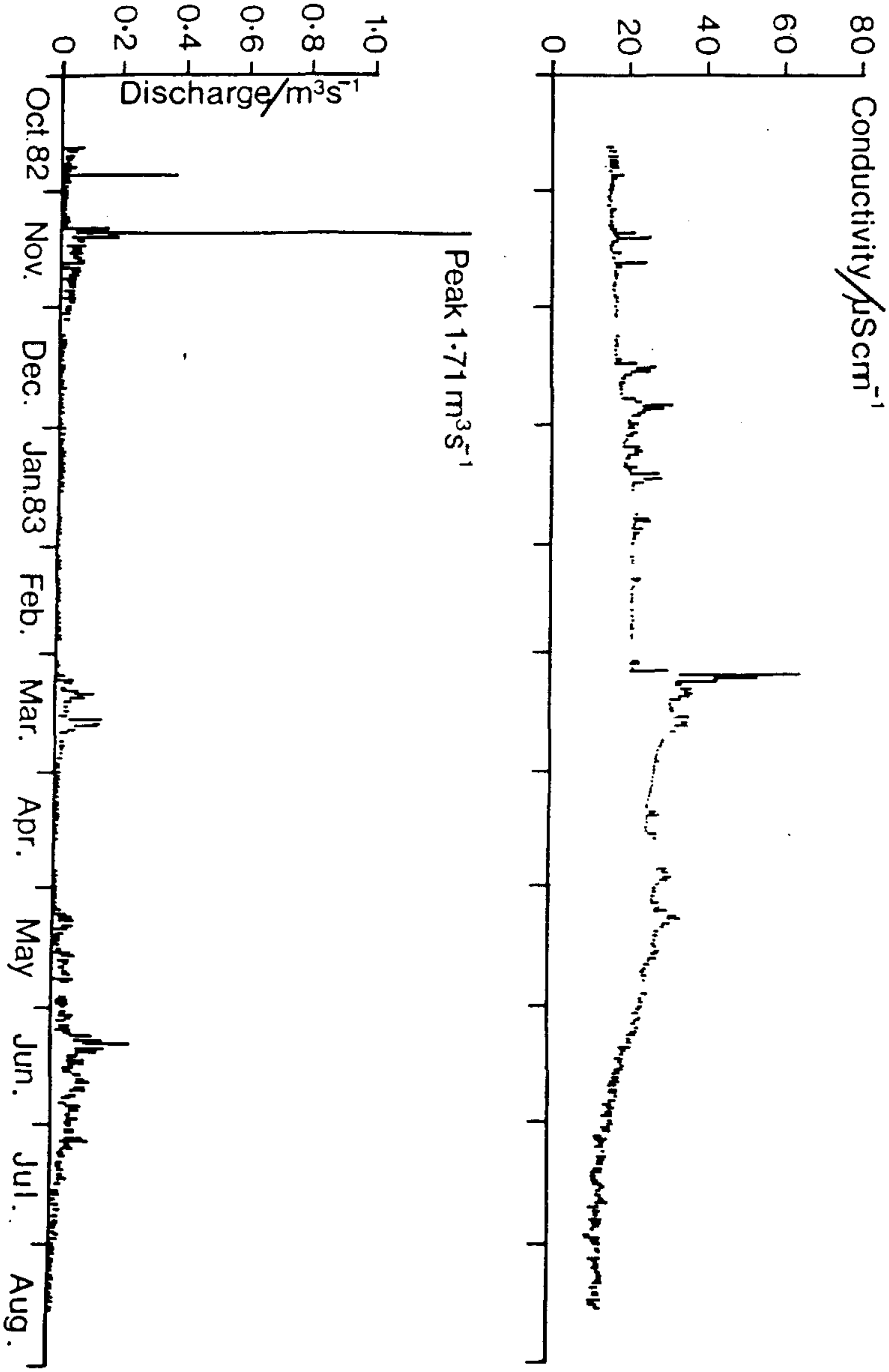
Skartveit, A. and Gjessing, Y.T. (1979). Chemical budgets and chemical quality of snow and runoff during spring snowmelt. Nordic Hydrology Vol. 10. p 141-154.

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.


Conductivity/µScm^{-1}
80
60
40
20
0
Discharge/ m^{3}s^{-1}
0·1
0·05
0
4 Mar 83
TIME/ days
15
20
25



Conductivity/µS cm⁻¹
80
60
40
20
0
Discharge/m³s⁻¹
1·0
0·8
0·6
0·4
0·2
0
Peak 1·71 m³s⁻¹
Oct.82
Nov.
Dec.
Jan.83
Feb.
Mar.
Apr.
May
Jun.
Jul.
Aug.

Appendix 1

The Allt a Mharcaidh Catchment Study

1. THE ALLT Á MHARCAIDH CATCHMENT STUDY

1.1 DATA COLLECTION RESPONSIBILITIES

The IH contribution to the SWAP catchment study in the Allt á Mharcaidh is to provide;

- stream flow data
- precipitation data
- weather stations
- continuous water quality monitoring
- snow surveys and snowmelt chemical analysis

and to undertake subsequent data management, analysis and interpretation. The extent to which these commitments have been achieved, results to date and examples of data available, are set out below.

1.2 INSTRUMENTATION AND RESULTS TO DATE

Work on the instrumentation for the Allt á Mharcaidh began at the outset of the project to enable a rapid deployment of equipment following planning approval. All monitoring equipment was purchased from commercial outlets or manufactured at IH and in both cases considerable development was necessary prior to field installation. Commercial equipment had to be made site specific to establish a compatible interface between data recorders and loggers whilst custom built equipment required design, construction and extensive testing. In both cases the necessity for employing equipment which is not only robust enough to survive the Cairngorm environment and transport over rough terrain, but also semi-permanent so as to comply with the planning agreement, posed considerable problems. Nevertheless, following planning approval in late August 1985, installation of instruments began and much of the agreed data collection commitment is underway.

In addition to the field instrumentation a temporary laboratory has been erected and furnished at Grantown-on-Spey and is fully equipped for sample analysis, storage and data translation.

1.2.1 Stream Water Quality land Quantity Data

A stream gauging station has been established at the bottom of the catchment, (Figure 1). It consists of a fixed stilling well housing pressure transducers for stage measurement and a pHOX 100 DPM water quality monitoring unit. Stage, pH, conductivity and temperature are logged at 20 minute intervals and the data is transferred to a solid state store. The system is powered by a 12 volt supply which is continuously charged by a wind generator thereby preventing data loss due to battery failure in cold weather.

The system has been in operation since 10:10:85 and results analysed to date demonstrate that the stream is susceptible to rainfall induced acid pulses. Figures 2(a)-(d) summarise stream data for the period 23:10:85 to 6:11:85. Initially, dry antecedent conditions and low rainfall input lowered the stream to baseflow level and pH rose to c.6.7. This pattern was broken by heavy rain and snowfall on 4:11:85 causing a rapid response in stream stage and a corresponding decrease in pH to c.5.5.

The raw 20-minute interval data illustrated in Figure 2 are now available and with a salt dilution-gauging programme in progress, discharge data will be available in the Spring 1986 after a stage-discharge rating curve has been established.

1.2.2 Weather Data

An automatic weather station has been installed in the centre of the catchment at a height of c.575m (Figure 1). Again, to prevent data loss through battery failure the station is connected to a wind generator. Rainfall, wind speed and direction net radiation, total incoming radiation, dry bulb temperature and wet bulb depression are logged at 5 minute intervals. These five minute data are summarised to produce hourly averages totals of all parameters.

The weather station has been operational since 11:9:85 and Figures 3(a)-(e) illustrates an example of the output covering the period 26:10:85 to 6:11:85. The data show that for the storm on the 4/5th November, temperatures were mild during the rainfall event and then dropped sharply; wind direction moved from SW to NE and wind speed is generally lower immediately after the storm. This situation is clearly indicative of a cold front moving in an easterly direction across Scotland.

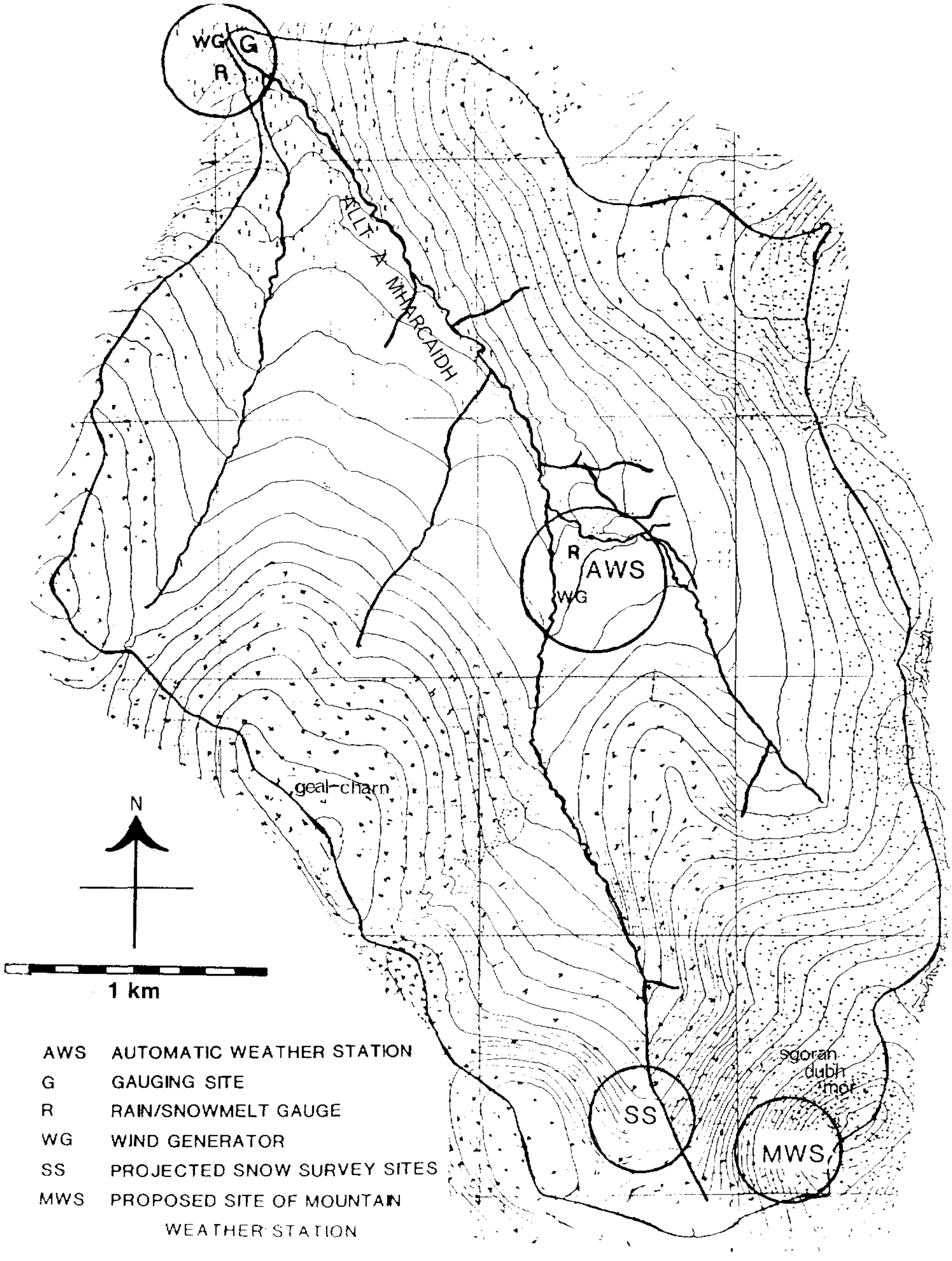


Figure 1 Allt à Mharcaidh Catchment

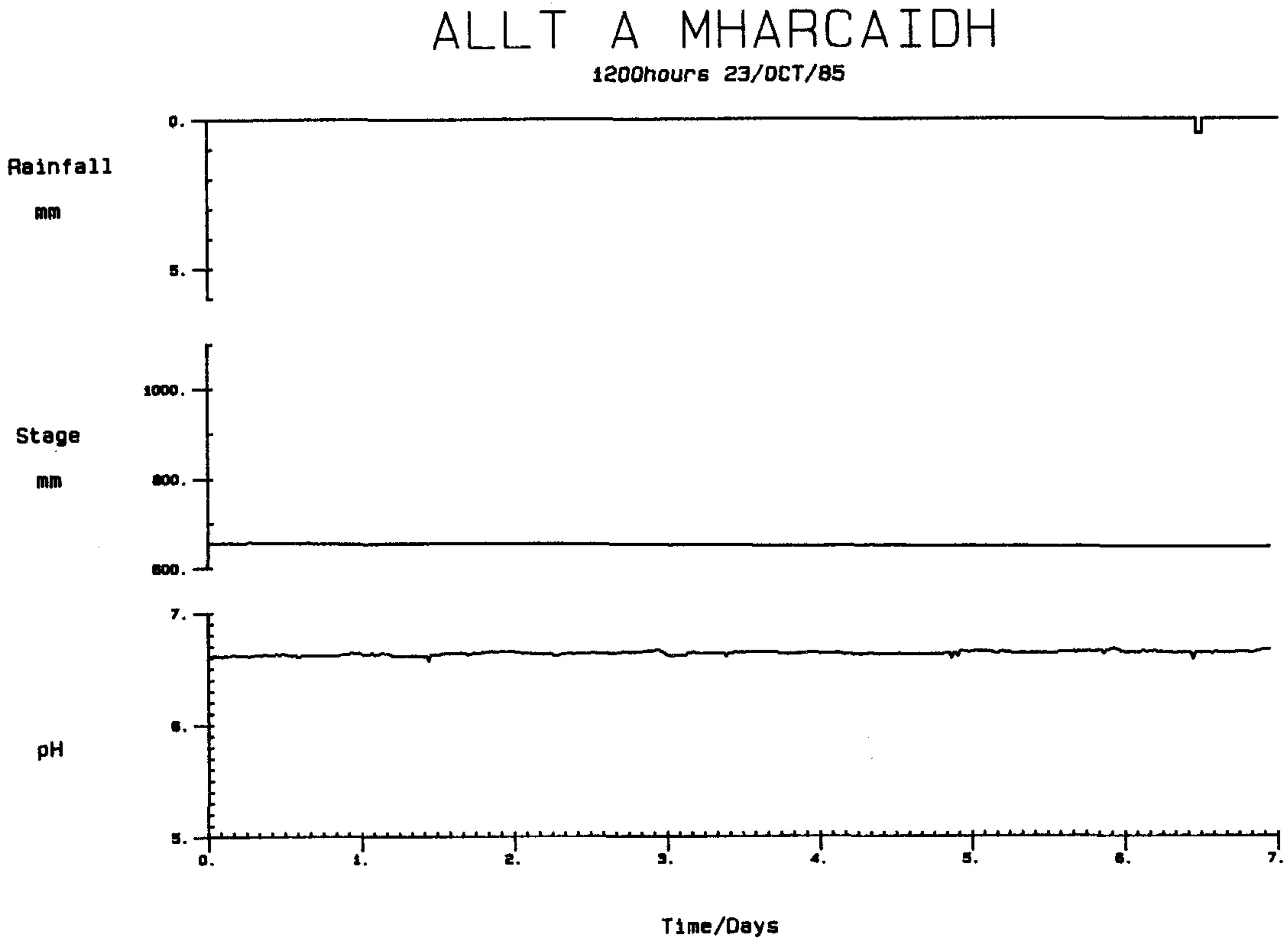


Figure 2a Stream Data For The Period Beginning at 12.00 on the 23.10.85

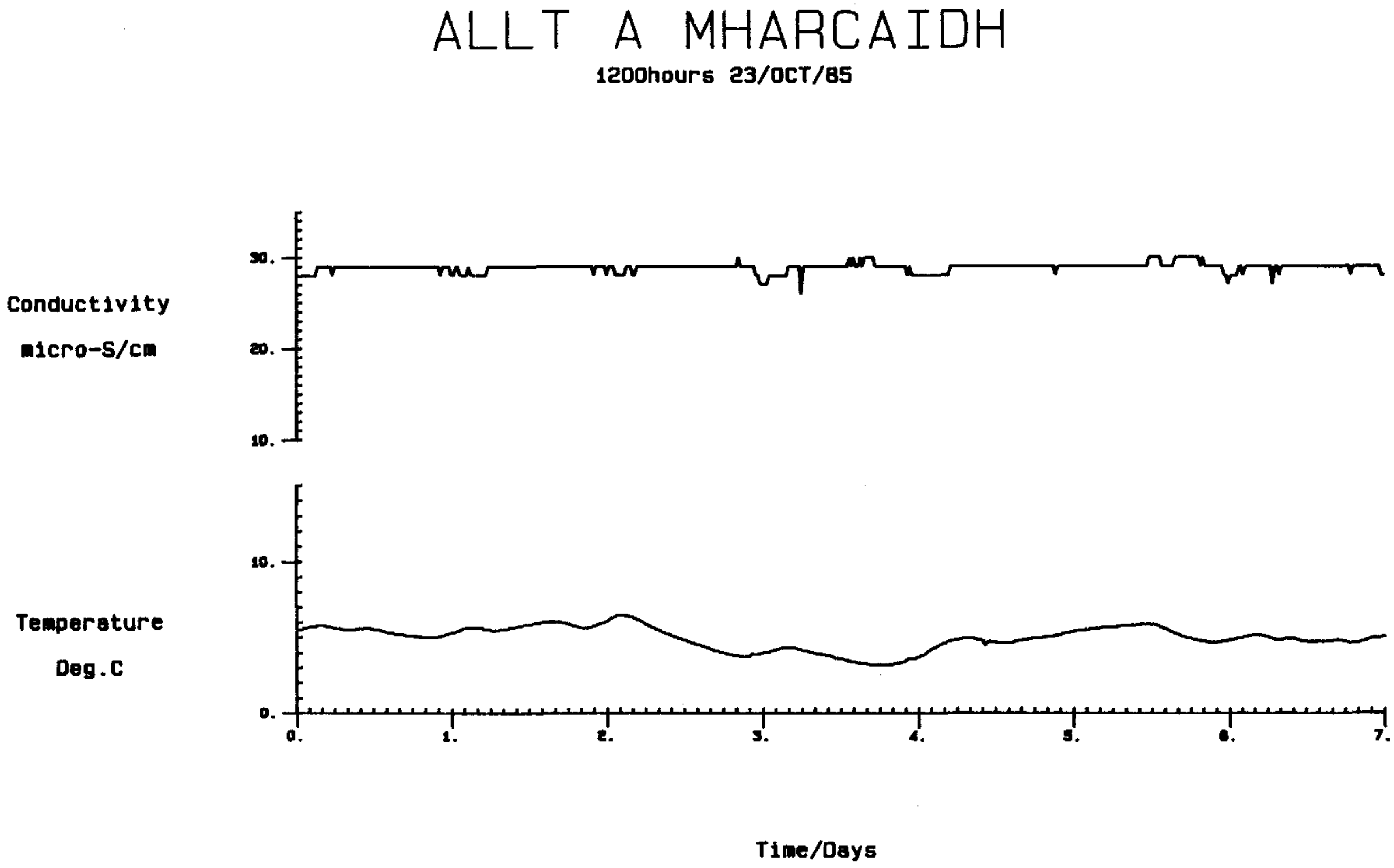


Figure 2b Stream Data For The Period Beginning at 12.00 on the 23.10.85

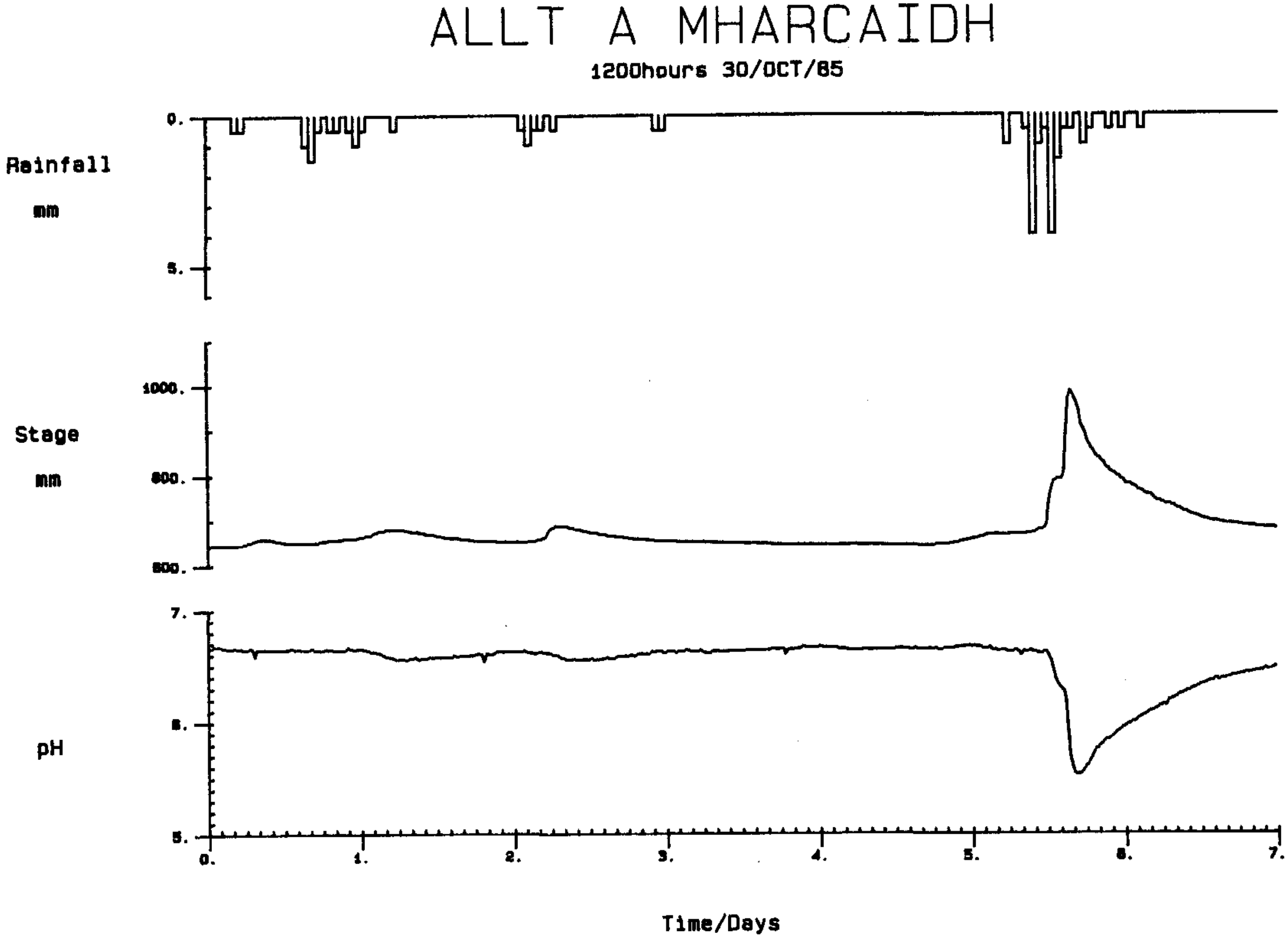


Figure 2c Stream Data For The Period Beginning at 12.00 on the 30.10.85

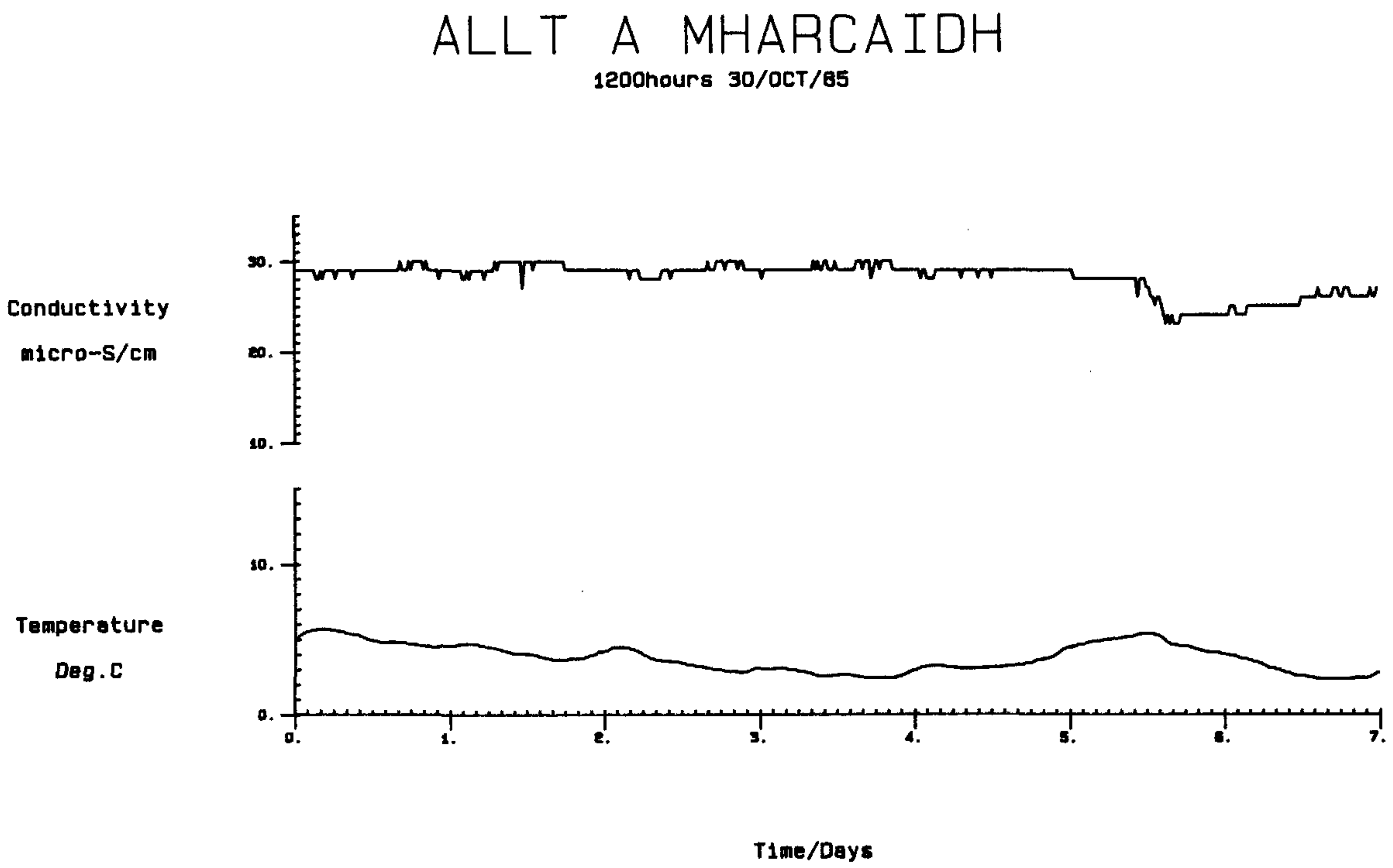


Figure 2d Stream Data For The Period Beginning at 12.00 on the 30.10.85

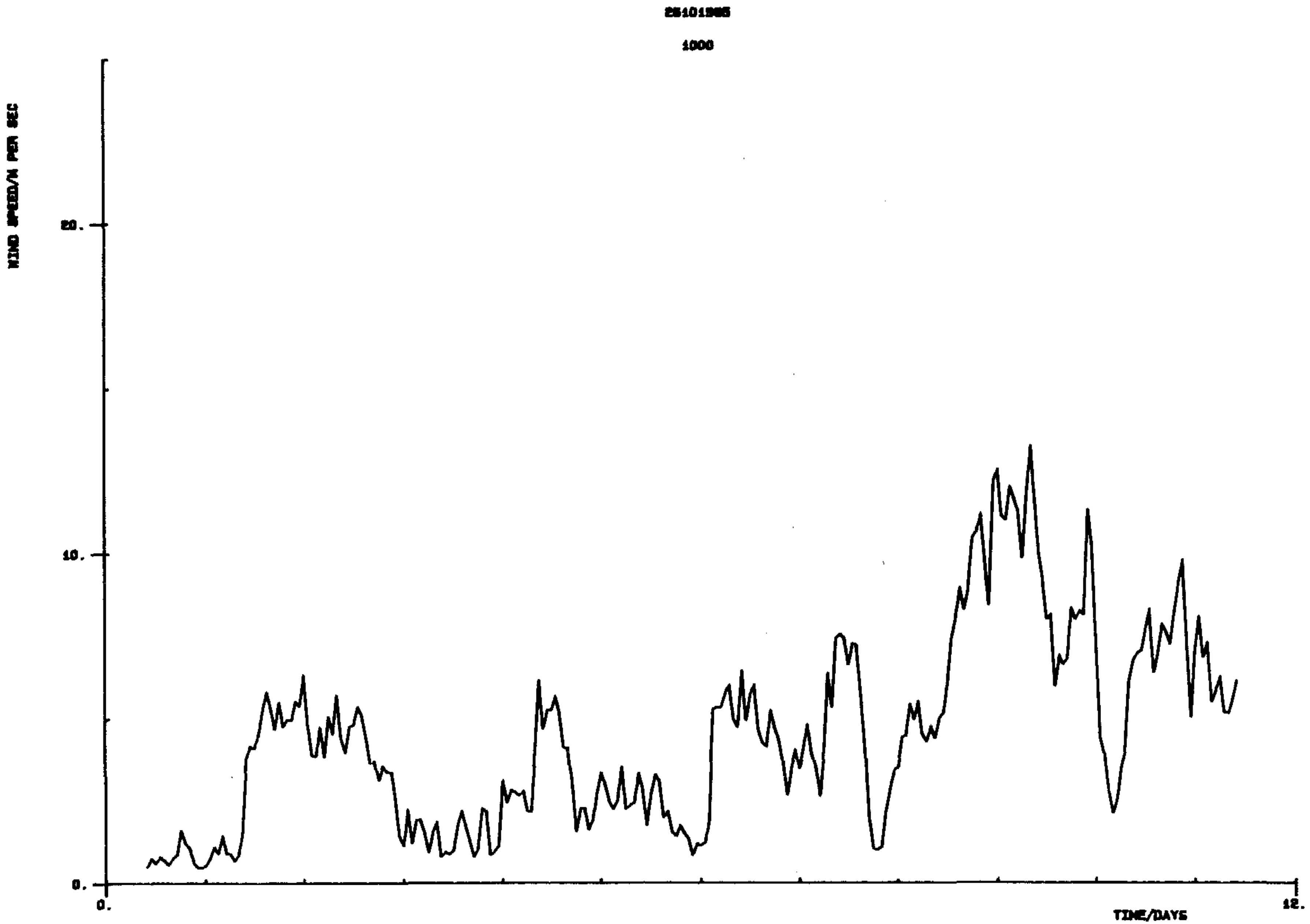


Figure 3a Automatic Weather Station Data For The Period Beginning 10.00 on The 26.10.85

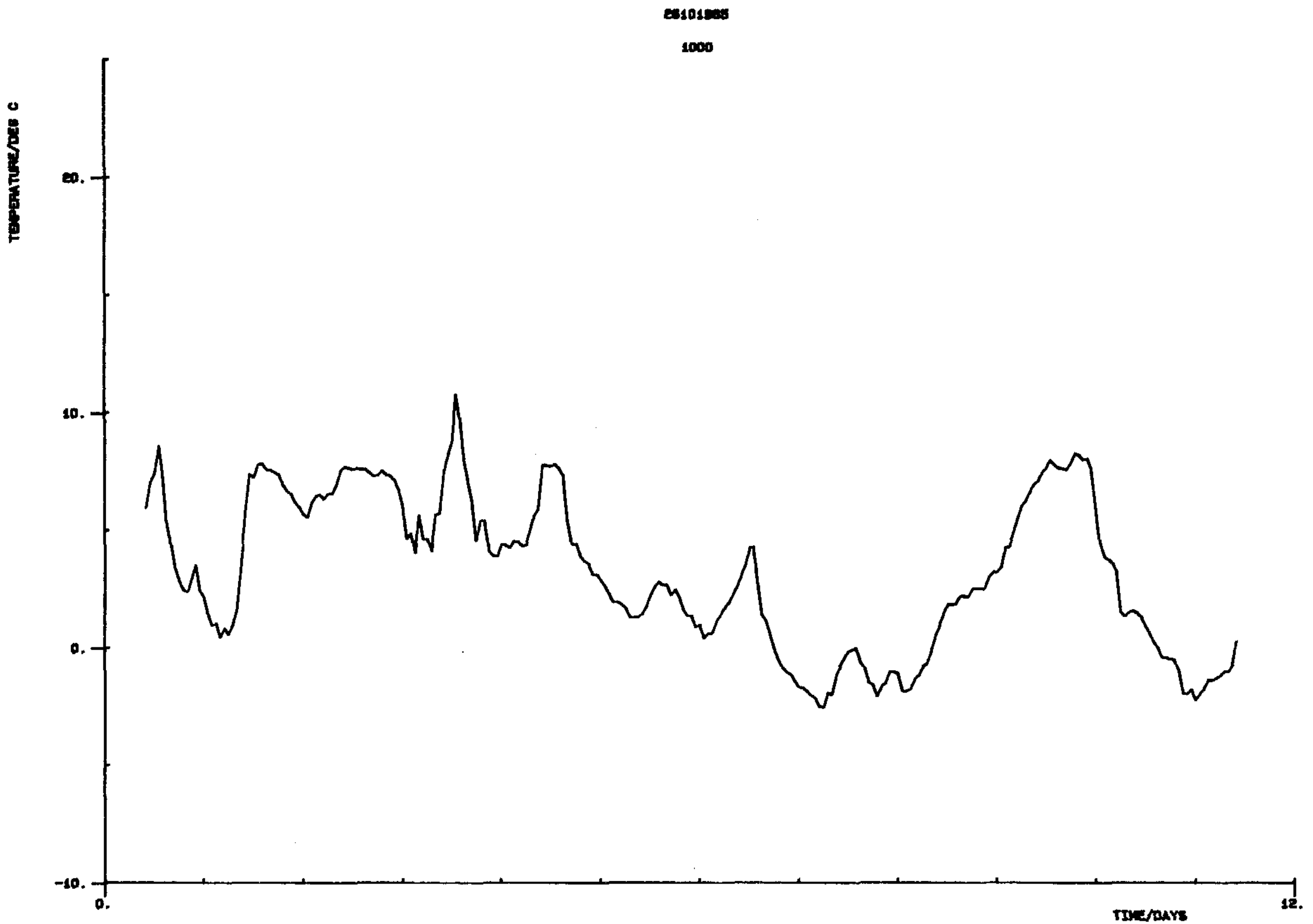


Figure 3b Automatic Weather Station Data For The Period Beginning 10.00 on The 26.10.85

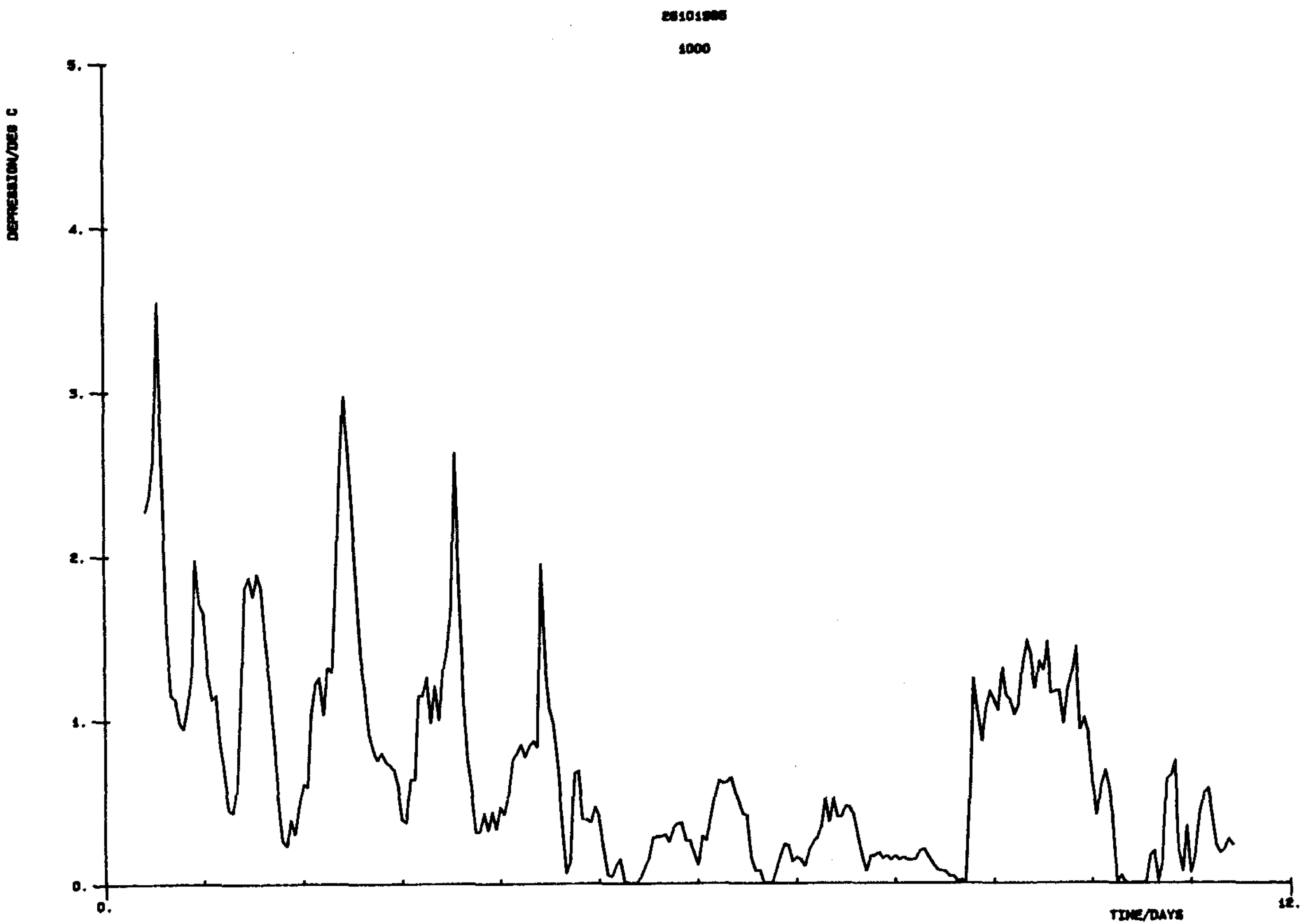


Figure 3c Automatic Weather Station Data For The Period Beginning 10.00 on The 26.10.85

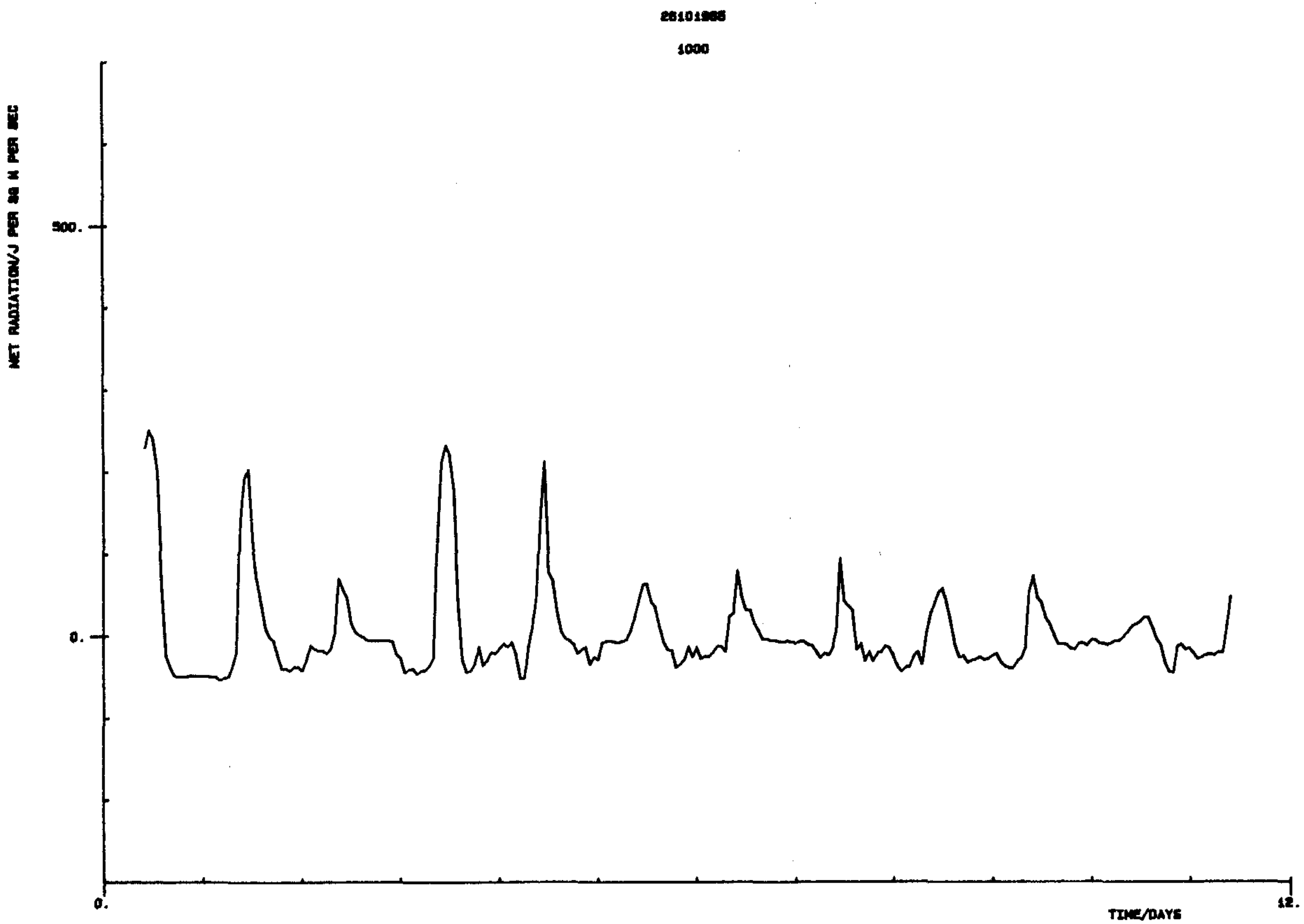


Figure 3d Automatic Weather Station Data For The Period Beginning 10.00 on The 26.10.85

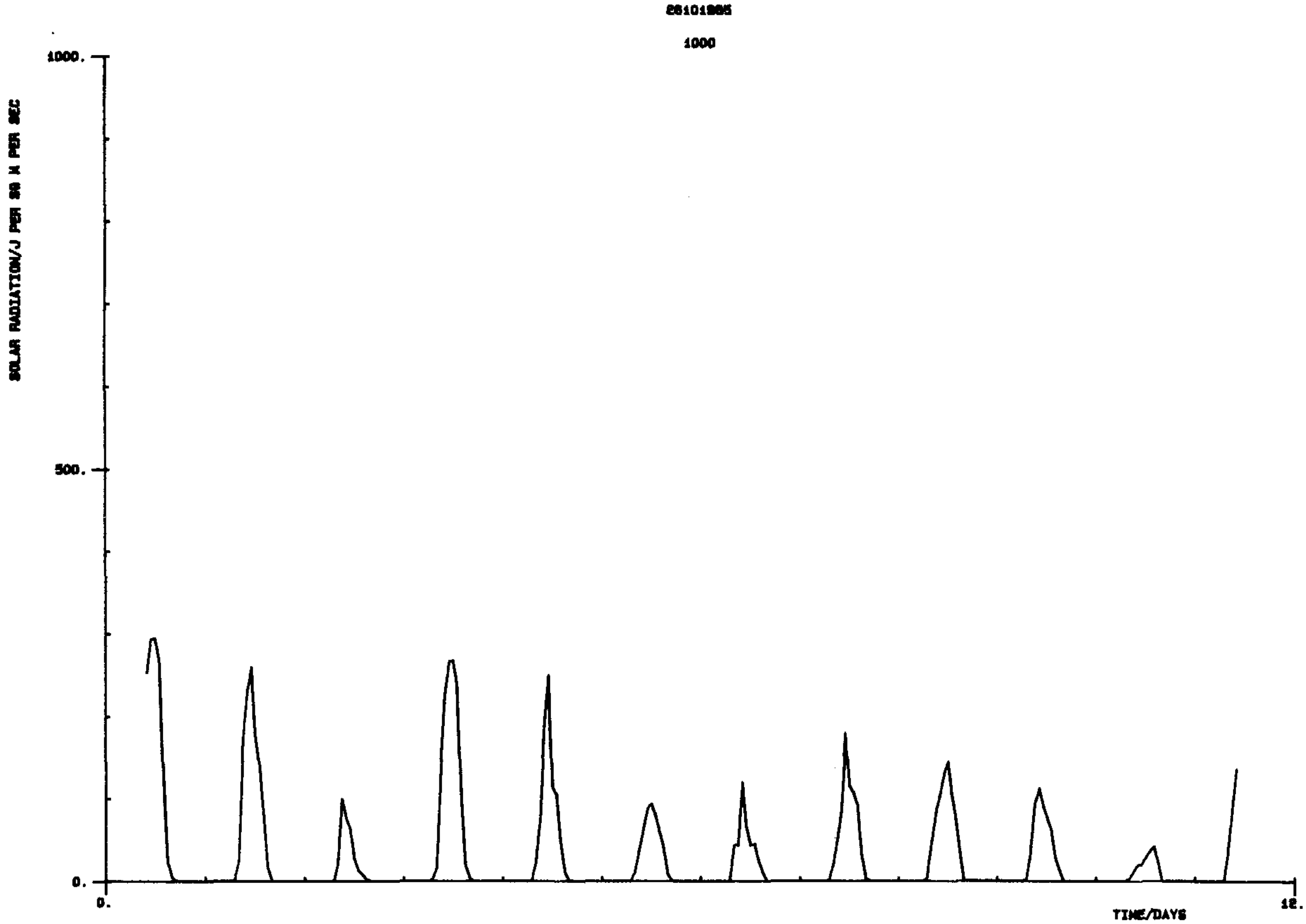


Figure 3e Automatic Weather Station Data For The Period Beginning 10.00 on The 26.10.85

1.2.3 Precipitation Data

In addition to the raingauge associated with the AWS, two further raingauges have been deployed in the catchment (Figure 1). These ground level gauges may be converted to snowmelt gauges during the winter. The raingauge cabled to the AWS remains on the surface at all times. The two ground level gauges have operated since 4:10:85 and hourly rainfall intensities from both sites are available until 10:12:85.

Precipitation quality is monitored by weekly sampling of bulk collectors installed at the stream gauging site and at the AWS site. These were deployed in December. Chemical analysis of collected samples will be carried out by the Macaulay Institute.

1.2.4 Snowmelt Data

Estimation of rate of snowmelt is obtained by converting the two ground-level raingauges to snow-melt gauges. This has been achieved by covering the grids with 'artificial grass' thereby allowing a snow cover to build up over the gauge. Snowmelt data are available from 10:12:85. In addition, snowmelt quality is monitored using a bulk collector at the AWS site and is sampled weekly during thaw conditions. Work is underway to install further collectors higher in the catchment.

1.3 INSTRUMENTATION IN PROGRESS

Further instrumentation is underway and installations to be completed include;

- a mountain weather station at a height of c.1000m together with associated rain and snowmelt gauges.

- two automatic snowmelt samplers to be located at the snow survey site. (NB. The 'shells' of these samplers have already been transported to the site).

- an automatic rainfall sampler capable of taking discrete samples during the course of a storm event.

- automatic stream samplers to be triggered on rising stream stage and conductivity.

TABLE OF CONTENTS

Appendix 2

The Lyn Brianne Catchment Study

SUMMARY

This reports describes the preliminary data analysis and modelling studies being undertaken jointly by the Institute of Hydrology, Welsh Water and Swansea University.

1. Data Transfer and the Data Base at IH

A system has been established between Welsh Water and IH for the transfer of hydrological and chemical data. The data from the continuous flow and quality monitoring equipment and from the chemical analysis of routine rainfall, stream and storm event samples is being transferred via magnetic tape from the WW computers to IH. Weather Station data is also being processed and automatically transferred to the IH data base. The data is stored on a relational database system (ORACLE) available on the new IBM computer at IH. In total over 3 million items of data are being generated each year in the Brianne Study and an extensive suite of computer programs have been developed to handle the storage, retrieval, preliminary statistical analysis and plotting of this large data set.

2. Preliminary Data Analysis

Preliminary analysis of the data has been undertaken including:-

a) Plotting of routine and storm event chemistry data
b) Plotting of hydrological and water quality data from the continuous monitors
c) Statistical analysis of hydrological and chemical data including means, max, min, standard deviation, cummulative distribution information and correlation analysis.

The interpretation of these statistical results is being undertaken to evaluate the principal chemical characteristics of each sub-catchment and present a summary of the pre-treatment condition.

3. Preliminary Modelling Studies

The continuous data is being used initially to evaluate catchment dynamics. The response time of the catchment hydrology and water quality can be evaluated using time series techniques with the models satisfactorily reproducing observed flow patterns following a storm event. The models provide basic information on the catchment response which will be essential in later studies to evaluate the complex acidification processes operating and the interactions with land use change.

4. Advanced Modelling Studies (MAGIC)

MAGIC (Model of Acidification of Groundwater In Catchments) is probably the most sophisticated model available at present. It includes a wide range of chemical processes considered to be controlling acidification in catchments and is being used in the Brianne study to determine long term trends and predict the effects of land use change.

1. DATA TRANSFER AND THE DATA BASE AT IH

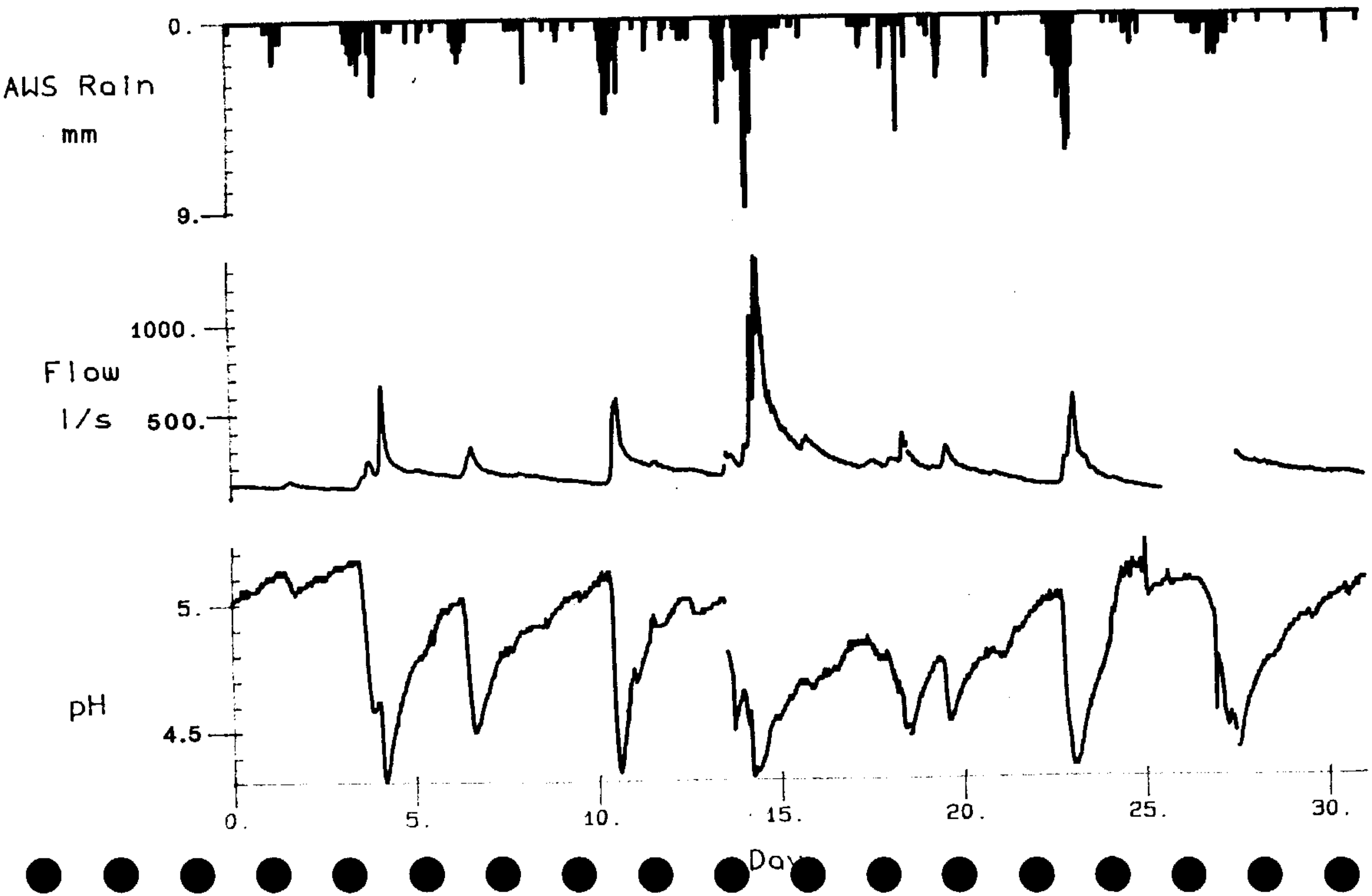
A system has been established between Welsh Water and IH for the transfer of hydrological and chemical data. The data from the continuous flow and quality monitoring equipment and from the chemical analysis of routine rainfall, stream and storm event samples is being transferred via magnetic tape from the WW computers to IH. This has not been straightforward, however, because of the basic incompatibility of ICL and IBM computers. A special computer program has been written to translate the data from the Welsh Water ICL machine to the IH IBM machine. There have also been problems transferring data from the Welsh Water Data General machine to IH. However, now that these difficulties have been largely resolved the data is being stored on a relational database system (ORACLE) available on the IBM machine at IH. Weather station data is also processed and transferred to the IH database system. In total over 3 million items of data are being generated each year in the Llyn Brianne Study and an extensive suite of computer programs have been developed to handle the storage, retrieval, preliminary statistical analysis and plotting of this large data set.

2. CONTINUOUS HYDROLOGICAL AND WATER QUALITY DATA

Continuous data is being obtained from monitors in the Llyn Brianne catchments recording flow, pH, conductivity and water temperature. The sampling interval is 15 minutes which is sufficiently fast to detect all storm events. In addition the IH weather station, based at Lynn Brianne, monitors soil and air temperature, rainfall intensity, relative humidity, wind speed and direction and solar radiation. All of this data is stored on the IH data base and is available for analysis and modelling purposes. The data is being examined in detail by members of the catchment characteristics group and a report is in preparation. A typical plot of rainfall, flow and pH is shown in Figure 1 for catchment LI1 and indicates the rapid response of the catchment flow and pH to rainfall events. This rapid response is being investigated using the time series modelling techniques at IH and preliminary results are presented in section 6. Figure 1b also shows rainfall, flow and pH but this time over a snowmelt event in March; the pH is reduced from 6 to 4 in under eight hours indicating the importance of snowmelt events in Wales.

Llyn Brianne site LI1

August 1985



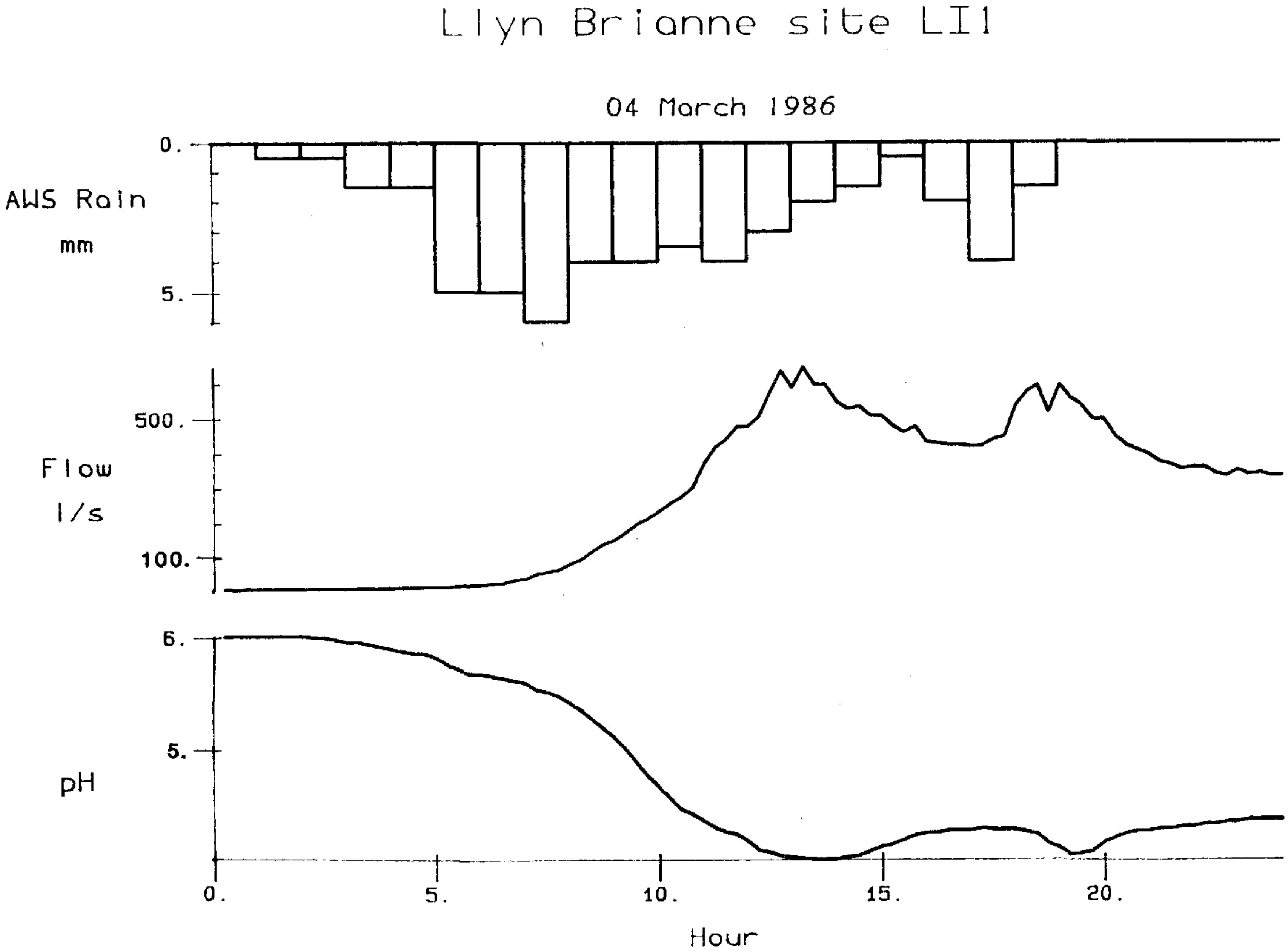


Figure 1b. Rainfall, Flow and pH during the snowmelt event in March.

3. RAINFALL AND STREAM CHEMISTRY.

Introduction

Table 1b lists the catchments for which data are available and some of their main characteristics. Figures 2a and 2b define their locations and those of the two bulk precipitation sampling sites. Where appropriate the results are expressed in ueq l^{-1}, elsewhere mg l^{-1}, are used. The analysis is presented in four parts. First, the bulk precipitation data are summarised. Second, the conifer afforested catchment data. Third, the acidified moorland stream data. And fourth, the unacidified moorland and oak woodland stream data. Storm event samples are not included in the analysis.

Bulk precipitation chemistry

Tables 2a and 3a show that the composition of bulk precipitation at Llyn Brianne is dominated by marine salts and terrestrially derived anions. At C7 in the Camddwr catchment pH ranged from 3.1 to 6.9, with a rainfall-weighted mean of 4.19. Corresponding levels at L3 ranged from 3.4 to 7.1 and averaged 4.12. Consequently, acidity levels can be considered moderate but with the occurrence of some highly acidic events. Indeed, 25% of those samples taken (Q1), exhibited a pH of 4.4 and 4.3 or less at C7 and L3 respectively.

SO_4 concentrations also exhibit a large range at both sites, with rainfall-weighted means of 71.04 ueq l^{-1} and 77.0 ueq l^{-1} at C7 and L3 respectively. Moreover, 25% of those samples taken exceeded 83.3 ueq l^{-1} (C7) and 117.1 ueq l^{-1} (L3). "Excess" - SO_4 concentrations averaged 63.5 ueq l^{-1} (C7) and 71 ueq l^{-1} (L3). Thus , sulphate contributions to acid events are sometimes significant and reflect the presence of anthropogenic sources of sulphates. In addition, the higher levels found at L3 probably

Table 1a Conversion factors, units and notations

Notation	Conversion to ueq l	Name	Unit
pH	–	pH	pH units
Cu	–	Copper	mg l^{-1}
Cd	–	Cadmium	mg l^{-1}
Zn	–	Zinc	mg l^{-1}
Al	–	Aluminium	mg l^{-1}
Pb	–	Lead	mg l^{-1}
Cr	–	Chromium	mg l^{-1}
Mn	–	Manganese	mg l^{-1}
Fe	–	Iron	mg l^{-1}
Ni	–	Nickel	mg l^{-1}
Na	* 1000 / 23.0	Sodium	ueq l^{-1}
K	* 1000 / 39.09	Potassium	ueq l^{-1}
Mg	* 2000 / 24.31	Magnesium	ueq l^{-1}
Ca	* 2000 / 40.08	Calcium	ueq l^{-1}
Cl	* 1000 / 35.46	Chloride	ueq l^{-1}
NO_2	* 1000 / 14.01	Nitrite	ueq l^{-1}
CO_2	–	Free Carbon dioxide	mg l^{-1}
OPO_4	–	Orthophosphate	mg l^{-1}
SiO_2	–	Silicate	mg l^{-1}
SO_4	* 2000 / 96.06	Sulphate	ueq l^{-1}
Amm.N	–	Ammoniacal nitrogen ≙ NH_4	mg l^{-1}
TON	* 1000 / 14.01	Total oxidised nitrogen ≙ NO_3	ueq l^{-1}
T.Alk	* 2000 / 100.05	Total alkalinity (as $CaCO_3$)	ueq l^{-1}
T.H.	–	Total Hardness (as $CaCO_3$)	mg l^{-1}
Cond.	–	Conductivity	µs cm^{-1}
Turb	–	Turbidity	FTU
H.Acid	–	Humic acid	mg l^{-1}
P. solids	–	Particulate solids	mg l^{-1}
DOC	–	Dissolved Organic Carbon (as C)	mg l^{-1}
F. pH	–	Field pH	pH units
I. Flow	–	Instantaneous flow	m^3 s^{-1}
W. Temp	–	Water temperature	°C
UV	–	U V wavelength	NM
Staff	–	Water level	m
H^+	antilog (6.0 – pH)	Hydrogen ion	ueq l^{-1}

Table 1b. The Llyn Brianne Study Catchments.

Notation	Catchment	Function Control/ Managed	Land use	Area km^2	Slope[1] $m\ km^{-1}$
LI1	Nant y Bustach	C	Mature forest	2.525	67.7
LI2	Nant y Fannog	M	Bankside clearance and liming	1.053	89.8
LI3	Nant y Craflwyn	M	Bankside clearance	0.643	96.6
LI4	Nant y Cwmbys	M	Helicopter liming	0.328	121.7
LI8	Trawsnant	C	Juvenile forest	0.659	146.5
CI3	Nant y Gelli	M	Grassland improvement	0.836	71.1
CI4	Nant Gruffydd	M	Ploughing w/o planting	0.491	94.0
CI5	Nant y Coeleth	M	Standard liming	0.342	112.7
CI6	Nant y Gronwen	C	Acid moorland	0.717	67.1
UC4	Nant yr Adar	M	Ploughing and planting conifers	-	-
LI6	Nant Esgair Garn S	C	Unacidic moorland	0.68	194.4
GI1	Nant Melyn tributary	C	Acidic oak woodland	-	-

1. Main stream slope (Boon, 1986).

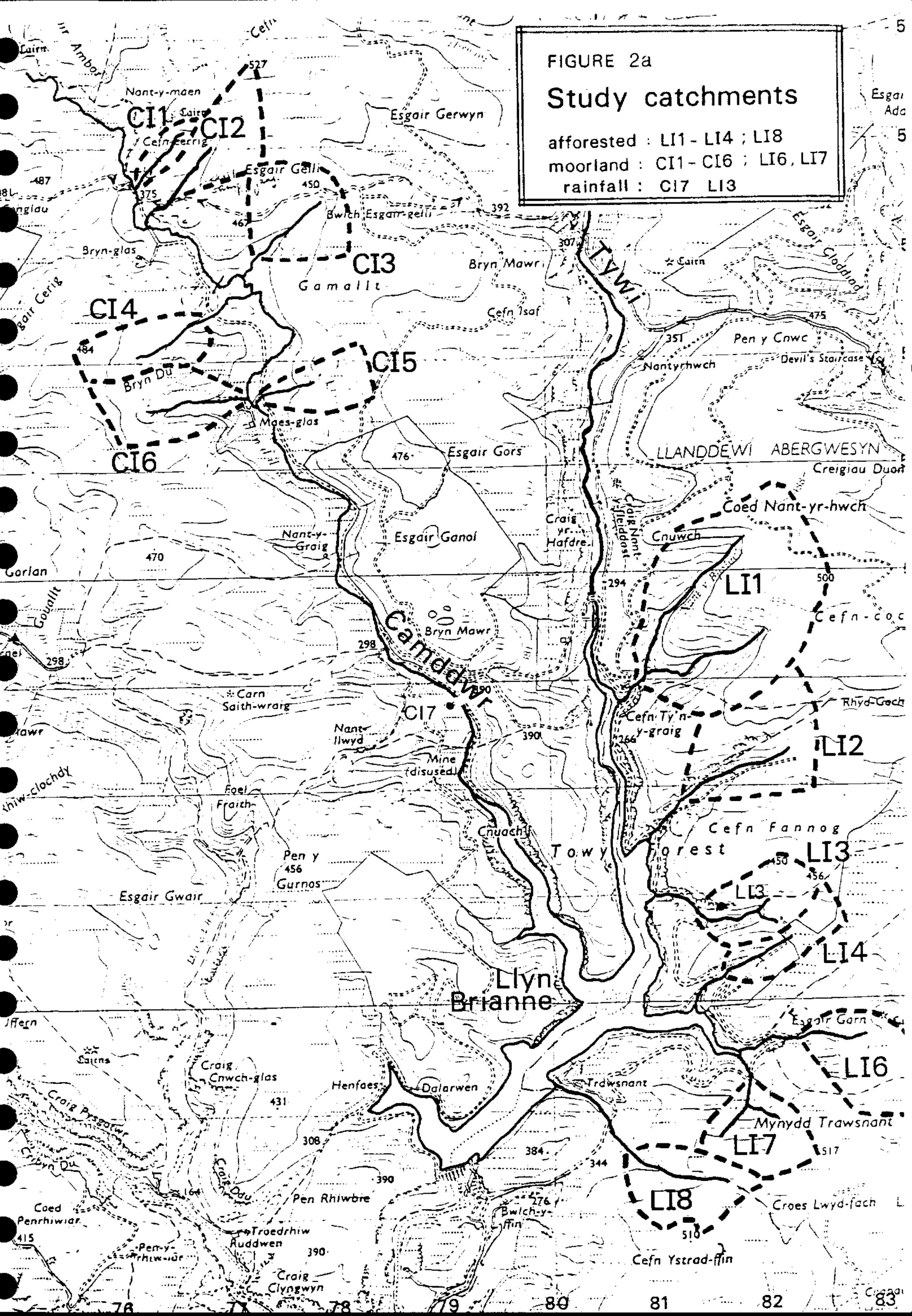


FIGURE 2a

Study catchments

afforested : LI1 - LI4 ; LI8
moorland : CI1 - CI6 ; LI6, LI7
rainfall : CI7 LI3

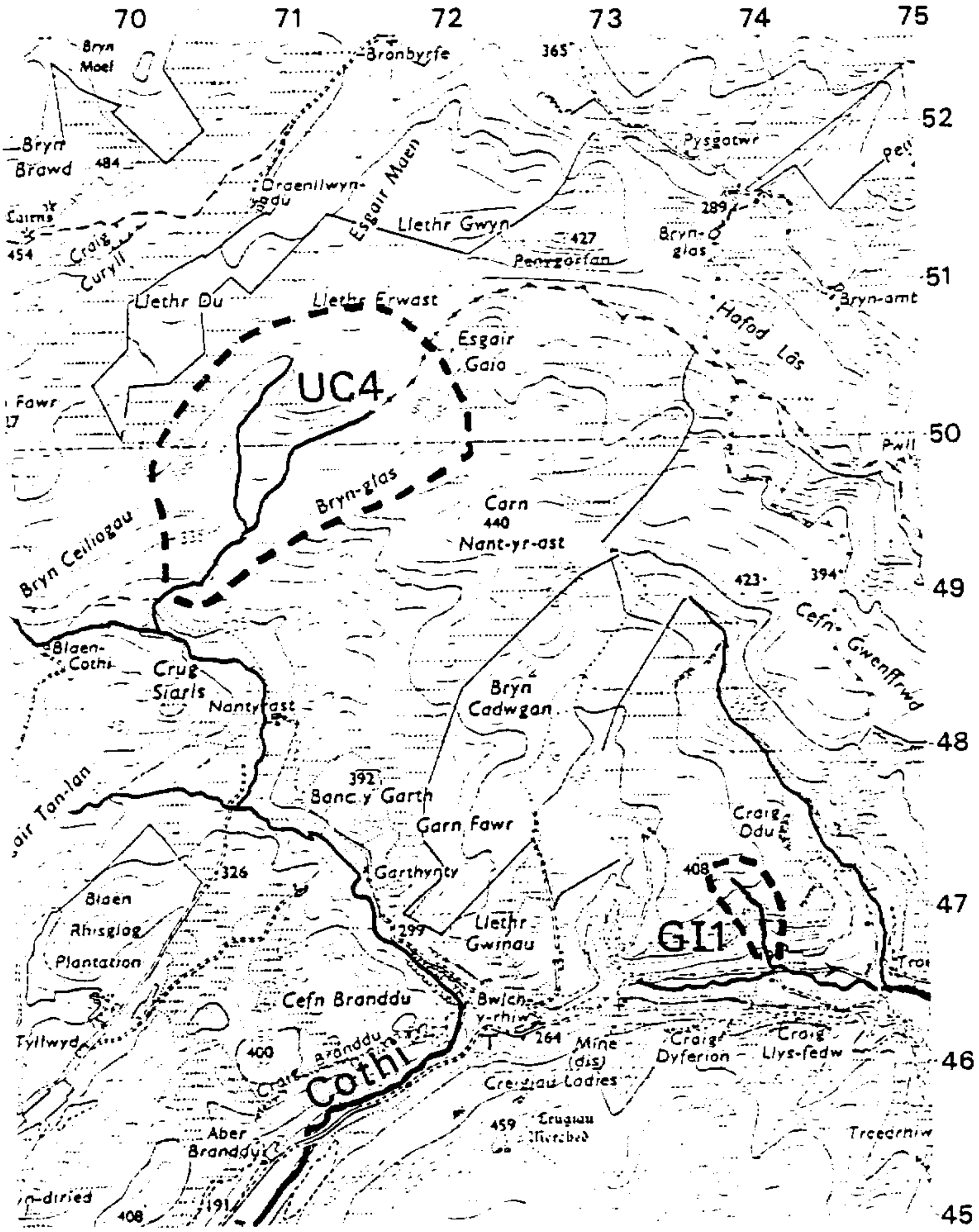


FIGURE 2b

Upper Cothi and Gwenffrwd sites (UC4 & GI1)

Table 2a CI7 rainfall chemistry (1984)

	N	N*	MEAN	MEDIAN	TRMEAN	STDEV	SEMEAN		MIN	MAX	Q1	Q3	Mean (Rainfall weighted)
PH	34	5	4.772	4.600	4.733	0.310	0.139	PH	4.100	6.900	4.400	5.075	4.19
COND	31	8	51.0	28.0	40.6	63.4	11.4	COND	9.0	350.0	17.0	63.0	40 6
AMM_N	35	4	30.86	15.00	25.44	36.93	6.24	AMM_N	2.14	150.00	7.14	37.14	30 8
TON	35	4	44.1	14.3	30.6	71.1	12.0	TON	7.1	307.1	7.1	42.9	44.4
NO2	35	4	0.3306	0.2857	0.3064	0.1297	0.0219	NO2	0.2857	0.9286	0.2357	0.2357	—
TH	33	6	2.958	1.400	2.362	3.895	0.678	TH	0.200	17.700	0.550	3.700	4.07
FCO2	25	14	5.95	3.00	4.52	8.68	1.74	FCO2	1.50	43.50	1.95	6.05	—
TA	15	24	22.25	17.93	18.14	22.97	5.93	TA	2.00	95.72	7.99	25.98	—
CL	35	4	177.3	56.4	143.8	241.2	40.8	CL	22.2	874.5	23.2	169.3	142.4
F	1	38	0.00E+00	0.00E+00	0.00E+00	*	*	F	0.00E+00	0.00E+00	*	*	—
OPO4	35	4	0.02171	0.02000	0.02000	0.00857	0.00145	OPO4	0.02000	0.07000	0.02000	0.02000	—
SIO2	35	4	0.20000	0.20000	0.20000	0.00000	0.00000	SIO2	0.20000	0.20000	0.20000	0.20000	—
SO4	35	4	75.59	62.46	68.89	55.85	9.44	SO4	20.92	239.43	31.23	83.28	71.04
NA	34	5	147.0	61.1	120.8	198.0	34.0	NA	10.4	700.1	32.2	165.5	113.8
K	34	5	7.84	3.71	6.73	8.25	1.41	K	0.26	36.31	2.56	13.10	7.7
CU	24	15	0.00337	0.00200	0.00309	0.00315	0.00064	CU	0.00100	0.01200	0.00100	0.00450	—
MG	34	5	36.20	16.45	29.58	47.86	8.21	MG	3.45	173.52	7.91	34.93	27.95
CA	33	6	20.67	11.98	17.17	21.97	3.82	CA	2.99	109.73	5.99	28.19	17 22
ZN	32	7	0.01572	0.01250	0.01429	0.01320	0.00233	ZN	0.00100	0.05600	0.00525	0.02100	—
CD	33	6	0.00093	0.00080	0.00088	0.00043	0.00007	CD	0.00040	0.00240	0.00080	0.00100	—
AL	31	8	0.02716	0.02400	0.02685	0.01595	0.00286	AL	0.00500	0.05400	0.01500	0.04300	—
PB	33	6	0.01079	0.00900	0.01024	0.00728	0.00127	PB	0.00200	0.02800	0.00500	0.01450	—
CR	24	15	0.00162	0.00100	0.00159	0.00092	0.00019	CR	0.00100	0.00300	0.00100	0.00300	—
MN	33	6	0.00385	0.00200	0.00321	0.00415	0.00072	MN	0.00100	0.02000	0.00100	0.00650	—
FE	33	6	0.03415	0.02400	0.03203	0.02650	0.00461	FE	0.00500	0.09500	0.01250	0.05500	—
NI	24	15	0.00321	0.00300	0.00309	0.00196	0.00040	NI	0.00100	0.00800	0.00100	0.00500	—
UV	13	26	0.01038	0.00500	0.00955	0.00946	0.00262	UV	0.00000	0.03000	0.00500	0.01250	—
RAIN	36	3	45.86	39.50	38.19	54.15	9.03	RAIN	0.00	290.40	8.12	53.77	—
HUMIC	24	15	0.2750	0.2000	0.2500	0.1675	0.0342	HUMIC	0.2000	0.9000	0.2000	0.2750	—
HION	34	5	62.9	25.1	34.3	143.0	24.5	HION	0.1	794.3	8.8	39.8	58.8

Table 2b Correlation matrices

(i) normal

	PH	COND	AMM_N	TON	NO2	TH	FCO2	TA	CL	OPO4	SO4	NA	K	CU	MG	CA
COND	-0.269															
AMM_N	-0.301	0.393														
TON	-0.418	0.290	0.436													
NO2	-0.189	0.207	0.557	0.132												
TH	0.497	0.296	0.027	0.036	0.198											
FCO2	-0.647	0.896	0.404	0.377	0.315	-0.242										
TA	0.943	0.434	0.633	-0.108	*	0.688	-0.451									
CL	0.493	0.215	-0.177	-0.062	0.043	0.929	-0.292	0.478								
OPO4	0.017	-0.101	0.047	-0.045	0.004	-0.099	-0.001	*	-0.103							
SO4	-0.041	0.235	0.812	0.379	0.417	0.459	0.027	0.714	0.257	-0.010						
NA	0.471	0.223	-0.222	-0.070	0.038	0.920	-0.278	0.470	0.996	-0.117	0.220					
K	0.195	0.554	0.156	0.295	0.422	0.774	0.249	0.607	0.659	0.015	0.427	0.650				
CU	-0.591	0.785	0.467	0.345	0.555	0.432	0.798	-0.672	0.122	-0.191	0.343	0.151	0.733			
MG	0.481	0.213	-0.169	-0.056	0.045	0.936	-0.292	0.485	0.997	-0.115	0.271	0.997	0.653	0.109		
CA	0.204	0.374	0.432	0.269	0.179	0.754	-0.034	0.900	0.474	-0.072	0.672	0.443	0.623	0.539	0.483	
ZN	-0.571	0.391	0.707	0.655	0.396	0.042	0.443	-0.182	-0.212	0.115	0.675	-0.226	0.523	0.724	-0.200	0.685
CD	-0.399	0.433	0.310	0.264	0.575	-0.265	0.674	-0.009	-0.383	-0.063	0.059	-0.374	0.310	0.670	-0.399	0.091
AL	-0.222	0.237	0.540	0.242	0.345	0.022	0.270	0.499	-0.190	-0.046	0.523	-0.232	0.244	0.544	-0.200	0.446
PB	-0.252	-0.013	0.200	-0.009	0.169	-0.276	0.178	-0.107	-0.349	-0.145	0.017	-0.403	-0.031	0.110	-0.393	0.016
CR	0.111	-0.253	-0.404	-0.321	-0.213	-0.223	-0.414	-0.637	0.090	-0.171	-0.342	0.133	-0.293	-0.234	0.101	-0.356
MN	-0.303	0.304	0.829	0.472	0.493	0.124	0.260	0.714	-0.165	-0.009	0.822	-0.193	0.453	0.605	-0.151	0.608
FE	-0.170	0.247	0.605	0.261	0.340	0.168	0.138	0.430	-0.019	-0.047	0.703	-0.043	0.201	0.513	-0.006	0.462
NI	-0.185	0.113	-0.151	-0.140	0.090	-0.075	0.008	-0.394	0.052	-0.285	-0.164	0.093	0.166	0.269	-0.023	-0.080
UV	-0.324	0.245	0.471	0.455	-0.012	0.074	0.190	-0.468	-0.044	-0.012	0.432	-0.043	-0.107	-0.170	-0.011	0.427
RAIN	0.014	-0.136	-0.366	-0.251	-0.260	-0.105	-0.217	-0.299	0.060	0.057	-0.270	0.057	-0.199	-0.348	0.041	-0.259
HUMIC	-0.367	0.329	0.861	0.377	0.587	0.692	0.190	*	0.037	0.063	0.912	-0.061	0.380	0.338	0.126	0.817
HION	-0.592	0.913	0.363	0.345	0.717	-0.136	0.993	-0.666	-0.197	-0.067	0.052	-0.174	0.197	0.724	-0.191	0.050

	ZN	CD	AL	PB	CR	MN	FE	NI	UV	RAIN	HUMIC
CD	0.466										
AL	0.626	0.328									
PB	0.103	0.521	0.077								
CR	-0.420	0.075	-0.296	0.267							
MN	0.796	0.401	0.595	0.260	-0.299						
FE	0.546	0.101	0.846	-0.148	-0.232	0.631					
NI	0.053	0.573	0.033	0.596	0.430	-0.031	-0.146				
UV	0.460	-0.011	0.123	-0.122	-0.791	0.136	0.103	-0.620			
RAIN	-0.275	-0.272	-0.373	-0.195	0.282	-0.353	-0.278	-0.041	-0.195		
HUMIC	0.679	0.199	0.567	-0.078	-0.311	0.836	0.833	-0.176	0.816	-0.274	
HION	0.403	0.643	0.252	0.162	-0.249	0.268	0.165	0.109	0.280	-0.196	0.225

(ii) logarithmic

	Al C71	Mn C72	Fe C73	Na C74	K C75	Mg C76	Ca C77	Cl C78	CO C79	SO4 C81	NH4 C82	TON C83	TA C84	TH C85	Con C86	Hum C87
C72	0.663															
C73	0.794	0.740														
C74	-0.313	-0.262	-0.066													
C75	0.071	0.131	0.131	0.663												
C76	-0.216	-0.132	0.062	0.969	0.642											
C77	0.306	0.530	0.508	0.433	0.553	0.622										
C78	-0.180	-0.134	0.057	0.951	0.658	0.966	0.542									
C79	0.347	0.517	0.157	-0.599	-0.153	-0.585	-0.027	-0.597								
C81	0.393	0.671	0.651	0.255	0.377	0.408	0.777	0.417	0.059							
C82	0.506	0.761	0.553	-0.275	0.155	-0.140	0.502	-0.174	0.666	0.689						
C83	0.375	0.653	0.442	-0.183	0.109	-0.064	0.449	-0.111	0.654	0.525	0.715					
C84	-0.150	0.105	0.317	0.694	0.576	0.658	0.729	0.642	-0.692	0.596	0.547	-0.033				
C85	0.036	0.244	0.303	0.809	0.673	0.901	0.880	0.841	-0.328	0.646	0.201	0.231	0.666			
C86	0.177	0.451	0.392	0.430	0.504	0.493	0.772	0.476	0.499	0.602	0.499	0.563	0.490	0.706		
C87	0.562	0.673	0.743	-0.041	0.313	0.212	0.845	0.135	0.427	0.337	0.750	0.673	*	0.641	0.627	
C89	0.210	0.331	0.193	-0.292	-0.195	-0.376	-0.002	-0.386	0.814	-0.005	0.214	0.441	-0.780	-0.229	0.575	0.463

H

Table 3a LI3 rainfall chemistry (1984)

	N	N*	MEAN	MEDIAN	TRMEAN	STDEV	SEMEAN	MIN	MAX	Q1	Q3	Mean (Rainfall - weighted)
PH	33	7	4.355	4.600	4.793	0.877	0.153	3.400	7.100	4.300	5.000	4.12
COND	27	13	41.37	30.00	37.96	31.72	6.10	13.00	155.00	19.00	57.00	33.2
AMM_N	34	6	39.47	23.21	32.74	48.01	8.23	1.43	221.43	7.50	46.21	38.8
TON	34	6	37.51	21.43	29.76	49.28	8.45	7.14	242.86	7.14	42.86	36.5
NO2	34	6	0.29931	0.28570	0.29046	0.03719	0.00638	0.28570	0.42860	0.28570	0.28570	–
TH	31	9	2.810	2.000	2.444	2.928	0.526	0.100	14.100	0.600	4.100	4.08
FCC2	23	17	4.174	3.400	3.976	2.714	0.566	1.100	11.400	2.200	5.900	–
TA	15	25	42.5	18.0	34.6	60.5	15.6	2.0	195.3	10.0	24.0	–
CL	34	6	143.5	56.4	113.8	182.7	31.3	28.2	874.5	23.2	197.5	113.0
F	2	33	2.63	2.63	2.63	3.72	2.63	0.00	5.26	*	*	–
OPO4	34	6	0.02441	0.02000	0.02167	0.01284	0.00220	0.02000	0.03000	0.02000	0.02000	–
SIO2	34	6	0.2912	0.2000	0.2000	0.3753	0.0644	0.2000	2.0000	0.2000	0.2000	–
SO4	34	6	85.5	54.6	80.0	64.6	11.1	20.8	239.4	41.5	117.1	77.0
NA	32	8	108.5	60.7	93.7	107.7	19.0	11.3	421.8	27.4	177.0	90.4
K	32	8	7.18	4.35	6.03	7.92	1.40	0.51	36.31	2.37	10.16	7.0
CU	25	15	0.00596	0.00200	0.00496	0.00786	0.00157	0.00100	0.03400	0.00200	0.00600	–
MG	32	8	29.48	16.04	26.04	29.61	5.23	4.28	104.44	8.16	39.39	25.2
CA	32	8	30.24	21.21	24.49	36.29	6.42	2.49	183.13	7.11	44.66	27.7
ZN	31	9	0.02726	0.02100	0.02430	0.02507	0.00450	0.00100	0.11300	0.00800	0.03900	–
CD	31	9	0.00109	0.00090	0.00103	0.00061	0.00011	0.00040	0.00270	0.00030	0.00120	–
AL	30	10	0.04010	0.02700	0.03227	0.04235	0.00773	0.00500	0.17900	0.01625	0.05150	–
PB	30	10	0.02093	0.01100	0.01254	0.04543	0.00830	0.00200	0.25500	0.00500	0.01475	–
CR	25	15	0.00164	0.00100	0.00161	0.00091	0.00018	0.00100	0.00300	0.00100	0.00300	–
MN	31	9	0.01429	0.00300	0.00674	0.03183	0.00572	0.00100	0.14500	0.00200	0.01400	–
FE	31	9	0.04519	0.03200	0.03781	0.04758	0.00855	0.00600	0.24500	0.01400	0.04900	–
NI	25	15	0.00344	0.00300	0.00309	0.00299	0.00060	0.00100	0.01400	0.00100	0.00450	–
UV	10	30	0.00850	0.00500	0.00687	0.00851	0.00269	0.00000	0.03000	0.00500	0.01125	–
RAIN	37	3	44.70	36.30	35.73	56.83	9.34	0.00	290.40	8.25	53.35	–
HUMIC	25	15	0.416	0.200	0.257	0.815	0.163	0.200	4.300	0.200	0.300	–
HICN	33	7	43.5	25.1	30.3	73.2	12.7	0.1	398.1	10.0	50.1	49.5

Table 3b Correlation matrices

(i) normal

	PH	COND	AMM_N	TON	NO2	TH	FCO2	TA
COND	-0.294							
AMM_N	-0.179	0.479						
TON	-0.296	0.446	0.933					
NO2	0.417	0.162	0.401	0.247				
TH	0.440	0.288	0.102	0.172	0.095			
FCO2	-0.617	0.412	0.674	0.744	-0.133	-0.212		
TA	0.993	0.254	-0.084	-0.070	0.073	0.690	-0.400	
CL	0.415	0.134	-0.130	-0.123	0.148	0.575	-0.431	0.506
F	*	*	*	*	*	*	*	*
CPO4	-0.261	0.370	0.689	0.753	0.243	0.198	0.520	-0.167
SO4	0.181	0.442	0.617	**0.655**	0.372	0.621	0.276	0.461
NA	0.285	0.072	-0.258	-0.229	-0.041	0.651	-0.599	0.211
K	0.363	0.311	0.534	0.369	0.507	0.222	0.286	0.011
CU	0.030	0.424	0.809	0.763	0.323	0.131	0.756	-0.041
MG	0.326	0.142	-0.161	-0.135	-0.068	**0.833**	-0.502	0.456
CA	0.451	0.357	0.327	0.382	0.212	**0.904**	0.038	0.732
ZN	0.094	0.395	0.863	0.845	0.340	0.393	0.624	0.460
CD	0.167	-0.003	0.402	0.289	0.265	-0.064	0.364	-0.041
AL	-0.147	0.194	0.543	**0.611**	0.078	0.371	0.697	-0.180
PB	-0.197	0.396	0.659	0.729	-0.038	0.247	0.586	0.431
CR	-0.139	-0.262	-0.377	-0.307	-0.175	-0.172	-0.453	-0.473
MN	0.074	0.016	-0.029	0.037	0.033	0.430	0.165	-0.005
FE	-0.206	0.400	0.801	0.878	0.095	0.239	0.706	-0.068
NI	0.041	-0.195	-0.037	-0.061	-0.077	-0.096	-0.174	-0.166
UV	-0.613	0.499	0.804	0.878	*	0.313	0.567	-0.293
RAIN	-0.067	-0.114	-0.363	-0.331	-0.228	-0.016	-0.301	-0.289
HUMIC	-0.245	0.458	0.807	0.866	0.013	0.213	0.654	-0.198
HION	-0.580	0.814	0.302	0.293	-0.169	-0.173	[illegible]	-0.112

	CL	F	CPO4	SO4	NA	K	CU	MG
F	*							
CPO4	-0.092	*						
SO4	0.329	*	0.432					
NA	**0.963**	*	-0.105	0.132				
K	0.106	*	0.303	0.221	0.163			
CU	-0.130	*	0.577	0.377	-0.169	0.326		
MG	**0.874**	*	-0.049	0.276	**0.941**	0.106	-0.151	
CA	0.229	*	0.337	0.761	0.295	0.236	0.302	0.524
ZN	-0.133	*	0.629	0.494	-0.142	0.653	0.853	0.003
CD	-0.273	*	0.200	0.117	-0.264	0.573	0.561	-0.281
AL	-0.106	*	0.523	0.402	0.007	0.352	0.496	0.212
PB	-0.100	*	0.717	0.425	-0.167	0.338	0.709	-0.047
CR	0.336	*	-0.279	-0.199	0.217	-0.323	-0.305	0.034
MN	0.105	*	0.058	0.212	0.273	0.137	-0.014	0.431
FE	-0.052	*	0.634	0.526	-0.130	0.336	0.790	-0.019
NI	-0.076	*	-0.096	-0.039	-0.067	0.108	0.093	-0.141
UV	-0.034	*	*	0.825	-0.125	0.047	0.942	0.014
RAIN	0.131	1.000	-0.161	-0.388	0.336	-0.210	-0.305	0.266
HUMIC	-0.088	*	0.803	0.457	-0.175	0.426	0.779	-0.045
HION	-0.219	*	0.197	0.032	-0.292	-0.081	0.155	-0.248

	CA	ZN	CD	AL	PB	CR	MN	FE
ZN	0.609							
CD	0.090	0.458						
AL	0.423	0.605	0.184					
PB	0.390	0.651	0.442	0.565				
CR	-0.312	-0.471	0.209	-0.344	-0.087			
MN	0.363	0.165	-0.004	0.750	0.052	-0.013		
FE	0.397	0.768	0.315	0.743	0.764	-0.272	0.121	
NI	-0.086	-0.040	0.726	-0.139	0.194	0.491	-0.156	-0.002
UV	0.874	0.918	0.211	0.579	0.230	-0.662	0.877	0.740
RAIN	-0.240	-0.433	-0.333	-0.092	-0.191	0.260	-0.040	-0.264
HUMIC	0.341	0.754	0.377	0.644	0.966	-0.180	0.055	0.904
HION	-0.071	0.135	0.001	0.098	0.259	-0.206	-0.101	0.228

	NI	UV	RAIN	HUMIC
UV	-0.749			
RAIN	-0.127	-0.320		
HUMIC	0.097	0.899	-0.167	
HION	-0.156	0.705	-0.170	0.279

(ii) logarithmic

	C71	C72	C73	C74	C75	C76	C77	C78
C72	0.742							
C73	0.827	0.507						
C74	-0.088	0.249	-0.116					
C75	0.277	0.442	0.345	0.357				
C76	0.123	0.417	0.075	**0.942**	0.383			
C77	0.496	0.732	0.546	0.441	0.565	0.620		
C78	-0.069	0.200	0.007	**0.910**	0.322	**0.915**	0.466	
C79	0.516	0.535	0.505	-0.749	-0.017	-0.537	-0.048	-0.627
C80	-0.010	0.435	0.049	0.315	-0.277	0.332	0.439	0.294
C81	0.493	0.569	0.679	0.083	0.273	0.245	0.667	0.357
C82	0.314	0.085	0.478	-0.450	0.409	-0.366	0.143	-0.232
C83	0.504	0.449	0.397	-0.510	0.405	-0.140	0.491	-0.114
C84	-0.376	0.172	-0.039	0.354	-0.137	0.390	0.388	0.536
C85	0.359	0.447	0.553	0.717	0.552	0.361	0.390	0.754
C86	0.272	0.207	0.155	0.277	0.213	0.230	0.476	0.336
[illegible]7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]8	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

SiO2

	C79	C80	C81	C82	C83	C84	C85	C86
C80	-0.214							
C81	0.232	0.323						
C82	0.615	-0.490	0.476					
C83	0.657	-0.053	0.725	0.792				
C84	-0.392	0.377	0.140	-0.278	-0.047			
C85	-0.340	0.353	[illegible]	-0.045	0.246	0.327		
C86	0.035	0.222	0.527	0.265	0.575	0.155	0.437	
[illegible]7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]8	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

reflect the greater amounts of occult and dry deposition characteristic of its forestry location.

T.O.N. concentrations (approximately equivalent to NO_3) average 44.4 ueq l^{-1} (C7) and 36.5 ueq l^{-1} (L3) and exhibit similar patterns at both sites which match SO_4 variations but are affected by occasional samples showing very high levels. Hence, at times the NO_3 component of acid rainfall can be quite substantial. On the other hand, both sites indicate the presence of comparable concentrations of ammoniacal nitrogen (approximating to NH_4 at low pH), averaging 30.8 ueq l^{-1} (C7) and 38.8 ueq l^{-1} (L3) and offering a limited capability to neutralise some of the rainfall's acidity.

As mentioned previously, the marine salts (Na , Mg and Cl) are present in large concentrations, with rainfall-weighted means of 113.8 ueq l^{-1} , 27.95 ueq l^{-1} and 142.4 ueq l^{-1} (C7) and 90.4 ueq l^{-1} , 25.2 ueq l^{-1} and 113 ueq l^{-1} (L3) . The higher levels at C7, probably reflect the sites closer proximity to the coast. Hence, sea-salt effects are likely to be significant in the study area. Sodium to chloride ratios averaging 1.25 at each site, also support the suggestion that much of the chloride is sea-derived.

Terrestrially derived Ca, total alkalinity and total hardness concentrations are all low on average suggesting that there are limited amounts available in bulk precipitation to buffer against acid inputs. Nevertheless, some samples have exhibited high alkalinity and hardness levels offering considerable buffering capacity on occasions.

Lastly, in all cases trace metal concentrations were very low with only aluminium and iron being present in any significant amounts. Thus, there is little evidence of any acute atmospheric metal pollution at Llyn Brianne.

To sum up, a comparison of the bulk precipitation quality data for 1984 with those already reported by Stoner et al. (1984) for 1981-82 are presented in Table 4. First, acidity concentrations are seen to be generally higher than in 1981-82 for all of the major components (i.e. H^+, SO_4^{2-} and NO_3^-), although the NH_4^+ concentrations are similar. However, this might be explained by the fact that the earlier years were not only non rainfall-weighted, but also (Figure 3) wetter, with annual rainfalls of 2050mm and 1943mm in 1981 and 1982 respectively, (recorded at Nant y maen) and 1699mm in 1984. Hence the acidic inputs were likely to have been diluted in the earlier years. Nevertheless, these factors may not account for the entire difference and suggests that a more detailed programme sampling wet, occult and dry deposition needs to be implemented. Other factors such as the changing magnitude and frequency of heavy rainfalls, rainfall seasonality, changing synoptic frequencies and evaporation effects also need to be considered.

Comparison with other sites in the British Isles thus indicates that levels are comparable with many of the more contaminated areas in terms of H^+ at least. In addition, sulphate and nitrate levels were certainly higher in 1984 and compare with those recorded in Central Scotland and the South Pennines. High sodium and chloride concentrations meanwhile, confirm the importance of marine salts at Llyn Brianne.

Correlation matrices relating all of the chemical determinants are given in Tables 2b and 3b. As is expected pH is significantly and positively correlated with total alkalinity and to a lesser extent total hardness at each site. Moreover, it is significantly and negatively correlated with free CO_2 and H^+. SO_4 and NH_4^+ are also highly positively correlated, suggesting their common source. The major marine derived ions are also highly and

Table 4. Some rainfall quality comparisons for the British Isles.

Study and location	Concentration (ueq l^{-1}) H^+	SO_4^{2-}	[2] Excess SO_4^{2-}	NO_3^-	NH_4^+	Na^+	Cl^-	Mg^{2+}	Ca^{2+}	K^+
1. C7 This report (1984)	59	71	64	44	31	114	142	28	17	8
1. L3 This report (1984)	49	77	71	37	39	90	113	25	28	7
3. Llyn Brianne (1981-82) (Stoner *et al.*, 1984)	27	54	39	17	31	136	148	34	35	12
Central Scotland (Harriman and Morrison, 1982)	40	83	73	7	16	93	101	24	23	7
South Pennines (Brown and Martin, 1980)	45	91	77	27	29	105	140	27	45	5
East Midlands (Martin and Barber, 1978)	73	171	157	80	129	80	140	27	57	13
Rothamstead (Williams, 1976)	50	103	86	78	122	84	167	34	91	18
Mid Wales (Cryer, 1976)	11	-	-	-	-	96	115	28	70	3
Dyfed (Martin, 1980)	20	54	43	16	13	89	107	23	15	6

1. rainfall - weighted mean using Nant-y-maen daily rainfalls
2. Excess SO_4 = Total SO_4 -0.1035 Cl^- concentrations
3. not rainfall - weighted

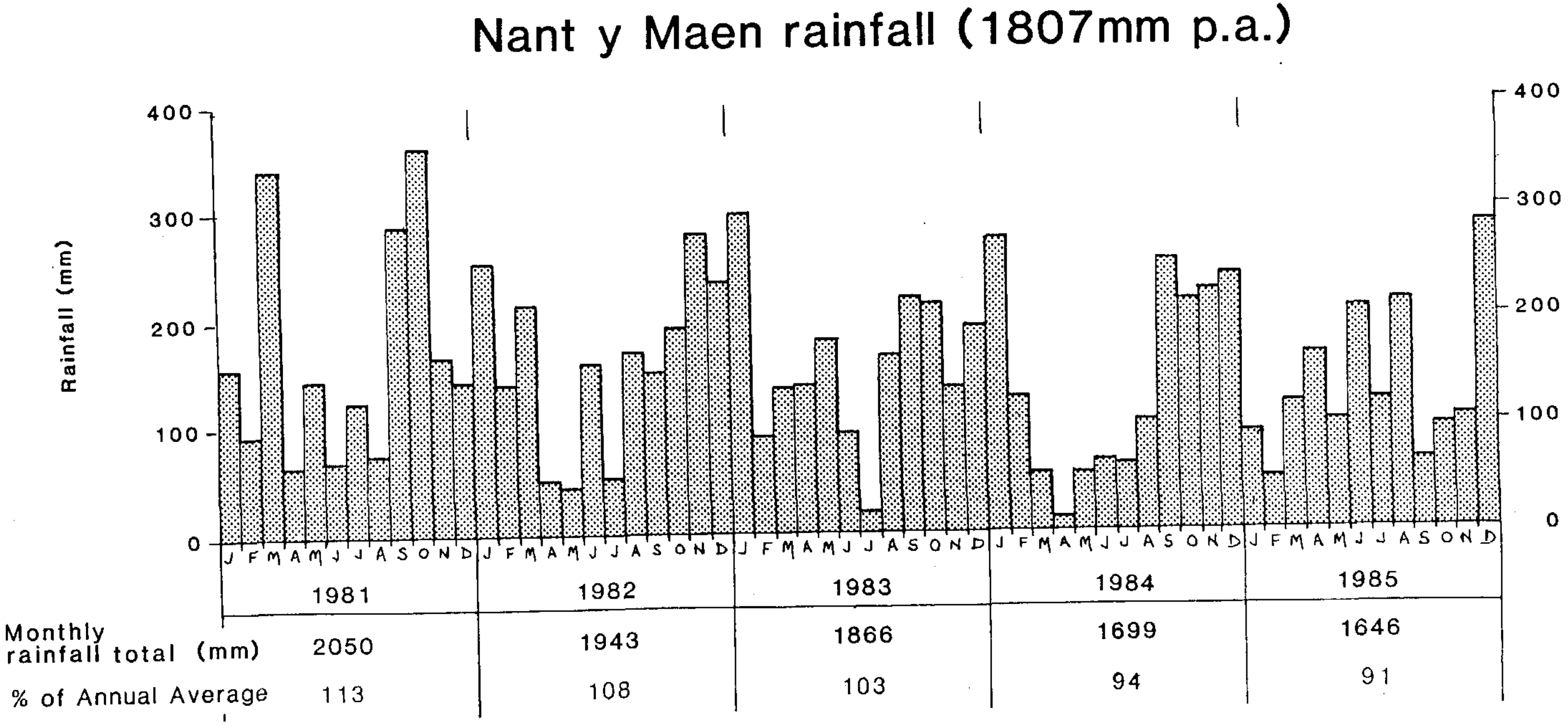


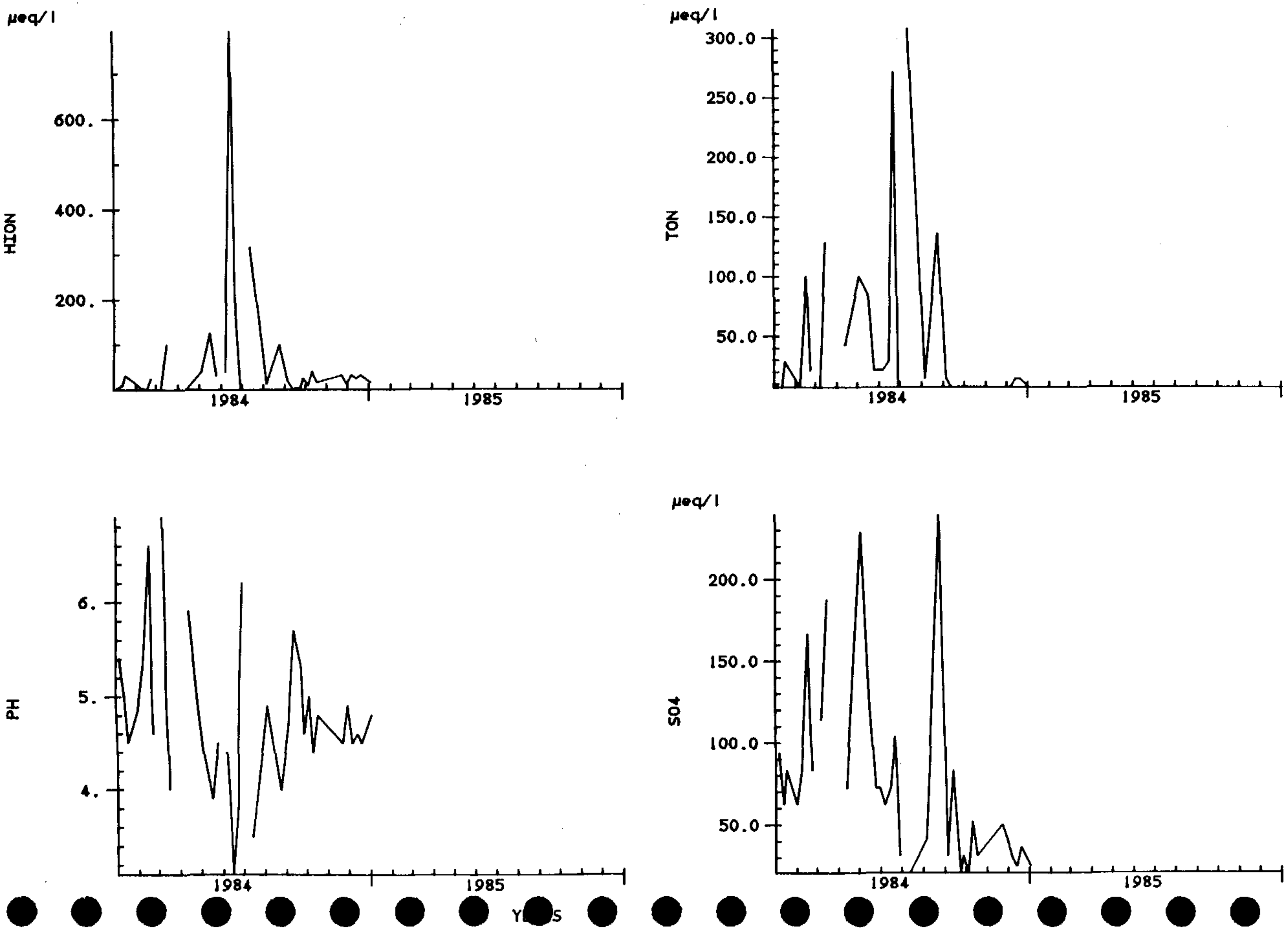
Figure 3 Monthly rainfall at Nant y Maen (1981 - 1985)

positively intercorrelated at both sites, reflecting their common source. Few other significant correlations exist and H^+ concentrations rarely correlate with any other determinand, with the obvious exceptions of pH, conductivity, free CO_2 and total alkilinity. Of the metals, dissolved aluminium shows some indication of a positive correlation with manganese and iron at both sites, few other consistent relationships are apparent. Logarithmic transformations improve the correlations between Al, Mn and Fe at both sites and confirm the correlations found between determinands prior to their transformation.

Any temporal patterns in rainfall chemistry must be viewed in the context of the varying rainfall amounts received in the area (Figure 3). Furthermore, within each year monthly rainfalls also vary. For example, not only was 1984 a dry year, but also its rainfall seasonality was unusual in the sense that from February to August, rainfall inputs were extremely low. In addition, the low rainfall period was characterised by a much greater frequency of easterly-type airflows than was the case for the rest of the year which was dominated by westerly and anticyclonic airflows.

Thus, at C7 and L3 (Figures 4 and 5) without exception, the most acid events (< pH 4.5) were recorded in the period March to August, with H^+ concentrations rising well above 30 ueq l^{-1}. June saw the most acid sample, with a pH of 3.1 at C7, following a long dry period. Presumably such a situation arose as a result of the flushing of accumulated dry particles from the atmosphere and their collection in the sampling instrument over a considerable period. Both SO_4 and NH_4^+ levels were also elevated during the long dry period and show two major peaks in early May and August. Both correspond to short periods dominated by the

Figure 4 RAINFALL (CI7)



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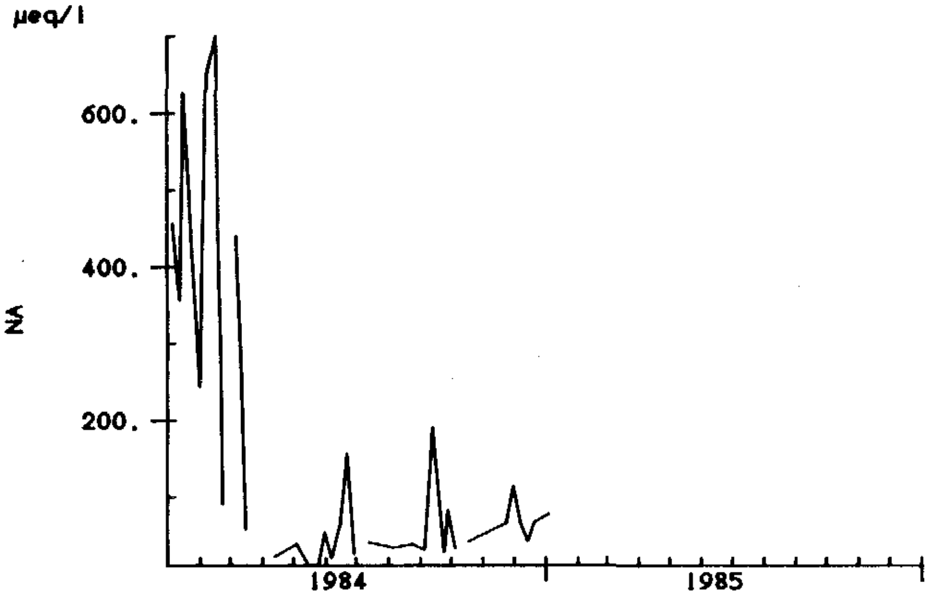

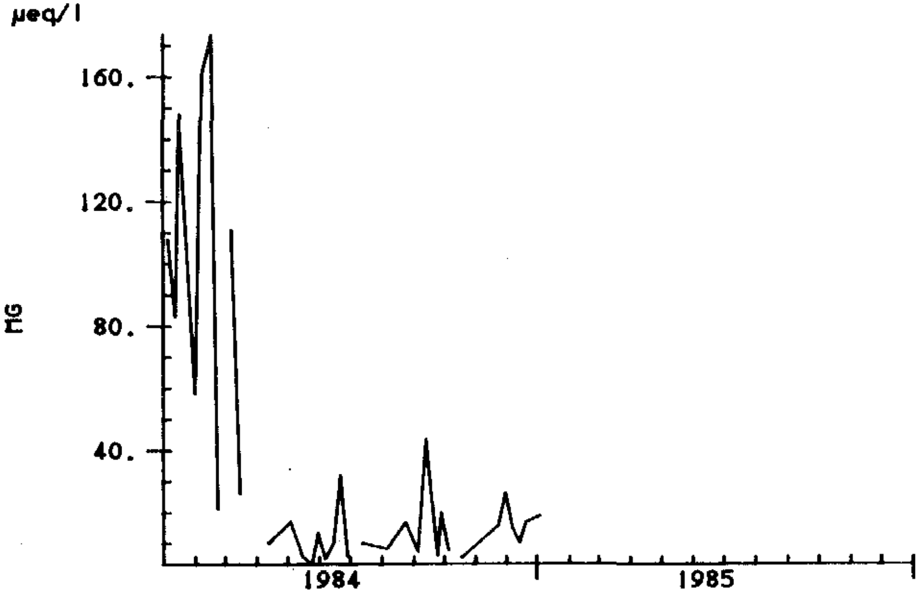

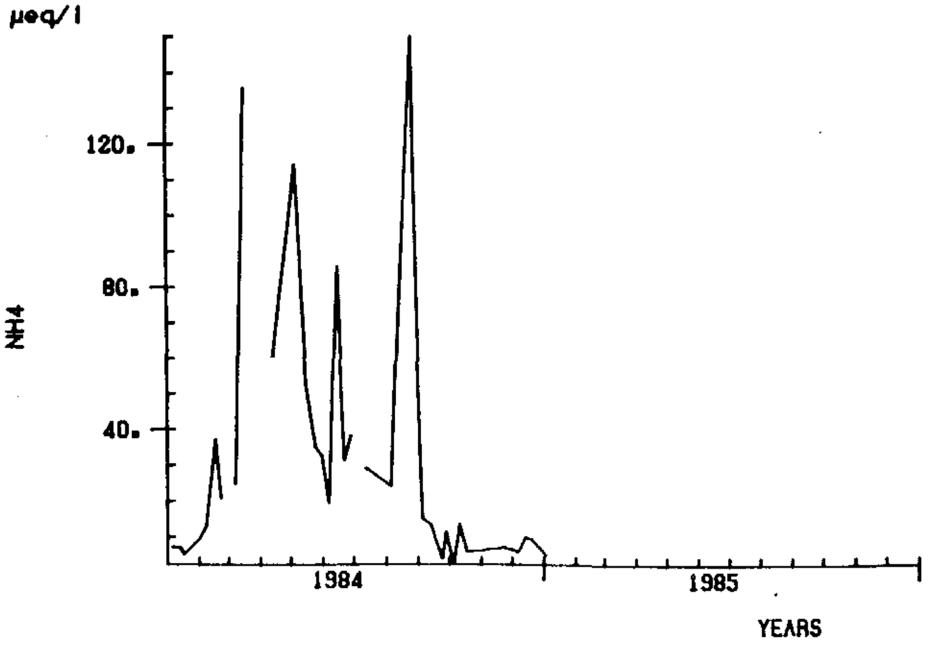

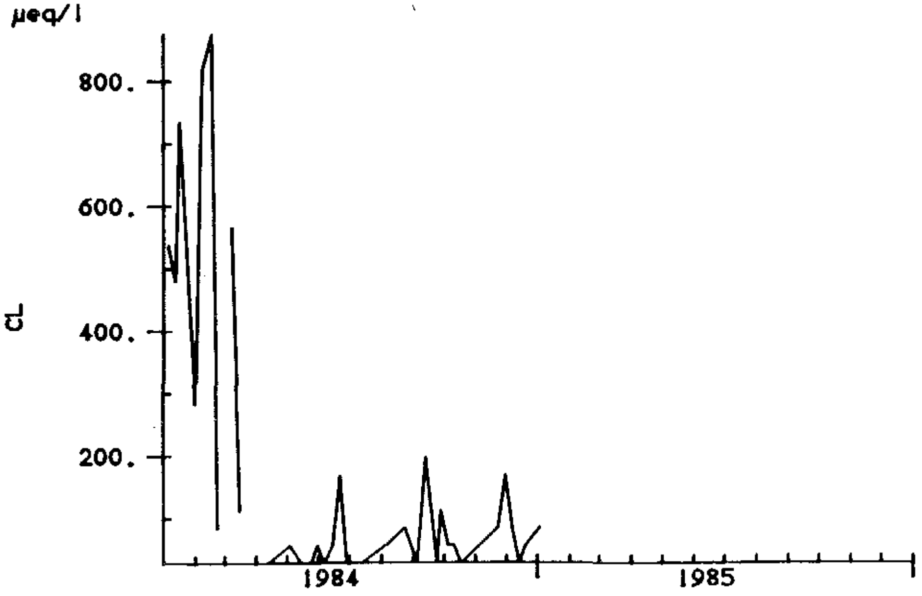

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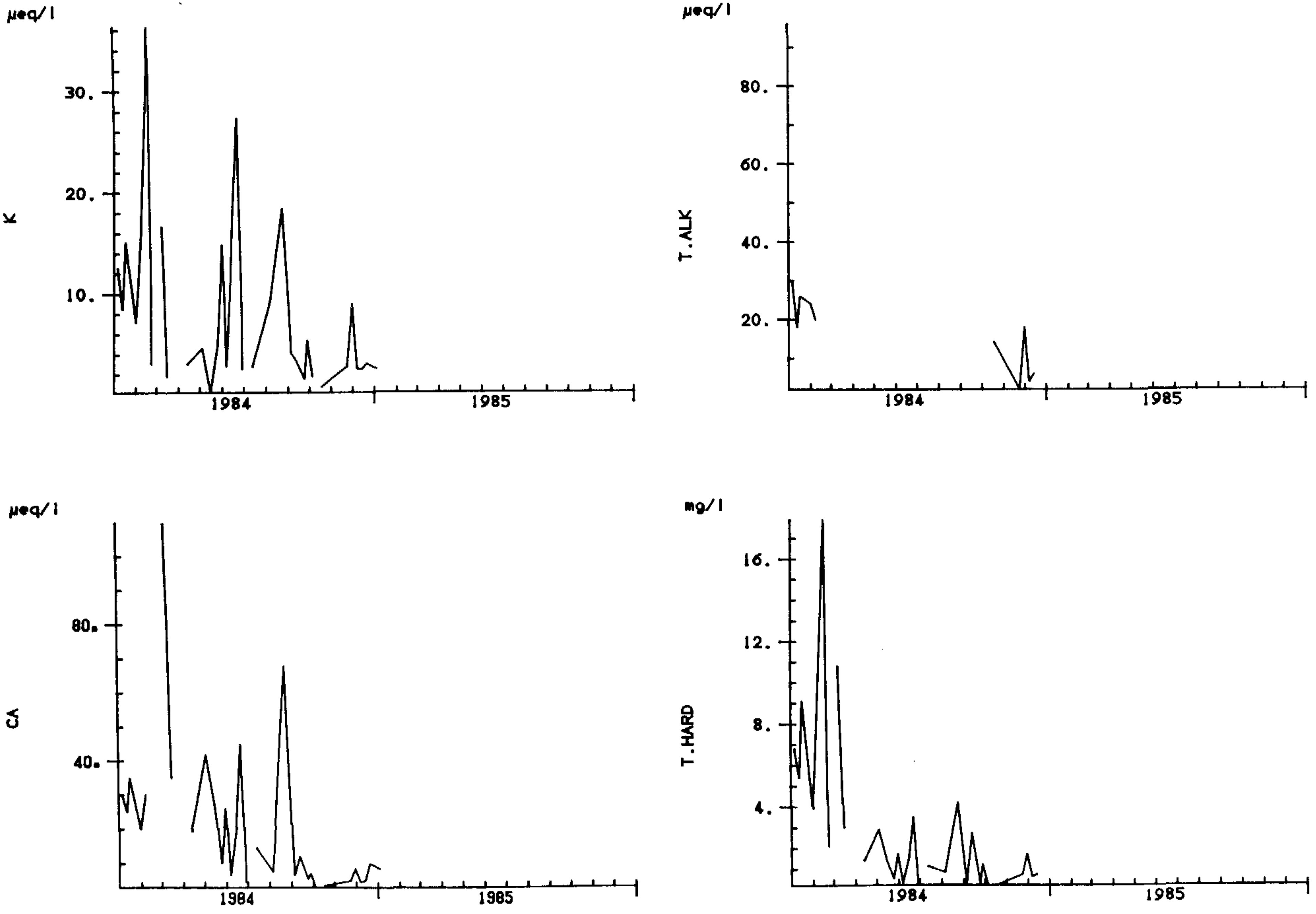

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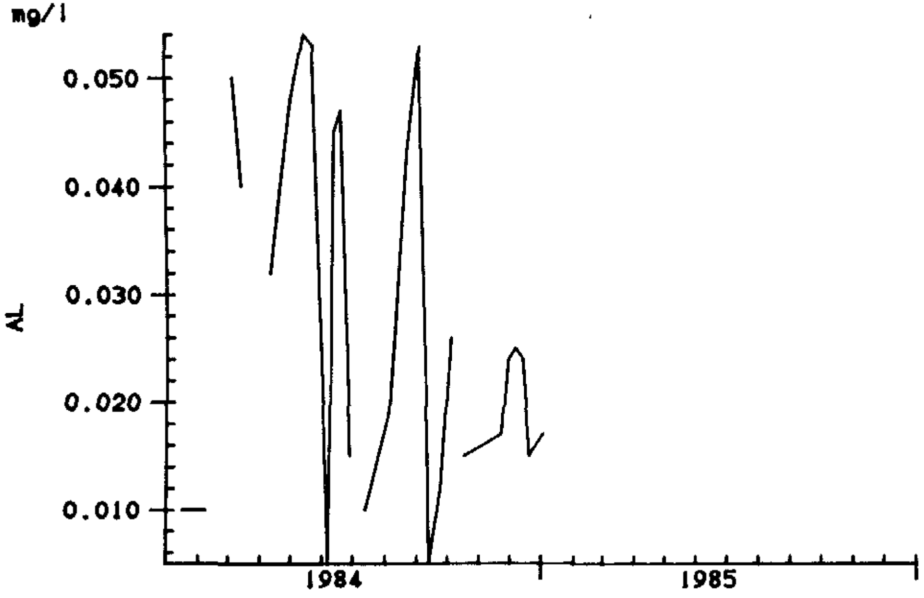

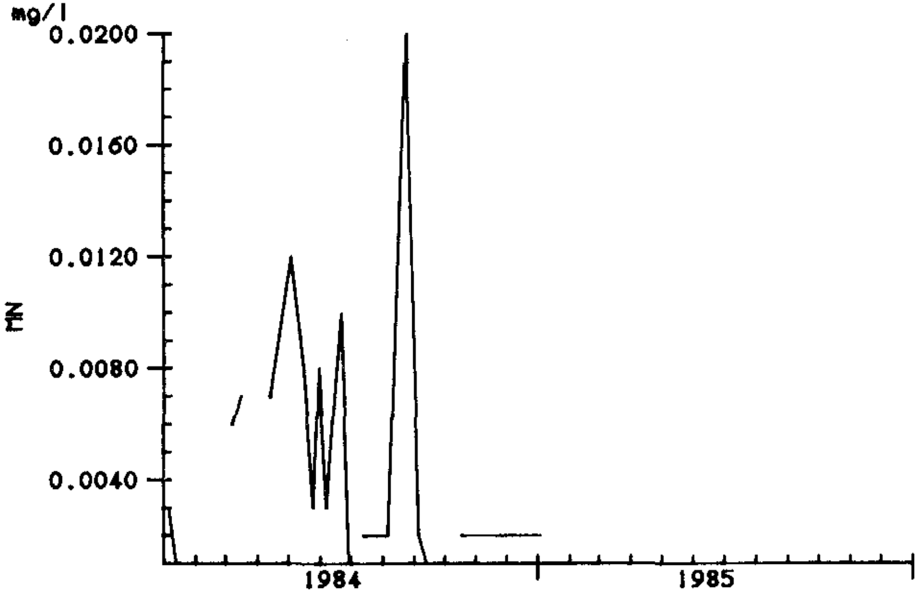

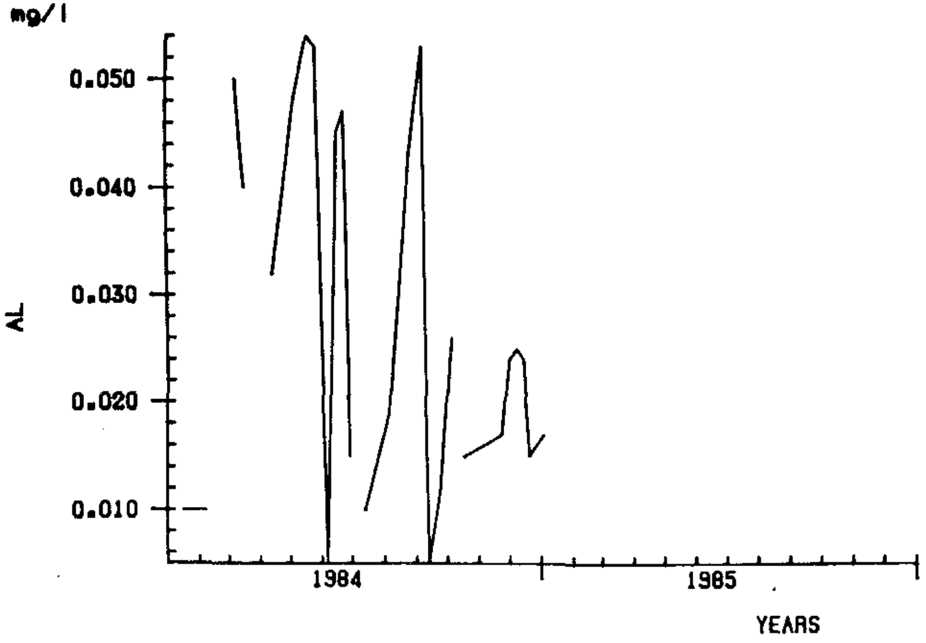

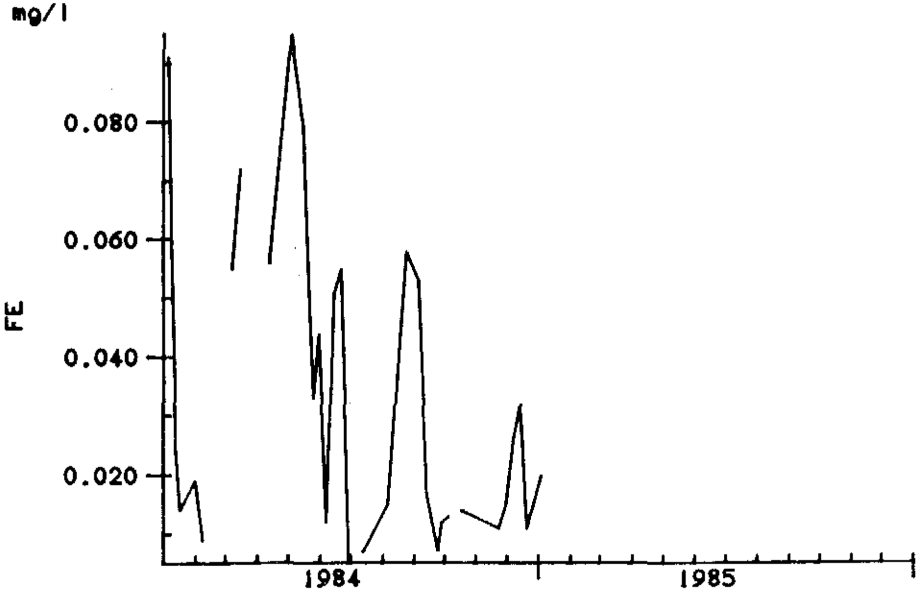

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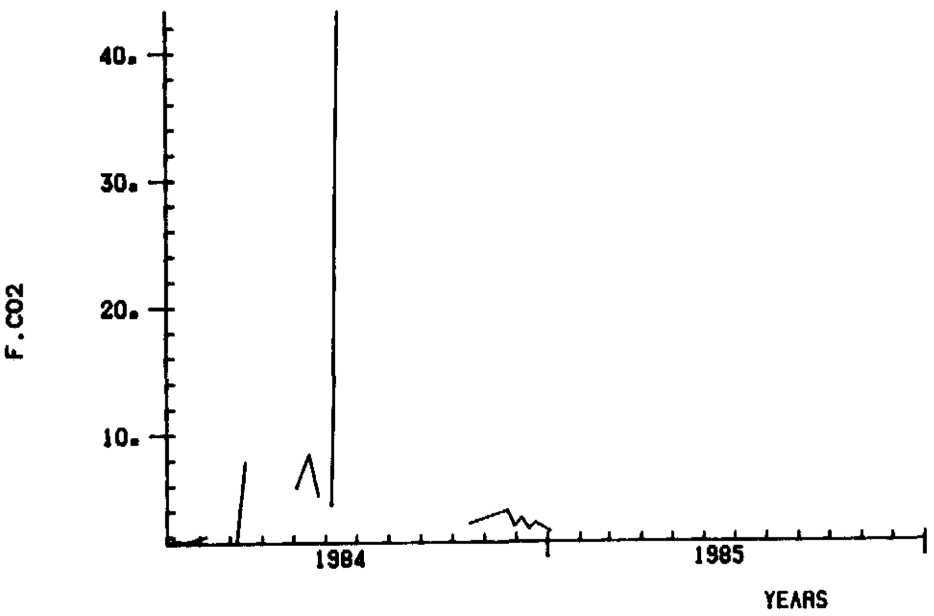
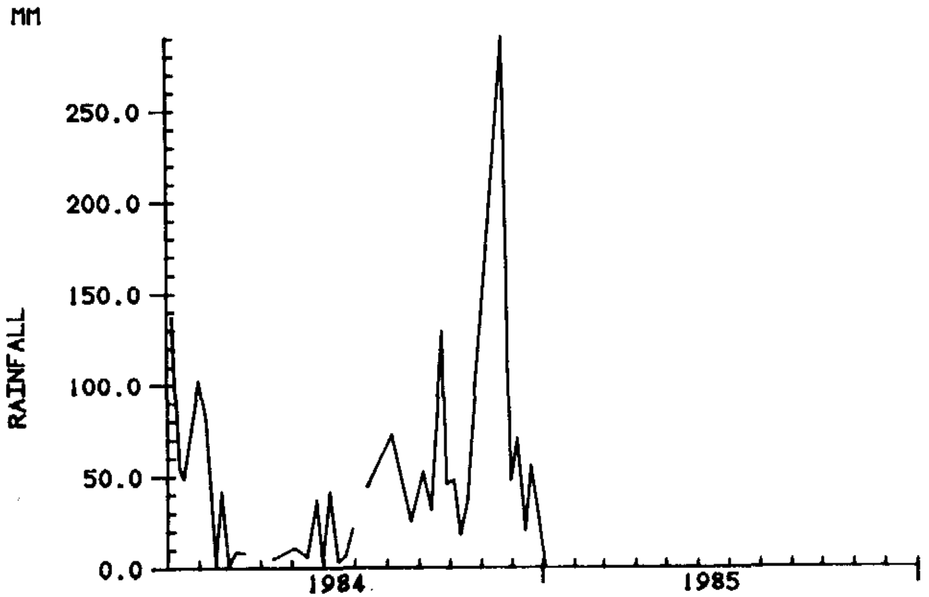




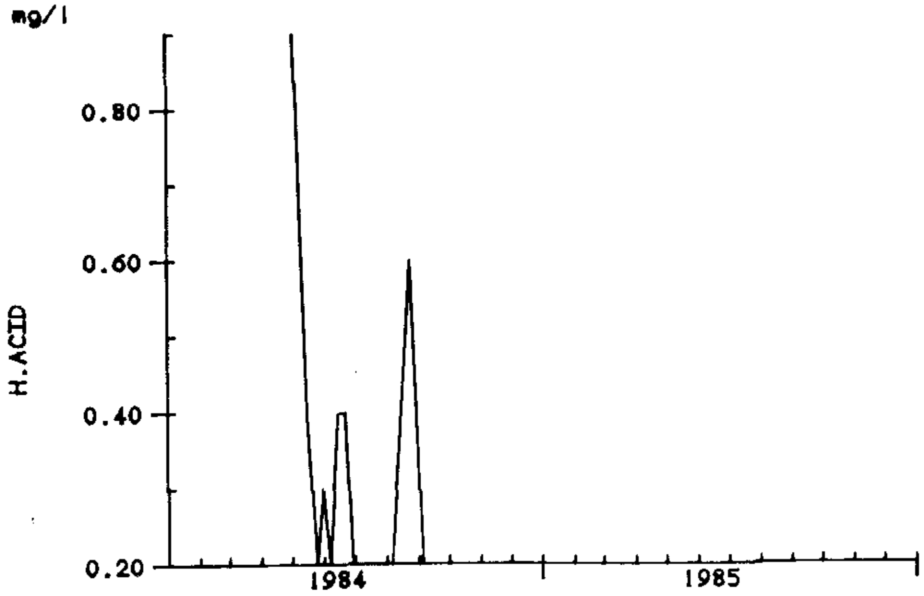
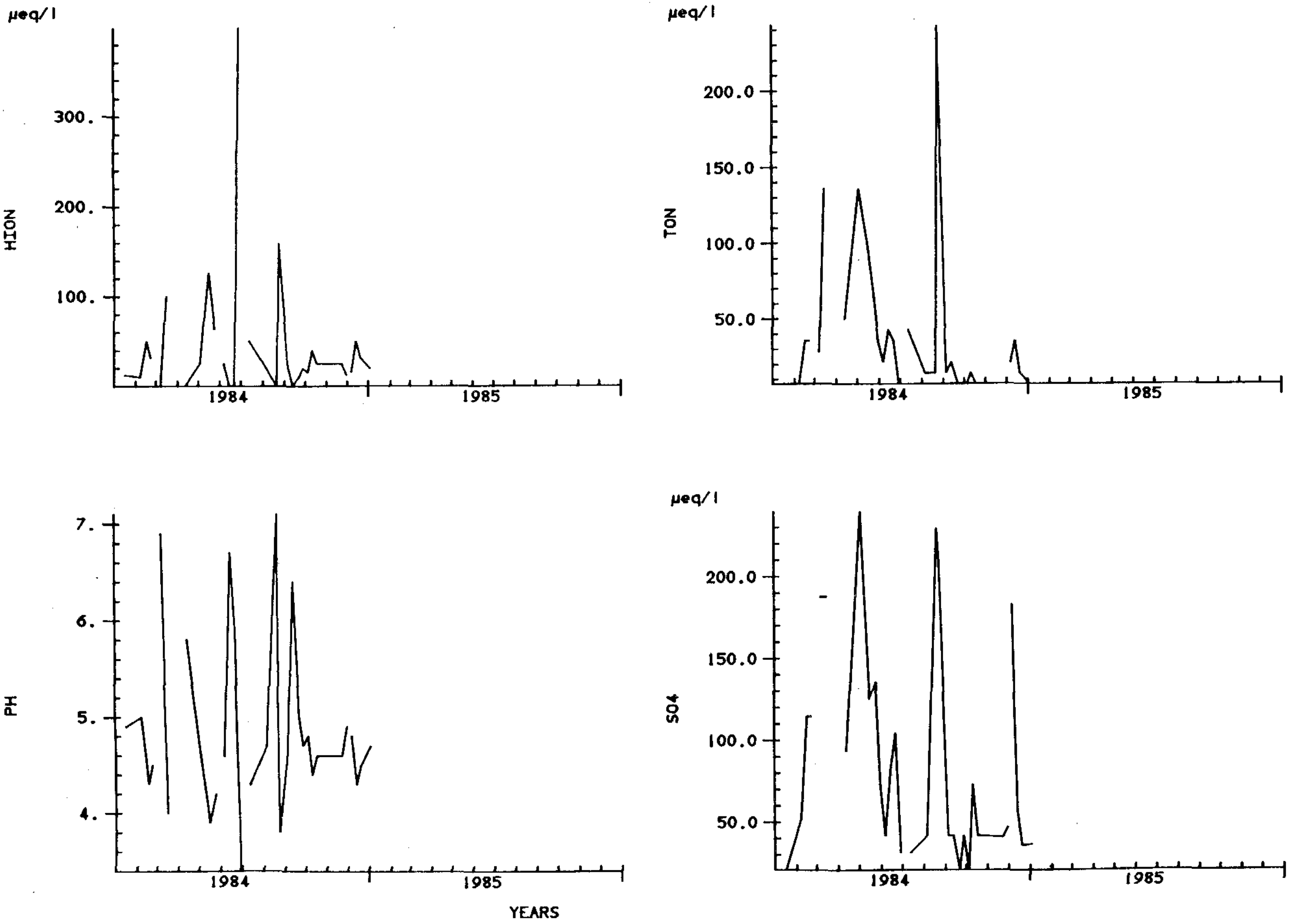


Figure 5

RAINFALL (LI3)



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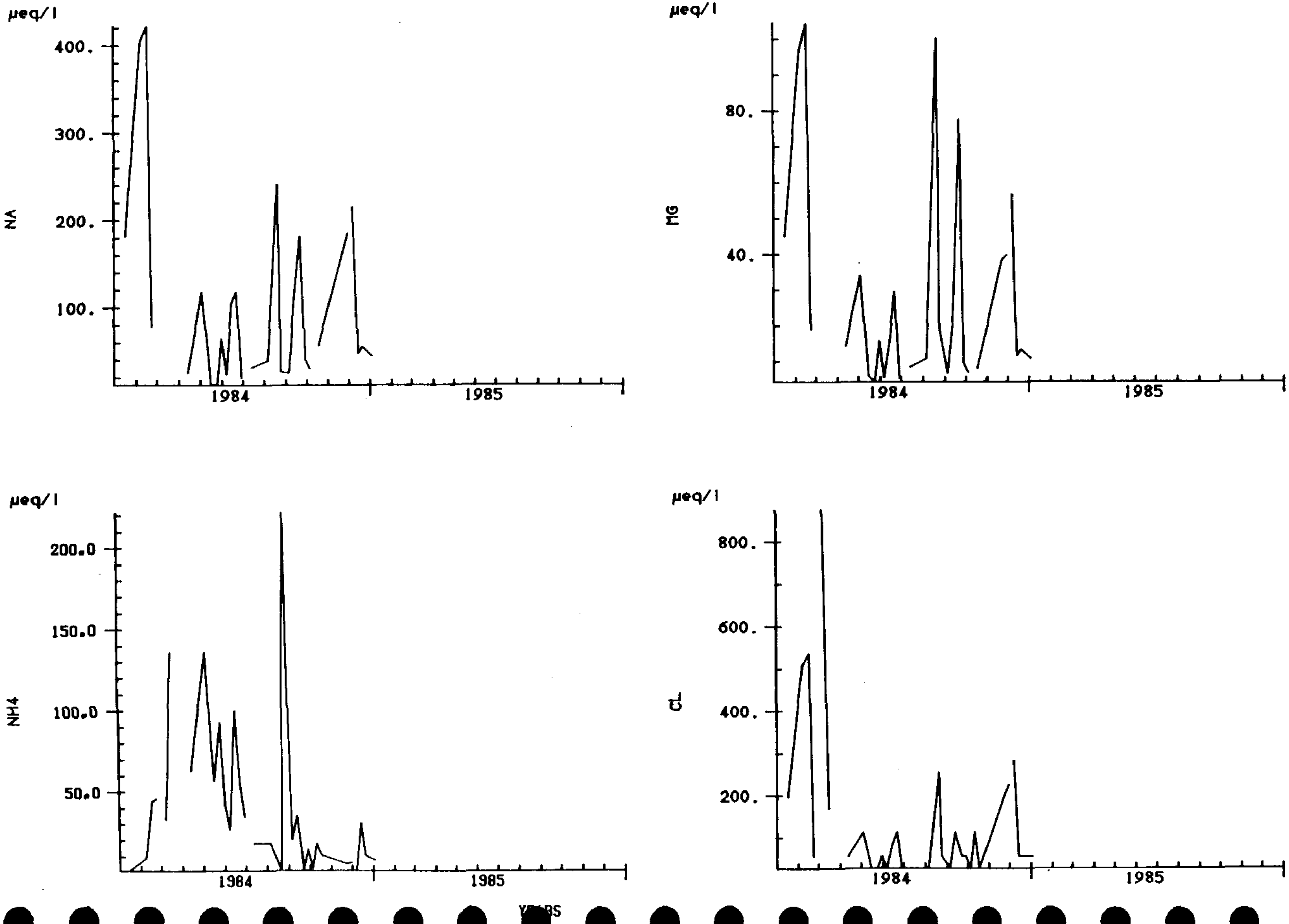

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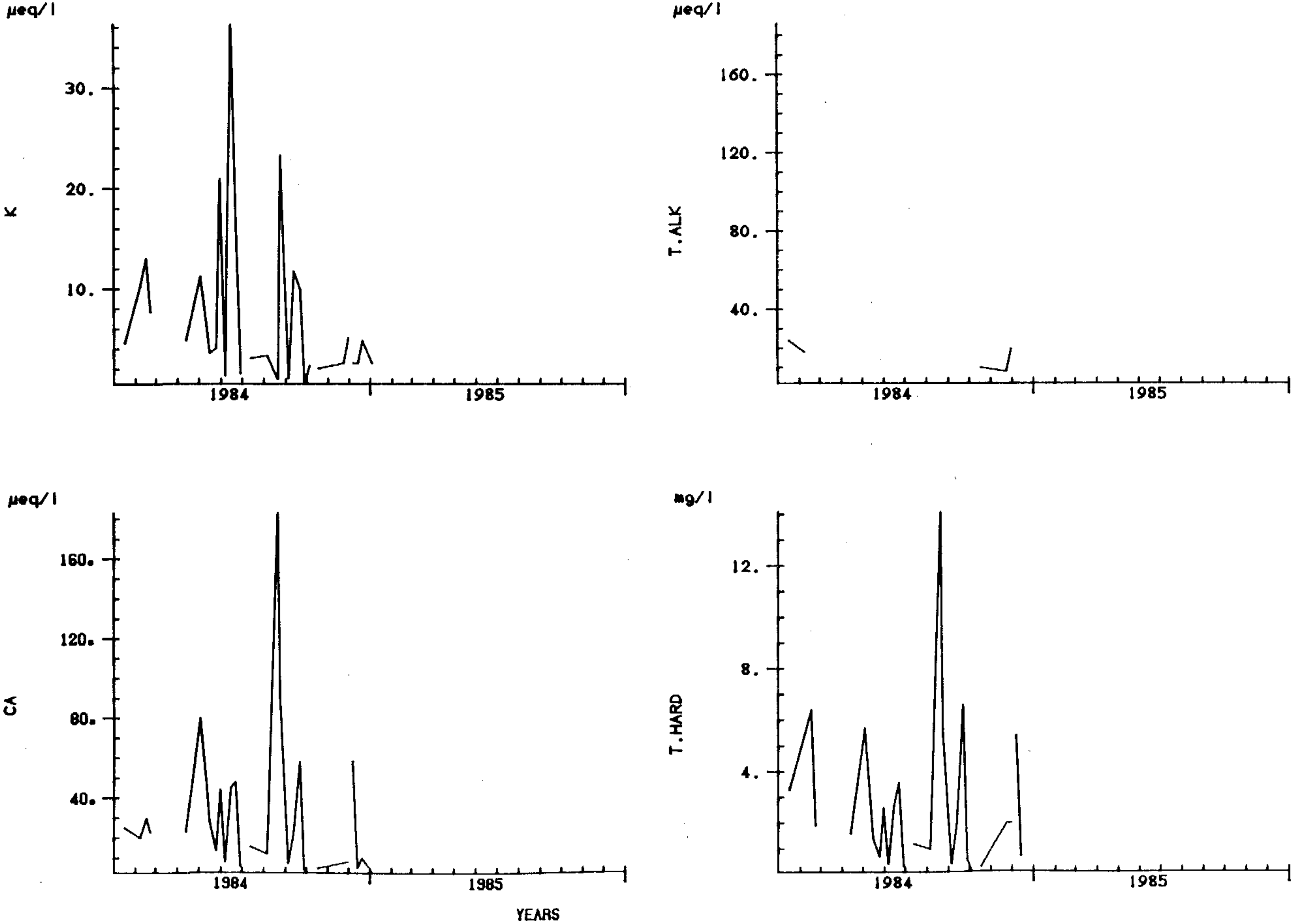

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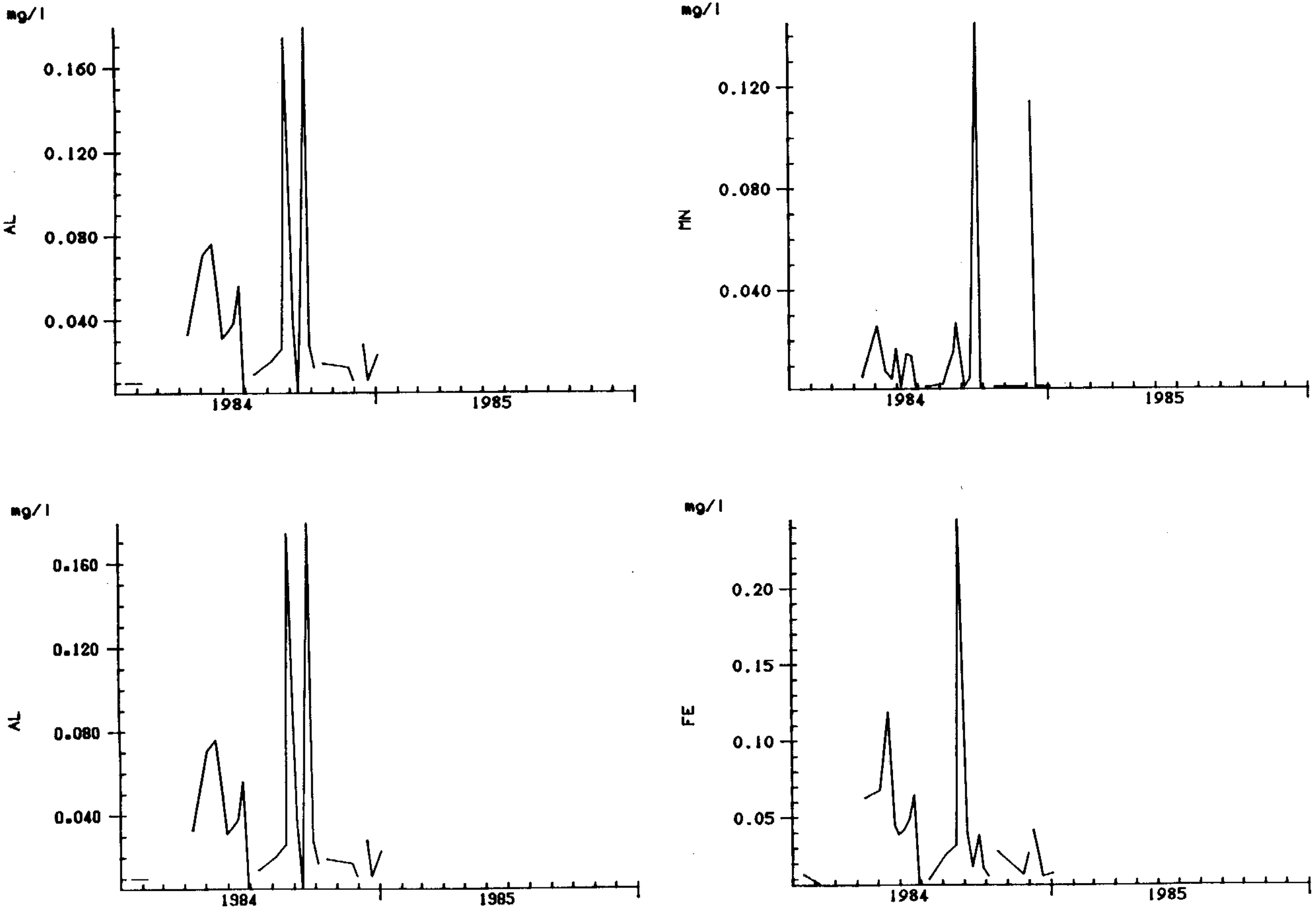

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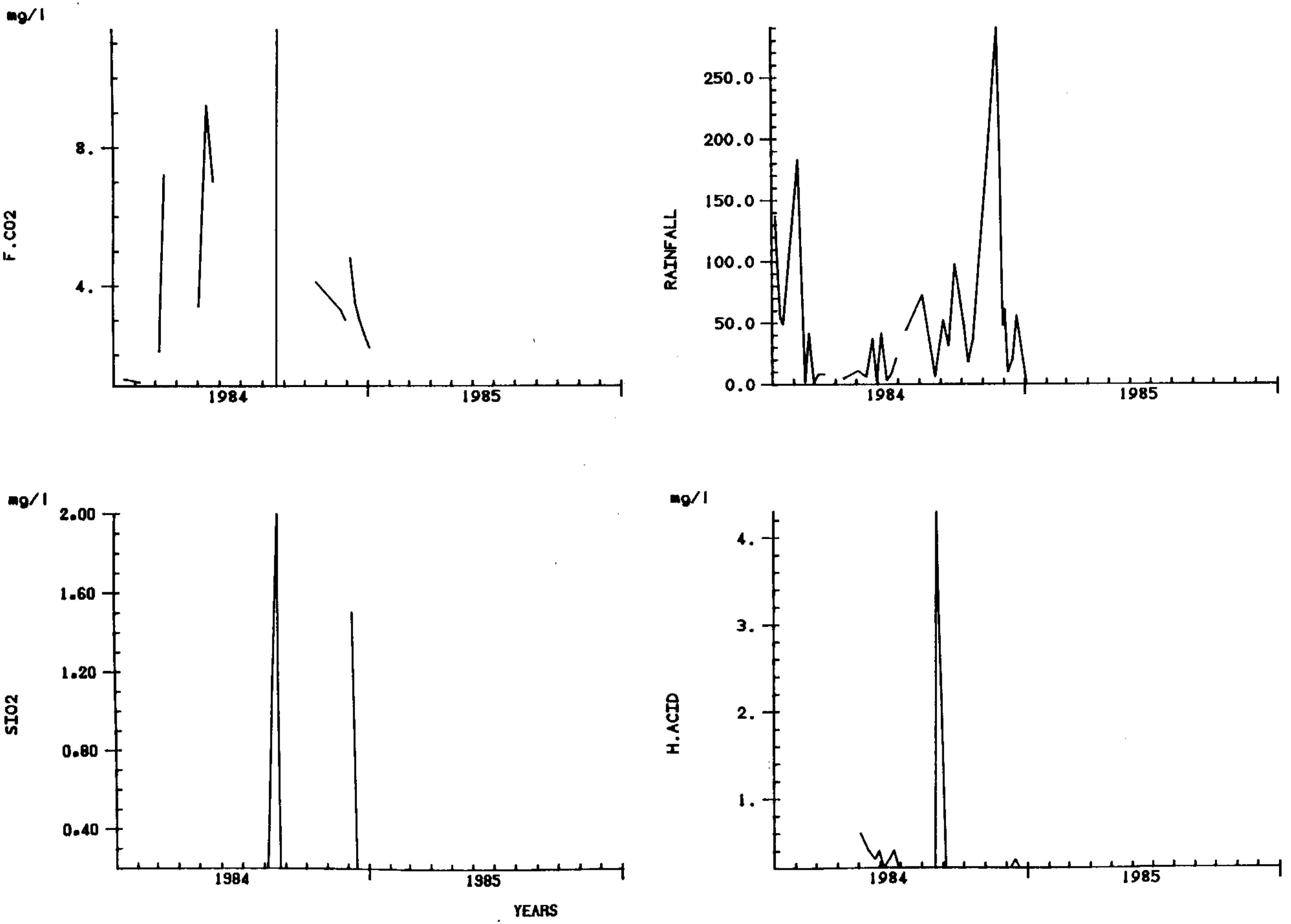


occurrence of easterly airflows, suggesting some industrial emission influence on the rainfall quality at Llyn Brianne.

The strong maritime influence is reflected in the patterns of Na, Mg and Cl concentrations at each site. Levels are highest during the wet month of January in particular. Other isolated peaks correspond to isolated storm events occuring during the year. Overall concentrations were slightly reduced at L3, probably due to its more remote inland location. Not surprisingly, the terrestrially derived Ca concentrations were highest during the low rainfall months, when the fall out contribution was at a maximum.

In conclusion, the rainfall while dominated by marine salts and terrestrially derived anions, is sometimes moderately acidic, especially during or following periods of easterly airflow. In addition the area also receives a large volume of mildy acid rainfall, averaging 1807 mm p.a. at Nant-y-maen, although the amount and seasonality is subject to extensive variability.

Stream chemistry

The major potential sources of acidity in poorly buffered streams such as those found at Llyn Brianne are atmospherically derived anions and terrestially derived inorganic anions and humic acids. As shown in Table 1, the sampled catchments are subject to two major and contrasting land uses, that of conifer afforestation and rough moorland pasture. These generally contribute to a contrasting water quality as will be seen in the remainder of this report. Of the streams being monitored, the conifer-afforested catchments will be considered first.

Conifer afforested catchments (LI1, LI2, LI3, LI4 and LI8)

LI1 is the largest of the catchments monitored (2.53 km^2) and the main stream slope is not surprisingly almost the lowest, hence response times and flow velocities might be expected to be lower than at other sites. Table 5a indicates that pH averaged 4.87 and H^+ 18.2 ueq l^{-1} over the period August 1984 to December 1985. However, levels of 4.3 have been sampled and 25% of all samples indicated a pH of 4.6 or less. Such levels are comparable to the mean pH of bulk precipitation at L3 (without rainfall-weighting) and suggest a very limited buffering capacity in this catchment. Similarly, Table 6a indicates that LI2 (which drains an area less than half that of LI1 and with a steeper mean slope), exhibits a mean pH of 4.62; with 25% of the much reduced sample number yielding levels of pH 4.5 or less. Furthermore, H^+ concentrations average 26 ueq l^{-1} at this site. The latter may be a product of the reduced sample size, or alternatively, they may reflect the reduction in catchment size and hence reduced residence times in LI2. Meanwhile, at LI3 (Table 7a) conditions are less acid with pH averaging 5.2 and H^+ averaging 10 ueq l^{-1}. This catchment is even smaller than LI2 and far steeper than either of the previous streams, hence residence times would presumably be reduced. One reason for the slight improvement might be the bankside clearance of conifers in LI3, a treatment which had not been performed in LI2 during the period being studied. However, conclusive proof of the above awaits a further, more detailed examination of the situation. Too few samples have been taken from LI4, the smallest catchment being monitored, hence little real indication of its chemistry can be gained. Lastly, LI8 (which is of a comparable size to LI3 but much steeper), drains an area dominated by young conifers and pH averaged 5.38 and H^+ averaged 8 ueq l^{-1} (Table 8a). The acidity

Table 5a LI1 streamwater quality (1984-5)

```
                N      N*      MEAN    MEDIAN    TRMEAN     STDEV    SEMEAN                 MIN        MAX         Q1         Q3
T_CU           24      78   0.00346   0.00200   0.00286   0.00366   0.00075    T_CU    0.00100    0.01700    0.00200    0.00375
T_ZN           23      79   0.01439   0.01300   0.01410   0.00512   0.00107    T_ZN    0.00700    0.02300    0.01000    0.01700
T_CD           24      78   0.00105   0.00100   0.00102   0.00015   0.00003    T_CD    0.00100    0.00170    0.00100    0.00100
T_AL           25      77    0.3370    0.3400    0.3383    0.1303    0.0261    T_AL     0.0950     0.5430     0.2335     0.4650
T_PB           23      79   0.00391   0.00200   0.00353   0.00362   0.00075    T_PB    0.00200    0.01300    0.00200    0.00500
T_CR           24      78   0.00300   0.00300   0.00300   0.00000   0.00000    T_CR    0.00300    0.00300    0.00300    0.00300
T_MN           24      78   0.08983   0.08400   0.08841   0.02353   0.00480    T_MN    0.04500    0.16600    0.07725    0.10125
T_FE           23      79    0.1213    0.0950    0.1130    0.1021    0.0213    T_FE     0.0300     0.3330     0.0470     0.1300
T_NI           24      78   0.00321   0.00300   0.00309   0.00072   0.00015    T_NI    0.00300    0.00600    0.00300    0.00300
PH            101       1    4.8740    4.8000    4.8217    0.4430    0.0441    PH      4.3000     7.0000     4.5000     5.0000
COND          101       1    52.592    55.000    52.559     7.328     0.729    COND    39.000     67.667     47.000     58.000
TURB            1     101  0.00E+00  0.00E+00  0.00E+00         *         *    TURB  0.00E+00   0.00E+00          *          *
AMM_N         102       0    1.5117    1.4286    1.4431    0.4021    0.0398    AMM_N   1.4286     5.0000     1.4286     1.4286
TON           102       0    10.457     7.143     9.836     4.991     0.494    TON      7.143     28.571      7.143     14.286
NO2           102       0   0.28710   0.28570   0.28570   0.01415   0.00140    NO2    0.28570    0.42860    0.28570    0.28570
TH             99       3     5.739     5.600     5.644     1.730     0.174    TH       2.000     11.400      4.500      6.500
FCO2           79      23     4.654     4.500     4.557     1.980     0.223    FCO2     1.200     11.457      3.300      5.700
TA             68      34     24.09     23.98     22.46     15.58      1.89    TA        0.00      97.92      16.49      27.98
CL            102       0    246.91    253.88    247.84     60.80      6.02    CL      112.34     366.72     197.45     310.30
OPO4          101       1   0.02040   0.02000   0.02000   0.00242   0.00024    OPO4   0.02000    0.04000    0.02000    0.02000
SIO2          102       0    1.4182    1.5000    1.4289    0.1940    0.0192    SIO2    0.7000     1.8000     1.3250     1.5000
SO4            95       7    154.42    151.02    152.38     30.10      3.09    SO4      97.90     260.37     135.31     169.76
NA             99       3    203.53    200.46    202.43     52.55      5.28    NA        4.35     434.41     169.59     239.16
K              95       7     5.331     4.102     4.902     3.397     0.400    K        0.769     25.640      2.564      6.923
CU            100       2   0.00247   0.00200   0.00219   0.00190   0.00019    CU     0.00100    0.01300    0.00200    0.00200
MG             99       3     59.61     59.05     59.07     15.35      1.54    MG       21.35     102.22      49.10      66.78
CA            100       2     59.27     55.39     58.04     20.32      2.03    CA       13.47     128.74      44.91      71.86
ZN            100       2   0.02074   0.01900   0.02034   0.00820   0.00082    ZN     0.00400    0.05000    0.01600    0.02500
CD            100       2   0.00106   0.00100   0.00098   0.00059   0.00006    CD     0.00030    0.00630    0.00100    0.00100
AL            100       2    0.3848    0.4065    0.3830    0.1947    0.0195    AL      0.0300     0.8510     0.2437     0.5245
PB            100       2   0.00954   0.00650   0.00873   0.00762   0.00076    PB     0.00200    0.04800    0.00500    0.01300
CR            100       2   0.00257   0.00300   0.00258   0.00101   0.00010    CR     0.00100    0.00800    0.00225    0.00300
MN            100       2   0.09946   0.10000   0.10029   0.03013   0.00301    MN     0.00800    0.17300    0.08000    0.12075
FE            100       2   0.06827   0.05600   0.06398   0.04642   0.00464    FE     0.00300    0.24300    0.03700    0.09052
NI            100       2   0.00318   0.00300   0.00292   0.00185   0.00019    NI     0.00100    0.01200    0.00300    0.00300
HUMIC          99       3    0.8846    0.5000    0.7548    0.9439    0.0949    HUMIC   0.2000     5.3000     0.3000     1.1000
IQ              2     100    0.0395    0.0395    0.0395    0.0559    0.0395    IQ      0.0000     0.0790          *          *
TEMP           10      92     10.17     10.75     10.71      4.21      1.33    TEMP      0.00      15.00       9.17      12.12
T_NA            1     101  0.00E+00  0.00E+00  0.00E+00         *         *    T_NA  0.00E+00   0.00E+00          *          *
T_K             1     101  0.00E+00  0.00E+00  0.00E+00         *         *    T_K   0.00E+00   0.00E+00          *          *
T_MG            1     101  0.00E+00  0.00E+00  0.00E+00         *         *    T_MG  0.00E+00   0.00E+00          *          *
T_CA            1     101  0.00E+00  0.00E+00  0.00E+00         *         *    T_CA  0.00E+00   0.00E+00          *          *
ACID            1     101  0.00E+00  0.00E+00  0.00E+00         *         *    ACID  0.00E+00   0.00E+00          *          *
UV              1     101  0.00E+00  0.00E+00  0.00E+00         *         *    UV    0.00E+00   0.00E+00          *          *
F_PH           11      91     4.982     5.500     5.367     1.756     0.529    F_PH     0.000      6.500      4.300      6.000

STAGE           1     101  0.00E+00  0.00E+00  0.00E+00         *         *    STAGE 0.00E+00   0.00E+00          *          *
P_SOLID        12      90     1.667     1.500     1.500     0.388     0.256    P_SOLID  1.000      4.000      1.000      2.000
DOC             1     101  0.00E+00  0.00E+00  0.00E+00         *         *    DOC   0.00E+00   0.00E+00          *          *
HICN          101       1     18.17     15.85     17.73     11.59      1.15    HICN      0.10      50.12      10.00      25.12
```

Table 5b Correlation matrices

(i) normal

			_N	TC		TH	FCC2		CL	OPO4	SIO2	SO4	NA	K	CU	MG
COND	-0.257															
AMM_N	-0.200	0.044														
TON	-0.133	0.017	-0.215													
NO2	-0.385	-0.159	-0.021	-0.066												
TH	0.703	0.134	0.167	0.016	*											
FCC2	-0.742	0.412	-0.006	0.232	*	-0.544										
TA	0.958	0.177	0.076	-0.232	*	0.709	-0.665									
CL	0.067	0.248	0.073	-0.009	-0.174	0.262	0.245	0.180								
OPO4	0.029	-0.143	-0.034	0.135	-0.016	0.133	0.003	-0.071	0.020							
SIO2	0.571	0.065	-0.070	-0.133	-0.216	0.422	-0.505	0.454	0.331	0.157						
SO4	0.172	0.427	-0.355	0.197	*	0.400	0.070	0.348	0.452	0.092	0.027					
NA	0.065	0.464	0.032	-0.063	*	0.301	0.097	0.277	0.402	0.032	-0.002	0.315				
K	0.184	0.301	-0.015	-0.004	*	0.330	-0.114	0.279	0.764	0.061	0.117	0.223	0.144			
CU	-0.134	-0.244	-0.021	-0.027	*	-0.294	-0.018	-0.126	-0.245	-0.055	-0.034	-0.154	-0.233	-0.062		
MG	0.587	0.376	0.174	0.056	*	0.952	-0.377	0.637	0.440	0.109	0.367	0.477	0.461	0.371	-0.313	
CA	0.747	0.049	0.136	0.011	*	0.971	-0.638	0.723	0.174	0.131	0.452	0.317	0.264	0.367	-0.243	0.861
ZN	-0.343	0.709	-0.154	0.041	*	-0.031	0.401	-0.255	0.243	-0.033	-0.155	0.195	0.334	0.340	-0.013	0.029
CD	-0.104	-0.207	0.022	-0.103	*	-0.154	0.196	-0.258	-0.205	-0.033	-0.041	-0.034	-0.090	-0.036	0.189	-0.136
AL	-0.698	0.292	-0.093	0.132	*	-0.416	0.700	-0.586	0.103	-0.014	-0.455	0.040	0.218	-0.187	0.162	-0.249
PB	-0.155	0.434	-0.123	-0.083	*	-0.026	0.330	-0.059	0.454	-0.022	-0.032	0.173	0.422	0.201	-0.014	0.078
CR	-0.247	-0.402	-0.086	-0.076	*	-0.138	-0.039	-0.512	-0.350	-0.014	-0.065	-0.443	-0.270	-0.124	0.327	-0.229
MN	-0.246	0.416	-0.320	0.161	*	0.114	0.220	-0.260	0.293	0.157	0.121	0.135	0.375	0.033	-0.190	0.190
FE	-0.284	-0.001	0.151	-0.191	*	-0.123	0.389	0.030	-0.124	0.063	-0.473	0.053	0.053	0.041	0.047	-0.111
NI	-0.166	-0.052	-0.155	0.040	*	-0.195	0.170	-0.274	-0.044	-0.016	-0.109	-0.019	0.068	0.070	0.354	-0.201
HUMIC	-0.326	-0.078	0.043	-0.127	0.260	-0.244	0.441	0.030	-0.250	-0.015	-0.546	0.029	-0.038	-0.016	0.063	-0.246
IQ	1.000	1.000	*	*	*	1.000	*	*	1.000	*	*	1.000	1.000	1.000	-1.000	1.000
TEMP	0.612	0.336	0.053	0.044	*	0.630	-0.503	0.825	0.523	0.113	0.435	0.483	0.511	0.719	-0.550	0.609
F_PH	0.687	0.346	-0.034	0.104	*	0.659	-0.395	0.735	0.598	0.098	0.567	0.475	0.661	0.705	-0.941	0.663
P_SOLID	-0.411	0.818	*	0.485	*	0.058	0.373	-0.265	0.577	*	-0.331	0.351	-0.598	-0.316	-0.192	0.212
HICN	-0.800	0.174	-0.039	0.063	0.116	-0.596	0.815	-0.982	-0.090	-0.065	-0.724	-0.067	0.004	-0.101	0.029	-0.470

	CA	ZN	CD	AL	PB	CR	MN	FE	NI	HUMIC	IQ	TEMP	F_PH	P_SOLID
ZN	-0.149													
CD	-0.120	0.034												
AL	-0.512	0.395	0.079											
PB	-0.076	0.362	0.121	0.386										
CR	-0.151	-0.144	0.168	0.144	-0.059									
MN	0.061	0.572	-0.067	0.207	0.181	-0.235								
FE	-0.127	0.208	0.037	0.275	0.020	-0.076	0.034							
NI	-0.169	0.228	0.209	0.253	0.543	0.237	-0.044	-0.071						
HUMIC	-0.237	0.116	-0.018	0.252	-0.058	-0.138	-0.034	0.880	-0.129					
IQ	1.000	1.000	*	-1.000	1.000	1.000	-1.000	-1.000	*	-1.000				
TEMP	0.618	-0.185	-0.135	-0.323	0.451	-0.570	-0.228	-0.006	-0.111	-0.219	*			
F_PH	0.610	0.192	-0.755	-0.673	0.535	-0.941	0.304	-0.262	-0.335	-0.678	*	0.912		
P_SOLID	-0.003	0.613	*	0.450	0.000	*	0.596	0.788	*	0.658	*	*	*	
HICN	-0.647	0.273	0.046	0.711	0.201	0.048	0.036	0.514	0.067	0.539	-1.000	-0.654	-0.841	0.335

(ii) logarithmic

	Al c1	Mn c2	Fe c3	Na c4	K c5	Mg c6	Ca c7	Cl c8	CO c9	SiO2 c10	SO4 c11	NH4 c12	TON c13	TA c14	TH c15	Con c16	Hum c17
C2	0.281																
C3	0.149	-0.015															
C4	0.015	0.129	0.125														
C5	-0.213	-0.022	0.124	0.258													
C6	-0.244	0.014	-0.013	0.280	0.407												
C7	-0.471	-0.062	-0.053	0.171	0.341	0.793											
C8	0.044	0.135	0.023	0.257	0.512	0.429	0.149										
C9	0.733	0.314	0.295	0.012	-0.127	-0.425	-0.654	0.174									
C10	-0.395	0.012	-0.110	0.021	0.231	0.334	0.430	0.332	-0.504								
C11	-0.075	-0.030	0.067	0.210	0.331	0.433	0.317	0.439	-0.014	0.274							
C12	-0.033	-0.422	0.114	0.037	0.002	0.128	0.108	-0.011	0.017	-0.035	0.237						
C13	0.126	0.151	-0.050	-0.033	-0.019	0.073	0.012	0.003	0.270	-0.114	0.171	0.033					
C14	-0.555	-0.222	-0.142	0.107	0.232	0.445	0.514	0.143	-0.233	0.455	0.252	0.257	-0.257				
C15	-0.395	-0.031	-0.050	0.240	0.330	0.943	0.944	0.272	-0.535	0.403	0.122	0.141	0.023	0.511			
C16	0.190	0.111	0.016	0.262	0.432	0.380	0.031	0.848	0.231	0.270	0.510	-0.303	0.052	0.012	0.137		
C17	0.164	-0.354	0.700	0.061	0.040	-0.160	-0.137	-0.176	0.751	-0.477	0.371	0.255	-0.147	-0.157	-0.135	0.017	
H C18	0.768	[illegible]	0.227	-0.153	-0.225	-0.507	-0.556	-0.084	0.377	-0.532	-0.177	0.015	0.156	-0.755	-0.617	0.043	[illegible]

Table 6a LI2 streamwater quality (1984-5)

```
              N     N*     MEAN    MEDIAN    TRMEAN     STDEV    SEMEAN
T_CU         22      7  0.00364   0.00200   0.00345   0.00252   0.00054
T_ZN         22      7  0.01373   0.01650   0.01790   0.00707   0.00151
T_CD         22      7  0.00159   0.00100   0.00109   0.00234   0.00050
T_AL         22      7   0.5194    0.5150    0.5203    0.1131    0.0241
T_PB         21      3  0.01629   0.01500   0.01567   0.00924   0.00202
T_CR         22      7  0.00509   0.00300   0.00300   0.00043   0.00009
T_MN         22      7  0.08841   0.08600   0.03755   0.01245   0.00266
T_FE         22      7   0.1597    0.0700    0.0934    0.3293    0.0703
T_NI         22      7  0.00364   0.00300   0.00345   0.00155   0.00033
PH           28      1   4.6248    4.6100    4.6242    0.1819    0.0344
COND         28      1   48.114    48.000    48.013     2.862     0.541
TURB          5     24    0.548     0.610     0.543     0.358     0.160
AMM_N        29      0   1.4348    1.4286    1.4330    0.0184    0.0034
TON          29      0    12.93     14.29     12.56      6.06      1.13
NO2          29      0  0.28570   0.28570   0.28570   0.00000   0.00000
TH           25      3    4.790     4.800     4.773     0.874     0.171
FCO2         19     10    5.539     5.300     5.553     1.018     0.233
TA           14     15     78.2      16.0      14.7     242.1      64.7
CL           29      0    213.2     197.5     201.8      84.4      15.7
OPO4         29      0  0.02034   0.02000   0.02000   0.00186   0.00034
SIO2         29      0   1.5624    1.5750    1.5670    0.1769    0.0328
SO4          26      3   131.21    131.23    135.15     31.88      6.25
NA           25      4   174.04    165.24    173.76     23.59      4.72
K            23      6    3.163     2.564     3.049     1.597     0.333
CU           26      3  0.00320   0.00200   0.00301   0.00182   0.00036
MG           26      3    46.54     46.79     46.41      6.85      1.34
CA           26      3    52.81     54.39     52.61     11.03      2.16
ZN           26      3  0.01997   0.01750   0.01968   0.00682   0.00134
CD           26      3  0.00107   0.00100   0.00104   0.00018   0.00003
AL           26      3   0.4332    0.5104    0.4838    0.1026    0.0201
PB           26      3  0.01309   0.01200   0.01272   0.00932   0.00183
CR           26      3  0.00300   0.00300   0.00300   0.00000   0.00000
MN           26      3  0.07991   0.08260   0.08103   0.01849   0.00363
FE           26      3  0.06222   0.04800   0.05907   0.04110   0.00806
NI           26      3  0.00327   0.00300   0.00312   0.00093   0.00018
HUMIC        27      2    0.899     0.600     0.799     0.935     0.180
IQ            1     28 0.00E+00  0.00E+00  0.00E+00         *         *
TEMP          1     28 0.00E+00  0.00E+00  0.00E+00         *         *
T_NA          1     28 0.00E+00  0.00E+00  0.00E+00         *         *
T_K           1     28 0.00E+00  0.00E+00  0.00E+00         *         *
T_MG          1     28 0.00E+00  0.00E+00  0.00E+00         *         *
T_CA          1     23 0.00E+00  0.00E+00  0.00E+00         *         *
ACID          1     28 0.00E+00  0.00E+00  0.00E+00         *         *
UV            1     28 0.00E+00  0.00E+00  0.00E+00         *         *
F_PH          1     23 0.00E+00  0.00E+00  0.00E+00         *         *

STAGE         1     28 0.00E+00  0.00E+00  0.00E+00         *         *
P_SOLID      12     17    1.750     1.000     1.600     1.055     0.305
DOC           1     23 0.00E+00  0.00E+00  0.00E+00         *         *
HICN         28      1    25.34     24.55     25.43     11.11      2.10

                MIN       MAX        Q1        Q3
T_CU        0.00200   0.00900   0.00200   0.00525
T_ZN        0.01000   0.04400   0.01400   0.02200
T_CD        0.00100   0.01200   0.00100   0.00100
T_AL         0.2900    0.7200    0.4475    0.6070
T_PB        0.00300   0.03300   0.01050   0.02050
T_CR        0.00300   0.00500   0.00300   0.00300
T_MN        0.02300   0.12500   0.07300   0.09475
T_FE         0.0390    1.6150    0.0495    0.1225
T_NI        0.00300   0.01300   0.00300   0.00300
PH           4.3000    4.7667    4.5000    4.8000
COND         42.943    56.000    46.000    50.000
TURB          0.000     0.990     0.240     0.810
AMM_N        1.4286    1.4331    1.4286    1.4286
TON            7.14     28.57      7.14     14.29
NO2         0.28570   0.28570   0.28570   0.28570
TH            3.400     6.600     4.100     5.321
FCO2          4.000     7.800     4.700     6.100
TA              0.0     919.2      10.0      13.0
CL            141.0     592.4     169.3     216.0
OPO4        0.02000   0.03000   0.02000   0.02000
SIO2         1.2000    1.9000    1.4314    1.7000
SO4            0.04    167.31    120.31    152.36
NA           134.30    217.59    155.46    194.90
K             0.513     8.205     2.564     2.820
CU          0.00200   0.00900   0.00200   0.00492
MG            35.36     60.36     40.13     51.73
CA            35.43     74.85     42.74     62.75
ZN          0.01000   0.03700   0.01475   0.02305
CD          0.00100   0.00130   0.00100   0.00102
AL           0.2700    0.6300    0.4035    0.5600
PB          0.00200   0.03300   0.00475   0.01965
CR          0.00300  -0.00300   0.00300   0.00300
MN          0.00900   0.12500   0.07375   0.08600
FE          0.02600   0.17400   0.03750   0.06400
NI          0.00300   0.00700   0.00300   0.00300
HUMIC         0.200     4.100     0.300     1.000
IQ         0.00E+00  0.00E+00         *         *
TEMP       0.00E+00  0.00E+00         *         *
T_NA       0.00E+00  0.00E+00         *         *
T_K        0.00E+00  0.00E+00         *         *
T_MG       0.00E+00  0.00E+00         *         *
T_CA       0.00E+00  0.00E+00         *         *
ACID       0.00E+00  0.00E+00         *         *
UV         0.00E+00  0.00E+00         *         *
F_PH       0.00E+00  0.00E+00         *         *

STAGE      0.00E+00  0.00E+00         *         *
P_SOLID       1.000     4.000     1.000     2.750
DOC        0.00E+00  0.00E+00         *         *
HICN          10.80     52.12     15.45     31.62
```

Table 6b Correlation matrices

(i) normal

	T_NI	PH	COND	TURB	AMM_N	TON	TH	FCO2
PH	-0.035							
COND	-0.200	-0.133						
TURB	*	0.939	-0.302					
AMM_N	*	0.333	0.107	0.771				
TON	-0.160	-0.443	0.774	-0.570	-0.129			
TH	-0.205	0.748	0.015	0.934	0.193	-0.424		
FCO2	-0.301	-0.535	0.292	*	*	0.634	-0.656	
TA	-0.359	0.538	-0.136	1.000	1.000	-0.196	0.595	-0.344
CL	-0.100	0.093	0.077	0.140	0.200	-0.179	-0.154	0.235
OPO4	-0.093	-0.350	-0.008	*	-0.064	0.496	-0.325	0.121
SIO2	-0.329	0.511	0.074	-0.167	-0.092	-0.117	0.613	-0.710
SO4	0.007	0.062	0.221	0.977	0.269	0.113	0.309	0.055
NA	-0.234	0.534	0.140	0.938	0.344	-0.267	0.799	-0.405
K	0.347	0.201	0.217	0.668	0.469	-0.078	0.131	-0.343
CU	0.325	-0.060	0.092	0.322	0.154	0.033	-0.112	-0.040
MG	-0.230	0.692	0.261	0.754	0.188	-0.294	0.912	-0.595
CA	-0.136	0.693	-0.139	0.927	0.164	-0.477	0.949	-0.710
ZN	0.450	0.061	0.110	0.362	0.301	-0.098	0.095	-0.194
CD	0.538	0.105	-0.298	0.508	0.135	-0.352	-0.054	-0.188
AL	-0.110	-0.561	0.410	-0.655	0.132	0.261	-0.421	0.587
PB	0.555	-0.052	-0.330	0.459	0.187	-0.375	-0.196	0.042
FE	0.249	-0.653	-0.364	-0.984	-0.204	0.109	-0.460	0.430
NI	0.637	-0.044	-0.095	0.498	0.376	-0.157	-0.141	0.000
HUMIC	0.504	-0.572	-0.343	-0.933	-0.154	0.022	-0.578	0.569
P_SOLID	-0.000	-0.025	-0.170	*	*	-0.243	0.332	-0.434
HION	-0.021	-0.982	0.157	-0.921	-0.329	0.518	-0.757	0.611

	TA	CL	OPO4	SIO2	SO4	NA	K	CU
CL	-0.077							
OPO4	*	-0.100						
SIO2	-0.601	0.121	-0.177					
SO4	0.002	0.093	0.000	-0.070				
NA	0.411	-0.015	-0.270	0.300	0.433			
K	0.118	-0.135	-0.032	-0.205	0.254	0.293		
CU	-0.299	-0.054	-0.155	-0.163	0.216	0.217	0.629	
MG	0.573	-0.083	-0.244	0.600	0.362	0.396	0.220	0.010
CA	0.530	-0.151	-0.321	0.543	0.224	0.651	0.065	-0.139
ZN	-0.379	0.027	-0.179	-0.133	0.532	0.471	0.443	0.561
CD	0.412	-0.252	-0.080	-0.498	0.097	0.031	0.326	0.267
AL	-0.578	-0.043	0.153	-0.629	0.302	-0.070	0.243	0.245
PB	-0.529	0.130	-0.243	-0.535	0.064	-0.064	0.238	0.393
FE	-0.748	-0.239	0.237	-0.653	-0.073	-0.554	-0.064	0.082
NI	*	0.134	-0.038	-0.420	0.001	-0.127	0.293	0.192
HUMIC	-0.096	-0.177	0.171	-0.779	-0.074	-0.577	0.116	0.208
P_SOLID	0.192	-0.215	*	0.251	0.364	-0.156	-0.239	-0.224
HION	-0.403	-0.151	0.428	-0.543	-0.081	-0.592	-0.219	0.014

	MG	CA	ZN	CD	AL	PB	FE	NI
CA	0.759							
ZN	0.162	0.033						
CD	-0.066	-0.053	0.149					
AL	-0.293	-0.479	0.174	0.180				
PB	-0.330	-0.061	0.433	0.533	0.272			
FE	-0.658	-0.275	-0.133	0.291	0.378	0.453		
NI	-0.172	-0.118	0.112	0.743	0.189	0.452	0.325	
HUMIC	-0.654	-0.433	-0.052	0.633	0.363	0.516	0.828	0.574
P_SOLID	0.316	0.333	-0.132	*	-0.002	-0.109	0.269	*
HION	-0.699	-0.716	-0.115	-0.117	0.641	0.004	0.653	0.003

	HUMIC	P_SOLID
P_SOLID	0.126	
HION	0.578	0.012

(ii) logarithmic

	C1	C2	C3	C4	C5	C6	C7	C8
C2	-0.080							
C3	0.437	-0.036						
C4	-0.071	0.000	-0.599					
C5	0.192	0.226	0.093	0.293				
C6	-0.278	0.070	-0.671	0.391	0.278			
C7	-0.470	0.107	-0.405	0.675	0.166	0.763		
C8	-0.021	-0.131	-0.352	0.063	-0.419	0.022	-0.084	
C9	0.535	-0.031	0.373	-0.407	-0.336	-0.602	-0.725	0.174
C10	-0.604	-0.139	-0.639	0.340	-0.190	0.623	0.571	0.201
C11	0.492	0.024	0.244	0.049	0.061	0.050	-0.019	0.039
C12	0.189	0.064	-0.357	0.337	0.407	0.199	0.181	0.254
C13	0.293	-0.080	0.119	-0.224	0.081	-0.247	-0.475	-0.163
C14	-0.242	0.239	-0.433	0.302	0.111	0.499	0.430	-0.120
C15	-0.196	0.145	-0.537	0.305	0.242	0.903	0.955	-0.074
C16	0.371	0.013	-0.274	0.143	0.172	0.274	-0.137	0.149
C17	0.514	0.106	0.537	-0.533	0.007	-0.798	-0.629	-0.163
C18	0.633	-0.093	0.750	-0.535	-0.151	-0.707	-0.737	-0.159

	C9	C10	C11	C12	C13	C14	C15	C16	C17
C10	-0.705								
C11	0.177	-0.141							
C12	-0.000	-0.073	0.039						
C13	0.671	-0.047	0.217	-0.093					
C14	0.142	-0.731	-0.173	0.357	-0.034				
C15	-0.565	0.621	0.025	0.203	-0.405	0.423			
C16	0.290	0.111	0.232	0.114	0.424	-0.090	0.020		
C17	0.567	-0.301	0.273	-0.151	0.029	-0.173	-0.719	-0.214	
C18	0.575	-0.511	0.172	-0.358	0.390	-0.744	-0.765	0.176	0.784

Table 7a LI3 streamwater quality (1984-5)

	N	N*	MEAN	MEDIAN	TRMEAN	STDEV	SEMEAN	MIN	MAX	Q1	Q3
T_CU	25	30	0.00320	0.00200	0.00243	0.00334	0.00077	0.00200	0.02100	0.00200	0.00500
T_ZN	25	30	0.01512	0.01400	0.01461	0.00530	0.00116	0.00700	0.01500	0.01150	0.01750
T_CD	25	30	0.00103	0.00100	0.00104	0.00027	0.00005	0.00100	0.00210	0.00100	0.00100
T_AL	25	30	0.3119	0.3000	0.3112	0.1330	0.0266	0.0400	0.5500	0.1500	0.4500
T_PB	24	31	0.00404	0.00200	0.00318	0.00525	0.00107	0.00200	0.02500	0.00200	0.00450
T_CR	25	30	0.00300	0.00300	0.00300	0.00000	0.00000	0.00300	0.00300	0.00300	0.00300
T_MN	25	30	0.11420	0.11500	0.11453	0.02928	0.00586	0.02500	0.14200	0.10150	0.12750
T_FE	25	30	0.0956	0.0540	0.0833	0.0658	0.0133	0.0010	0.1700	0.0540	0.1150
T_NI	25	30	0.00340	0.00300	0.00317	0.00141	0.00023	0.00100	0.00700	0.00300	0.00300
PH	54	1	5.1722	5.0000	5.1437	0.4881	0.0664	4.5000	6.3000	4.8000	5.4000
COND	54	1	47.574	50.500	50.033	6.532	0.889	16.000	60.000	46.000	54.000
TURB	1	54	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
AMM_N	55	0	1.701	1.429	1.501	0.727	0.125	1.429	6.429	1.429	1.429
TON	55	0	20.73	21.43	20.26	9.94	1.34	7.14	50.00	14.29	23.57
NO2	55	0	0.28570	0.28570	0.28570	0.00000	0.00000	0.28570	0.28570	0.28570	0.28570
TH	53	2	7.339	7.100	7.074	7.242	0.995	0.600	57.900	5.650	8.350
FCO2	49	6	3.303	3.700	3.757	1.517	0.217	1.700	7.100	2.350	5.000
TA	48	7	27.49	25.78	27.06	14.12	2.05	4.00	67.74	18.48	35.17
CL	55	0	202.59	197.46	204.37	37.65	5.08	56.42	232.09	169.25	225.67
OPO4	55	0	0.02291	0.02000	0.02000	0.02025	0.00273	0.02000	0.17000	0.02000	0.02000
SIO2	55	0	1.4413	1.5000	1.4633	0.2529	0.0341	0.2000	1.3000	1.3000	1.6000
SO4	53	2	152.97	160.39	156.79	37.49	5.15	0.04	221.21	136.79	174.36
NA	52	3	184.88	182.63	185.52	35.95	4.98	45.22	276.56	166.76	207.64
K	50	5	3.692	3.077	3.595	1.582	0.224	0.513	7.692	2.564	4.745
CU	53	2	0.00257	0.00200	0.00232	0.00138	0.00019	0.00100	0.00900	0.00200	0.00300
MG	53	2	56.59	57.48	56.39	13.71	1.88	10.69	106.91	48.93	64.06
CA	53	2	105.1	87.3	88.3	141.3	19.4	3.5	1097.8	66.4	109.8
ZN	53	2	0.01900	0.01700	0.01726	0.01173	0.00161	0.00500	0.05200	0.01300	0.02050
CD	53	2	0.00110	0.00100	0.00103	0.00033	0.00004	0.00100	0.00240	0.00100	0.00100
AL	53	2	0.3513	0.3400	0.3418	0.2199	0.0302	0.0130	0.3790	0.1450	0.5100
PB	53	2	0.00870	0.00500	0.00685	0.01119	0.00154	0.00200	0.05500	0.00200	0.01150
CR	53	2	0.00296	0.00300	0.00300	0.00027	0.00004	0.00100	0.00300	0.00300	0.00300
MN	53	2	0.11319	0.11300	0.11396	0.03221	0.00442	0.00200	0.13600	0.09700	0.12650
FE	53	2	0.05555	0.05100	0.05351	0.02542	0.00349	0.00800	0.15500	0.03800	0.06750
NI	53	2	0.00374	0.00300	0.00343	0.00173	0.00024	0.00300	0.01000	0.00300	0.00300
HUMIC	55	0	0.4236	0.2000	0.3816	0.3260	0.0440	0.2000	1.7000	0.2000	0.5000
IG	1	54	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
TEMP	1	54	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
T_NA	1	54	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
T_K	1	54	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
T_MG	1	54	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
T_CA	1	54	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
ACID	1	54	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
UV	1	54	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
F_PH	1	54	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
STAGE	1	54	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
P_SOLID	12	43	3.250	3.000	3.100	1.765	0.509	1.000	7.000	2.000	4.750
DOC	1	54	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
HICN	54	1	10.47	10.00	10.03	7.94	1.08	3.50	31.52	5.44	15.25

Table 7b Correlation matrices

(i) normal

	PH	COND	AMM_N	TCN	TH	FCO2	TA	CL
COND	0.079							
AMM_N	0.003	-0.351						
TCN	-0.169	0.517	-0.052					
TH	0.372	0.025	0.036	0.253				
FCO2	-0.921	0.207	-0.122	0.265	-0.154			
TA	0.960	0.045	-0.067	-0.213	0.375	-0.780		
CL	0.093	0.276	-0.190	0.398	-0.055	0.122	0.098	
OPO4	0.053	0.121	0.274	0.123	0.020	-0.070	0.021	0.193
SIO2	0.591	0.532	-0.326	0.127	0.242	-0.343	0.593	0.487
SO4	-0.107	0.570	-0.256	0.263	0.073	0.199	-0.128	0.555
NA	0.310	0.609	-0.245	0.291	0.150	-0.289	0.360	0.621
K	-0.093	0.229	0.075	0.136	-0.039	0.082	-0.069	0.282
CU	-0.153	0.130	-0.041	-0.309	0.010	0.139	-0.072	0.287
MG	0.372	0.478	-0.142	0.386	0.235	-0.312	0.354	0.315
CA	0.344	-0.016	0.046	0.223	0.996	-0.123	0.350	-0.079
ZN	-0.353	0.335	-0.129	0.045	-0.087	0.406	-0.317	0.117
CD	-0.164	0.185	-0.096	-0.098	-0.084	0.230	-0.141	0.078
AL	-0.746	0.432	-0.315	0.275	-0.295	0.306	-0.705	0.421
PB	-0.294	0.294	-0.050	0.188	-0.165	0.372	-0.313	0.326
CR	0.107	-0.092	0.042	-0.307	0.025	-0.115	0.078	-0.082
MN	0.153	0.390	-0.451	0.038	0.165	-0.044	0.180	0.344
FE	-0.198	-0.105	-0.241	-0.175	0.009	0.178	-0.210	-0.212
NI	-0.245	0.216	-0.130	0.052	-0.113	0.305	-0.224	0.221
HUMIC	-0.359	-0.264	-0.070	-0.235	-0.112	0.463	-0.326	-0.355
P_SOLID	0.187	-0.039	-0.045	0.403	0.233	-0.282	0.068	-0.359
HION	-0.987	-0.149	0.043	0.095	-0.334	0.813	-0.886	-0.200

	OPO4	SIO2	SO4	NA	K	CU	MG	CA
SIO2	0.135							
SO4	0.049	0.176						
NA	0.134	0.566	0.557					
K	0.147	0.030	0.032	0.242				
CU	-0.061	0.213	0.175	0.102	0.437			
MG	0.146	0.439	0.213	0.377	0.307	-0.155		
CA	0.006	0.202	0.059	0.104	-0.067	0.026	0.146	
ZN	-0.045	-0.110	0.311	0.141	0.134	0.155	0.021	-0.091
CD	-0.047	-0.035	0.175	-0.166	0.142	0.302	-0.200	-0.066
AL	-0.060	-0.249	0.479	0.073	0.133	0.220	-0.270	-0.272
PB	-0.049	-0.159	0.259	-0.165	0.087	0.203	-0.254	-0.141
CR	-0.047	0.081	-0.034	0.069	0.103	0.057	-0.013	0.031
MN	-0.079	0.303	0.435	0.500	-0.025	-0.030	0.125	0.157
FE	-0.094	-0.066	-0.012	-0.134	0.032	0.223	-0.155	0.016
NI	-0.047	-0.122	0.262	-0.118	0.287	0.550	-0.236	-0.091
HUMIC	-0.100	-0.340	-0.117	-0.312	0.054	0.005	-0.264	-0.095
P_SOLID	*	0.071	0.293	0.316	-0.130	-0.357	0.082	0.262
HION	-0.107	-0.697	-0.051	-0.473	0.072	0.028	-0.447	-0.299

	ZN	CD	AL	PB	CR	MN	FE	NI	HUMIC	P_SOLID
CD	0.608									
AL	0.377	0.253								
PB	0.157	0.608	0.512							
CR	-0.036	0.044	-0.179	0.046						
MN	0.045	-0.069	0.257	0.023	0.066					
FE	0.094	0.184	0.161	0.082	0.130	0.325				
NI	0.358	0.730	0.397	0.580	-0.183	-0.084	0.196			
HUMIC	0.035	0.042	0.168	-0.075	0.094	0.082	0.504	0.048		
P_SOLID	-0.418	*	-0.251	0.669	*	0.230	0.586	-0.000	-0.019	
HION	0.317	0.133	0.691	0.280	-0.093	-0.157	0.241	0.200	0.458	-0.215

(ii) logarithmic

	C1	C2	C3	C4	C5	C6	C7	C8
C2	0.482							
C3	0.367	0.551						
C4	0.353	0.791	0.246					
C5	0.056	-0.021	0.032	0.207				
C6	0.105	0.560	0.200	0.798	0.260			
C7	-0.058	0.609	0.315	0.692	0.139	0.754		
C8	0.500	0.717	0.144	0.769	0.152	0.615	0.446	
C9	0.733	-0.037	0.174	-0.193	0.026	-0.254	-0.286	0.075
C10	0.220	0.734	0.365	0.795	0.091	0.768	0.753	0.733
C11	0.440	0.217	0.042	0.219	0.034	0.137	0.076	0.203
C12	-0.443	-0.607	-0.355	-0.395	0.039	-0.306	-0.233	-0.362
C13	0.309	0.172	-0.113	0.367	0.144	0.442	0.304	0.473
C14	-0.496	0.255	-0.143	0.454	0.106	0.406	0.578	0.233
C15	-0.081	0.565	0.2[illegible]7	0.625	0.154	0.775	0.994	0.426
C16	[illegible]	0.751	0.272	0.7[illegible]4	0.125	0.738	0.566	0.922
C17	0.319	0.116	0.367	-0.203	-0.015	-0.172	-0.103	-0.243
C18	0.701	-0.201	0.155	-0.314	0.019	-0.386	-0.536	-0.142

	C9	C10	C11	C12	C13	C14	C15	C16	C17
C10	-0.194								
C11	0.250	0.263							
C12	-0.056	-0.457	-0.070						
C13	0.319	0.215	0.143	-0.324					
C14	-0.750	0.497	-0.175	-0.077	-0.165				
C15	-0.240	0.722	0.334	-0.302	0.540	0.555			
C16	0.13[illegible]	0.32[illegible]	0.21[illegible]	-0.447	0.527	0.161	0.559		
C17	0.37[illegible]	-0.134	[illegible]	-0.076	-0.305	-0.4[illegible]	-0.117	-0.151	
C18	0.[illegible]71	-0.430	0.2[illegible]	0.307	0.175	-0.450	-0.523	-0.121	[illegible]

Table 8a LI8 streamwater quality (1984-5)

	N	N*	MEAN	MEDIAN	TRMEAN	STDEV	SEMEAN	MIN	MAX	Q1	Q3
T_CU	22	103	0.00244	0.00200	0.00235	0.00084	0.00018	0.00200	0.00510	0.00200	0.00300
T_ZN	22	103	0.02234	0.02050	0.02132	0.01018	0.00217	0.00900	0.05600	0.01675	0.02425
T_CD	22	103	0.00125	0.00100	0.00113	0.00078	0.00017	0.00100	0.00370	0.00100	0.00100
T_AL	23	102	0.2135	0.2000	0.2149	0.0614	0.0128	0.1300	0.3900	0.1800	0.2600
T_PB	23	102	0.00310	0.00200	0.00292	0.00162	0.00034	0.00200	0.00800	0.00200	0.00500
T_CR	22	103	0.00311	0.00300	0.00300	0.00051	0.00011	0.00300	0.00540	0.00300	0.00300
T_MN	23	102	0.09103	0.08900	0.09013	0.01927	0.00402	0.06100	0.14000	0.07800	0.09200
T_FE	23	102	0.1962	0.1400	0.1849	0.1391	0.0290	0.0470	0.5636	0.0890	0.2400
T_NI	22	103	0.00330	0.00300	0.00317	0.00083	0.00018	0.00300	0.00600	0.00300	0.00300
PH	125	0	5.3814	5.2000	5.3564	0.5624	0.0503	4.4000	6.8000	5.0000	5.7633
COND	125	0	46.471	47.000	46.549	5.921	0.530	32.370	61.500	44.000	50.000
TURB	1	124	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
AMM_N	125	0	1.5625	1.4286	1.4602	0.5118	0.0458	1.4286	4.2857	1.4286	1.4286
TON	125	0	16.173	14.286	15.172	10.193	0.912	7.143	57.142	7.143	21.428
NO2	125	0	0.28570	0.28570	0.28570	0.00000	0.00000	0.28570	0.28570	0.28570	0.28570
TH	123	2	7.169	6.700	7.060	2.252	0.203	0.900	13.750	5.700	8.400
FCO2	97	28	4.167	3.800	3.833	3.116	0.316	1.900	32.390	3.000	4.600
TA	94	31	66.7	32.0	38.9	223.1	23.0	6.0	2171.8	25.7	44.0
CL	125	0	211.13	225.67	212.32	40.83	3.65	84.63	310.30	197.46	239.78
OPO4	125	0	0.02443	0.02000	0.02000	0.04566	0.00408	0.02000	0.53000	0.02000	0.02000
SIO2	125	0	1.0231	1.0000	1.0291	0.1515	0.0136	0.4000	1.4000	1.0000	1.1000
SO4	121	4	135.22	135.39	132.79	34.03	3.09	85.40	364.52	114.57	145.81
NA	122	3	161.75	164.15	160.72	37.55	3.40	36.55	368.51	140.83	178.28
K	120	5	7.766	7.339	7.447	4.426	0.404	1.026	21.538	4.359	9.743
CU	112	13	0.00231	0.00200	0.00213	0.00144	0.00014	0.00100	0.00900	0.00100	0.00300
MG	123	2	72.25	69.08	71.24	21.18	1.91	9.29	131.91	58.55	80.59
CA	123	2	75.66	70.36	74.46	25.53	2.30	9.48	154.94	57.33	88.82
ZN	124	1	0.02527	0.02400	0.02441	0.01183	0.00106	0.00600	0.07700	0.01700	0.03100
CD	124	1	0.00105	0.00100	0.00095	0.00075	0.00007	0.00040	0.00800	0.00030	0.00100
AL	124	1	0.2029	0.2020	0.1958	0.1252	0.0112	0.0050	0.7170	0.1051	0.2767
PB	124	1	0.00810	0.00500	0.00713	0.00746	0.00067	0.00200	0.05100	0.00500	0.01300
CR	112	13	0.00228	0.00300	0.00227	0.00105	0.00010	0.00100	0.00530	0.00100	0.00300
MN	124	1	0.08061	0.08000	0.07964	0.03403	0.00306	0.00300	0.22300	0.06100	0.09775
FE	124	1	0.08848	0.06800	0.08084	0.06090	0.00547	0.00500	0.33000	0.05225	0.10475
NI	112	13	0.00321	0.00300	0.00298	0.00202	0.00019	0.00100	0.01300	0.00200	0.00388
HUMIC	109	16	1.215	0.700	1.013	1.411	0.135	0.200	8.400	0.400	1.350
IQ	71	54	0.03346	0.02300	0.02998	0.03212	0.00381	0.00000	0.15400	0.00900	0.04800
TEMP	37	88	9.731	10.000	9.865	3.702	0.609	0.000	15.500	6.500	12.325
T_NA	1	124	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
T_K	1	124	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
T_MG	1	124	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
T_CA	1	124	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
ACID	1	124	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
UV	23	102	0.01957	0.01000	0.01690	0.02088	0.00435	0.00000	0.09500	0.00500	0.03000
F_PH	18	107	5.500	5.750	5.675	1.673	0.394	0.000	8.200	4.875	6.250
STAGE	56	69	0.1300	0.0575	0.0970	0.1958	0.0262	0.0000	1.1500	0.0300	0.1500
P_SOLID	11	114	4.18	2.00	2.33	6.71	2.02	1.00	24.00	1.00	4.00
DOC	1	124	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
HION	125	0	7.493	6.310	6.886	6.929	0.620	0.159	39.811	1.726	10.000

Table 8b Correlation matrices

(i) normal

	F_	[illegible]	[illegible]	AMM_	[illegible]	[illegible]	CO2	T
[illegible]	0.1							
CCO3	0.340	0.211						
AMM_N	0.395	-0.022	0.111					
TCA	-0.171	-0.475	0.010	0.790				
TH	0.135	0.537	0.014	0.023	-0.177			
FCO2	-0.221	-0.315	-0.279	-0.043	0.032	-0.147		
TA	0.571	0.029	-0.172	-0.047	-0.165	0.015	0.900	
CL	0.268	0.077	0.723	-0.023	-0.053	0.313	-0.344	-0.303
OPO4	0.577	0.031	0.021	-0.007	-0.076	0.072	-0.068	-0.014
SIO2	-0.060	0.239	0.173	-0.126	0.017	0.144	-0.252	-0.223
SO4	0.222	0.013	0.304	0.133	-0.119	0.377	-0.116	-0.135
NA	0.159	0.037	0.443	0.053	-0.052	0.495	-0.239	-0.196
K	0.066	0.427	0.472	-0.021	-0.142	0.509	-0.073	0.105
CU	0.351	-0.265	-0.142	0.170	0.033	-0.175	0.219	0.211
MG	0.259	0.574	0.670	0.013	-0.204	0.957	-0.231	-0.021
CA	0.293	0.534	0.570	0.040	-0.166	0.977	-0.178	0.032
ZN	0.736	-0.570	0.047	0.025	0.229	-0.211	0.153	-0.058
CD	0.792	-0.091	0.064	0.040	-0.103	0.021	-0.059	-0.023
AL	-0.069	-0.714	-0.025	0.055	0.392	-0.335	0.164	-0.069
PB	-0.025	-0.139	0.131	-0.041	-0.066	0.005	0.008	-0.051
CR	0.596	-0.389	-0.429	0.190	0.321	-0.324	0.016	-0.014
MN	0.040	-0.542	0.021	0.100	0.121	-0.189	0.079	-0.101
FE	0.135	-0.197	-0.222	0.077	-0.110	-0.104	0.345	0.355
NI	0.596	-0.422	-0.114	0.072	0.179	-0.203	0.252	0.192
HUMIC	0.241	-0.152	-0.196	0.086	-0.119	-0.060	0.553	0.532
IQ	*	-0.690	0.029	0.100	0.291	-0.342	0.359	-0.390
TEMP	*	0.663	0.347	0.008	-0.636	0.562	-0.520	0.701
UV	*	-0.550	-0.043	-0.152	0.414	-0.314	0.383	-0.365
F_PH	*	0.620	0.744	0.104	-0.409	0.612	-0.453	0.598
STAGE	*	-0.273	0.092	-0.037	0.383	-0.092	0.348	-0.179
P_SOLID	0.991	0.321	0.878	0.369	-0.183	0.907	-0.301	0.681
HION	-0.109	-0.231	-0.088	0.064	0.416	-0.437	0.334	0.061

	CL	OPO4	SIO2	SO4	NA	K	CU	MG
OPO4	[illegible]							
SIO2	0.025	0.075						
SO4	0.455	-0.218	-0.155					
NA	0.255	0.029	-0.056	0.335				
K	0.367	-0.046	0.051	0.355	0.255			
CU	-0.157	-0.033	-0.077	-0.053	-0.014	-0.162		
MG	0.477	0.072	0.172	0.359	0.529	0.510	-0.223	
CA	0.226	0.072	0.194	0.325	0.458	0.514	-0.105	0.908
ZN	0.099	-0.031	-0.140	0.213	0.062	-0.164	0.175	-0.176
CD	0.067	0.065	-0.011	0.173	0.495	-0.008	0.132	0.061
AL	-0.114	-0.075	-0.277	0.027	0.240	-0.251	0.276	-0.126
PB	0.130	0.120	0.141	0.236	0.075	0.053	0.053	-0.051
CR	-0.393	-0.071	0.027	-0.373	-0.058	-0.425	0.346	-0.378
MN	0.172	-0.085	-0.133	0.338	0.210	-0.241	0.184	-0.144
FE	-0.314	-0.044	-0.525	0.045	0.025	-0.147	0.273	-0.077
NI	-0.134	-0.016	-0.030	-0.021	-0.015	-0.215	0.551	-0.281
HUMIC	-0.137	0.169	-0.443	0.197	-0.258	0.010	0.125	-0.091
IQ	0.115	-0.104	-0.518	0.129	0.355	-0.282	0.183	-0.320
TEMP	0.052	0.104	0.125	0.337	0.075	0.473	-0.065	0.550
UV	-0.114	-0.152	-0.672	-0.333	0.008	-0.128	0.037	-0.302
F_PH	0.479	0.000	-0.373	0.666	0.401	0.740	-0.593	0.622
STAGE	0.154	-0.037	-0.371	0.211	0.072	-0.151	-0.152	-0.059
P_SOLID	0.924	0.992	-0.163	0.875	0.903	0.145	0.573	0.933
HION	-0.112	-0.067	-0.410	0.011	-0.021	-0.240	0.151	-0.422

	CA	ZN	CD	AL	PB	CR	MN	FE
ZN	-0.223							
CD	0.144	0.152						
AL	-0.373	0.511	0.086					
PB	0.042	0.233	0.214	0.299				
CR	-0.241	0.180	0.122	0.433	0.055			
MN	-0.201	0.468	0.265	0.456	0.102	0.150		
FE	-0.098	0.215	0.062	0.303	-0.031	0.223	0.255	
NI	-0.128	0.423	0.283	0.434	0.695	0.420	0.195	0.115
HUMIC	-0.033	0.103	0.145	0.054	-0.076	0.005	0.218	0.640
IQ	-0.368	0.521	0.130	0.339	0.159	0.355	0.482	0.333
TEMP	0.564	-0.556	0.293	-0.567	0.341	-0.279	-0.258	-0.186
UV	-0.333	0.689	-0.577	0.561	-0.233	0.249	0.037	0.640
F_PH	0.598	-0.446	0.032	-0.517	0.568	-0.901	-0.272	0.002
STAGE	-0.130	0.423	-0.024	0.221	-0.121	-0.157	0.396	0.216
P_SOLID	0.939	0.347	0.930	-0.337	0.932	0.960	0.328	0.530
HION	-0.440	0.454	0.031	0.695	0.154	0.235	0.378	0.333

	NI	HUMIC	IQ	TEMP	UV	F_PH	STAGE	P_SOLID
HUMIC	0.064							
IQ	0.443	0.193						
TEMP	-0.107	0.220	-0.406					
UV	-0.388	0.491	0.679	-0.241				
F_PH	-0.850	0.331	-0.134	0.777	0.281			
STAGE	-0.079	0.204	0.511	-0.263	0.931	0.133		
P_SOLID	0.980	0.322	*	*	*	*	*	
HION	0.385	0.216	0.220	-0.527	0.767	-0.553	0.352	-0.300

(ii) logarithmic

	C1	C2	C3	C4	C5	C6	C7	C8
C2	0.519							
C3	0.406	0.332						
C4	0.310	0.150	0.142					
C5	-0.275	-0.134	-0.133	0.210				
C6	-0.177	0.105	0.091	0.505	0.463			
C7	-0.207	0.037	0.077	0.446	0.452	0.911		
C8	-0.136	-0.000	-0.352	0.272	0.453	0.343	0.229	
C9	0.356	0.112	0.175	-0.293	-0.163	-0.304	-0.276	-0.369
C10	-0.282	-0.131	-0.463	-0.022	-0.004	0.135	0.233	0.254
C11	0.013	0.205	0.014	0.342	0.359	0.458	0.395	0.518
C12	0.052	0.116	0.052	0.071	0.026	0.043	0.069	0.000
C13	0.353	0.197	-0.307	-0.051	-0.064	-0.193	-0.190	0.028
C14	-0.561	-0.393	0.145	0.354	0.342	0.352	0.407	-0.063
C15	-0.193	0.066	0.011	0.457	0.438	0.953	0.951	0.272
C16	-0.157	-0.099	-0.207	0.425	0.552	0.553	0.447	0.806
							-0.022	-0.145

	C9	C10	C11	C12	C13	C14	C15	C16
C10	-0.272							
C11	-0.037	-0.070						
C12	-0.039	-0.121	0.144					
C13	0.139	0.021	-0.123	0.257				
C14	0.057	0.022	0.074	-0.111	-0.326			
C15	-0.274	0.223	0.431	0.255	-0.145	0.313		
C16	-0.155	0.203	0.529	0.257	0.034	0.125	0.479	
	0.211	-0.325	0.110	0.197	-0.170	0.121	-0.022	-0.168

is markedly reduced in this catchment, presumably because the open canopy reduces stemflow, occult deposition, atmospheric scavenging and evapotranspirational losses. All of the above factors are considered to be of major importance in determining stream acidity in afforested catchments. Nevertheless, acid events do occur as indicated by the minimum recorded pH of 4.4. In addition, 25% of all samples exhibit a pH of 5.0 or less, even in an open canopy conifer forest area. Hence, some of the aspects of such a land use which contribute to stream acidity, are clearly already present prior to its maturity.

Second, SO_4 concentrations are high at LI1 averaging 154 ueq l^{-1}, with 25% of all samples exhibiting concentrations of 170 ueq l^{-1} or more. Hence on average, concentrations are more than double those found in bulk precipitation and presumably reflect the large evapotranspirational losses (typically 30% or more) and enhanced sulphate scavenging capacity associated with such a land use, as well as the possibility of enhanced sulphate contributions from the forest soils. Average SO_4 concentrations in LI2 are even higher (174 ueq l^{-1}), although the sample size is much smaller. On the other hand, in LI3 levels are only slightly lower averaging 153 ueq l^{-1}, suggesting that bankside clearance has done little to affect sulphate concentrations. Concentrations in LI8 however, average 135 ueq l^{-1} indicating a significant reduction presumably as a result of its juvenile status causing reduced evapotranspiration and scavenging.

Third, NO_3 concentrations are very low at LI1, averaging 10.5 ueq l^{-1}, some 25 to 30% of that found in the bulk precipitation. Clearly these low concentrations reflect the large uptake of nitrates by the mature conifer vegetation cover. Hence, LI2 and LI3 also exhibit low concentrations averaging 12.9 ueq l^{-1} and 20.8 ueq l^{-1} respectively. More surprisingly, levels only average 16 ueq l^{-1} at LI8, suggesting that nutrient uptake rates are comparable with those of the mature forests.

Similarly, the low ammoniacal nitrogen concentrations found at all sites contrast with the higher levels found in the bulk precipitation. Again this reflects the effects of plant uptake, as well as the utilisation of ammonia in neutralising any stream acidity.

The marine salts (Na, Cl and Mg) are all present at quite high concentrations at LI1, averaging 204 ueq l^{-1} , 247 ueq l^{-1} and 60 ueq l^{-1} respectively. Hence all three are present at average concentrations more than 100% higher than those found in bulk precipitation at L3. Consequently, all three reflect the strong sea-salt influence in the area and the very effective scavenging capability of the forest, with its large evapotranspirational losses. In addition, LI2 and LI3 exhibit similar, although slightly lower concentrations of all three due to their comparable land use , lithology and climate. On the other hand, concentrations at LI8 while similar in the case of Na and Cl, are higher for Mg averaging 72 ueq l^{-1} . Thus, while scavenging capacities and evapotranspirational losses are similar, there appears to be an additional source of Mg, possibly present in the catchment soils due to the reduced base cation uptake of a younger forest cover. Terrestrially derived Ca concentrations are very low at LI1, averaging 59 ueq l^{-1} , confirming its limited buffering capacity with levels only slightly higher than that found in bulk precipitation. At LI2, concentrations are even lower (averaging 53 ueq l^{-1}) while at LI3 they are considerably higher (averaging 105 ueq l^{-1}), although the latter is clearly influenced by a single very high concentration. Nevertheless, LI3 does seem to posess a greater buffering capacity despite its similar land use, possibly this is due to the effects of the bankside conifer clearance. Again though, the conclusion is necessarily speculative given the available information. Meanwhile at LI8 Ca concentrations average 76 ueq l^{-1} slightly higher than at LI1 and LI2, but lower than at LI3. Hence its buffering capacity is slightly enhanced relative to a mature forest probably due to its open canopy and reduced base cation uptake.

Not surprisingly, dissolved aluminium levels are elevated at LI1 with average concentrations of 0.38 mg l^{-1} and peaks of up to 0.85 mg l^{-1}. This represents a major increase on that found in the bulk precipitation and reflects the enhanced dissolution of alumina silicate minerals in the forest soils since aluminium acts as a powerful buffer to acidity in the absence of available base cation buffering capacity (i.e. low hardness and low alkalinity waters). Thus, with total hardness averaging only 5.7 mg l^{-1}, the above process contributes large amounts of aluminium into the stream during acid events. Aluminium levels are similarly elevated in LI2 and LI3, averaging 0.48 mg l^{-1} and 0.35 mg l^{-1} respectively, with total hardness averaging 4.8 mg l^{-1} and 7.9 mg l^{-1} respectively. Thus, again LI3 gives an indication of its slightly enhanced buffering capacity possibly resulting from the bankside clearance, although its soils need to be thoroughly examined before any such effect can be confirmed. Conceivably, removal of the trees might result in the creation of less acid soil conditions on the banks, through and/or over which runoff would have to pass. In addition, the scavenging capability of the catchment would be reduced slightly. Both factors would presumably contribute to a slight reduction in its acidity. Meanwhile LI8 exhibits slightly lower dissolved aluminium concentrations averaging 0.2 mg l^{-1}, although a maximum of 0.72 mg l^{-1} suggests that it too does suffer from the intermittent effects of acid events flushing out toxic aluminium.

Finally, Table 9 presents a comparison of selected streamwater chemistry for the afforested catchments. Clearly, LI1 and LI2 are most acidic with very low buffering capacities and consequently high levels of aluminium contamination. LI3 is less acid, while LI8 is even less so, due to its juvenile forest cover. Another factor of importance is the change in the catchment hydrology brought about by the forestry land use. For example, the installation of drainage ditches leads to a more rapid storm response and reduced baseflow components in storm hydrographs (Neal _et_ _al_., 1986). In addition, the increased evapotranspirational losses also affect catchment hydrology (UKAWRG, 1986).

Examination of the correlation matrices for each catchment reveals several common and significant parameter correlations (Tables 5b, 6b, 7b and 8b). LI1 shows a clear negative correlation between pH and dissolved aluminium ($r = -0.7$), suggesting that acid events are accompanied by enhanced concentrations of aluminium. Furthermore, high positive correlations between pH and total hardness, pH and alkalinity and pH and calcium concentrations, all support the suggestion that the limited buffering capacities are crucial to the generation of acid runoff and elevated aluminium concentrations. On the other hand SO_4 shows little correlation with any other variable, at least on the basis of the spot sampling data. In addition, the marine salts are not highly correlated (i.e. $r \leqslant 0.4$) suggesting that hydrochemical processes within the catchment serve to modify the inputs passing through LI1. Ca and Mg concentrations however, are well correlated ($r = 0.861$)

Table 9. A comparison of afforested streamwater chemistry (ueq l^{-1}).

	LI1	LI2	LI3[6]	LI4[3]	LI8
[1] pH					
[2] $\bar{x}$	4.87	4.62	5.17	-	5.38
max	7.00	5.0	6.3	-	6.8
min	4.3	4.3	4.5	-	4.4
H^+					
$\bar{x}$	18	26	10	-	8
max	50	50	32	-	40
min	0.1	11	0.5	-	0.2
SO_4^{2-}					
$\bar{x}$	154	131	153	-	135
max	260	168	221	-	365
min	98	0	0	-	85
NO_3^-					
$\bar{x}$	11	13	21	-	16
max	29	29	50	-	57
min	7	7	7	-	7
[5] NH_4^+					
$\bar{x}$	1.5	1.4	1.7	-	1.6
max	5.0	1.5	6.4	-	4.3
min	1.4	1.4	1.4	-	1.4
Na^+					
$\bar{x}$	204	174	185	-	162
max	434	220	277	-	368
min	4	135	45	-	37
Cl^-					
$\bar{x}$	247	213	203	-	211
max	367	592	282	-	310
min	113	141	56	-	85
Mg^{2+}					
$\bar{x}$	60	47	57	-	72
max	102	61	107	-	132
min	24	35	11	-	9
Ca^{2+}					
$\bar{x}$	59	53	105	-	76
max	129	75	1098	-	155
min	13	35	4	-	10
K^+					
$\bar{x}$	5	3	3.7	-	7.8
max	26	8.2	7.7	-	22
min	1	0.5	0.5	-	1
[4] Al					
$\bar{x}$	0.38	0.48	0.35	-	0.2
max	0.85	0.68	0.88	-	0.72
min	0.03	0.27	0.013	-	0.005

1. pH units.
2. $\bar{x}$ - arithmetic mean
3. n < 13
4. Dissolved Al. (mg l^{-1})
5. mg l^{-1}
6. n < 30

and both exhibit negative correlations with H^+, thus confirming the importance of limited buffering during acid events. Consequently, aluminium concentrations are also negatively correlated with alkalinity and calcium concentrations are positively correlated with free CO_2 and H^+, reflecting the combined effect of increased acidity and reduced buffering in contributing to enhanced aluminium levels. Logarithmic transformation merely confirms the existence of all of the above correlations.

At LI2, similar relationships were found for pH and dissolved aluminium ($r = -0.661$) and pH and total hardness ($r = 0.75$), alkalinity ($r = 0.54$) and calcium concentrations ($r = 0.7$). Again SO_4 shows little correlation with any other parameter and the marine salts are largely uncorrelated, although Na and Mg concentrations exhibit a high correlation ($r = 0.9$) reflecting their common source. On the other hand Ca and Mg levels are again highly correlated ($r = 0.76$) reflecting their common source in the catchments soils and geology. In addition, both exhibit negative correlations with H^+ confirming the importance of buffering capacities during acid events. Consequently, H^+ and aluminium concentrations are highly correlated ($r = 0.64$) as at LI1. Again logarithmic transformations confirm all of the above, as well as yielding a higher correlation ($r = 0.724$) between H^+ and humic acid concentrations. Hence both sources of acidity appear to contribute to the severity of acid events in LI2.

At LI3 pH and dissolved aluminium concentrations are again highly correlated ($r = -0.75$). As expected, free CO_2 is also highly negatively correlated with pH ($r = -0.821$) and alkalinity ($r = -0.78$) and positively correlated with H^+ ($r = 0.81$). Meanwhile, SO_4 and Cl are slightly correlated ($r = 0.56$) and Cl and Na are correlated ($r = 0.62$), presumably reflecting their common marine source. In addition, H^+ is positively correlated with dissolved aluminium (r = 0.691) as at the other sites, and negatively correlated with SiO_2 (r = -0.7) suggesting that silicate concentrations are reduced during acid events.

Lastly, at LI8 pH is again negatively correlated with dissolved aluminium levels (r = 0.73) and positively correlated with total hardness (r = 0.58). The marine salts meanwhile, show less evidence of intercorrelation between Na and Mg (r = 0.53). Ca and Mg levels are however highly correlated (r = 0.9) as at the previous sites and both show slight negative correlations with H^+. Not surprisingly, H^+ and Al also exhibit a positive correlation (r = 0.7), supporting the suggestion that acid events accompanied by elevated aluminium concentrations are also quite common even in a juvenile conifer catchment. Finally, logarithmic transformations merely confirm the above, although Cl and SO_4 also exhibit a positive correlation (r = 0.52) as do Al and Mn (r = 0.62), reflecting their common sources in marine salts and catchment soils respectively.

Temporal patterns

Figure 6 shows tha pH and H^+ concentration patterns for LI1 since 1981. The first point to make is the increase in sample numbers since mid - 1984. Secondly, in general pH and H^+ levels indicate that stream conditions were more acid in 1981 and 1982 and that the winter high rainfall and high flow months were more acid than the summer months. Clearly, one reason might be the occurrence of enhanced rainfall inputs in 1981 and 1982. Thus, although the rainfall acidity seems to have increased in 1984, the overall reduction in precipitation volume received has compensated for the former, producing slightly reduced levels of stream acidity. Moreover, an examination of the fractional

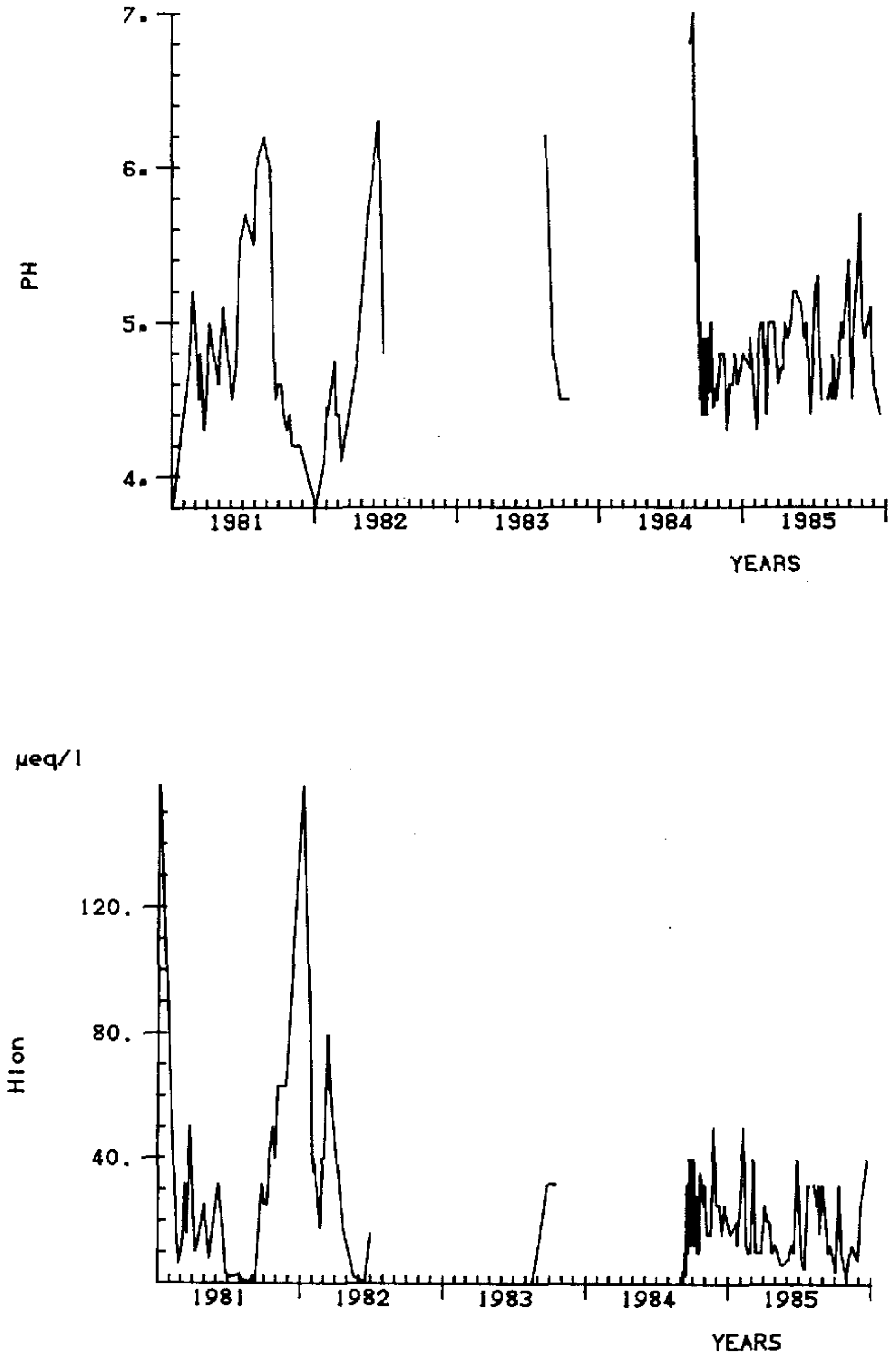


Figure 6 pH and H^+ patterns at LI 1 (1981 - 1985) cumulative frequency of H^+ samples taken during each year since 1981 confirm that both 1981 and 1982 were characterised by a higher frequency of more acid events (Figure 7). Clearly then, the frequency of occurence of large storm events seems to be a major factor in determining the magnitude of monitored acid events.

Subsequent analysis in the present report will concentrate upon the stream conditions monitored since 1984, with only occasional references to earlier samples. First, at LI1 the dry period from February to August 1984 was followed by high rainfall in September which resulted in a major increase in stream acidity (Figure 8). Presumably this pattern reflects a flushing effect following the dry period. Acidity continued at a fairly high level over the Winter high rainfall months, falling to a minimum in May 1985 before recovering until a further minimum in September. The latter coincided with a further period of unusually low rainfall from September to November. Thus the major factor influencing streamwater quality patterns appears to be the rainfall inputs. Consequently, the unusual nature of both 1984 and 1985 cannot be under-estimated. 1984 experienced an unusually dry Spring and early Summer and a total rainfall 94% of normal. Likewise, 1985 experienced an unusually dry late Winter and Autumn, yielding a total rainfall 91% of normal. Thus, both years to date make it difficult to establish the nature of any normal seasonal patterns in streamwater chemistry.

The higher SO_4 concentrations were recorded during August 1984, following the long dry period. Levels then declined during the latter part of the year before recovering during the low rainfall months of January to March 1985. Presumably the patterns reflect the influence of flushing effects following the

Llyn Brianne (LI1)

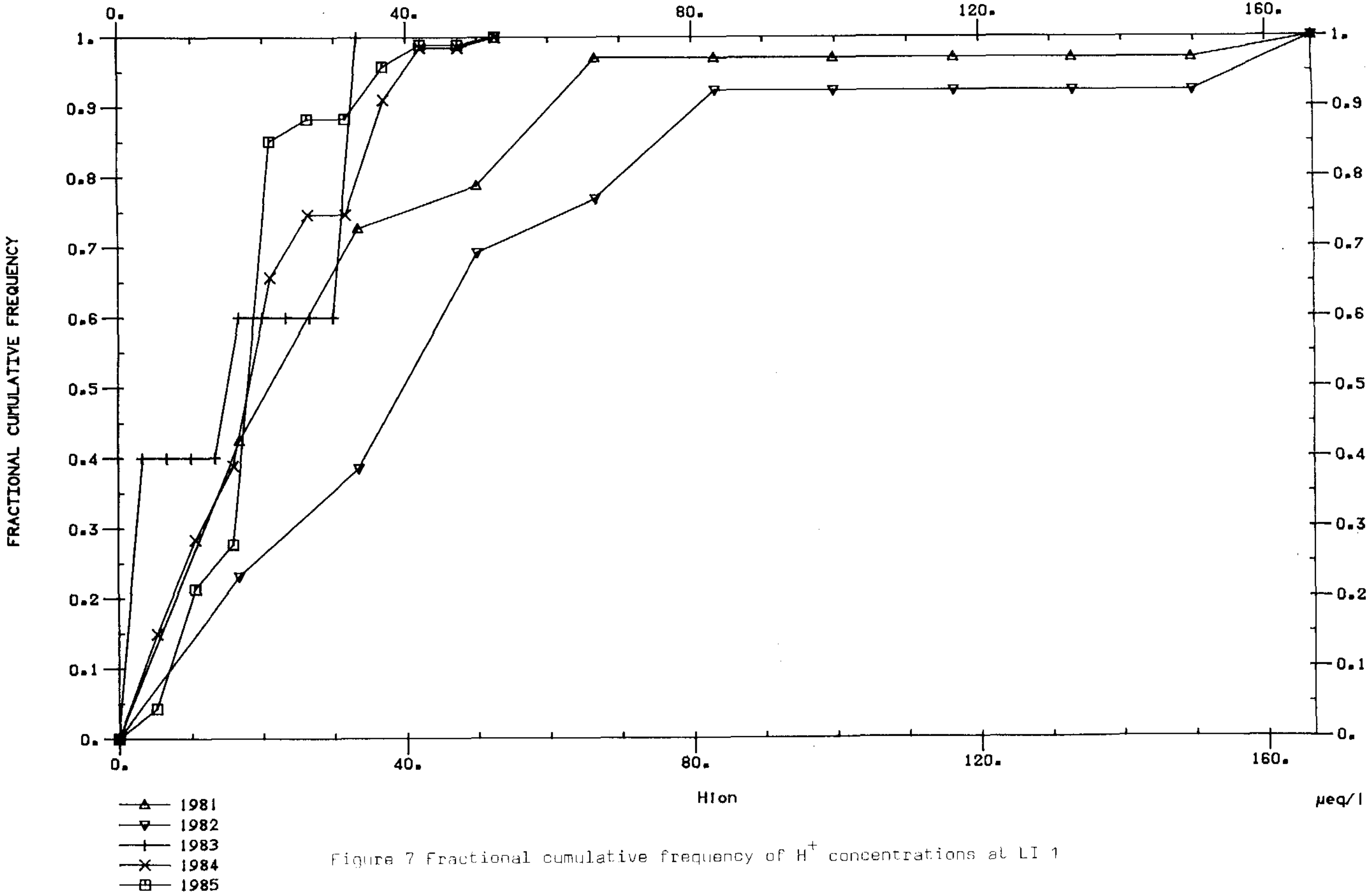
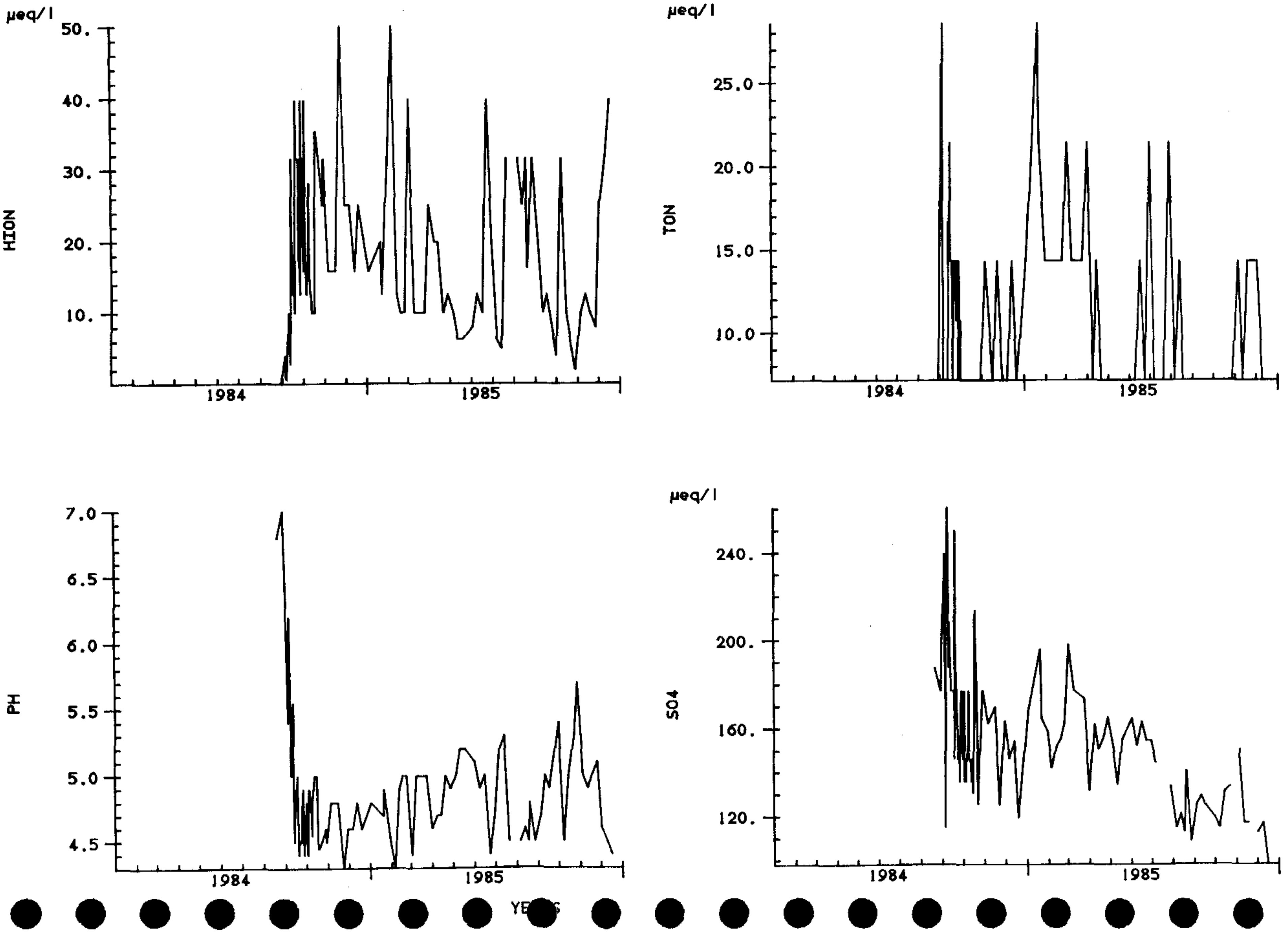
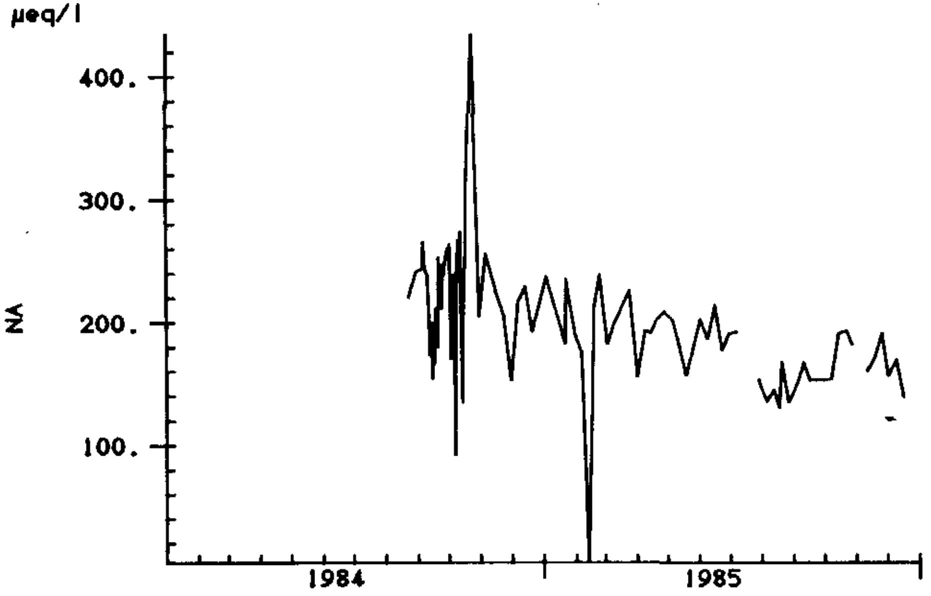


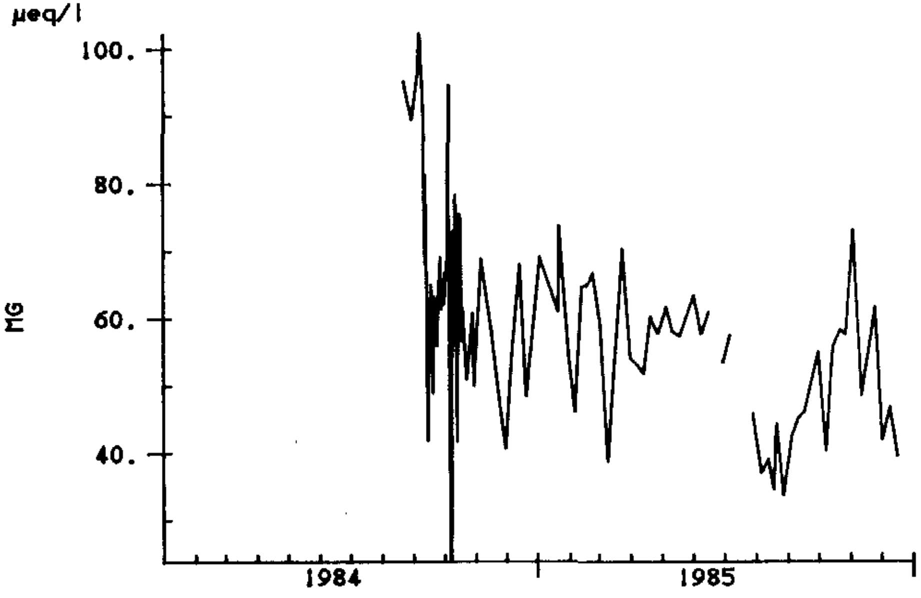
Figure 7 Fractional cumulative frequency of H^+ concentrations at LI 1

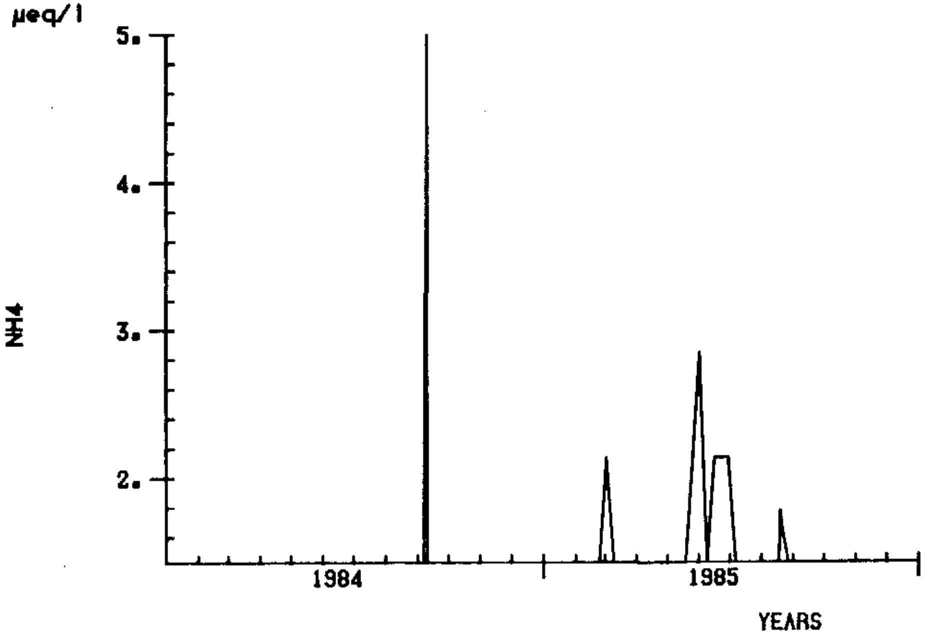
Figure 8 LLYN BRIANNE (LI1)

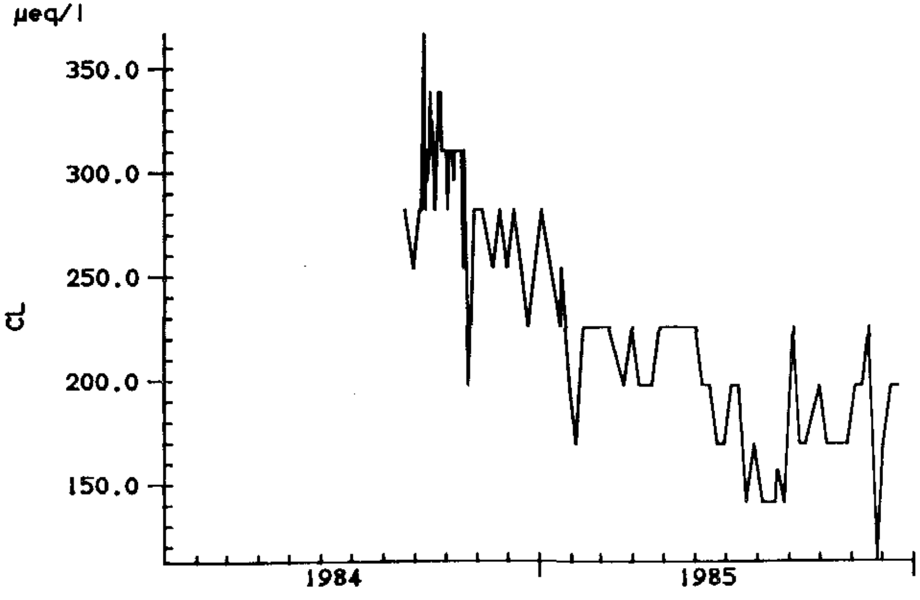


LLYN BRIANNE (LI1)

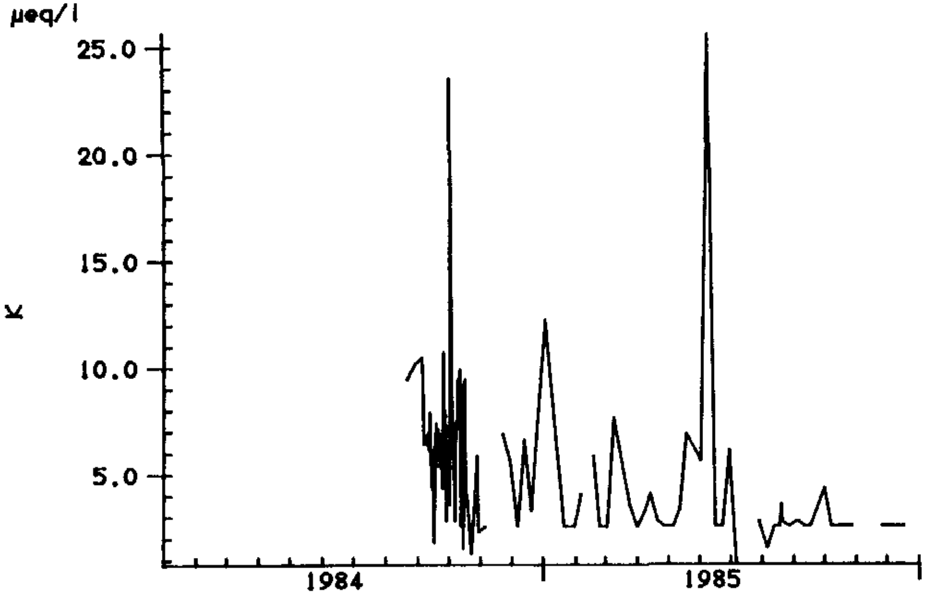


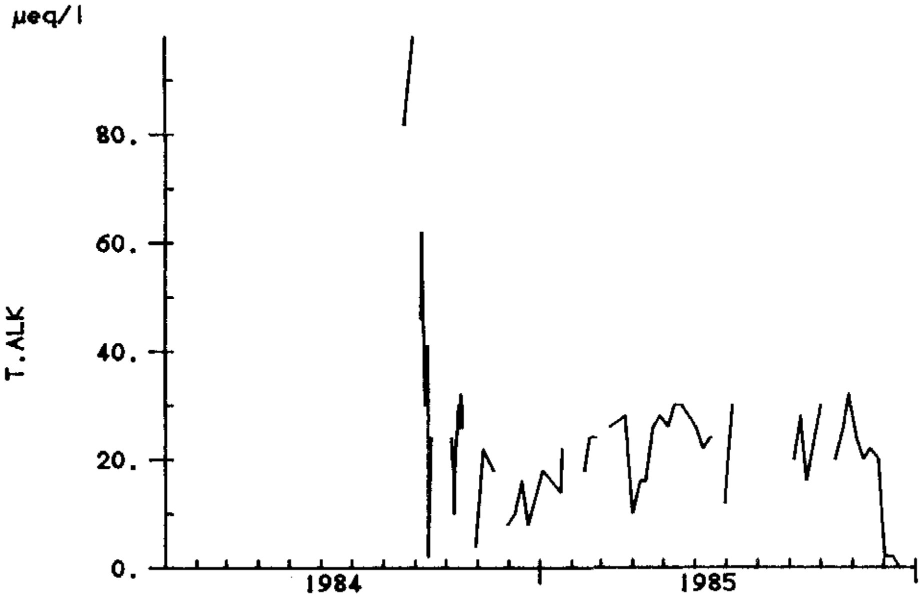


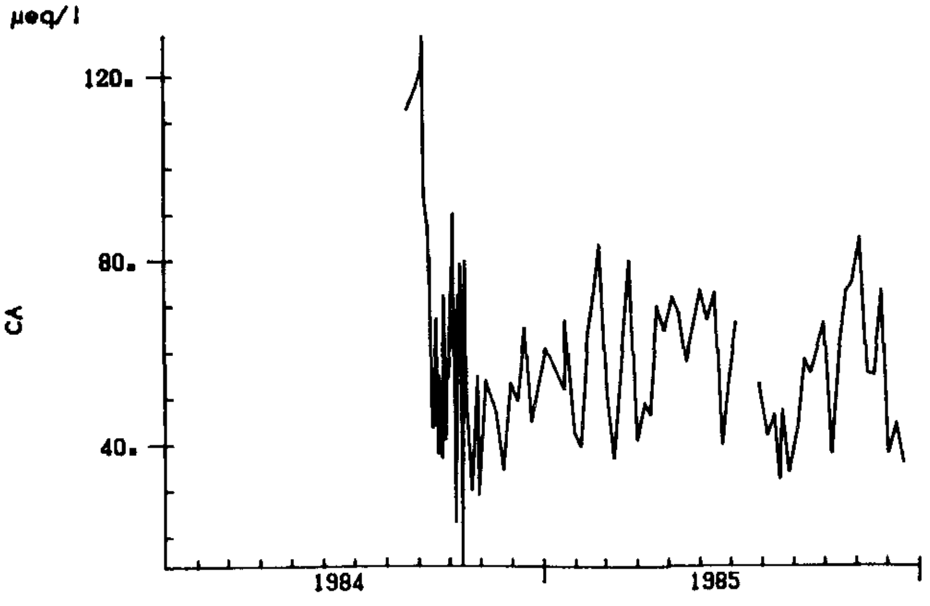


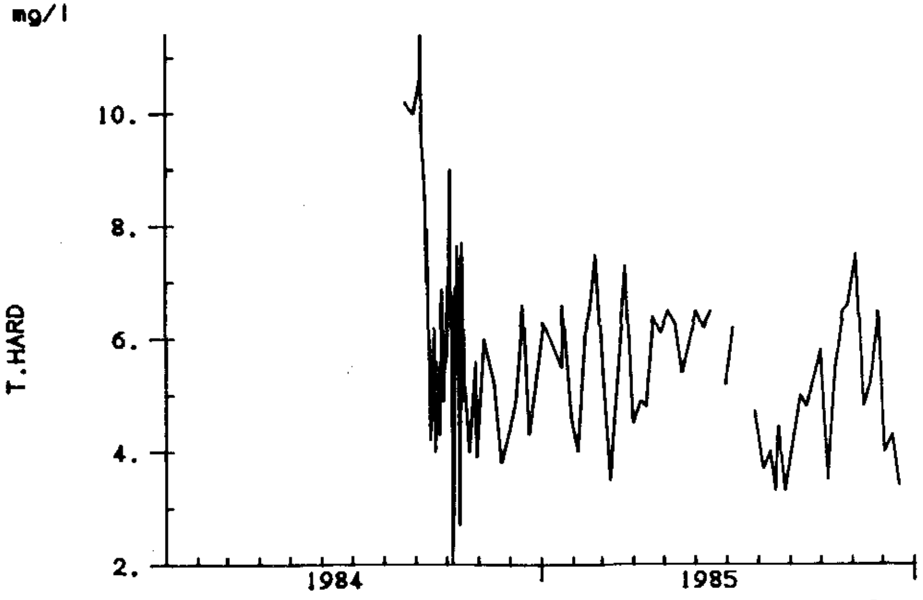


LLYN BRIANNE (LI1)

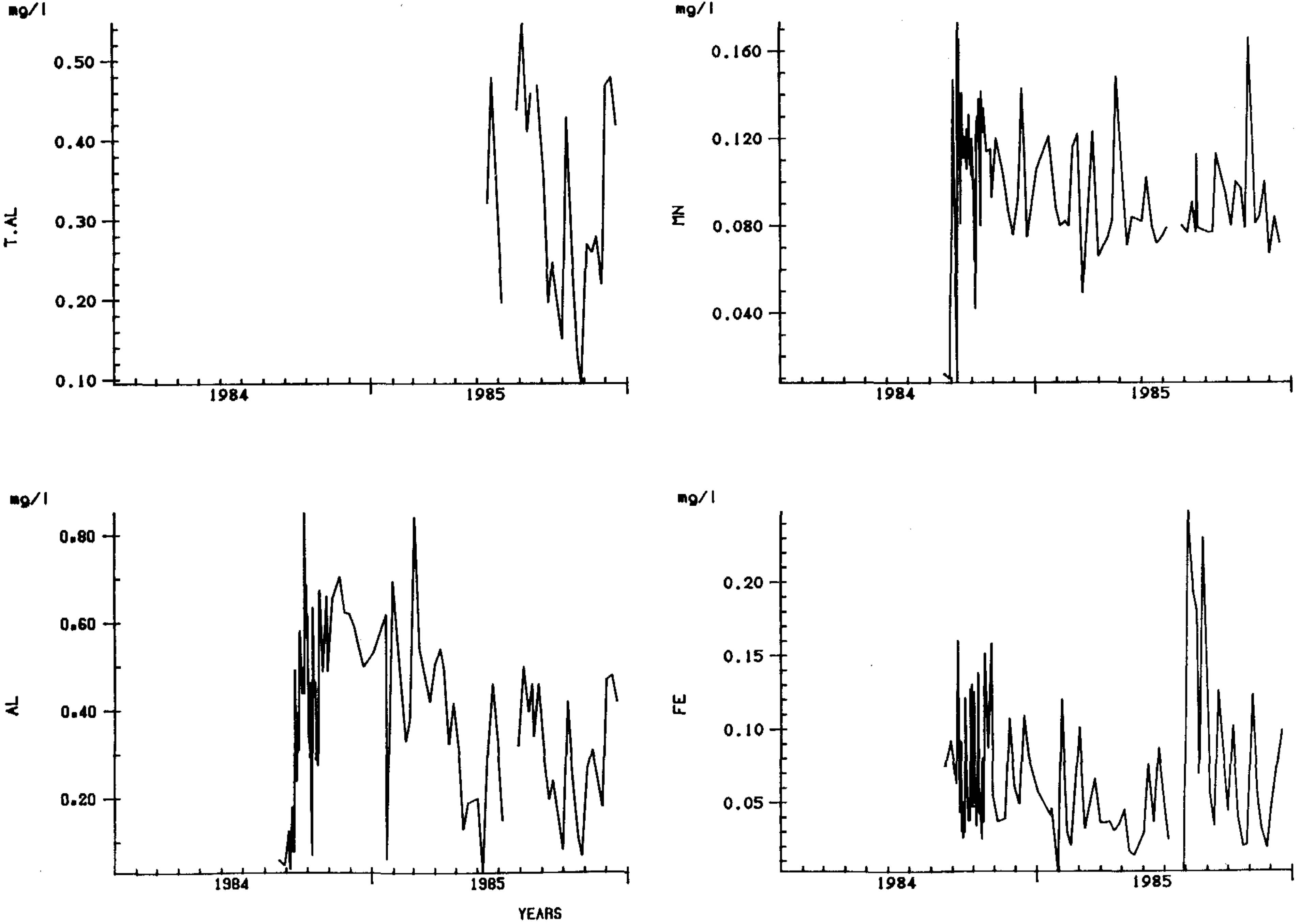




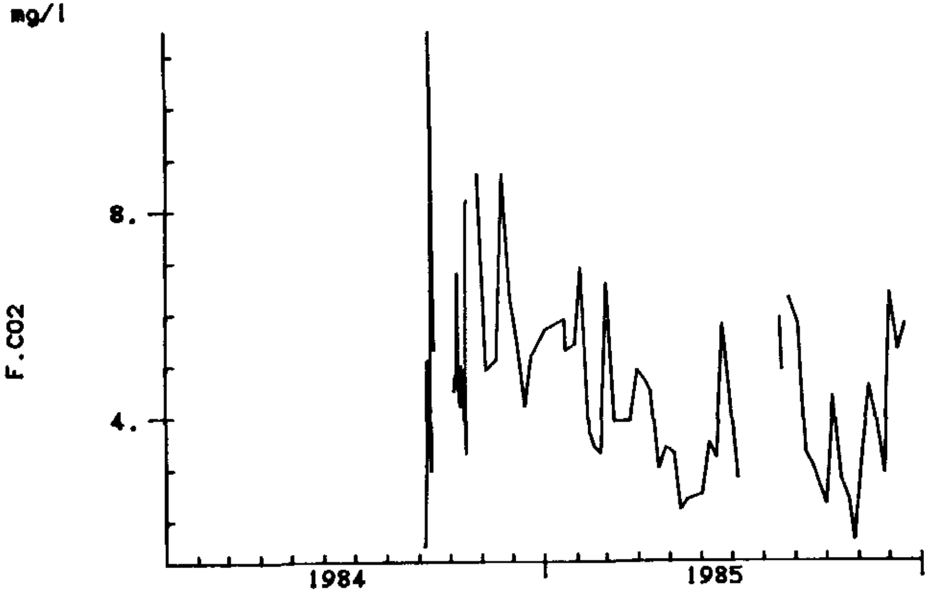


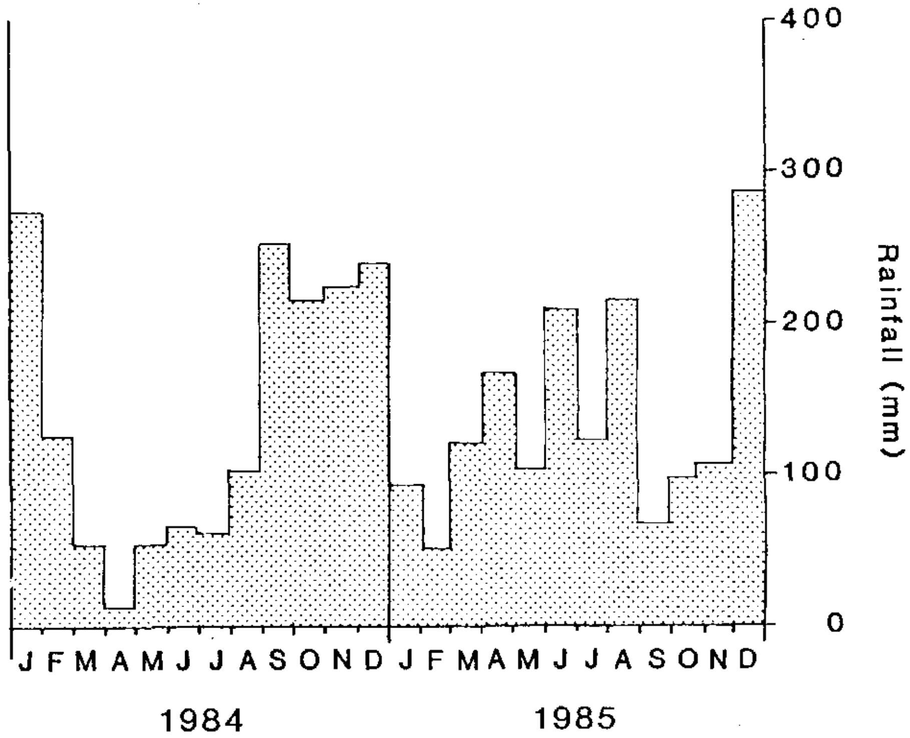


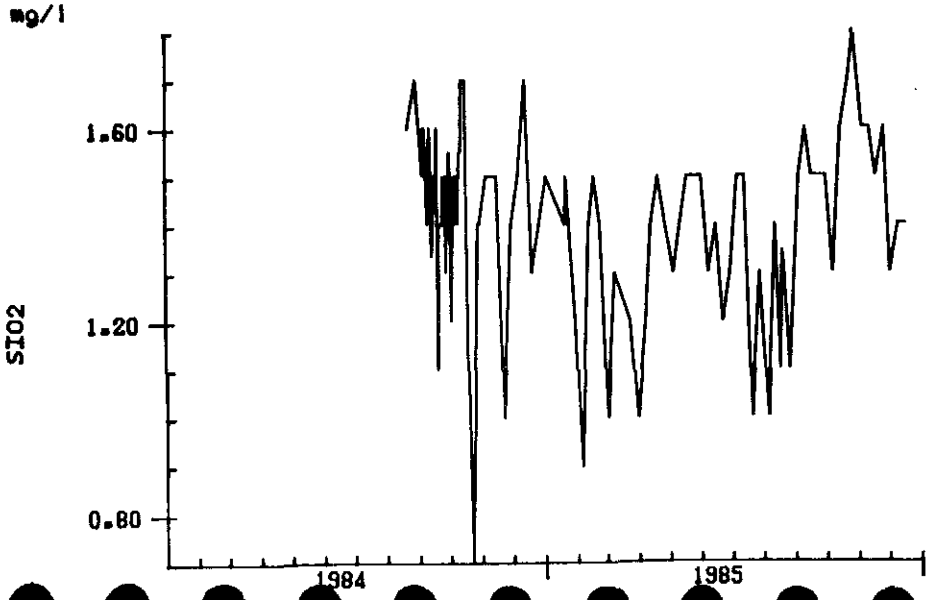
LLYN BRIANNE (LI1)

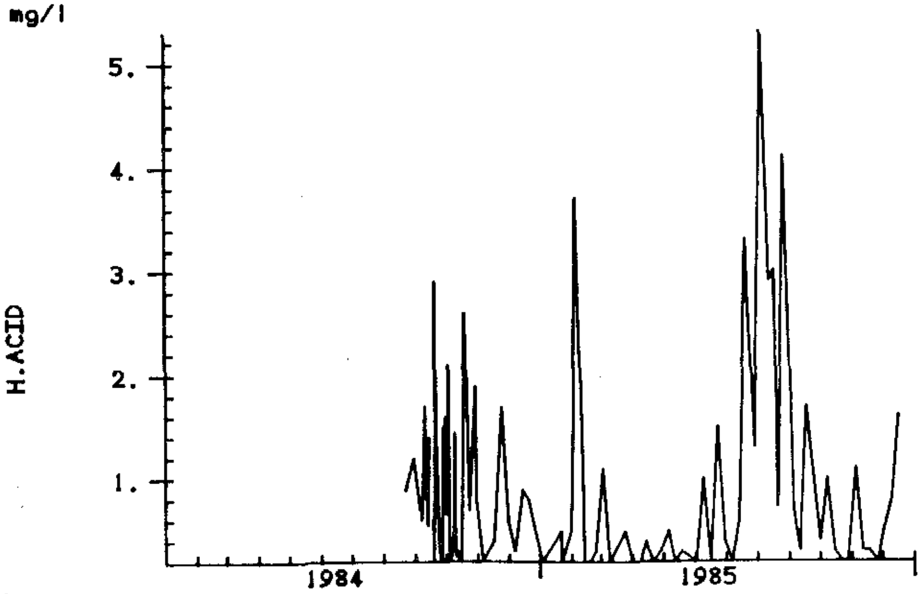


LLYN BRIANNE (LI1)









dry spell and the concentrating effects of reduced runoff draining the forest land use. The NO_3 concentrations also indicate the presence of a flushing effect in September 1984, with other peaks occuring in the Winter months especially, presumably when plant uptake of nutrients is at a minimum.

The marine salts all indicate a decreasing trend in 1984 with the high concentrations of Summer 1984 representing the concentrating effects of high evapotranspiration losses from February to August and subsequent flushing effects. Fluctuations in 1985 were fairly limited but with some evidence of a minimum in July and August.

Terrestrially derived calcium concentrations were low throughout the study period and gave little indication of a seasonal pattern, although some evidence of a flushing effect was apparent in early September 1984. In addition, in general the low rainfall months tended to record elevated Ca concentrations. Both total hardness and total alkalinity exhibit similar patterns. Hence, during low flow months when the baseflow component of streamflow is elevated, the limited stream buffering capacity is at its highest.

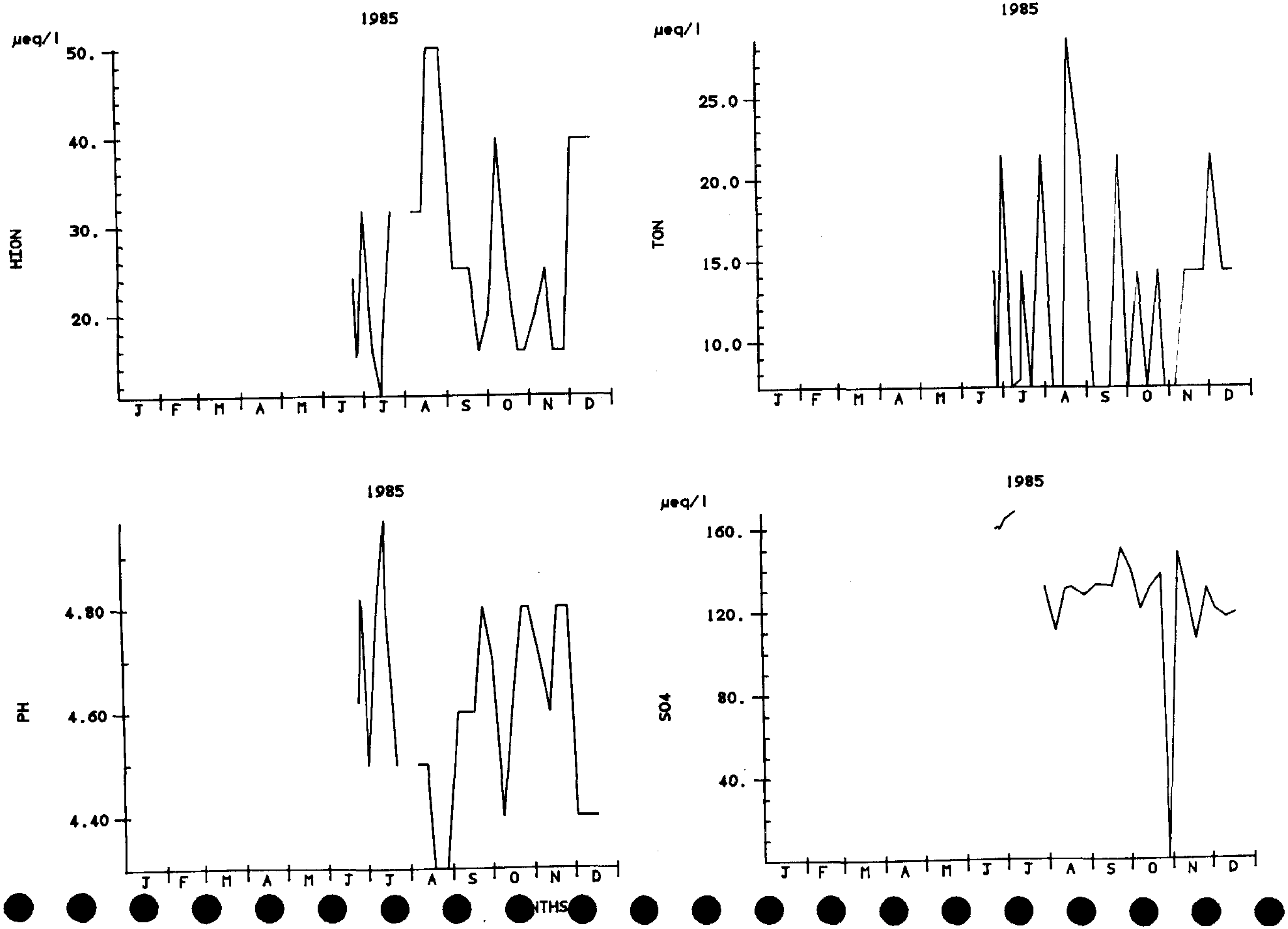
Of the metals, dissolved aluminium concentrations consistently peak during periods of high acidity and high runoff. Dissolved Fe and Mn concentrations exhibit a similar pattern, with peaks generally corresponding to rainfall events.

Free CO_2 levels not surprisingly mirror H^+ concentrations, while SiO_2 concentrations decrease when H^+ levels increase. Lastly, humic acid levels were reduced in March to June 1985 and recovered in July/August 1985 probably reflecting patterns in soil and vegetation conditions.

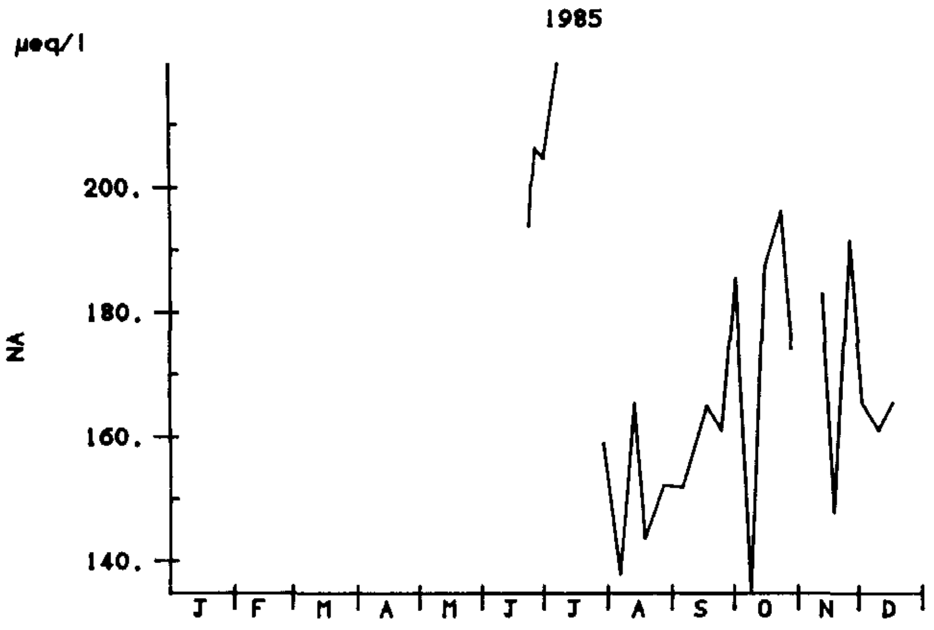
At LI2 data are only available since June 1985 making any analysis of trends impossible (Figure 9). The plots are thus

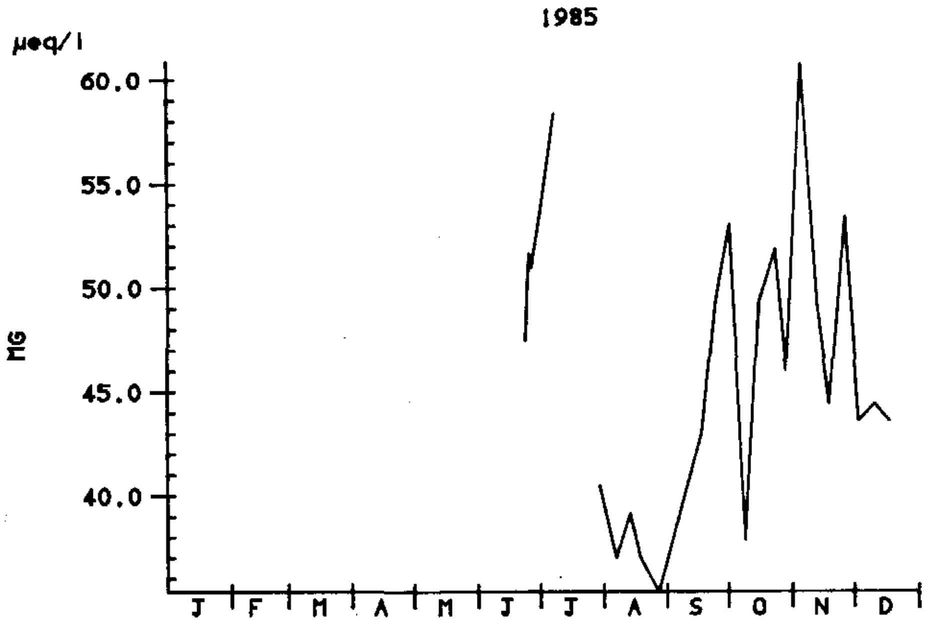
Figure 9

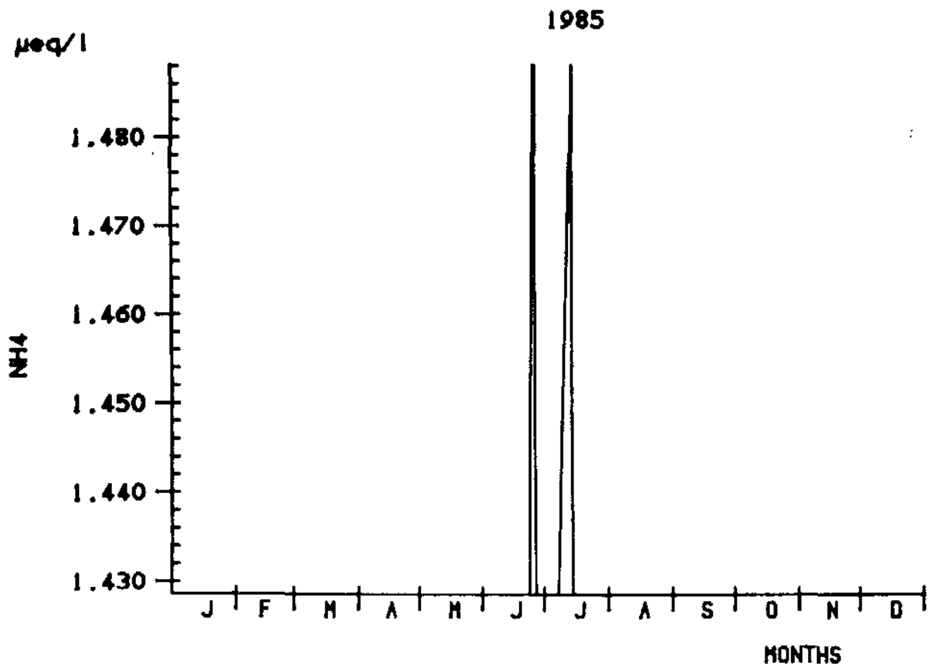
LLYN BRIANNE (LI2)

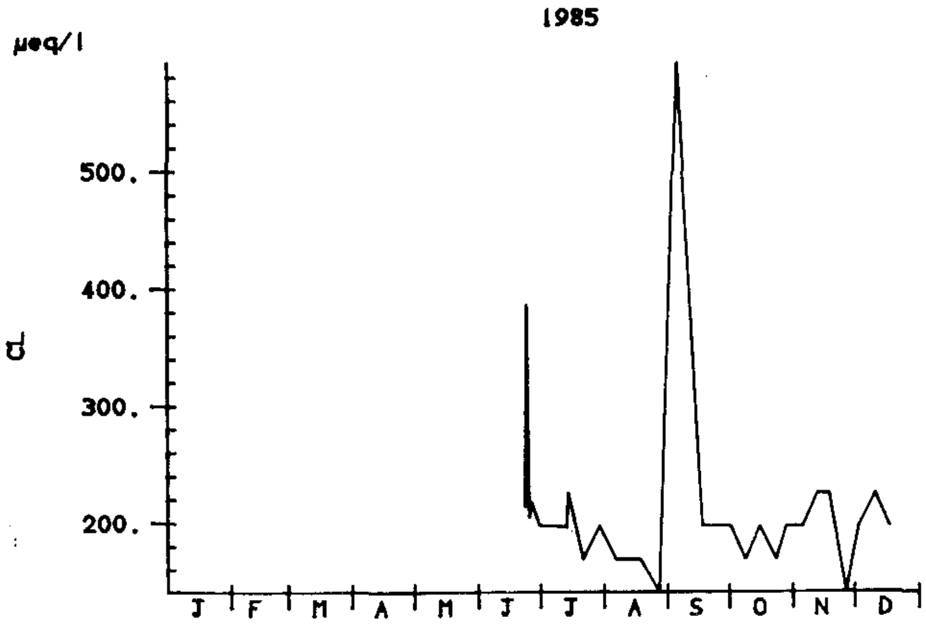


LLYN BRIANNE (LI2)









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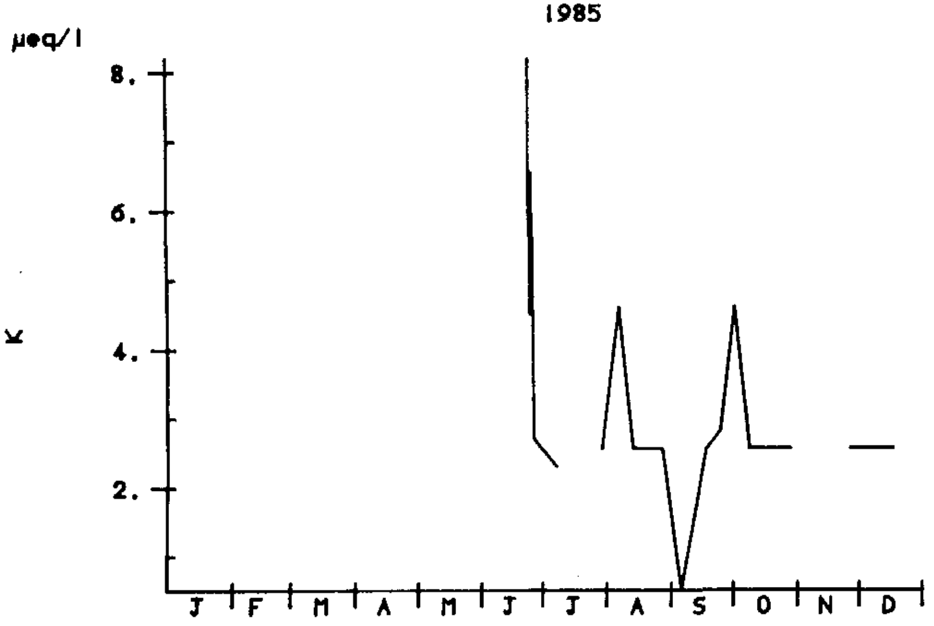
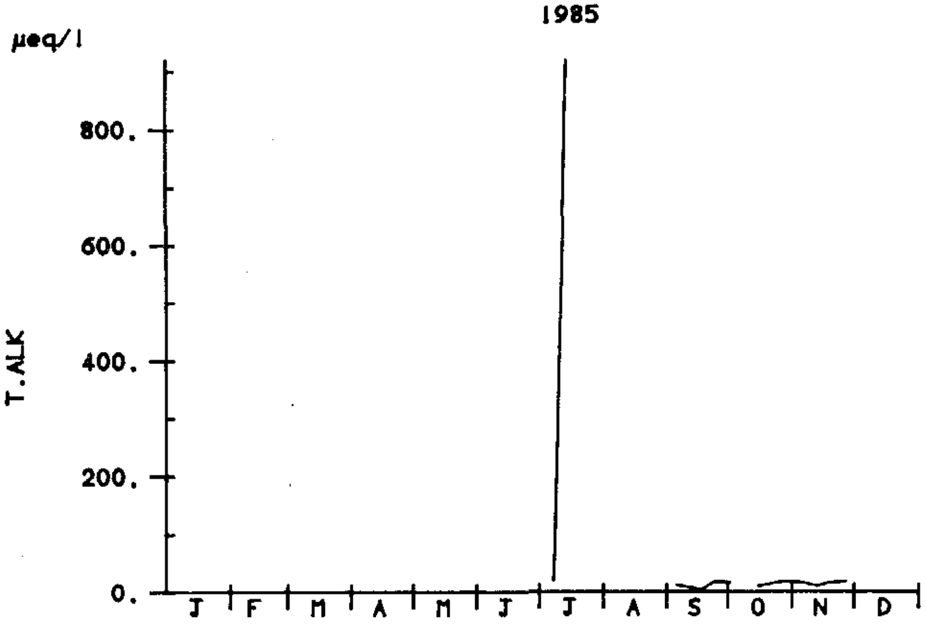
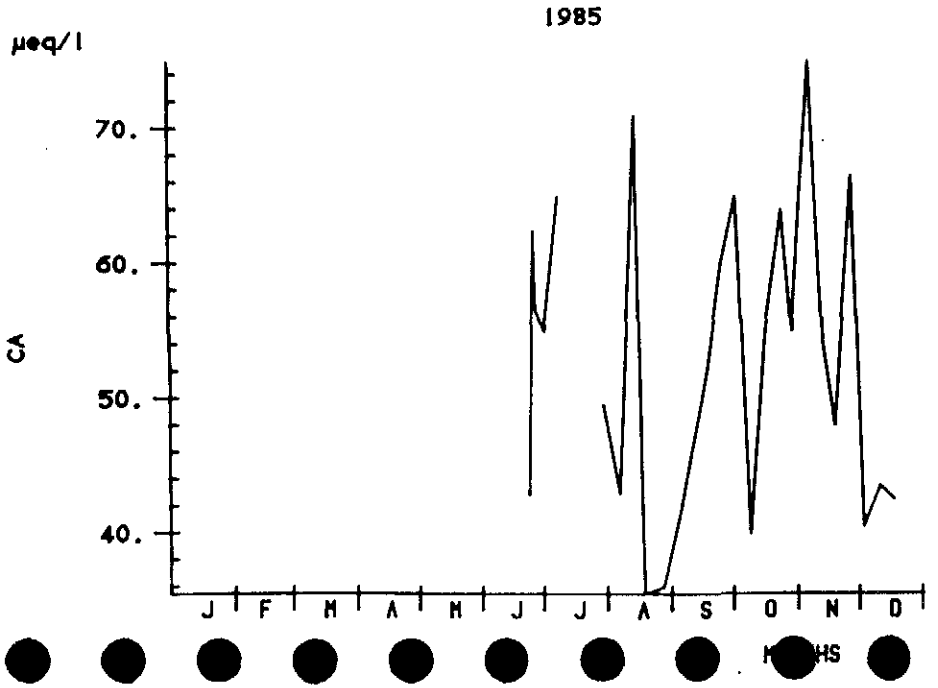
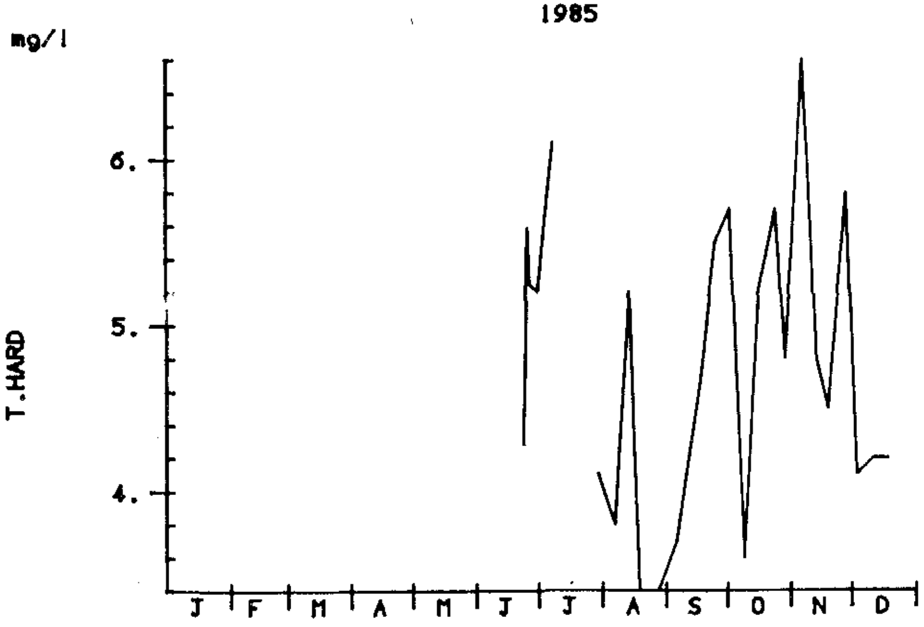
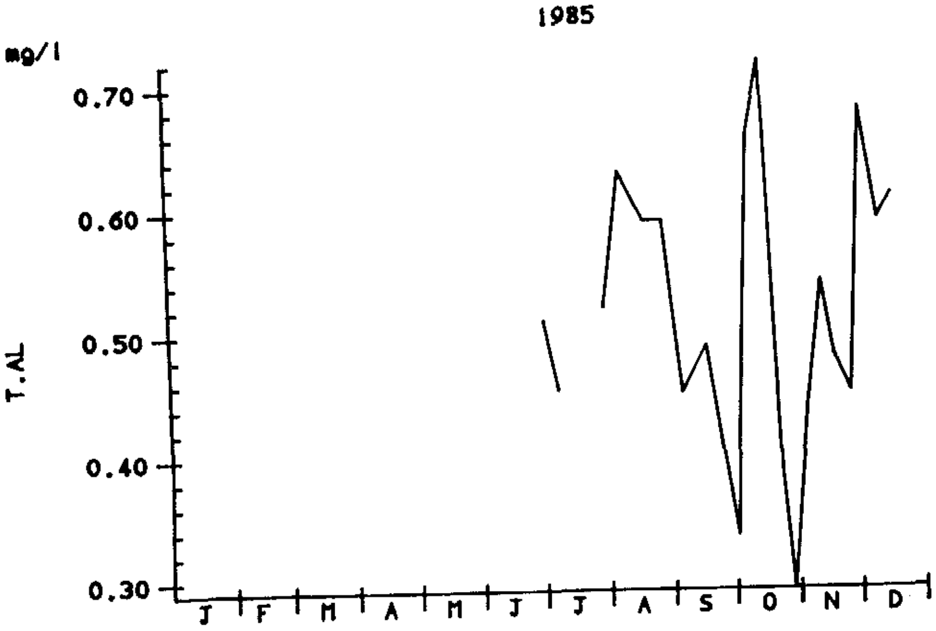


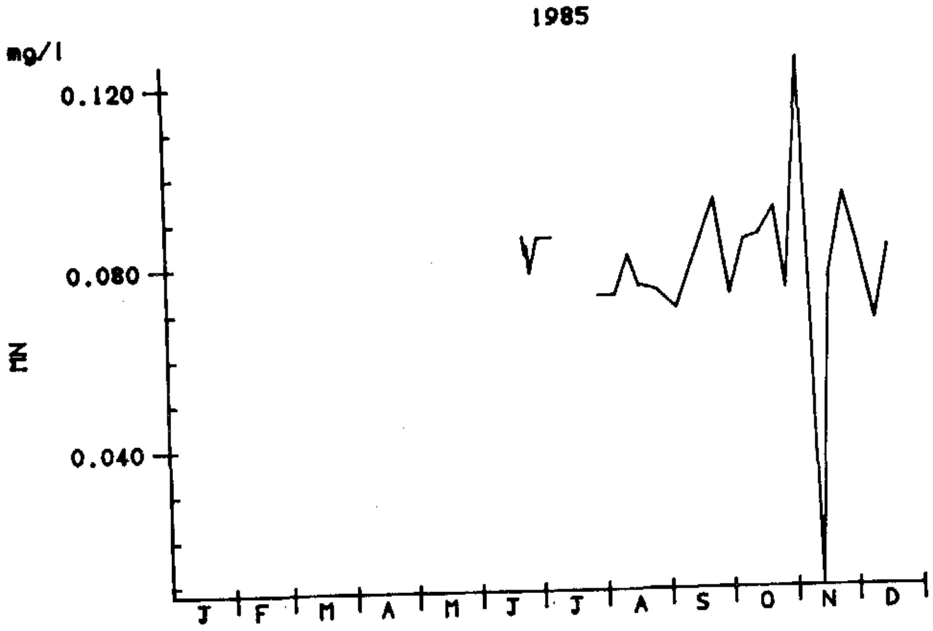


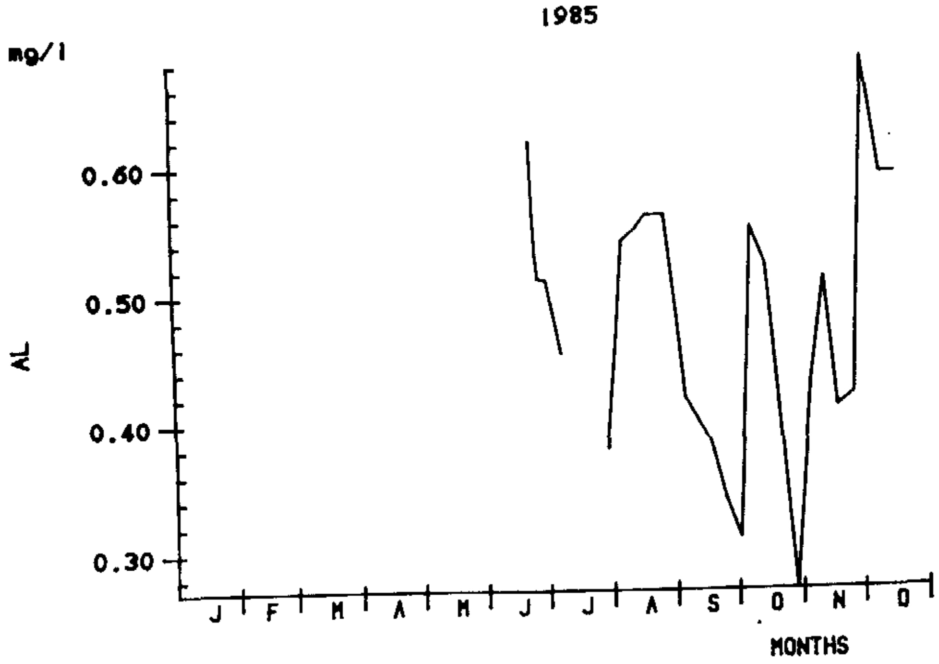


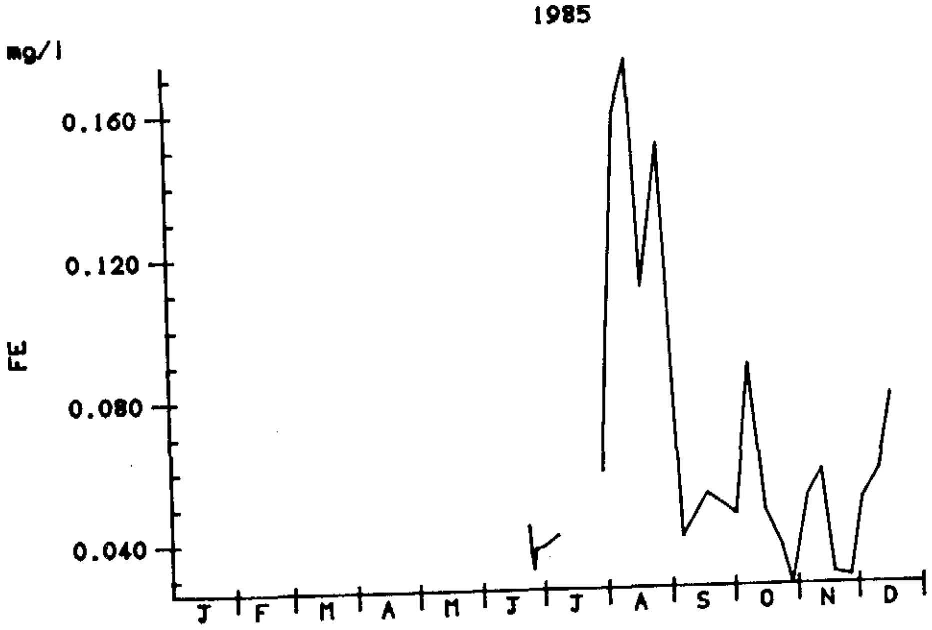


LLYN BRIANNE









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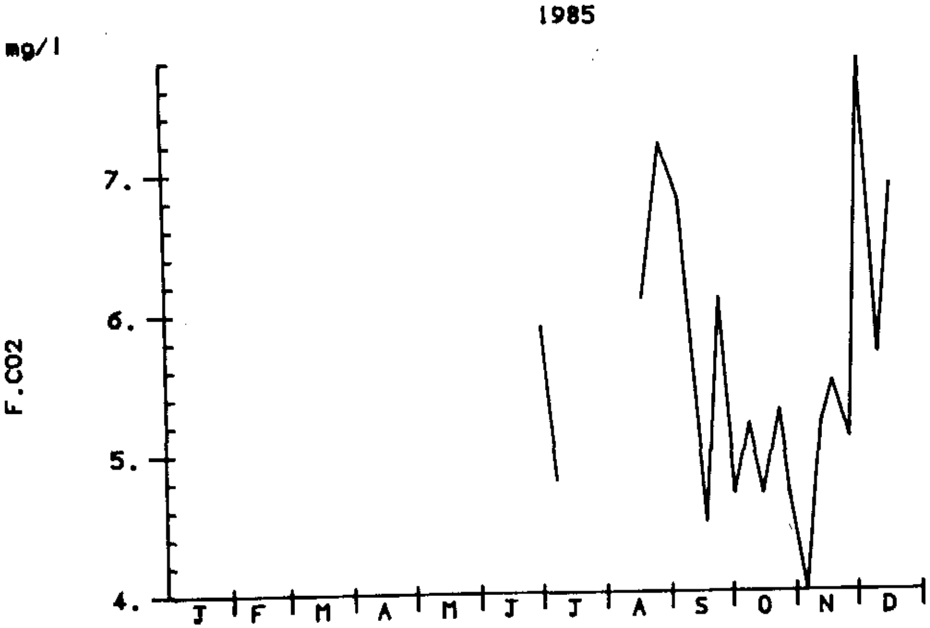

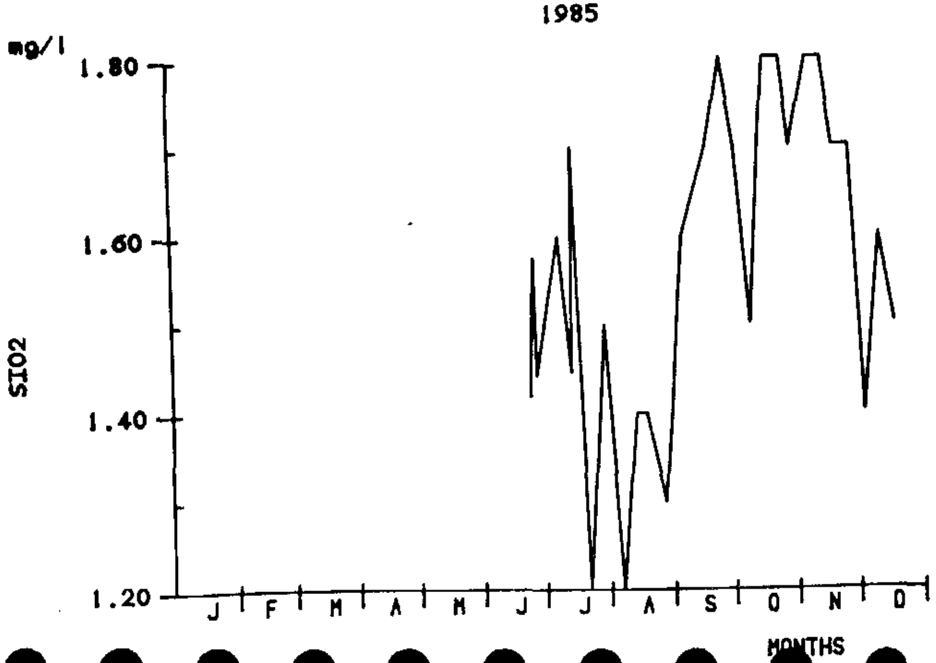

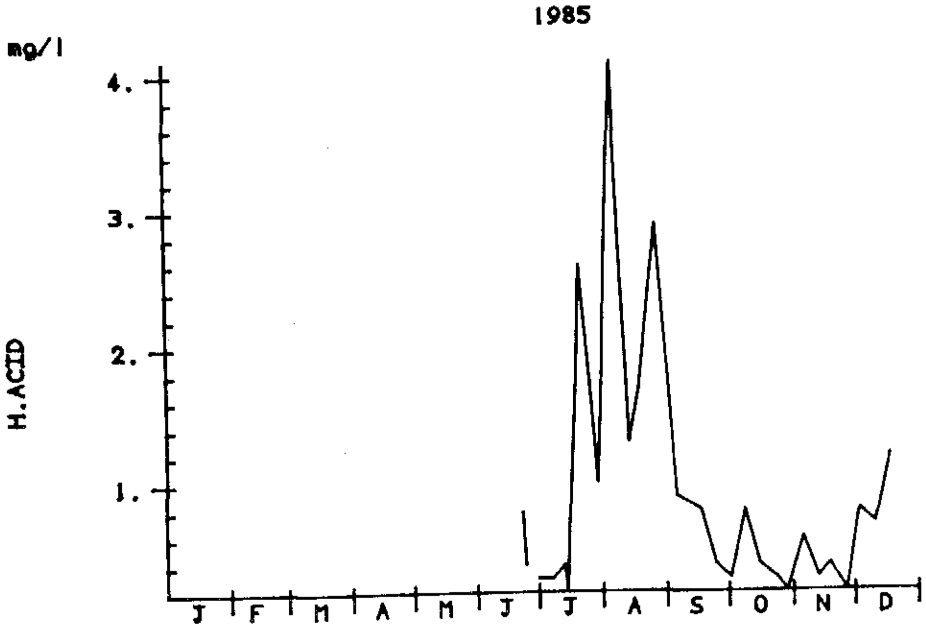

included merely for information. On the other hand, LI3 has been monitored since September 1984 (Figure 10). In summary, the patterns are very similar to those exhibited at LI1. pH and H^+ levels tend to exhibit acid conditions during the high rainfall/ high runoff periods. NO_3 levels also show peaks during the Winter when plant uptake is reduced. Likewise, the marine salts also show some evidence of a seasonal pattern with reduced concentrations in July to September 1985, as at LI1. Similarly, Ca, K, total hardness and total alkalinity patterns mirror those found in LI1, although K levels are lower and Ca and total hardness concentrations are occasionally much higher than at LI1. The latter might reflect a slightly greater buffering capacity as mentioned earlier. The patterns in aluminium concentration at LI3 are almost identical to that found in LI1 and thus high levels correspond to acid high runoff events.

Again, too few samples have been taken in LI4 since October 1985 to allow any sensible interpretation. Thus, conditions at LI8 are now reviewed (Figure 11). First, the availability of data since 1982 allows the determination of some seasonal trends which are probably common to all the afforested sites. Hence, pH and H^+ reveal clear seasonal patterns with peaks in acidity corresponding to the winter high rainfall and high runoff periods. More specifically, the obvious seasonal pattern in the two parameters is clearly lacking since mid - 1984 illustrating that periods atypical nature. Similarly, seasonal patterns in Ca and Mg concentrations with a clear Summer peak, also disappear in the latter part of the study period. However, in order to retain comparability further analysis is restricted to 1984 and 1985, but must be viewed in the context of its unusual nature.

Figure 10

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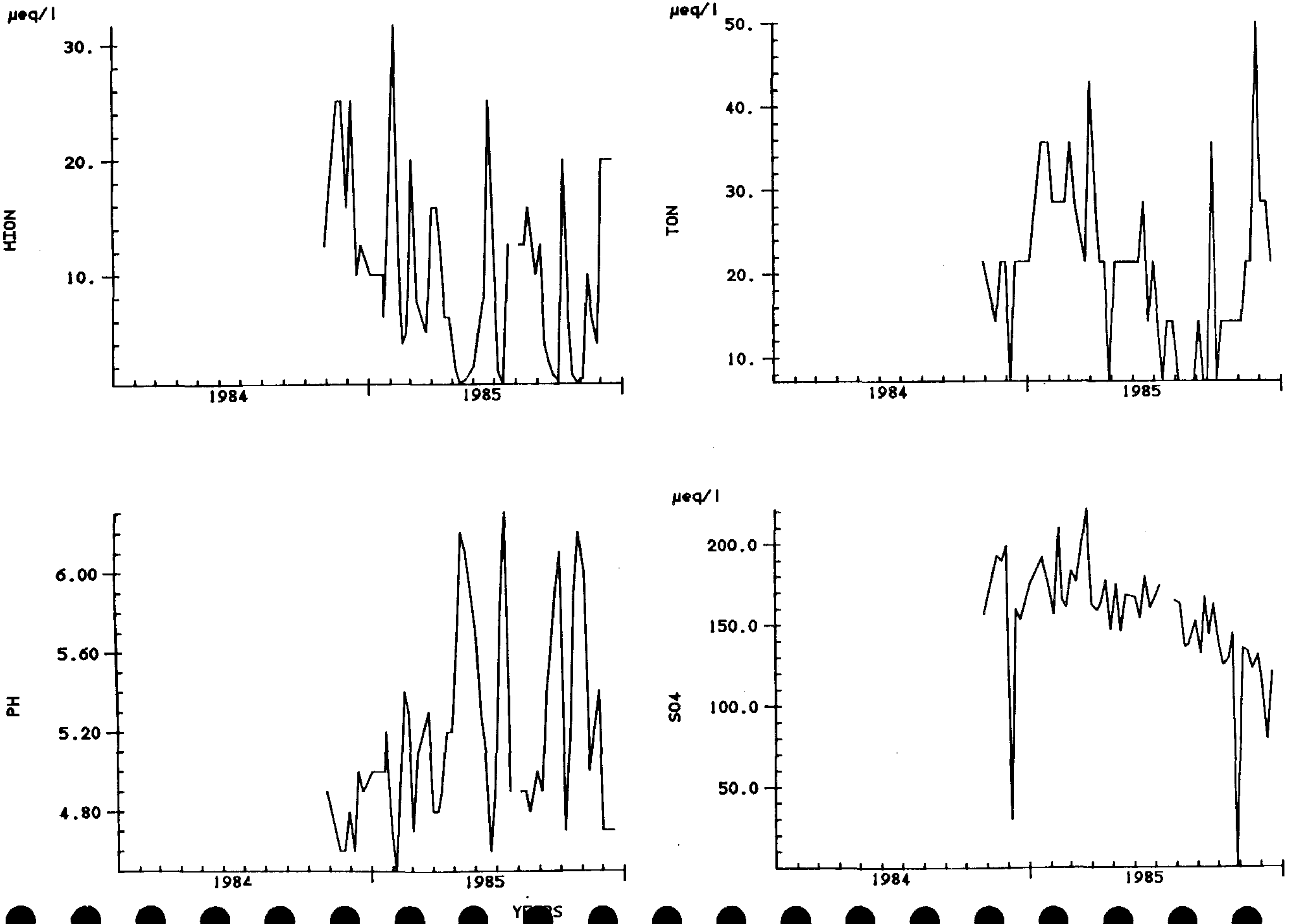

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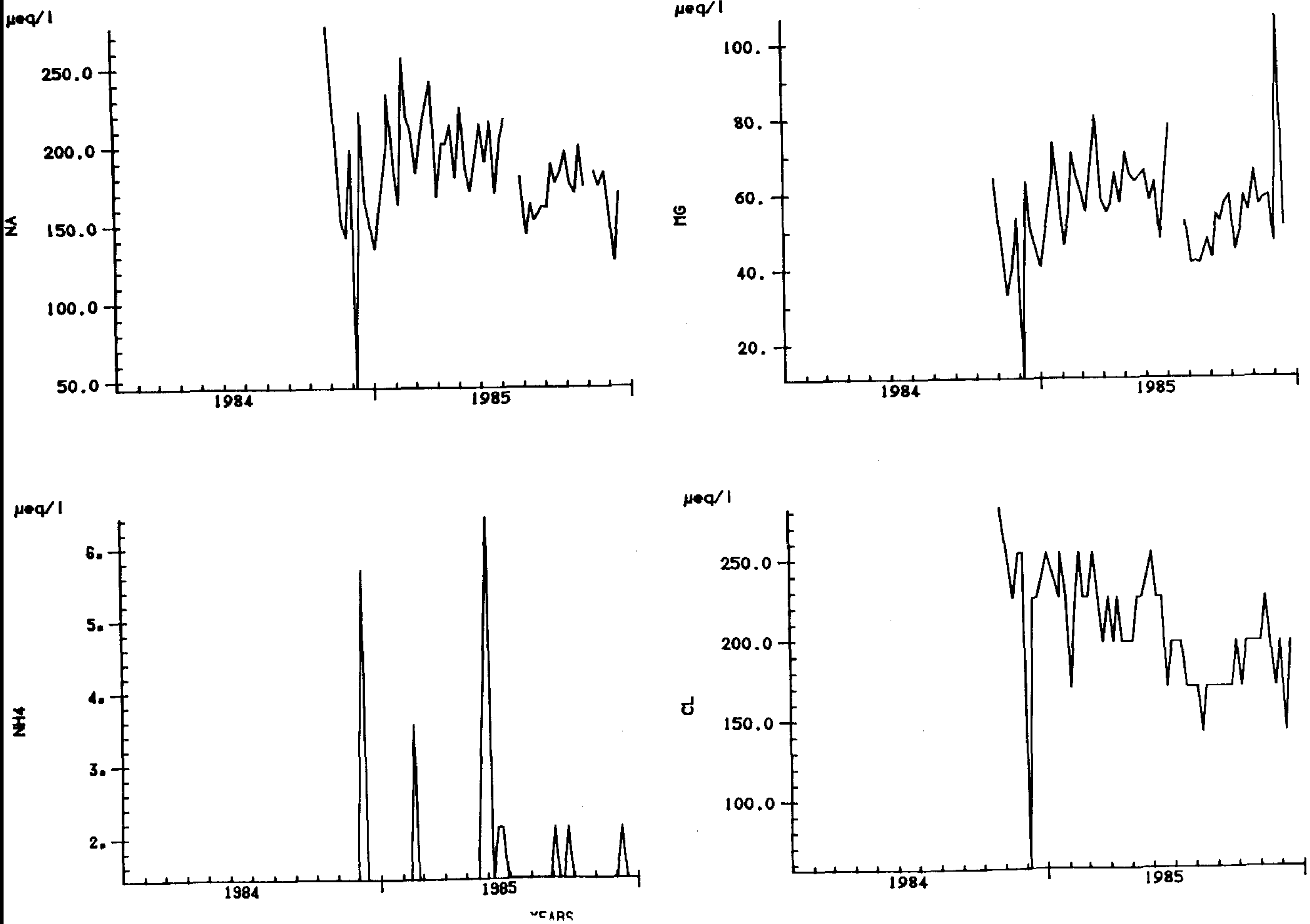

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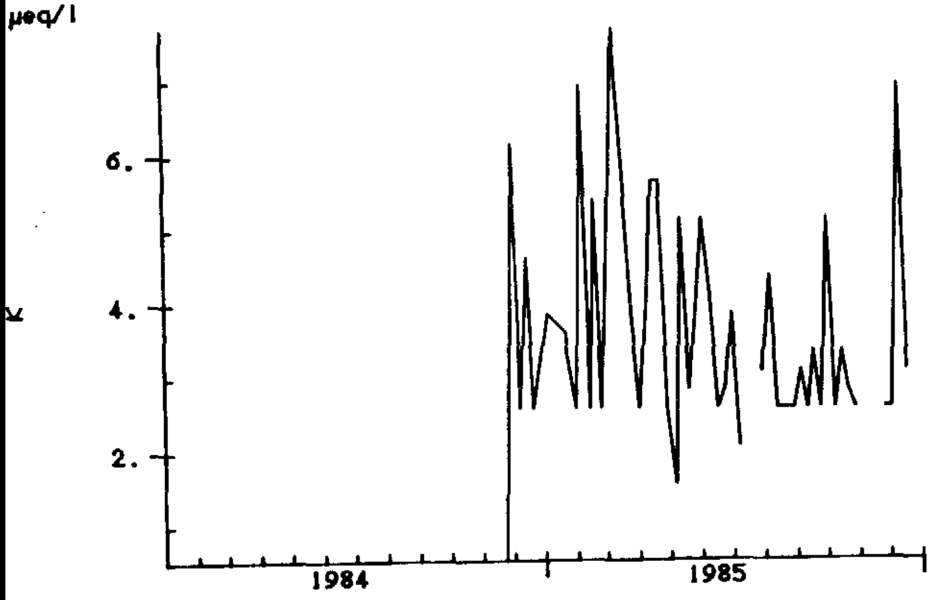
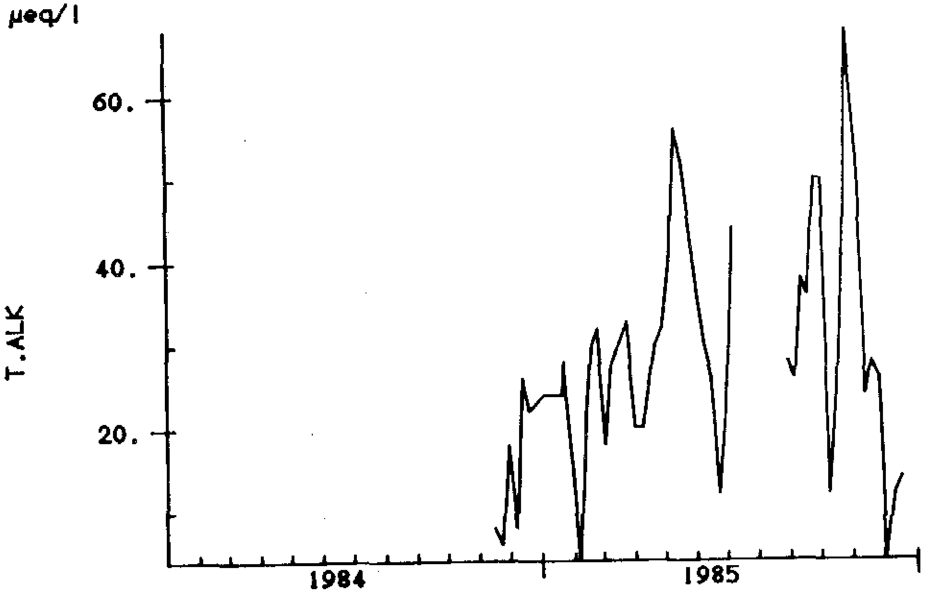
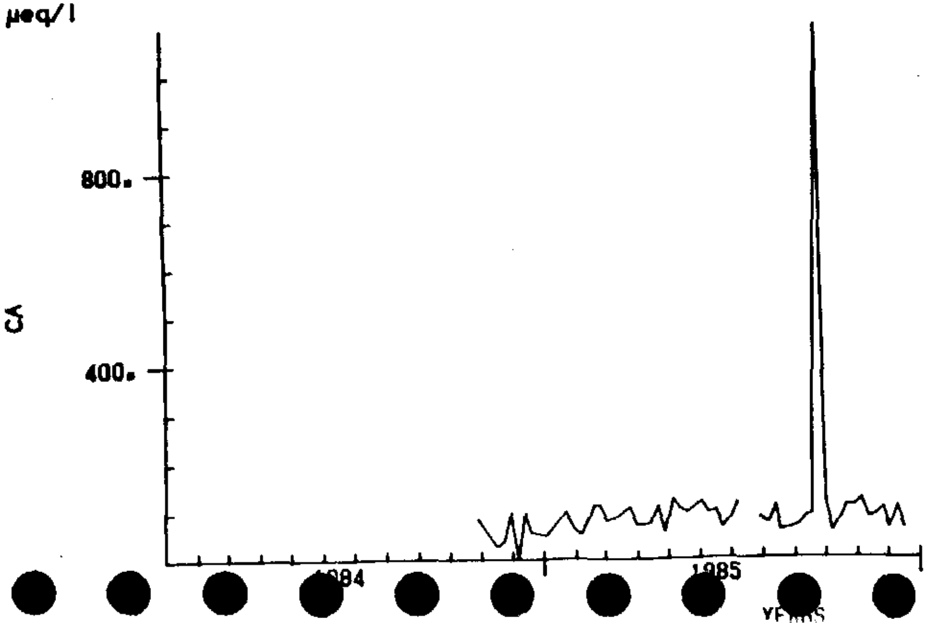
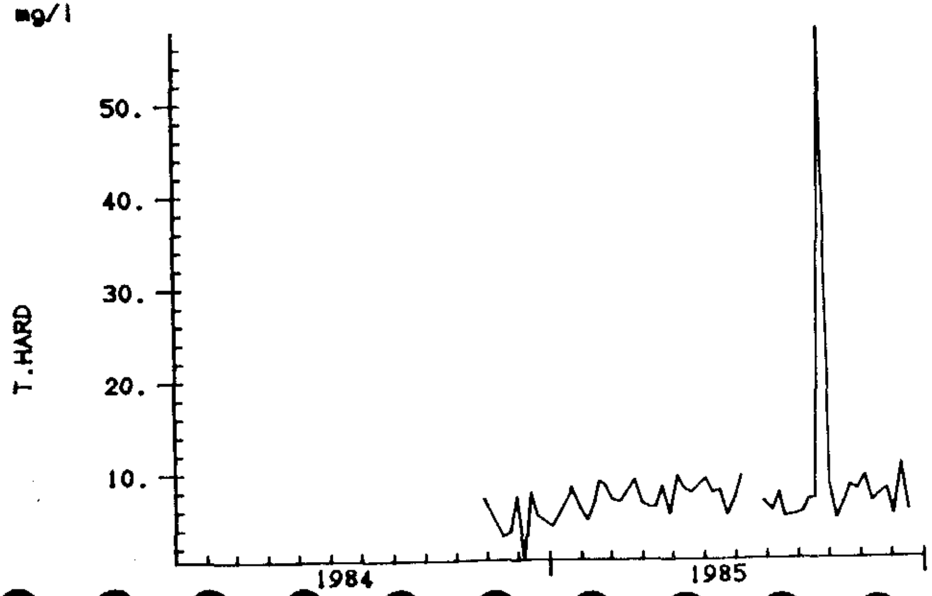
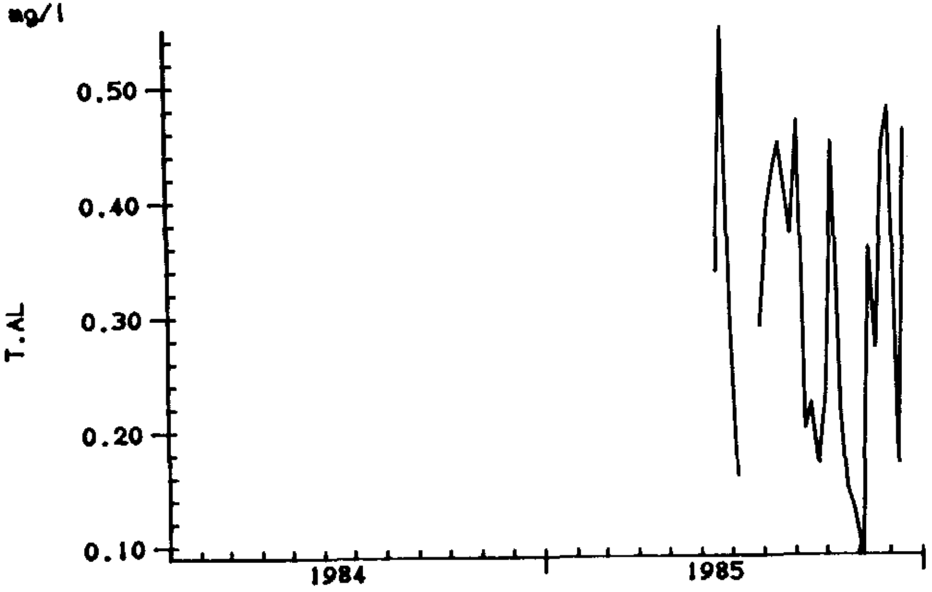


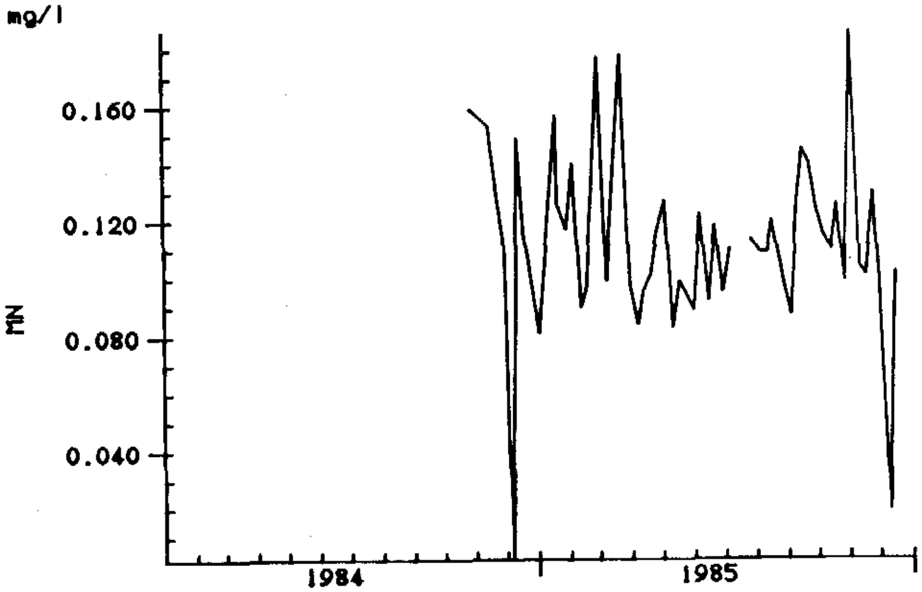


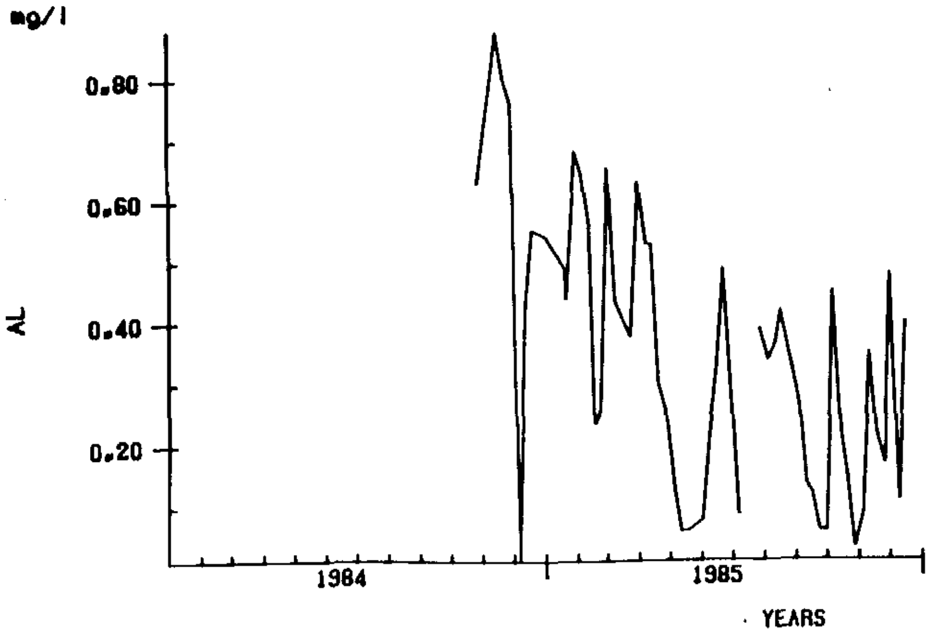


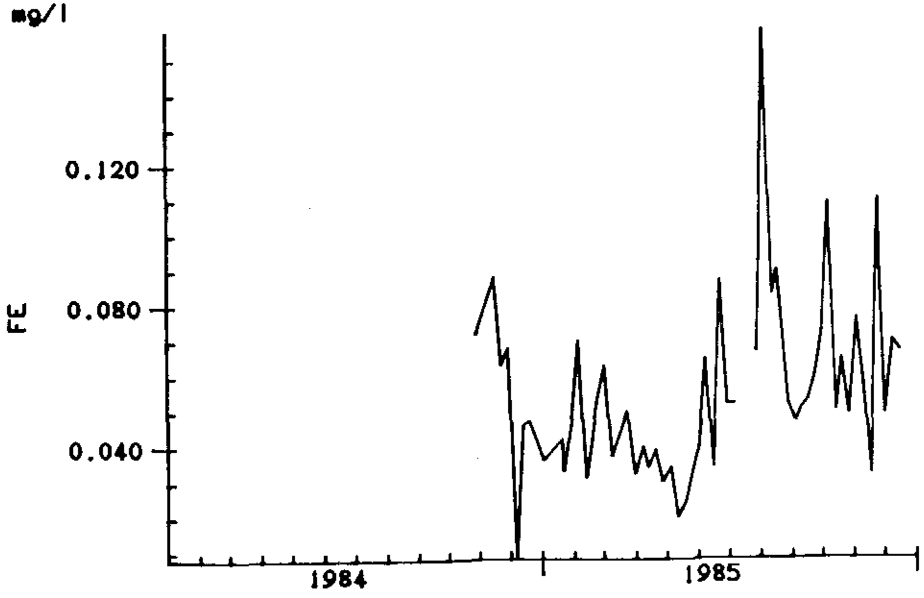


LLYN BRIANNE (LI3)









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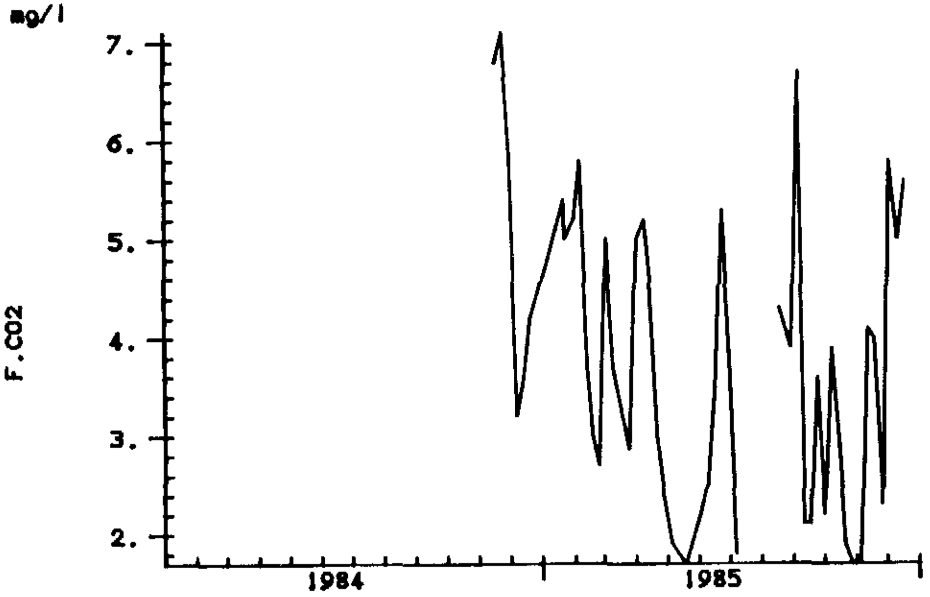
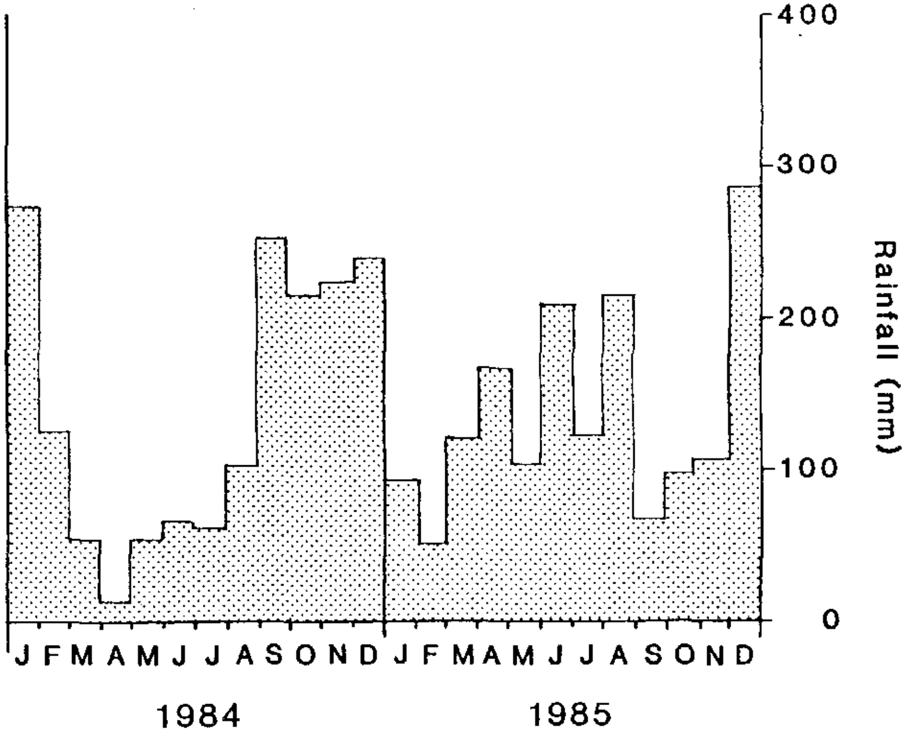
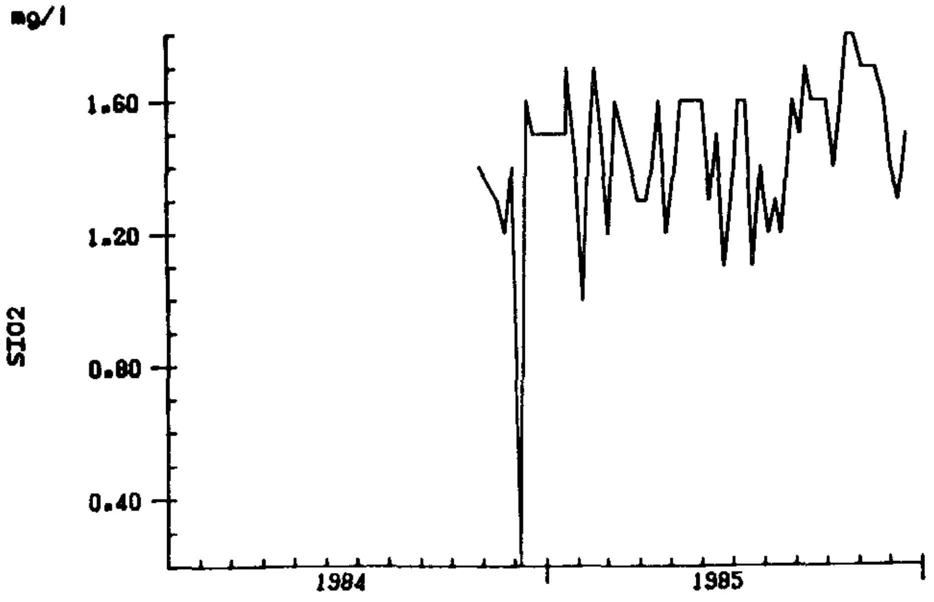
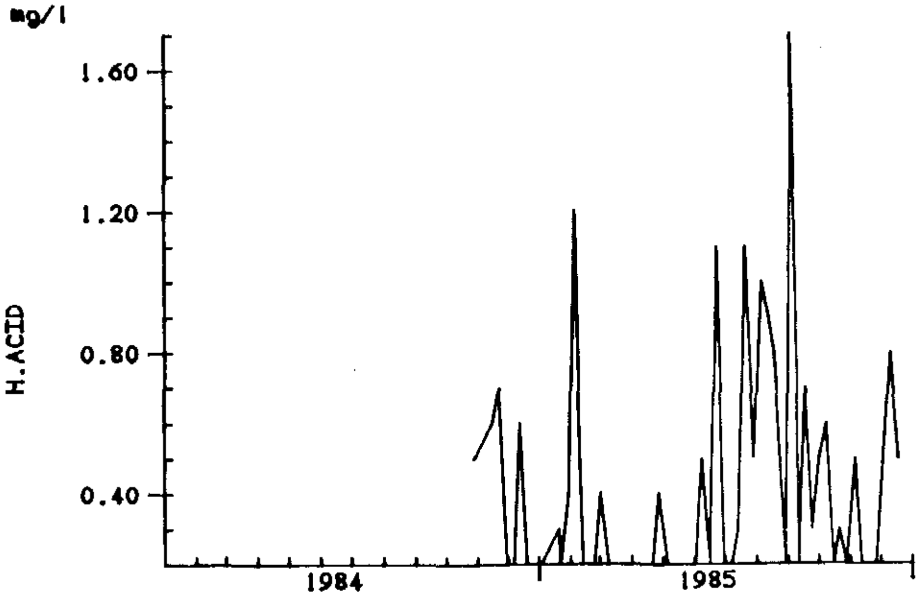








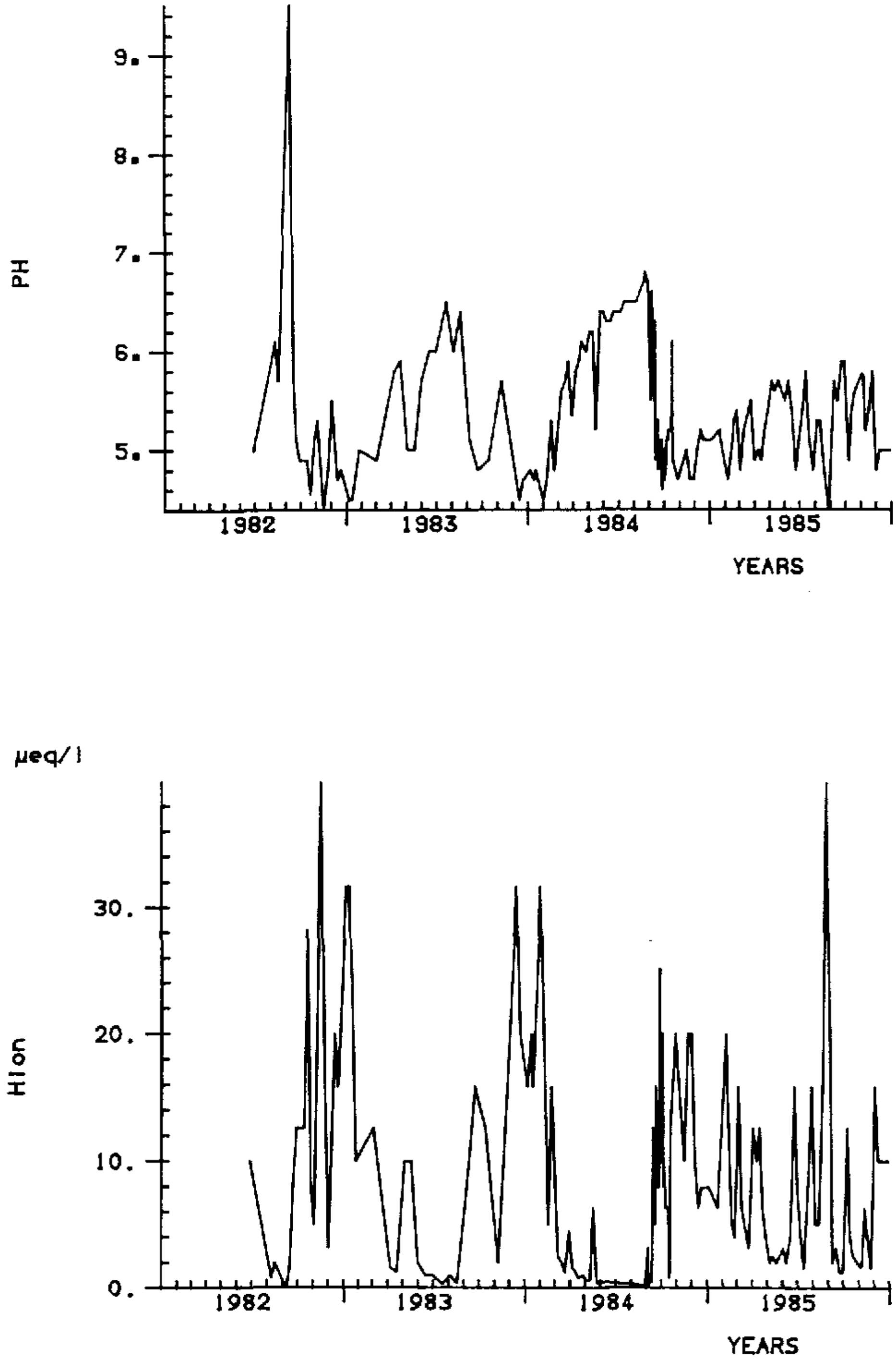
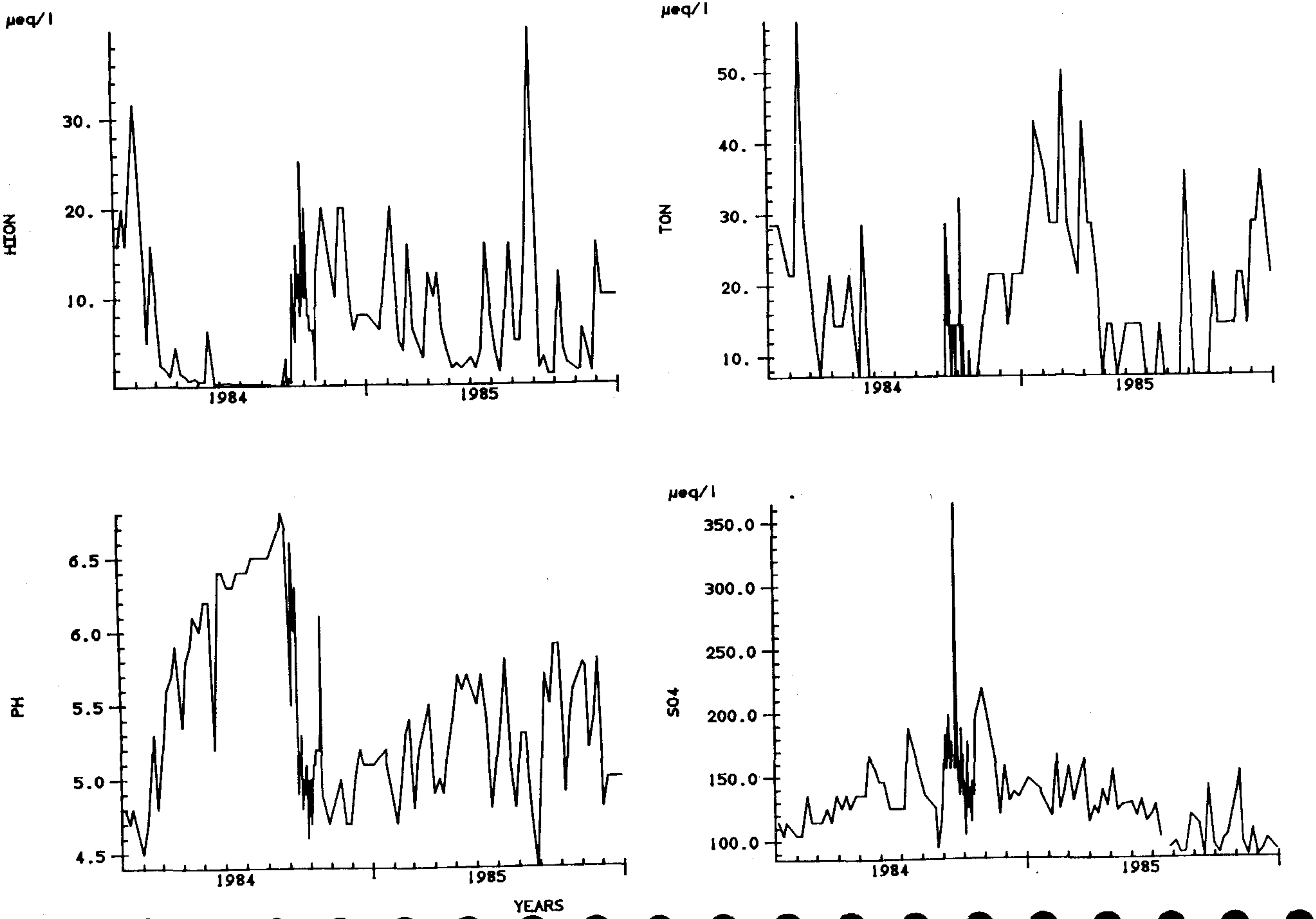


Figure 11a pH and H^+ patterns at LI 8 (1982 - 1985)

Figure 11b

LLYN BRIANNE (LI8)



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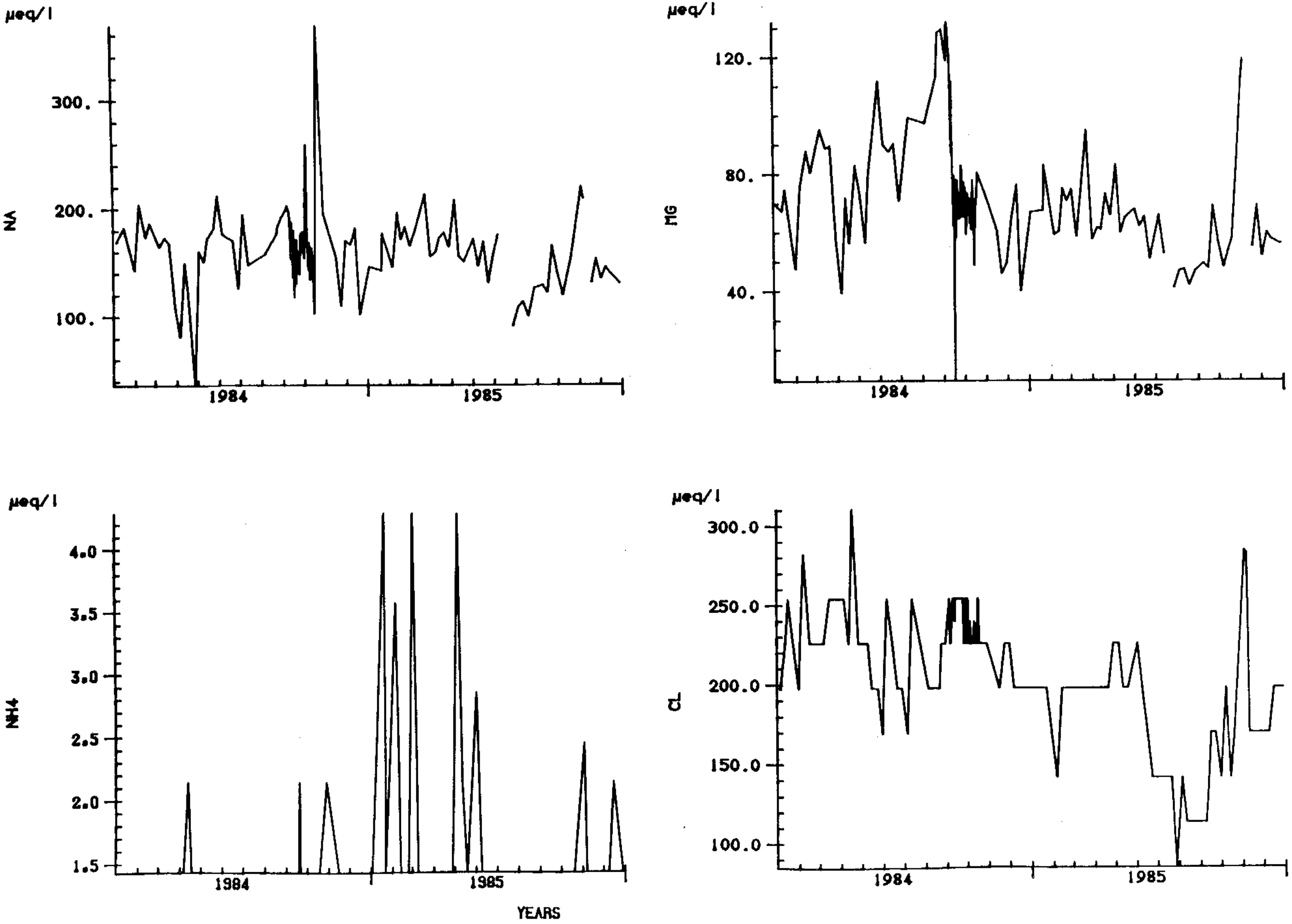

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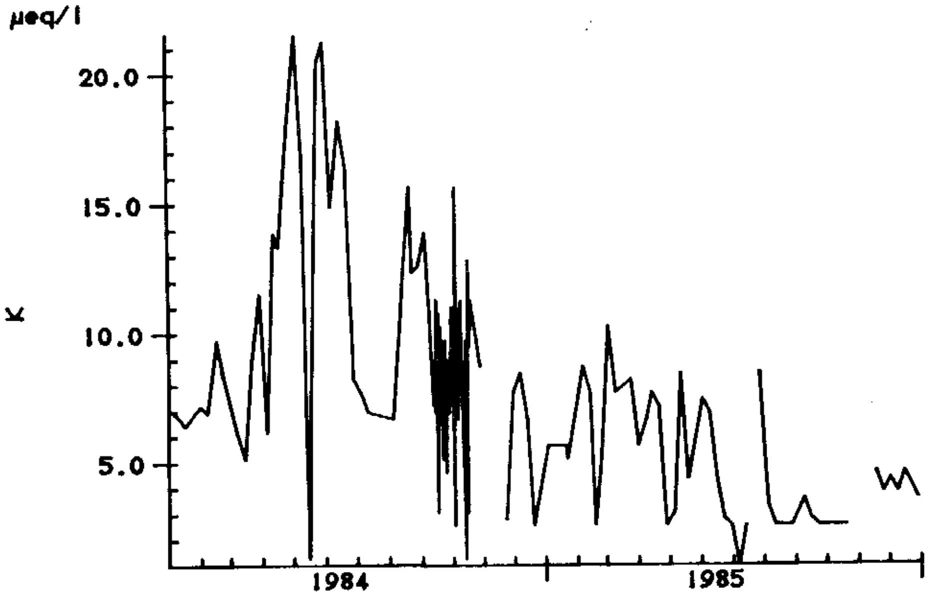

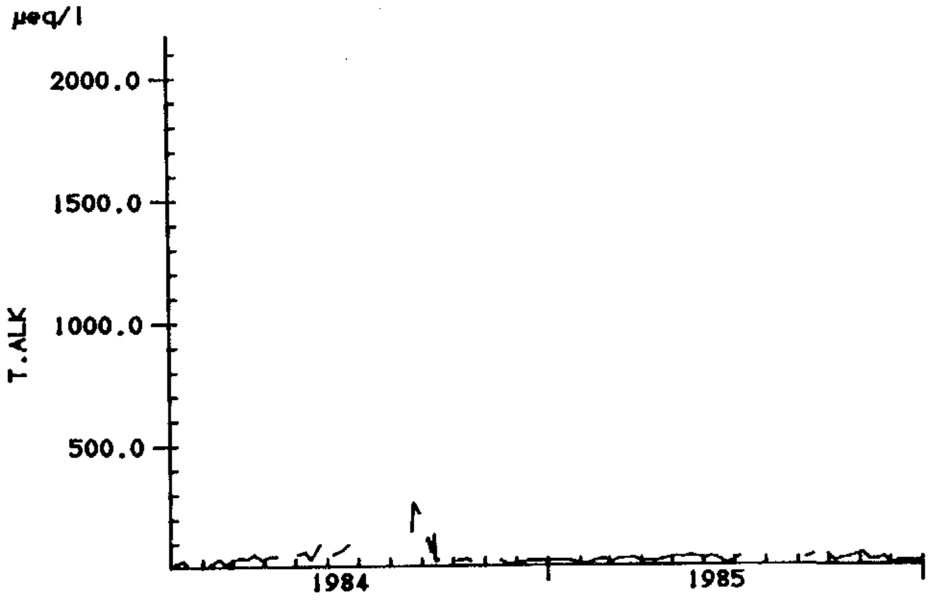

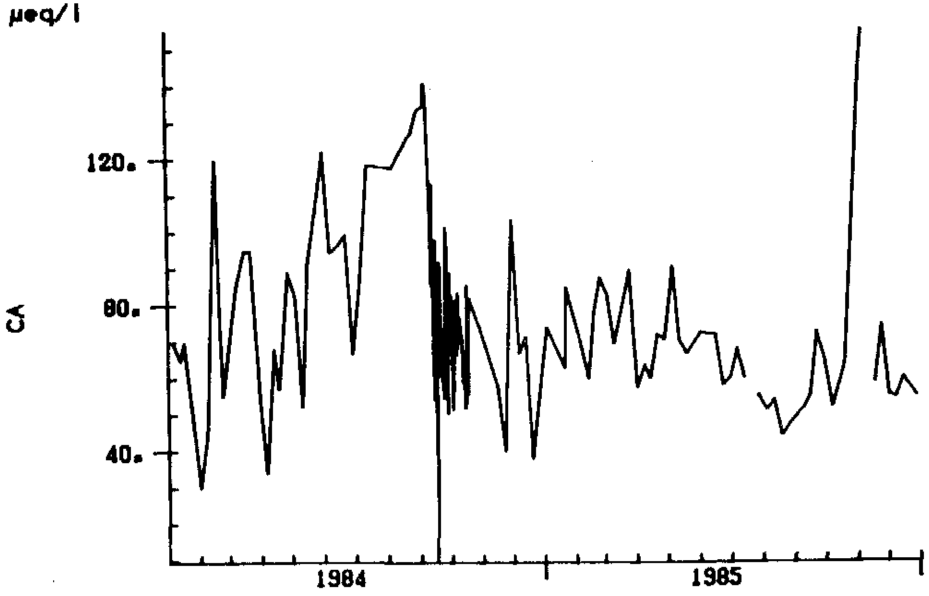

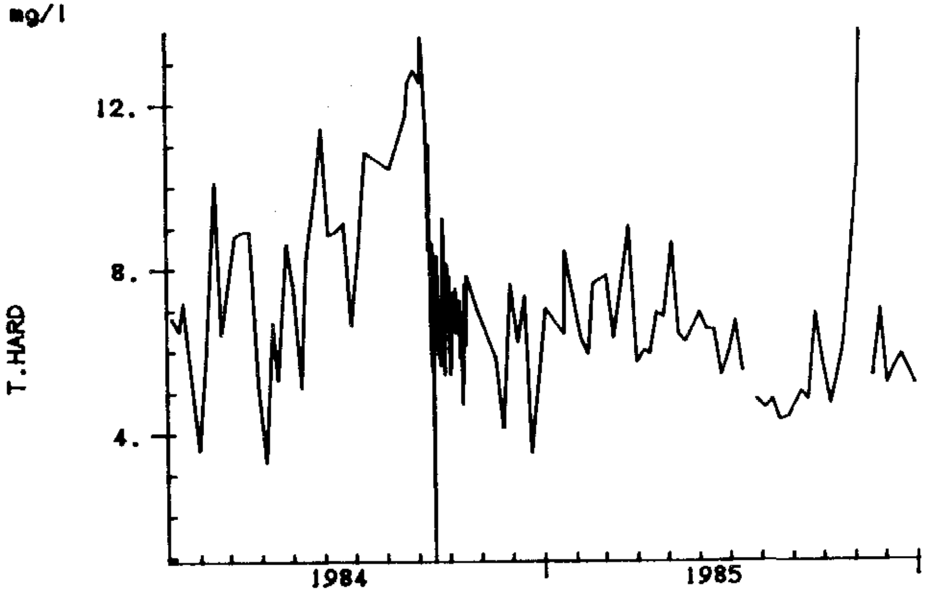

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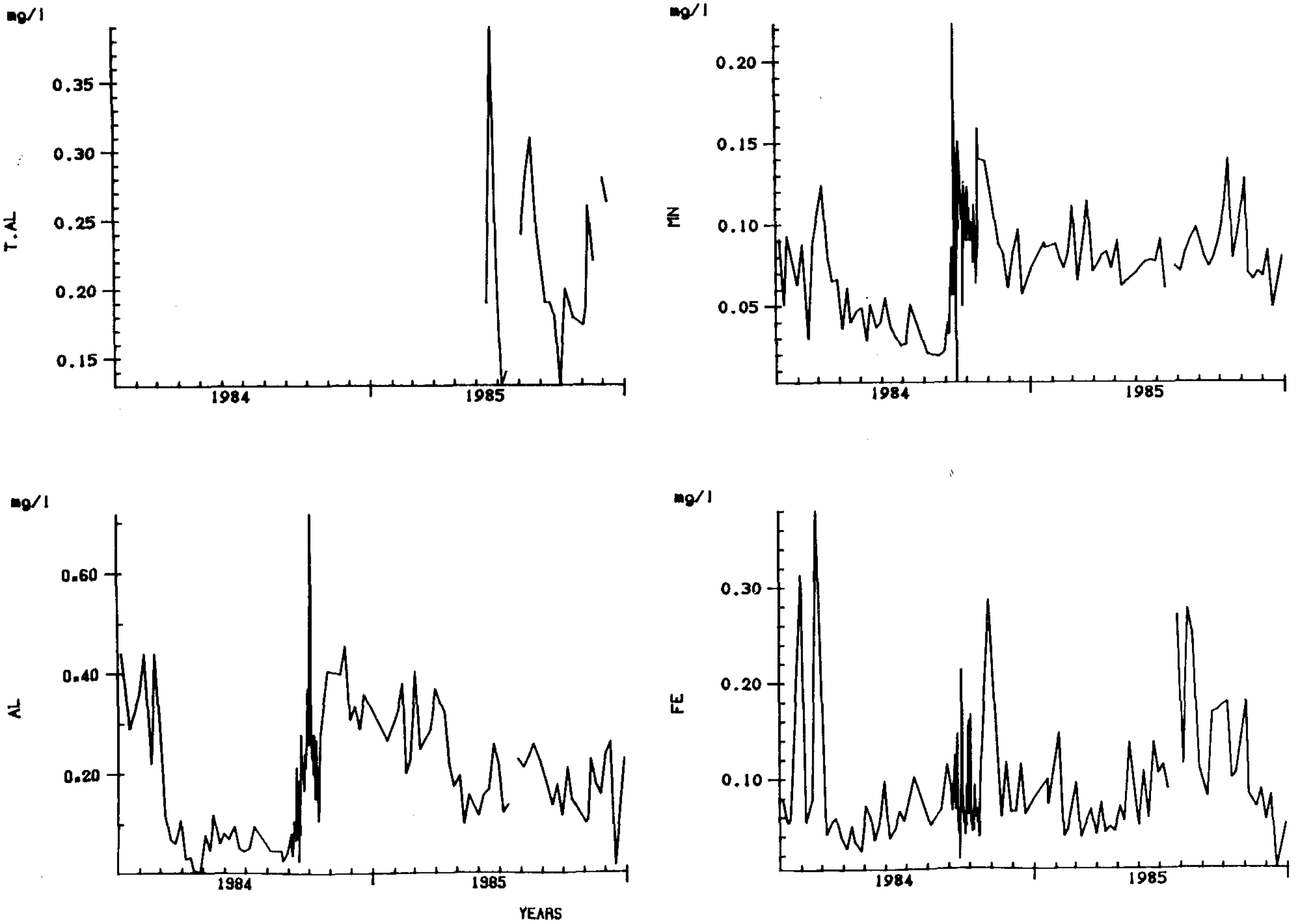

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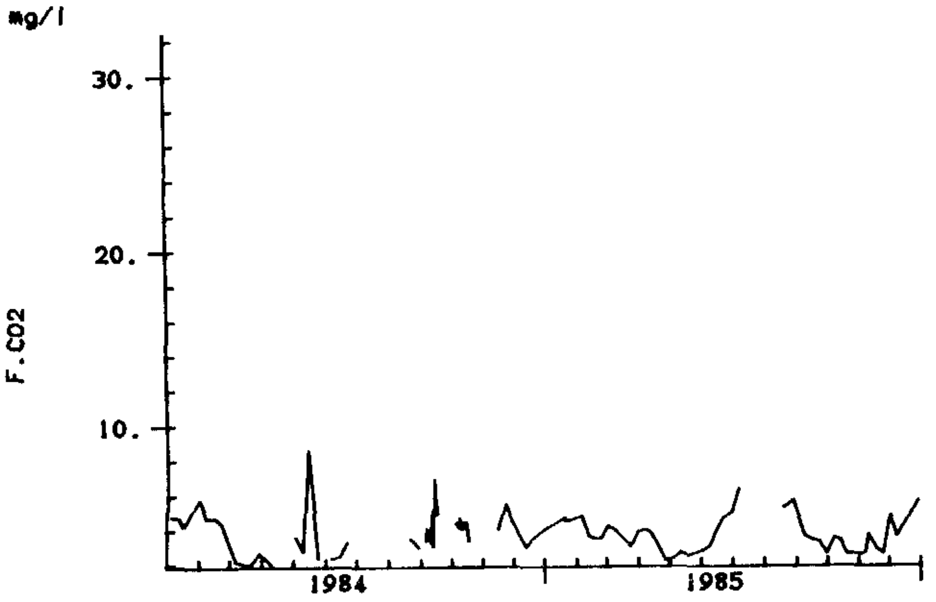
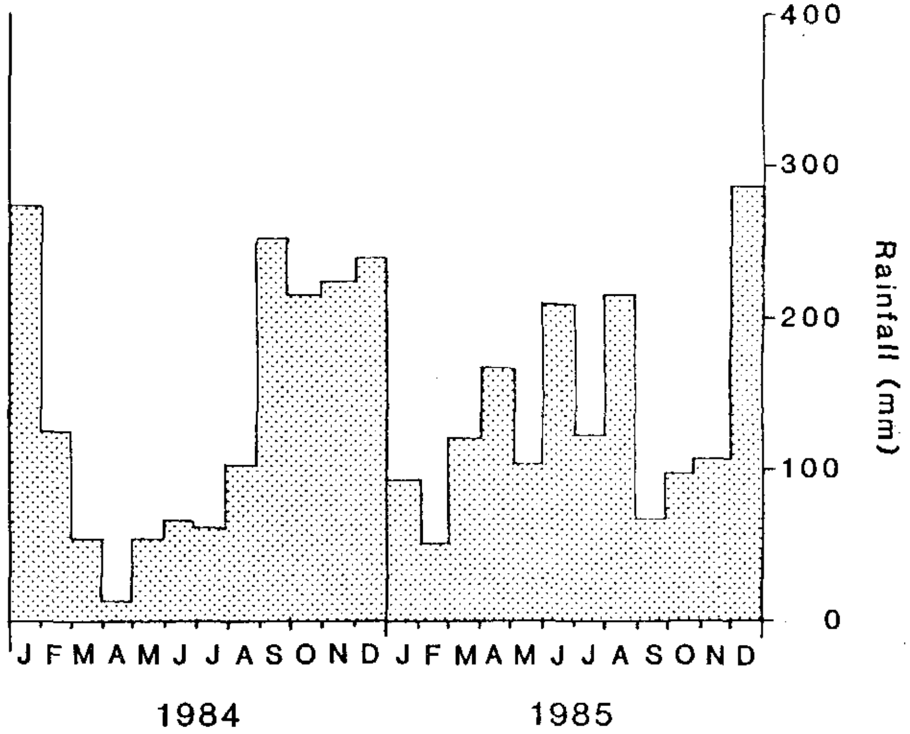
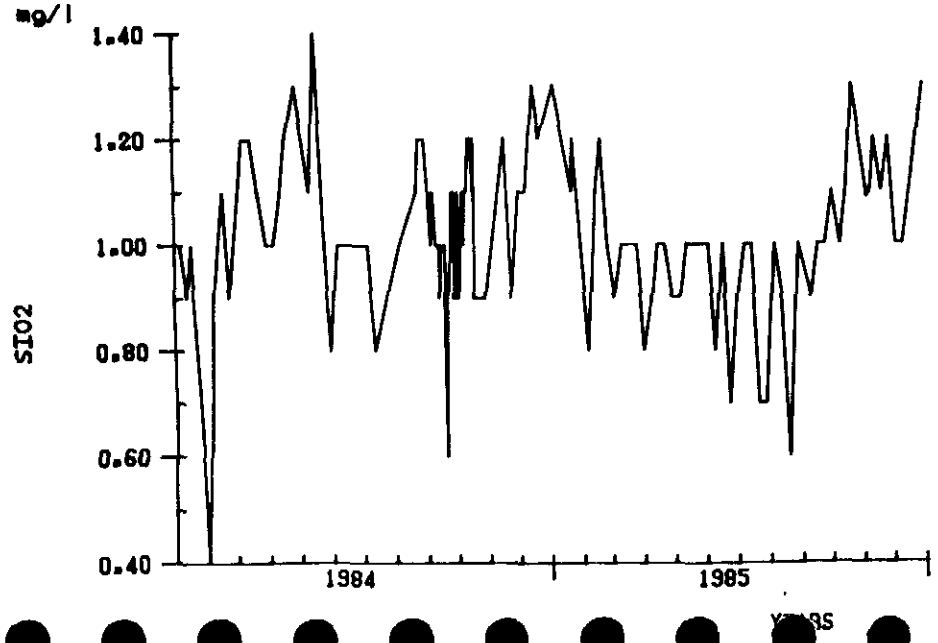
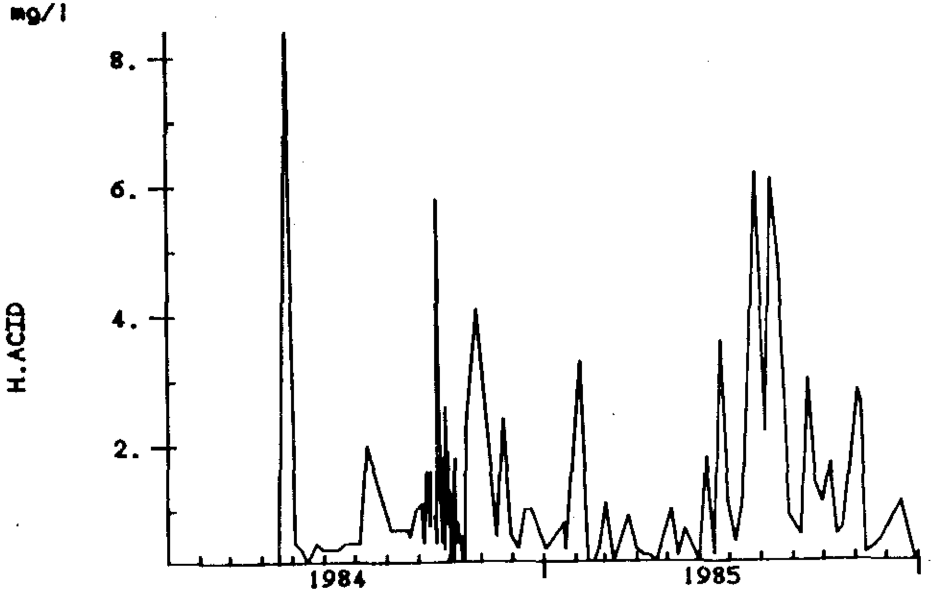








pH and H^+ levels again reflect the fluctuations in rainfall and runoff as at previous sites. In addition, the flushing effect suggested for September 1984 is confirmed. SO_4 levels meanwhile exhibit no real patterns although a peak was recorded during the high rainfalls of late 1984. NO_3 concentrations again exhibit a pattern of peaks corresponding to the Winter months as at previous sites. Similarly, the marine salts exhibit patterns almost identical to those found at LI1, as was the case for the terrestrially derived Ca and hardness concentrations, and dissolved aluminium.

Conclusion

In conclusion, afforestation has probably resulted in an approximate doubling of evapotranspirational losses (Law, 1956; Calder, 1985). In addition its presence can probably be linked to several other mechanisms contributing to streamwater acidity (Bache, 1983; Nilsson _et_ _al_., 1982; Harriman and Morrison, 1982; Neal _et_ _al_., 1986). These include the more effective scavenging of air pollutants, stemflow and throughfall contamination, the effects of acid leaf litter, increased base cation uptake, the effects of forest soil characteristics and forestry ploughing and drainage practices. Moreover, a forestry land use can encourage the generation of more rapid hydrological runoff processes such as overland flow, macropore flow and shallow throughflow. As a result of the above, residence times are reduced especially during storms, and baseflow contributions are reduced at all times due to evapotranspiration (UKAWRG, 1986). Small catchments such as the ones being studied are also more prone to fast reacting surface and shallow sub-surface runoff processes.

Clearly, residence times and the extent of water - rock contact are important in determining the stream chemistry. In general, baseflow is characterised by low acidity and Ca bearing streamwaters, and stormflow is characterised by high acidity and Al bearing waters. During storms the processes determining stream chemistry appear to be limited to the flushing and mixing of waters from the near surface soil layers, fed by dry deposition washed from the trees. On the other hand, under normal Summer low flow conditions, soil moisture deficits are high and water is supplied from the deeper inorganic horizons. During the Autumn storm period, however, the deficit decreases and streamwater is probably supplied from both soil matrix and macropore flow, mainly from the upper organic soil horizons.

Thus, conditions in all of the afforested catchments are similar, producing similar responses to rainfall inputs. The major differences in response can presumably be related to the juvenile status of the forest in the case of LI8. In the case of LI3 however, the link with the effects of bankside clearance and a slightly improved stream chemistry remains necessarily speculative and awaits further information about the catchment soils in particular.

Acidified moorland catchments (CI3, CI4, CI5, CI6, UC4).

CI3 is the largest of the Camddwr catchments (Table 1) and consequently one of the least steep. Table 10a indicates that CI3 is generally only slightly less acid than the afforested catchments, with the exception of LI8, with pH averaging 5.27 and H^+ 8.5 ueq l^{-1}. Hence, despite the reduced evapotranspirational losses of the moorland (typically 50% less) and its reduced scavenging capacity, the catchment is still prone to acid events. Indeed, 25% of all samples taken exhibited a pH of 5.0 or less. Tables 11A and 12a both indicate that

Table 10a CI3 streamwater quality (1984-5)

```
              N     N*      MEAN    MEDIAN    TRMEAN     STDEV    SEMEAN               MIN       MAX        Q1        Q3
T_CU         24     53   0.00229   0.00200   0.00232   0.00081   0.00016    T_CU   0.00200   0.00400   0.00200   0.00300
T_ZN         25     52   0.01076   0.01000   0.01057   0.00521   0.00104    T_ZN   0.00400   0.02200   0.00600   0.01400
T_CD         25     52   0.00102   0.00100   0.00100   0.00008   0.00002    T_CD   0.00100   0.00140   0.00100   0.00100
T_AL         26     51   0.10831   0.10550   0.10558   0.03416   0.00670    T_AL   0.04100   0.22100   0.08025   0.13050
T_PB         24     53   0.00343   0.00200   0.00329   0.00205   0.00042    T_PB   0.00200   0.00800   0.00200   0.00500
T_CR         25     52   0.00300   0.00300   0.00300   0.00000   0.00000    T_CR   0.00300   0.00300   0.00300   0.00300
T_MN         25     52   0.05260   0.05100   0.05257   0.00995   0.00199    T_MN   0.03100   0.07500   0.04600   0.05950
T_FE         25     52    0.1142    0.0790    0.0985    0.1103    0.0221    T_FE    0.0490    0.5420    0.0560    0.1235
T_NI         25     52   0.00320   0.00300   0.00309   0.00071   0.00014    T_NI   0.00200   0.00600   0.00300   0.00300
PH           76      1   5.27000    5.2000    5.2700    0.5062    0.0581    PH      4.1000    6.2000    5.0000    5.5000
COND         76      1    35.000     37.00     35.00     15.03      1.72    COND     24.00    53.000     27.40     40.00
TURB         10     67     0.764     0.711     0.799     0.372     0.113    TURB     0.000     1.243     0.592     1.132
AMM_N        77      0    1.5154    1.4286    1.4605    0.2830    0.0328    AMM_N   1.4286    2.8571    1.4286    1.4286
TON          76      1     14.60      7.14     12.61     41.71      4.78    TON       7.14    100.00      7.14     21.43
NO2          77      0   0.28570   0.28570   0.28570   0.00000   0.00000    NO2    0.28570   0.28570   0.28570   0.28570
TH           69      8     4.642     4.400     4.583     1.106     0.133    TH       3.100     8.200     3.800     5.300
FCO2         58     19     3.822     3.000     3.311     3.204     0.421    FCO2     1.000    20.800     2.700     3.700
TA           55     22     31.99     29.97     31.83     15.16      2.04    TA        2.00     69.94     21.98     41.96
CL           77      0    145.91    141.04    145.36     40.44      4.61    CL       76.93    225.67    112.84    169.25
OPO4         76      1   0.02014   0.02000   0.02000   0.00115   0.00013    OPO4   0.02000   0.03000   0.02000   0.02000
SIO2         77      0    0.8546    0.8000    0.8335    0.2703    0.0308    SIO2    0.4332    1.8000    0.7000    1.0000
SO4          72      5     94.99     93.74     94.56     16.15      1.90    SO4      63.32    131.65     82.30    105.17
NA           68      9    138.65    136.97    136.98     30.30      3.67    NA       77.84    277.86    118.21    153.28
K            67     10     5.211     4.359     4.870     3.305     0.404    K        1.795    21.794     2.564     7.179
CU           69      8   0.00254   0.00200   0.00242   0.00140   0.00017    CU     0.00100   0.00800   0.00200   0.00300
MG           69      8     53.92     51.81     53.20     13.53      1.63    MG       33.72     94.98     43.86     60.90
CA           69      8     42.97     40.42     42.48      9.37      1.13    CA       29.44     73.35     36.43     49.15
ZN           69      8   0.01292   0.01100   0.01236   0.00736   0.00089    ZN     0.00200   0.04400   0.00800   0.01600
CD           69      8   0.00163   0.00100   0.00126   0.00217   0.00026    CD     0.00080   0.01300   0.00100   0.00100
AL           69      8   0.12165   0.10400   0.11663   0.06923   0.00833    AL     0.02200   0.37700   0.06650   0.16100
PB           69      8   0.00772   0.00500   0.00660   0.00827   0.00100    PB     0.00200   0.04500   0.00200   0.01100
CR           67     10   0.00276   0.00300   0.00284   0.00065   0.00008    CR     0.00100   0.00310   0.00300   0.00300
MN           69      8   0.06423   0.05700   0.06111   0.04171   0.00502    MN     0.00400   0.25000   0.04350   0.07100
FE           69      8    0.0959    0.0570    0.0663    0.1769    0.0213    FE      0.0030    1.1590    0.0410    0.0770
NI           69      8   0.00337   0.00300   0.00323   0.00136   0.00016    NI     0.00100   0.00900   0.00300   0.00300
HUMIC        71      6    0.7861    0.7000    0.7272    0.5143    0.0610    HUMIC   0.2000    2.7000    0.4000    1.0000
IQ            1     76 0.00E+00 0.00E+00 0.00E+00          *         *    IQ    0.00E+00  0.00E+00         *         *
TEMP          1     76 0.00E+00 0.00E+00 0.00E+00          *         *    TEMP  0.00E+00  0.00E+00         *         *
T_NA          1     76 0.00E+00 0.00E+00 0.00E+00          *         *    T_NA  0.00E+00  0.00E+00         *         *

T_K           1     76 0.00E+00 0.00E+00 0.00E+00          *         *    T_K   0.00E+00  0.00E+00         *         *
T_MG          1     76 0.00E+00 0.00E+00 0.00E+00          *         *    T_MG  0.00E+00  0.00E+00         *         *
T_CA          1     76 0.00E+00 0.00E+00 0.00E+00          *         *    T_CA  0.00E+00  0.00E+00         *         *
ACID          1     76 0.00E+00 0.00E+00 0.00E+00          *         *    ACID  0.00E+00  0.00E+00         *         *
UV            1     76 0.00E+00 0.00E+00 0.00E+00          *         *    UV    0.00E+00  0.00E+00         *         *
F_PH          1     76 0.00E+00 0.00E+00 0.00E+00          *         *    F_PH  0.00E+00  0.00E+00         *         *
STAGE         1     76 0.00E+00 0.00E+00 0.00E+00          *         *    STAGE 0.00E+00  0.00E+00         *         *
P_SOLID      10     67     2.100     2.000     1.875     1.370     0.433    P_SOLID  1.000     5.000     1.000     2.500
DOC           1     76 0.00E+00 0.00E+00 0.00E+00          *         *    DOC   0.00E+00  0.00E+00         *         *
HICN         76      1      8.50      6.31      6.80     53.38      6.12    HICN      0.63     79.40      3.15     10.00
```

Table [illegible] Correlation matrices

(i) normal

	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	PH	COND	TURB	ALK_N	TDS	TH	FCO2	TA	CL
[illegible]	[illegible]															
[illegible]	[illegible]	[illegible]														
[illegible]	[illegible]	[illegible]	[illegible]													
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]												
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]											
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]										
PH	[illegible]	[illegible]	[illegible]	[illegible]	-0.110	[illegible]	0.051									
COND	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.212	-0.174	-0.609								
TURB	*	*	*	*	*	*	*	0.928	[illegible]							
ALK_N	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-0.065	-0.082	[illegible]	[illegible]						
TDS	[illegible]	[illegible]	[illegible]	[illegible]	-0.045	[illegible]	-0.152	-0.614	[illegible]	[illegible]	[illegible]					
TH	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-0.150	-0.310	0.287	[illegible]	[illegible]	[illegible]	[illegible]				
FCO2	[illegible]	[illegible]	[illegible]	[illegible]	-0.043	0.369	-0.034	-0.635	[illegible]	*	[illegible]	0.534	-0.049			
TA	[illegible]	[illegible]	[illegible]	[illegible]	-0.244	[illegible]	0.041	0.963	[illegible]	*	[illegible]	[illegible]	0.497	-0.361		
CL	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-0.156	0.026	[illegible]	-0.747	[illegible]	[illegible]	[illegible]	0.137	0.132	
OPO4	*	*	*	*	*	*	*	-0.052	[illegible]	[illegible]	[illegible]	-0.041	[illegible]	-0.017	-0.099	-0.018
SIO2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-0.310	0.252	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.502	0.471
SO4	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-0.467	-0.036	-0.031	[illegible]	0.294	[illegible]	[illegible]	[illegible]	0.151	-0.061	0.324
NA	[illegible]	[illegible]	[illegible]	0.083	-0.303	-0.167	-0.475	-0.012	0.319	-0.502	-0.035	0.158	0.647	0.098	0.165	0.598
K	[illegible]	[illegible]	[illegible]	0.150	-0.217	[illegible]	-0.280	0.163	0.256	-0.554	[illegible]	0.112	0.639	[illegible]	0.322	0.554
CU	[illegible]	[illegible]	[illegible]	0.192	0.431	0.262	0.392	0.026	-0.164	0.624	[illegible]	-0.047	-0.101	-0.194	-0.066	-0.347
MG	[illegible]	[illegible]	[illegible]	-0.146	-0.057	-0.205	-0.344	0.292	0.267	0.022	[illegible]	0.072	0.969	-0.007	0.449	0.695
CA	[illegible]	[illegible]	-0.113	0.001	-0.154	-0.223	-0.297	0.247	0.345	0.096	[illegible]	0.253	0.921	-0.094	0.497	0.470
ZN	[illegible]	[illegible]	[illegible]	[illegible]	-0.275	-0.419	-0.058	-0.245	0.221	0.364	[illegible]	0.226	0.103	0.095	-0.272	-0.003
CD	[illegible]	[illegible]	-0.026	-0.148	0.050	-0.067	0.825	-0.074	-0.103	0.595	0.147	-0.087	-0.258	0.037	-0.271	-0.165
AL	[illegible]	[illegible]	[illegible]	0.358	0.023	-0.238	0.091	-0.563	0.131	[illegible]	0.012	0.113	-0.026	0.222	-0.749	0.208
PB	[illegible]	[illegible]	[illegible]	0.649	0.100	0.179	-0.152	0.106	0.091	0.443	[illegible]	-0.066	0.363	0.106	0.129	0.467
CR	*	*	*	*	*	*	*	-0.007	-0.050	0.445	[illegible]	0.128	-0.240	-0.293	-0.034	-0.556
MN	[illegible]	[illegible]	0.049	-0.061	0.966	0.287	0.164	-0.507	[illegible]	0.747	[illegible]	[illegible]	-0.119	[illegible]	-0.685	0.325
FE	0.501	-0.232	-0.124	[illegible]	0.370	0.753	-0.040	-0.145	[illegible]	[illegible]	[illegible]	-0.071	-0.150	0.694	-0.252	0.026
NI	[illegible]	[illegible]	[illegible]	-0.202	0.164	-0.108	0.858	-0.052	-0.020	0.641	[illegible]	[illegible]	0.060	0.104	-0.164	-0.028
HUMIC	[illegible]	-0.279	[illegible]	[illegible]	[illegible]	0.444	0.103	0.246	-0.224	[illegible]	[illegible]	[illegible]	-0.212	-0.031	0.164	-0.106
F_SOLID	[illegible]	-0.113	0.022	-0.077	0.007	-0.150	*	-0.004	[illegible]	*	*	[illegible]	[illegible]	0.109	0.096	-0.481
HION	[illegible]	[illegible]	[illegible]	[illegible]	-0.145	[illegible]	-0.083	-0.667	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.670	-0.843	-0.048

	OPO4	SIO2	SO4	NA	K	CU	MG	CA	ZN	CD	AL	PB	CR	MN	FE	NI	HUMIC
SIO2	[illegible]																
SO4	[illegible]	[illegible]															
NA	[illegible]	[illegible]	[illegible]														
K	[illegible]	[illegible]	[illegible]	[illegible]													
CU	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]												
MG	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-0.154											
CA	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.031	0.813										
ZN	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.099	0.169									
CD	[illegible]	[illegible]	[illegible]	[illegible]	-0.154	0.409	-0.252	-0.196	[illegible]								
AL	[illegible]	[illegible]	[illegible]	0.197	0.071	-0.063	0.025	-0.055	[illegible]	[illegible]							
PB	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.303	0.305	[illegible]	[illegible]	[illegible]						
CR	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.374	-0.315	-0.073	[illegible]	[illegible]	[illegible]	-0.107					
MN	[illegible]	[illegible]	[illegible]	0.201	[illegible]	-0.140	[illegible]	-0.135	[illegible]	[illegible]	[illegible]	0.140	-0.495				
FE	[illegible]	[illegible]	[illegible]	[illegible]	-0.079	[illegible]	[illegible]	-0.199	0.049	[illegible]	[illegible]	0.042	-0.199	0.410			
NI	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.403	[illegible]	0.067	[illegible]	[illegible]	[illegible]	[illegible]	0.270	[illegible]	0.079		
HUMIC	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-0.190	-0.193	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.188	0.002	
F_SOLID	*	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.256	[illegible]	*	[illegible]	[illegible]	*	[illegible]	0.205	*	[illegible]
HION	[illegible]	[illegible]	[illegible]	0.102	[illegible]	[illegible]	[illegible]	0.120	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.042	0.009	-0.041	[illegible]

(ii) logarithmic

```
              C1        C2        C3        C4        C5        C6        C7        C8
C2         0.717
C3        -0.552     0.042
C4         0.153     0.065    -0.141
C5        -0.029    -0.257    -0.109     0.542
C6        -0.109    -0.239    -0.272     0.745     0.634
C7        -0.153    -0.225    -0.325     0.671     0.539     0.807
C8         0.079    -0.012    -0.117     0.659     0.546     0.744     0.507
C9         0.274     0.165     0.217     0.021     0.194     0.035    -0.115     0.195        C9       C10       C11       C12       C13       C14       C15       C16
C10       -0.112    -0.546    -0.077     0.307     0.468     0.500     0.335     0.529     0.042
C11        0.253     0.070    -0.107     0.490     0.354     0.632     0.533     0.324     0.108    -0.045
C12        0.219    -0.018    -0.074    -0.034    -0.049    -0.069     0.129    -0.227     0.074    -0.231     0.182
C13        0.307     0.120    -0.152     0.210     0.125     0.150     0.267     0.025     0.397     0.134     0.172     0.155
C14       -0.627    -0.313    -0.295     0.053     0.032     0.232     0.432    -0.080    -0.675     0.324    -0.105     0.005    -0.218
C15       -0.141    -0.245    -0.295     0.736     0.602     0.969     0.914     0.686    -0.015     0.463     0.608    -0.003     0.206     0.337
C16        0.157     0.046    -0.110     0.491     0.412     0.467     0.424     0.522     0.723     0.339     0.507     0.047     0.636    -0.267     0.482
C17       -0.377    -0.327     0.499    -0.444    -0.039    -0.319    -0.315    -0.221     0.071    -0.043    -0.431     0.026    -0.518     0.029    -0.338    -0.369       C17
C18        0.462     0.554     0.035     0.002    -0.118    -0.254    -0.245    -0.015     0.721    -0.163     0.015     0.089     0.508    -0.341    -0.254     0.575    -0.313
```

Table 11a CI4 streamwater quality (1984-5)

	N	N*	MEAN	MEDIAN	TRMEAN	STDEV	SEMEAN	MIN	MAX	Q1	Q3
T_CU	24	49	0.00352	0.00200	0.00255	0.00552	0.00113	0.00100	0.02900	0.00200	0.00275
T_ZN	25	48	0.01360	0.01000	0.01239	0.01039	0.00208	0.00600	0.04900	0.00800	0.01450
T_CD	25	48	0.00100	0.00100	0.00100	0.00000	0.00000	0.00100	0.00100	0.00100	0.00100
T_AL	26	47	0.13043	0.13550	0.13183	0.02431	0.00477	0.05900	0.17000	0.11300	0.14050
T_PB	24	49	0.00392	0.00200	0.00314	0.00452	0.00092	0.00200	0.02300	0.00200	0.00500
T_CR	25	48	0.00303	0.00300	0.00300	0.00040	0.00008	0.00300	0.00500	0.00300	0.00300
T_MN	24	49	0.1542	0.1315	0.1488	0.0741	0.0151	0.0490	0.3800	0.1003	0.2100
T_FE	25	48	0.5166	0.3060	0.4927	0.3817	0.0763	0.0910	1.5000	0.2435	0.7760
T_NI	25	48	0.00312	0.00300	0.00304	0.00044	0.00009	0.00300	0.00500	0.00300	0.00300
PH	72	1	5.2126	5.0000	5.1839	0.5957	0.0702	4.7000	7.0000	4.7000	5.7000
COND	72	1	34.320	35.000	34.812	6.444	0.759	21.061	59.000	30.000	32.750
TURB	1	72	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
AMM_N	73	0	1.5019	1.4286	1.4450	0.2224	0.0319	1.4286	2.3571	1.4286	1.4286
TON	72	1	9.921	7.143	9.375	4.574	0.539	7.143	21.429	7.143	14.286
NO2	73	0	0.28570	0.28570	0.28570	0.00000	0.00000	0.28570	0.28570	0.28570	0.28570
TH	67	6	4.644	4.500	4.539	1.455	0.178	2.300	10.400	3.700	5.400
FCO2	62	11	3.799	3.500	3.582	1.909	0.242	1.400	14.400	2.800	4.200
TA	61	12	37.97	29.97	33.97	33.13	4.24	2.00	177.35	16.99	47.96
CL	73	0	149.27	141.04	149.51	37.02	4.33	56.42	225.67	112.84	169.25
CPO4	72	1	0.02098	0.02000	0.02000	0.00715	0.00084	0.02000	0.08000	0.02000	0.02000
SIO2	73	0	0.7431	0.7000	0.7408	0.2044	0.0239	0.3000	1.2000	0.6000	0.9000
SO4	70	3	89.95	91.24	89.10	25.08	3.00	46.23	149.56	66.19	107.61
NA	66	7	130.24	132.63	130.32	29.12	3.59	61.54	191.33	112.73	149.58
K	65	8	4.912	4.359	4.756	2.661	0.330	0.513	12.051	2.564	6.666
CU	67	6	0.00247	0.00200	0.00226	0.00159	0.00019	0.00100	0.01200	0.00200	0.00200
MG	67	6	52.78	52.63	51.87	16.74	2.05	4.36	113.93	42.60	61.68
CA	67	6	42.17	40.42	41.20	15.29	1.87	10.48	100.90	33.93	49.90
ZN	67	6	0.01470	0.01300	0.01418	0.00672	0.00082	0.00500	0.03600	0.01000	0.01800
CD	67	6	0.00123	0.00100	0.00104	0.00127	0.00015	0.00030	0.01100	0.00100	0.00100
AL	67	6	0.12922	0.12100	0.12803	0.04333	0.00529	0.02500	0.25200	0.10600	0.15400
PB	67	6	0.00910	0.00500	0.00743	0.01155	0.00141	0.00200	0.07500	0.00200	0.01300
CR	65	8	0.00272	0.00300	0.00280	0.00070	0.00009	0.00100	0.00300	0.00300	0.00300
MN	67	6	0.13903	0.12300	0.13711	0.05377	0.00657	0.05900	0.26600	0.10400	0.17200
FE	66	7	0.2584	0.1835	0.2299	0.2290	0.0282	0.0520	1.1800	0.1100	0.2962
NI	67	6	0.00331	0.00300	0.00346	0.00258	0.00031	0.00100	0.01800	0.00300	0.00300
HUMIC	72	1	2.267	1.700	2.126	1.582	0.186	0.300	6.800	1.200	3.150
IO	1	72	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
TEMP	1	72	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
T_NA	1	72	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
T_K	1	72	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
T_MG	1	72	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
T_CA	1	72	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
ACID	1	72	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
UV	1	72	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
F_PH	1	72	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
STAGE	1	72	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
P_SOLID	10	63	1.900	1.000	1.375	1.912	0.605	1.000	7.000	1.000	2.250
DOC	1	72	0.00E+00	0.00E+00	0.00E+00	*	*	0.00E+00	0.00E+00	*	*
HION	72	1	11.72	10.00	10.57	11.71	1.38	0.10	57.10	2.00	19.75

Table 11b Correlation matrices

(i) normal

	PH	COND	AMM_N	TON	TH	FCO2	TA	CL	TPO4	SIO2	SO4	NA	K	CU	MG	CA
COND	[illegible]															
AMM_N	[illegible]	[illegible]														
TON	[illegible]	[illegible]	[illegible]													
TH	[illegible]	[illegible]	[illegible]	0.294												
FCO2	[illegible]	[illegible]	-0.017	-0.170	[illegible]											
TA	[illegible]	[illegible]	[illegible]	-0.214	[illegible]	-0.190										
CL	[illegible]	[illegible]	[illegible]	0.348	0.271	0.154	-0.237									
TPO4	-0.015	[illegible]	[illegible]	-0.024	-0.010	-0.061	-0.034	-0.108								
SIO2	[illegible]	[illegible]	[illegible]	[illegible]	0.205	[illegible]	0.244	0.105	[illegible]							
SO4	[illegible]	[illegible]	[illegible]	0.150	0.473	[illegible]	-0.028	0.480	[illegible]	[illegible]						
NA	[illegible]	[illegible]	-0.114	0.317	0.743	-0.340	0.212	0.489	[illegible]	[illegible]	[illegible]					
K	[illegible]	[illegible]	[illegible]	0.177	[illegible]	-0.099	0.278	0.230	-0.076	0.031	[illegible]	0.401				
CU	[illegible]	[illegible]	[illegible]	0.199	-0.315	0.017	-0.061	-0.052	-0.041	[illegible]	-0.146	-0.277	-0.136			
MG	0.475	[illegible]	-0.121	0.071	0.307	-0.149	0.599	0.393	-0.029	0.065	0.465	[illegible]	0.430	-0.226		
CA	[illegible]	[illegible]	[illegible]	0.020	[illegible]	-0.256	0.741	0.118	0.047	0.122	[illegible]	0.587	0.433	-0.318	0.836	
ZN	[illegible]	[illegible]	[illegible]	[illegible]	-0.027	0.139	-0.299	0.292	[illegible]	[illegible]	[illegible]	0.106	[illegible]	[illegible]	0.079	-0.048
CD	[illegible]	[illegible]	[illegible]	0.064	-0.139	-0.012	-0.141	-0.066	[illegible]	[illegible]	0.047	-0.127	-0.047	[illegible]	-0.119	-0.135
AL	-0.681	0.165	-0.130	-0.121	-0.417	0.241	-0.532	0.206	-0.048	-0.213	-0.000	-0.100	-0.065	0.006	-0.145	-0.347
PB	[illegible]	0.224	-0.126	-0.179	-0.174	0.069	-0.214	0.204	-0.051	0.102	0.344	-0.113	0.168	-0.015	-0.095	-0.171
CR	0.037	-0.667	0.116	0.260	-0.438	-0.433	-0.316	-0.417	0.056	[illegible]	-0.466	-0.182	-0.366	0.313	-0.530	-0.324
MN	-0.179	[illegible]	-0.208	-0.220	0.067	0.397	-0.011	0.324	[illegible]	0.071	0.004	0.051	-0.117	-0.161	0.207	-0.032
FE	[illegible]	[illegible]	[illegible]	[illegible]	-0.036	0.133	0.400	-0.319	[illegible]	[illegible]	[illegible]	-0.307	[illegible]	[illegible]	-0.069	0.084
NI	[illegible]	0.018	-0.045	-0.107	-0.314	0.050	-0.159	-0.018	-0.045	[illegible]	0.117	-0.261	0.116	0.220	-0.264	-0.254
HUMIC	[illegible]	-0.652	0.043	-0.313	-0.216	0.065	0.342	-0.564	[illegible]	[illegible]	-0.726	-0.493	-0.335	0.039	-0.243	-0.038
P_SOLID	0.321	[illegible]	*	-0.386	0.623	0.117	0.740	-0.430	*	0.564	[illegible]	0.442	-0.313	-0.165	0.584	0.663
HION	[illegible]	[illegible]	-0.069	-0.095	[illegible]	0.467	-0.672	0.339	-0.036	-0.400	[illegible]	-0.146	[illegible]	-0.117	-0.183	-0.385

	ZN	CD	AL	PB	CR	MN	FE	NI	HUMIC	P_SOLID
CD	[illegible]									
AL	[illegible]	[illegible]								
PB	[illegible]	[illegible]	[illegible]							
CR	[illegible]	[illegible]	-0.099	[illegible]						
MN	[illegible]	-0.074	0.374	-0.077	-0.341					
FE	[illegible]	[illegible]	[illegible]	[illegible]	0.115	0.427				
NI	[illegible]	[illegible]	0.245	0.765	0.163	-0.082	-0.060			
HUMIC	[illegible]	[illegible]	[illegible]	-0.321	0.214	0.172	0.259	-0.104		
P_SOLID	[illegible]	*	[illegible]	[illegible]	*	0.470	0.414	0.937	[illegible]	
HION	[illegible]	[illegible]	[illegible]	[illegible]	-0.464	0.179	-0.217	0.115	[illegible]	[illegible]

(ii) logarithmic

	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17
C2	[illegible]																
C3	[illegible]	[illegible]															
C4	[illegible]	[illegible]	[illegible]														
C5	[illegible]	[illegible]	-0.745	[illegible]													
C6	[illegible]	[illegible]	[illegible]	0.400	[illegible]												
C7	[illegible]	[illegible]	[illegible]	0.561	[illegible]	0.204											
C8	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.184										
C9	[illegible]	[illegible]	[illegible]	-0.417	[illegible]	-0.172	-0.364	0.069									
C10	[illegible]	[illegible]	[illegible]	[illegible]	0.114	0.016	0.075	0.218	[illegible]								
C11	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.305	0.292	0.535	[illegible]	[illegible]							
C12	[illegible]	[illegible]	[illegible]	-0.124	[illegible]	[illegible]	0.031	-0.105	[illegible]	[illegible]	[illegible]						
C13	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-0.029	0.097	[illegible]	[illegible]	[illegible]	[illegible]					
C14	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.203	0.436	-0.303	[illegible]	[illegible]	[illegible]	[illegible]	-0.137				
C15	[illegible]	[illegible]	[illegible]	[illegible]	0.746	0.495	0.727	0.374	-0.411	[illegible]	[illegible]	[illegible]	0.109	[illegible]			
C16	[illegible]	[illegible]	[illegible]	[illegible]	0.512	0.420	0.281	0.793	[illegible]	[illegible]	[illegible]	[illegible]	0.114	[illegible]	0.537		
C17	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-0.021	-0.531	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-0.256	-0.630	
C18	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-0.511	0.144	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-0.600	0.118	[illegible]

Table 12a CI5 streamwater quality (1984-5)

```
               N      N*      MEAN    MEDIAN    TRMEAN     STDEV    SEMEAN                 MIN       MAX        Q1        Q3
T_CU          24      80   0.00242   0.00200   0.00227   0.00106   0.00022    T_CU     0.00200   0.00600   0.00200   0.00200
T_ZN          25      79   0.01960   0.01000   0.01035   0.00413   0.00083    T_ZN     0.00500   0.02000   0.00700   0.01300
T_CD          25      79   0.00103   0.00100   0.00100   0.00040   0.00008    T_CD     0.00100   0.00300   0.00100   0.00100
T_AL          26      78   0.10081   0.09550   0.09979   0.03931   0.00771    T_AL     0.04600   0.18000   0.05875   0.12400
T_PB          24      80   0.00295   0.00200   0.00282   0.00168   0.00034    T_PB     0.00200   0.00700   0.00200   0.00450
T_CR          27      77   0.00300   0.00300   0.00300   0.00000   0.00000    T_CR     0.00300   0.00300   0.00300   0.00300
T_MN          24      80   0.04746   0.05000   0.04941   0.01011   0.00206    T_MN     0.02200   0.07100   0.04225   0.05450
T_FE          25      79    0.1074    0.0900    0.1027    0.0727    0.0145    T_FE      0.0400    0.3330    0.0555    0.1400
T_NI          25      79   0.00316   0.00300   0.00309   0.00055   0.00011    T_NI     0.00300   0.00500   0.00300   0.00300
PH           103       1    5.2226    5.2000    5.2102    0.3354    0.0330    PH        4.6000    6.0000    5.0000    5.5000
COND         103       1    37.363    39.000    37.536     5.938     0.585    COND      24.000    43.000    33.000    42.000
TURB           1     103  0.00E+00  0.00E+00  0.00E+00         *         *    TURB    0.00E+00  0.00E+00         *         *
AMM_N        104       0    1.5047    1.4286    1.4292    0.4093    0.0401    AMM_N     1.4286    5.0000    1.4286    1.4296
TON          103       1     14.84      7.14     13.29     11.78      1.16    TON         7.14     85.71      7.14     21.43
NO2          104       0   0.23570   0.23570   0.23570   0.00000   0.00000    NO2      0.23570   0.23570   0.23570   0.23570
TH            95       9     4.827     4.600     4.797     1.189     0.122    TH         2.700     7.500     3.900     5.600
FCO2          83      21    3.3312    3.2000    3.2992    0.7643    0.0839    FCO2      0.9000    5.7000    2.3000    3.7000
TA            83      21     29.62     27.98     29.26     10.37      1.14    TA         11.99     59.75     19.98     35.97
CL           104       0    167.63    169.25    168.95     42.12      4.13    CL         84.63    225.67    141.04    197.46
CFO4         103       1   0.02148   0.02000   0.02000   0.01033   0.00102    CFO4     0.02000   0.12000   0.02000   0.02000
SIO2         104       0    0.9178    0.8000    0.8219    0.1717    0.0168    SIO2      0.4000    1.1000    0.7000    1.0000
SO4          100       4    102.19    103.37    101.81     18.87      1.89    SO4        60.41    149.93     87.51    114.31
NA            94      10    149.03    146.32    148.02     31.72      3.27    NA         89.58    285.08    128.17    169.70
K             93      11     6.626     5.897     6.232     3.936     0.408    K          0.513    20.517     3.590     7.948
CU            83      21   0.00205   0.00200   0.00190   0.00116   0.00013    CU       0.00100   0.00800   0.00100   0.00200
MG            95       9     56.10     53.04     55.78     14.20      1.46    MG         32.99     91.04     43.59     68.09
CA            95       9     43.99     42.81     43.76     11.47      1.18    CA         19.96     71.36     36.43     50.40
ZN            95       9   0.01887   0.01600   0.01617   0.01694   0.00174    ZN       0.00400   0.12900   0.01200   0.02000
CD            95       9   0.00093   0.00100   0.00090   0.00032   0.00003    CD       0.00040   0.00280   0.00080   0.00100
AL            96       8    0.1624    0.1310    0.1538    0.1198    0.0122    AL        0.0050    0.6260    0.0672    0.2275
PB            95       9   0.00809   0.00500   0.00606   0.01262   0.00129    PB       0.00200   0.10750   0.00200   0.00700
CR            82      22   0.00247   0.00300   0.00235   0.00161   0.00018    CR       0.00100   0.01400   0.00100   0.00300
MN            94      10   0.07032   0.06750   0.06864   0.02798   0.00289    MN       0.02700   0.16400   0.04767   0.08725
FE            95       9   0.07967   0.05600   0.07213   0.06713   0.00689    FE       0.00100   0.34300   0.03300   0.11000
NI            82      22   0.00307   0.00300   0.00287   0.00173   0.00019    NI       0.00100   0.01000   0.00300   0.00300
HUMIC         89      15    0.3515    0.3000    0.3272    0.2182    0.0231    HUMIC     0.0500    1.4000    0.2000    0.5000
IG            50      54   0.01032   0.00600   0.00910   0.01037   0.00147    IG       0.00000   0.04800   0.00275   0.01700
TEMP          32      72     9.881    10.250     9.954     4.650     0.822    TEMP       0.000    17.000     5.625    14.000
T_NA           1     103  0.00E+00  0.00E+00  0.00E+00         *         *    T_NA    0.00E+00  0.00E+00         *         *

T_K            1     103  0.00E+00  0.00E+00  0.00E+00         *         *    T_K     0.00E+00  0.00E+00         *         *
T_MG           1     103  0.00E+00  0.00E+00  0.00E+00         *         *    T_MG    0.00E+00  0.00E+00         *         *
T_CA           1     103  0.00E+00  0.00E+00  0.00E+00         *         *    T_CA    0.00E+00  0.00E+00         *         *
ACID           1     103  0.00E+00  0.00E+00  0.00E+00         *         *    ACID    0.00E+00  0.00E+00         *         *
UV            24      80   0.01125   0.00500   0.01114   0.00811   0.00166    UV       0.00000   0.02500   0.00500   0.02000
F_PH           9      95     4.344     4.300     4.344     1.646     0.549    F_PH       0.000     5.400     4.650     5.000
STAGE         43      61    0.2630    0.0400    0.1949    0.4853    0.0740    STAGE     0.0000    2.5000    0.0300    0.2000
P_SOLID        9      95     1.773     1.000     1.778     1.093     0.364    P_SOLID    1.000     4.000     1.000     2.500
DOC            1     103  0.00E+00  0.00E+00  0.00E+00         *         *    DOC     0.00E+00  0.00E+00         *         *
HION         103       1     7.724     6.310     7.475     5.033     0.496    HION       1.000    25.119     3.162    10.000
```

Table 12b Correlation matrices

(i) normal

	[illegible]	[illegible]	[illegible]	[illegible]	TH	[illegible]	[illegible]	CL
[illegible]	[illegible]							
[illegible]	[illegible]	[illegible]						
[illegible]	[illegible]	[illegible]	[illegible]					
TH	[illegible]	[illegible]	[illegible]	[illegible]				
[illegible]	[illegible]	[illegible]	[illegible]	0.115	-0.133			
IC	[illegible]	[illegible]	[illegible]	[illegible]	0.441	-0.367		
CL	-0.074	[illegible]	[illegible]	[illegible]	[illegible]	0.249	0.122	
PO4	[illegible]	[illegible]	[illegible]	[illegible]	0.010	-0.149	-0.003	-0.074
SIO2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-0.202	0.195
SO4	[illegible]	[illegible]	[illegible]	[illegible]	0.475	[illegible]	0.011	0.301
NA	[illegible]	[illegible]	[illegible]	[illegible]	0.571	-0.020	0.175	0.579
K	[illegible]	[illegible]	[illegible]	[illegible]	0.569	0.026	0.179	0.502
CU	[illegible]	[illegible]	[illegible]	[illegible]	-0.446	0.041	-0.323	-0.428
MG	[illegible]	[illegible]	[illegible]	0.121	0.950	-0.053	0.329	0.717
CA	[illegible]	[illegible]	[illegible]	-0.071	0.927	-0.226	0.530	0.373
ZN	[illegible]	[illegible]	-0.127	0.103	0.002	0.239	-0.165	0.253
CD	[illegible]	-0.456	[illegible]	-0.111	-0.425	0.005	-0.205	-0.466
AL	[illegible]	[illegible]	[illegible]	0.330	-0.323	0.435	-0.699	0.163
PB	[illegible]	[illegible]	[illegible]	[illegible]	-0.125	0.269	-0.226	-0.059
CR	[illegible]	-0.299	[illegible]	[illegible]	-0.299	-0.017	-0.177	-0.367
MN	-0.266	0.542	-0.043	[illegible]	0.236	0.427	-0.150	0.578
FE	0.614	[illegible]	0.142	-0.071	0.372	-0.065	0.623	0.204
NI	[illegible]	-0.145	[illegible]	0.213	-0.446	0.156	-0.321	-0.190
HUMIC	[illegible]	-0.360	0.032	-0.226	[illegible]	-0.050	0.093	-0.303
IQ	[illegible]	[illegible]	-0.176	-0.064	-0.414	0.449	-0.479	0.073
TEMP	[illegible]	0.019	[illegible]	-0.661	0.537	-0.172	0.777	-0.067
UV	-0.145	-0.032	0.047	-0.118	-0.005	0.284	0.078	0.106
F_FH	[illegible]	[illegible]	*	0.257	0.496	0.130	0.574	0.805
STAGE	[illegible]	[illegible]	[illegible]	-0.051	-0.594	0.350	-0.561	-0.285
P_SOLID	-0.527	0.114	*	-0.052	-0.330	0.703	-0.459	-0.610
WICN	-0.935	[illegible]	-0.111	0.227	-0.376	0.552	-0.866	0.074

	[illegible]	SIO2	[illegible]	NA	K	CU	MG	CA
SIO2	[illegible]							
SO4	[illegible]	[illegible]						
NA	[illegible]	-0.047	[illegible]					
K	-0.037	0.143	0.429	[illegible]				
CU	-0.074	0.141	-0.017	[illegible]	-0.182			
MG	-0.021	[illegible]	0.475	0.737	0.563	-0.496		
CA	0.035	[illegible]	0.453	0.520	0.521	-0.360	0.784	
ZN	[illegible]	0.350	0.054	0.066	0.103	0.036	0.022	-0.033
CD	0.026	[illegible]	[illegible]	-0.442	-0.249	0.353	-0.493	-0.257
AL	-0.085	[illegible]	[illegible]	0.177	-0.058	0.243	-0.170	-0.450
PB	-0.015	-0.045	[illegible]	-0.139	-0.021	0.109	-0.144	-0.048
CR	0.011	0.253	-0.130	-0.198	-0.023	0.328	-0.332	-0.221
MN	-0.030	0.216	0.113	0.403	0.312	-0.272	0.399	0.140
FE	-0.020	0.119	0.153	0.150	0.373	-0.252	0.301	0.421
NI	-0.043	0.199	[illegible]	-0.336	-0.160	0.537	-0.431	-0.385
HUMIC	-0.030	[illegible]	[illegible]	-0.296	-0.160	-0.003	-0.327	-0.194
IQ	[illegible]	[illegible]	[illegible]	0.191	-0.275	-0.103	-0.322	-0.444
TEMP	0.132	-0.699	0.567	0.176	0.180	-0.336	0.466	0.591
UV	0.230	-0.203	-0.041	0.306	0.053	-0.152	-0.015	0.047
F_FH	*	-0.523	0.759	0.669	0.522	-1.000	0.683	0.250
STAGE	-0.077	0.173	0.073	-0.369	-0.287	0.529	-0.579	-0.539
P_SOLID	*	-0.409	0.112	0.036	-0.345	-0.267	-0.098	-0.455
WICN	-0.060	0.172	-0.076	-0.004	-0.148	0.159	-0.234	-0.531

	ZN	CD	AL	PB	CR	MN	FE	NI	HUMIC	IQ	TEMP	UV	F_FH	STAGE	P_SOLID
CD	0.046														
AL	0.252	0.071													
PB	0.143	0.731	0.123												
CR	0.011	0.261	0.155	0.067											
MN	0.272	-0.207	0.416	0.072	-0.146										
FE	-0.144	-0.201	-0.423	-0.132	-0.005	0.206									
NI	0.251	0.549	0.413	0.347	0.115	-0.057	-0.346								
HUMIC	-0.111	[illegible]	0.072	0.323	-0.001	0.001	-0.026	0.257							
IQ	0.225	-0.237	0.017	-0.033	-0.111	0.290	-0.471	0.406	[illegible]						
TEMP	-0.307	0.321	[illegible]	0.437	-0.131	-0.169	0.334	-0.142	[illegible]	[illegible]					
UV	[illegible]	[illegible]	[illegible]	[illegible]	0.391	0.225	-0.035	-0.371	[illegible]	[illegible]	0.173				
F_FH	[illegible]	[illegible]	0.176	0.312	-1.000	0.708	0.342	-1.000	*	[illegible]	0.202	0.471			
STAGE	[illegible]	[illegible]	[illegible]	[illegible]	0.176	0.207	-0.340	0.475	[illegible]	[illegible]	[illegible]	0.417	[illegible]		
P_SOLID	[illegible]	*	0.624	-0.267	0.000	0.627	-0.195	*	[illegible]	*	*	*	*	*	
WICN	[illegible]	[illegible]	0.797	0.041	0.073	0.117	-0.564	0.354	[illegible]	[illegible]	[illegible]	[illegible]	0.047	0.723	0.804

(ii) logarithmic

	C1	C2	C3	C4	C5	C6	C7	C8
C2	0.177							
C3	[illegible]	0.111						
C4	[illegible]	[illegible]	0.057					
C5	[illegible]	[illegible]	0.153	0.403				
C6	[illegible]	[illegible]	0.117	0.792	0.345			
C7	[illegible]	[illegible]	0.255	[illegible]	0.439	0.724		
C8	[illegible]	[illegible]	[illegible]	[illegible]	0.355	0.745	0.331	
C9	[illegible]	[illegible]	[illegible]	[illegible]	0.022	0.054	-0.162	0.260
C10	[illegible]	[illegible]	[illegible]	[illegible]	0.130	-0.072	-0.214	0.209
C11	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.517	0.442	0.347
C12	[illegible]	[illegible]	[illegible]	-0.111	[illegible]	-0.119	-0.017	-0.085
C13	[illegible]	[illegible]	[illegible]	0.070	0.192	0.134	-0.100	0.176
C14	[illegible]	[illegible]	[illegible]	[illegible]	0.112	0.305	0.520	0.107
C15	[illegible]	[illegible]	[illegible]	[illegible]	0.527	0.937	0.901	0.585
C16	[illegible]	[illegible]	[illegible]	[illegible]	0.537	0.764	0.570	0.578
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-0.155	-0.388
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

	C9	C10	C11	C12	C13	C14	C15	C16	
C10	[illegible]								
C11	[illegible]	[illegible]							
C12	[illegible]	[illegible]	[illegible]						
C13	[illegible]	[illegible]	0.212	[illegible]					
C14	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]				
C15	[illegible]	[illegible]	[illegible]	[illegible]	0.040	[illegible]			
C16	[illegible]	[illegible]	[illegible]	-0.115	[illegible]	[illegible]	0.617		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-0.276	-0.438	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.205	[illegible]

conditions in CI4 and CI5 are very similar with pH levels averaging 5.2 in each stream and H^+ averaging 12 ueq l^{-1} and 8 ueq l^{-1} respectively. Both catchments are much smaller than CI3, with steeper slopes and presumably reduced residence times, nevertheless they are comparable. In the case of CI4, 25% of all samples yielded a pH of 4.7 or less, while in CI5 the corresponding level was 5.0 or less.

On the other hand, Table 13a suggests that conditions in CI6 are slightly less acid with pH averaging 5.6 and H^+ 5 ueq l^{-1}. One factor contributing to the above might be its larger area compared to CI4 and CI5 and more importantly its very gentle slopes which would tend to favour increased residence times and perhaps encourage a reduction in overland flow processes. Moreover, the valley bottom is characterised by a large area of peat which probably increases residence times, reduces stormflows and controls the baseflow chemistry. Hence, the catchment may not be ideally representative of the Camddwr system. Lastly, Table 14a indicates that too few sample been taken at UC4 to allow any conclusions to be drawn, the data is merely provided for information.

SO_4 levels at CI3 averaged 95 ueq l^{-1}, less than 60% of those found at LI1 but still about 30% greater than was found in bulk precipitation at C7. Thus, the reduction in evapotranspiration and scavenging capacity in the moorland catchment has presumably led to the above, aided by a probable reduction in sulphates contributed from the soils. The other acidified moorland sites exhibit similar concentrations, although levels are slightly lower in CI6 averaging 88 ueq l^{-1} as might be expected given its slightly reduced acidity.

Despite the very different vegetation cover, NO_3 levels are similar to those found at the LI sites. Hence they are

Table 13a CI6 streamwater quality (1984-5)

```
             N     N*     MEAN   MEDIAN   TRMEAN    STDEV   SEMEAN              MIN       MAX        Q1        Q3
T_CU        24     52  0.00262  0.00200  0.00232  0.00176  0.00036   T_CU   0.00200   0.01000   0.00200   0.00200
T_ZN        25     51  0.00924  0.00900  0.00848  0.00555  0.00111   T_ZN   0.00400   0.03000   0.00630   0.01000
T_CD        25     51  0.00100  0.00100  0.00100  0.00002  0.00000   T_CD   0.00100   0.00110   0.00100   0.00100
T_AL        25     50  0.10433  0.09850  0.10446  0.02434  0.00487   T_AL   0.07000   0.15000   0.08450   0.13000
T_PB        24     52  0.00267  0.00200  0.00259  0.00124  0.00025   T_PB   0.00200   0.00500   0.00200   0.00275
T_CR        25     51  0.00300  0.00300  0.00300  0.00000  0.00000   T_CR   0.00300   0.00300   0.00300   0.00300
T_MN        25     51   0.1034   0.0760   0.1029   0.0648   0.0130   T_MN    0.0370    0.2500    0.0505    0.1540
T_FE        25     51    0.543    0.259    0.493    0.605    0.121   T_FE     0.055     2.200     0.113     0.733
T_NI        25     51  0.00304  0.00300  0.00300  0.00020  0.00004   T_NI   0.00300   0.00400   0.00300   0.00300
PH          75      1   5.5572   5.5000   5.5424   0.5339   0.0616   PH      4.5000    6.3000    5.2000    6.0000
COND        75      1   34.510   36.000   34.660    5.531    0.639   COND    22.000    44.000    30.000    33.000
TURB         1     75 0.00E+00 0.00E+00 0.00E+00        *        *   TURB  0.00E+00  0.00E+00         *         *
AMM_N       76      0   1.5321   1.4286   1.4812   0.3002   0.0344   AMM_N   1.4286    2.8571    1.4286    1.4286
TON         75      1    13.31     7.14    12.79     8.89     1.03   TON       7.14     42.86      7.14     14.29
NO2         76      0  0.28570  0.28570  0.28570  0.00000  0.00000   NO2    0.28570   0.28570   0.28570   0.28570
TH          68      8    5.126    5.100    5.032    1.321    0.160   TH       2.300     9.500     4.225     5.900
FCO2        62     14   2.7226   2.6000   2.6589   0.7657   0.0972   FCO2    1.7000    5.3000    2.1750    3.2000
TA          62     14    46.13    37.17    42.47    32.21     4.09   TA        4.00    175.35     25.93     52.46
CL          76      0   146.09   141.04   146.08    36.92     4.24   CL       55.42    225.67    112.34    169.25
OPO4        75      1  0.02030  0.02000  0.02000  0.00174  0.00020   OPO4   0.02000   0.03140   0.02000   0.02000
SIO2        76      0   0.7641   0.8000   0.7632   0.1948   0.0223   SIO2    0.3000    1.2000    0.6000    0.9000
SO4         72      4    88.22    93.74    88.59    21.35     2.52   SO4      33.33    131.65     72.90    104.15
NA          66     10   137.41   137.41   135.27    33.73     4.15   NA       76.97    266.12    117.08    152.52
K           65     11    5.946    5.128    5.556    4.169    0.517   K        0.256    25.896     2.820     7.692
CU          69      7  0.00260  0.00200  0.00224  0.00257  0.00031   CU     0.00100   0.02100   0.00200   0.00200
MG          68      8    53.63    54.48    52.95    13.30     1.61   MG       26.23     97.53     45.93     61.73
CA          68      8    52.72    50.65    51.67    14.45     1.75   CA       24.95    101.80     41.17     61.00
ZN          69      7  0.01287  0.01200  0.01265  0.00553  0.00067   ZN     0.00300   0.03100   0.00950   0.01600
CD          69      7  0.00118  0.00100  0.00103  0.00085  0.00010   CD     0.00080   0.00720   0.00100   0.00100
AL          68      8  0.10601  0.10200  0.10595  0.04241  0.00514   AL     0.01300   0.21500   0.08000   0.13225
PB          69      7  0.00772  0.00500  0.00619  0.01094  0.00132   PB     0.00200   0.03100   0.00200   0.00600
CR          68      8  0.00271  0.00300  0.00277  0.00071  0.00009   CR     0.00100   0.00500   0.00300   0.00300
MN          69      7  0.09998  0.09000  0.09760  0.04694  0.00565   MN     0.01200   0.23600   0.06400   0.12300
FE          69      7   0.2207   0.0970   0.1658   0.3435   0.0414   FE      0.0030    1.9000    0.0555    0.1305
NI          68      8  0.00345  0.00300  0.00310  0.00277  0.00034   NI     0.00100   0.02300   0.00300   0.00300
HUMIC       75      1    1.294    0.800    1.111    1.301    0.150   HUMIC    0.200     7.800     0.500     1.600
IQ           1     75 0.00E+00 0.00E+00 0.00E+00        *        *   IQ    0.00E+00  0.00E+00         *         *
TEMP         1     75 0.00E+00 0.00E+00 0.00E+00        *        *   TEMP  0.00E+00  0.00E+00         *         *
T_NA         1     75 0.00E+00 0.00E+00 0.00E+00        *        *   T_NA  0.00E+00  0.00E+00         *         *

T_K          1     75 0.00E+00 0.00E+00 0.00E+00        *        *   T_K   0.00E+00  0.00E+00         *         *
T_MG         1     75 0.00E+00 0.00E+00 0.00E+00        *        *   T_MG  0.00E+00  0.00E+00         *         *
T_CA         1     75 0.00E+00 0.00E+00 0.00E+00        *        *   T_CA  0.00E+00  0.00E+00         *         *
ACID         1     75 0.00E+00 0.00E+00 0.00E+00        *        *   ACID  0.00E+00  0.00E+00         *         *
UV           1     75 0.00E+00 0.00E+00 0.00E+00        *        *   UV    0.00E+00  0.00E+00         *         *
F_PH         1     75 0.00E+00 0.00E+00 0.00E+00        *        *   F_PH  0.00E+00  0.00E+00         *         *
STAGE        1     75 0.00E+00 0.00E+00 0.00E+00        *        *   STAGE 0.00E+00  0.00E+00         *         *
P_SOLID     10     66     4.70     2.50     3.75     3.62     1.15   P_SOLID   1.00     12.00      1.75      6.50
DOC          1     75 0.00E+00 0.00E+00 0.00E+00        *        *   DOC   0.00E+00  0.00E+00         *         *
HION        75      1    5.192    3.162    4.495    5.752    0.664   HION     0.159    31.623     1.000     6.310
```

Table 13b Correlation matrices

(i) normal

	PH	COND	AMM_N	TON	TH	FCO2	TA	CL	OPO4	SIO2	SO4	NA	K	CU	MG	CA
COND	-0.162															
AMM_N	0.091	-0.072														
TON	-0.167	0.152	[illegible]													
TH	0.604	[illegible]	[illegible]	0.004												
FCO2	-0.637	0.077	0.015	-0.071	-0.410											
TA	0.873	0.075	-0.015	-0.228	0.741	-0.433										
CL	-0.305	0.717	-0.045	-0.035	0.255	0.395	-0.185									
OPO4	0.069	-0.129	-0.059	0.054	-0.077	-0.024	-0.011	-0.108								
SIO2	0.109	0.441	[illegible]	0.220	0.405	-0.045	0.036	0.385	[illegible]							
SO4	-0.121	0.511	0.024	0.264	0.343	0.016	-0.220	0.268	-0.077	0.142						
NA	0.162	0.526	0.024	0.011	0.519	-0.315	0.215	0.408	-0.045	[illegible]	0.202					
K	0.049	0.473	0.257	0.243	0.490	0.003	0.127	0.278	-0.001	0.344	0.127	0.155				
CU	-0.072	-0.114	0.054	0.261	-0.080	-0.095	-0.112	-0.100	0.010	[illegible]	[illegible]	-0.110	0.211			
MG	0.479	0.574	-0.015	0.056	0.941	-0.256	0.612	0.371	-0.157	0.424	[illegible]	0.452	0.456	-0.094		
CA	0.707	0.445	0.012	0.026	0.959	-0.519	0.791	0.133	-0.057	[illegible]	0.114	0.555	0.462	-0.044	0.324	
ZN	-0.319	0.169	0.254	0.001	-0.006	0.113	-0.306	0.185	-0.010	-0.174	0.101	0.145	0.017	0.417	0.101	-0.059
CD	0.014	-0.155	0.078	-0.057	-0.156	-0.134	-0.068	-0.097	0.199	-0.109	-0.438	0.275	0.065	0.149	-0.338	0.039
AL	-0.554	0.182	0.024	0.204	-0.412	0.570	-0.752	0.275	-0.052	0.044	0.274	-0.147	0.044	0.174	-0.243	-0.542
PB	-0.313	0.226	0.059	-0.112	-0.027	0.228	-0.234	0.309	[illegible]	0.265	-0.052	0.025	0.367	0.178	0.027	-0.061
CR	0.033	-0.531	0.145	0.303	-0.329	-0.290	-0.398	-0.463	0.073	0.168	-0.001	-0.224	-0.192	0.212	-0.391	-0.238
MN	-0.181	0.177	-0.014	-0.174	-0.030	0.487	0.025	0.340	-0.087	0.145	-0.045	-0.081	0.071	-0.102	0.073	-0.088
FE	0.312	-0.159	0.093	-0.119	0.104	-0.055	0.351	-0.069	-0.058	0.359	-0.179	-0.067	-0.072	-0.072	0.028	0.172
NI	-0.188	-0.027	0.109	0.061	-0.127	0.075	-0.225	0.042	0.133	0.154	-0.161	-0.124	0.311	0.315	-0.136	-0.097
HUMIC	0.246	-0.283	0.012	-0.210	-0.068	0.035	0.315	-0.183	0.010	0.109	-0.489	-0.210	-0.102	-0.081	-0.137	0.015
P_SOLID	0.202	-0.287	0.654	-0.117	-0.015	0.079	-0.014	0.019	*	0.361	0.142	0.206	-0.422	-0.223	-0.042	-0.016
HION	-0.537	0.329	-0.069	0.041	-0.394	0.738	-0.586	0.376	-0.107	-0.173	0.080	-0.079	0.095	-0.020	-0.235	-0.497

	ZN	CD	AL	PB	CR	MN	FE	NI	HUMIC	P_SOLID
CD	0.009									
AL	0.324	-0.177								
PB	0.324	0.257	0.263							
CR	-0.050	0.169	0.064	0.233						
MN	-0.081	-0.209	0.316	0.061	-0.166					
FE	-0.324	-0.074	-0.100	-0.183	0.168	0.553				
NI	0.223	0.358	0.116	0.274	0.264	-0.017	-0.068			
HUMIC	-0.729	-0.030	-0.155	-0.132	0.227	0.572	0.922	-0.092		
P_SOLID	0.707	*	-0.030	0.747	*	-0.354	-0.041	0.000	-0.039	
HION	0.299	-0.068	0.225	0.111	-0.321	0.272	-0.245	0.113	-0.163	-0.372

(ii) logarithmic

	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17
C2	0.363																
C3	-0.141	0.344															
C4	-0.220	-0.072	-0.234														
C5	-0.075	0.053	-0.056	0.507													
C6	-0.242	0.127	-0.094	0.574	0.479												
C7	-0.523	-0.144	0.030	[illegible]	0.524	0.777											
C8	0.166	0.335	-0.102	[illegible]	0.552	0.455	0.204										
C9	0.402	0.555	0.076	-0.246	-0.097	-0.225	-0.570	0.313									
C10	0.016	0.153	0.274	[illegible]	0.368	0.480	0.416	0.443	[illegible]								
C11	0.246	0.053	[illegible]	[illegible]	0.095	0.590	0.214	0.258	[illegible]	0.352							
C12	0.217	-0.277	[illegible]	[illegible]	0.033	-0.009	0.097	-0.089	[illegible]	[illegible]	[illegible]						
C13	0.280	-0.262	-0.225	0.173	0.316	0.102	0.112	0.019	[illegible]	[illegible]	[illegible]	0.013					
C14	-0.774	-0.129	[illegible]	0.227	-0.010	0.426	0.714	-0.246	[illegible]	[illegible]	-0.149	0.017	[illegible]				
C15	-0.409	-0.221	[illegible]	[illegible]	0.348	0.915	0.954	0.348	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			
C16	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.440	0.807	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.610		
C17	[illegible]	[illegible]	[illegible]	[illegible]	-0.175	-0.307	-0.205	-0.291	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-0.273	-0.420	
C18	[illegible]	[illegible]	[illegible]	[illegible]	-0.035	[illegible]	-0.676	0.267	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-0.555	0.164	[illegible]

Table 14a UC4 streamwater quality (1984-5)

```
             N    N*      MEAN    MEDIAN    TRMEAN     STDEV    SEMEAN
T_CU        13     8   0.00238   0.00200   0.00213   0.00037   0.00024
T_ZN        13     8   0.01479   0.01100   0.01257   0.01109   0.00308
T_CD        13     8   0.00101   0.00100   0.00100   0.00003   0.00001
T_AL        13     8    0.0897    0.0800    0.0829    0.0370    0.0103
T_PB        12     9   0.00233   0.00200   0.00210   0.00089   0.00026
T_CR        13     8   0.00300   0.00300   0.00300   0.00000   0.00000
T_MN        13     8    0.0880    0.0600    0.0787    0.0615    0.0171
T_FE        13     8     0.901     0.450     0.536     1.395     0.387
T_NI        13     8   0.00308   0.00300   0.00300   0.00028   0.00008
PH          21     0     5.915     5.900     5.923     0.531     0.116
COND        21     0     33.56     34.00     33.30      6.24      1.36
TURB         3    18      2.91      3.90      2.81      2.47      1.42
AMM_N       21     0    1.4803    1.4286    1.4431    0.1618    0.0353
TON         21     0      8.16      7.14      7.14      4.68      1.02
NO2         21     0   0.28570   0.28570   0.28570   0.00000   0.00000
TH          20     1     5.736     5.300     5.673     1.451     0.324
FCO2        18     3     2.986     2.869     2.865     1.164     0.274
TA          18     3     69.10     53.95     64.37     39.75      9.37
CL          21     0    133.15    141.04    136.36     43.63      9.52
OPO4        21     0   0.02043   0.02000   0.02000   0.00218   0.00048
SIO2        21     0    0.7742    0.6000    0.7609    0.3841    0.0838
SO4         21     0     67.32     68.37     67.11     15.43      3.37
NA          20     1    136.55    137.63    136.82     27.52      6.15
K           19     2     4.753     3.346     4.528     3.145     0.722
CU          21     0   0.00287   0.00200   0.00275   0.00127   0.00028
MG          20     1     64.26     62.09     63.63     14.86      3.32
CA          20     1     54.09     49.15     53.50     14.02      3.13
ZN          21     0   0.01474   0.01200   0.01335   0.00945   0.00206
CD          21     0   0.00115   0.00100   0.00104   0.00052   0.00011
AL          21     0   0.06691   0.06810   0.06685   0.01592   0.00347
PB          21     0   0.00343   0.00200   0.00342   0.00154   0.00034
CR          21     0   0.00300   0.00300   0.00300   0.00000   0.00000
MN          21     0   0.06375   0.04700   0.05995   0.04104   0.00896
FE          21     0    0.3254    0.2863    0.3197    0.1637    0.0357
NI          21     0   0.00310   0.00300   0.00306   0.00027   0.00006
HUMIC       21     0     4.143     4.150     4.142     1.362     0.297
IG           1    20  0.00E+00  0.00E+00  0.00E+00         *         *
TEMP         1    20  0.00E+00  0.00E+00  0.00E+00         *         *
T_NA         1    20  0.00E+00  0.00E+00  0.00E+00         *         *

T_K          1    20  0.00E+00  0.00E+00  0.00E+00         *         *
T_MG         1    20  0.00E+00  0.00E+00  0.00E+00         *         *
T_CA         1    20  0.00E+00  0.00E+00  0.00E+00         *         *
ACID         1    20  0.00E+00  0.00E+00  0.00E+00         *         *
UV           1    20  0.00E+00  0.00E+00  0.00E+00         *         *
F_PH         1    20  0.00E+00  0.00E+00  0.00E+00         *         *
STAGE        1    20  0.00E+00  0.00E+00  0.00E+00         *         *
P_SOLID      7    14      4.71      3.00      4.71      4.72      1.78
DOC          1    20  0.00E+00  0.00E+00  0.00E+00         *         *
HION        21     0     2.437     1.259     1.852     3.532     0.771

                 MIN       MAX        Q1        Q3
T_CU         0.00200   0.00300   0.00200   0.00250
T_ZN         0.00600   0.04300   0.00700   0.01715
T_CD         0.00100   0.00110   0.00100   0.00100
T_AL          0.0540    0.2000    0.0670    0.0990
T_PB         0.00200   0.00500   0.00200   0.00200
T_CR         0.00300   0.00300   0.00300   0.00300
T_MN          0.0390    0.2390    0.0445    0.1165
T_FE           0.311     5.500     0.372     0.720
T_NI         0.00200   0.00400   0.00300   0.00300
PH             4.900     6.800     5.543     6.300
COND           25.00     47.00     27.50     36.00
TURB            0.00      4.62      0.00      4.62
AMM_N         1.4286    2.1428    1.4286    1.4286
TON             7.14     28.57      7.14      7.14
NO2          0.28570   0.28570   0.28570   0.28570
TH             3.600     9.300     4.600     6.775
FCO2           1.500     6.400     2.162     3.400
TA             23.78    181.85     42.96     87.43
CL             34.63    225.67    107.71    169.25
OPO4         0.02000   0.03000   0.02000   0.02000
SIO2          0.2000    1.6000    0.5000    1.1000
SO4            42.70     95.92     54.16     76.63
NA             85.66    182.63    115.41    158.06
K              0.513    17.820     2.564     5.204
CU           0.00200   0.00600   0.00200   0.00320
MG             41.86     97.96     52.43     73.81
CA             33.93     84.83     44.14     67.12
ZN           0.00600   0.04990   0.00900   0.01800
CD           0.00100   0.00350   0.00100   0.00100
AL           0.04100   0.09400   0.05250   0.08000
PB           0.00200   0.00500   0.00200   0.00500
CR           0.00300   0.00300   0.00300   0.00300
MN           0.02980   0.17000   0.03600   0.07650
FE            0.1240    0.6350    0.1774    0.4300
NI           0.00300   0.00400   0.00300   0.00300
HUMIC          2.400     5.900     2.500     5.500
IG          0.00E+00  0.00E+00         *         *
TEMP        0.00E+00  0.00E+00         *         *
T_NA        0.00E+00  0.00E+00         *         *

T_K         0.00E+00  0.00E+00         *         *
T_MG        0.00E+00  0.00E+00         *         *
T_CA        0.00E+00  0.00E+00         *         *
ACID        0.00E+00  0.00E+00         *         *
UV          0.00E+00  0.00E+00         *         *
F_PH        0.00E+00  0.00E+00         *         *
STAGE       0.00E+00  0.00E+00         *         *
P_SOLID         1.00     15.00      2.00      5.00
DOC         0.00E+00  0.00E+00         *         *
HION           0.159    15.849     0.515     2.877
```

Table 14b. Correlation matrices

(i) normal

	PH	COND	TURB	AMM_N	TON	TH	FCO2	TA
COND	0.4[illegible]							
TURB	-0.?61	-0.[illegible]						
AMM_N	-0.[illegible]	0.?7?	[illegible]					
TON	-0.4?1	-0.241	*	-0.?7?				
TH	0.907	0.?73	-0.?92	0.2??	-0.?14			
FCO2	-0.5?1	-0.527	0.240	-0.070	0.000	-0.520		
TA	0.?77	0.?57	-0.675	-0.076	-0.000	0.?5?	-0.409	
CL	0.?34	0.?51	-0.?52	0.?51	-0.??1	0.657	-0.257	0.144
OPO4	0.?3?	0.?3	0.?0	0.?31	-0.?50	0.422	-0.040	0.043
SIO2	0.?14	0.?0?	-0.??2	0.341	-0.164	0.525	-0.169	0.450
SO4	0.101	0.367	-0.9??	0.02?	-0.566	0.107	-0.501	-0.264
NA	0.55?	0.??3	-0.?71	0.?73	-0.455	0.75?	-0.701	0.451
K	-0.145	0.4?7	-0.7??	-0.[illegible]	-0.169	0.061	-0.151	-0.258
CU	0.??1	0.2??	0.?57	0.47?	-0.157	0.0?4	-0.191	-0.093
MG	0.761	0.912	-0.9??	0.363	-0.355	0.97?	-0.506	0.747
CA	0.?35	0.?12	-0.795	0.2??	-0.334	0.9?5	-0.500	0.873
ZN	-0.214	-0.05?	0.?40	0.?05	-0.139	-0.212	-0.095	-0.324
CD	-0.??0	-0.373	0.?12	0.259	-0.066	-0.333	-0.057	-0.322
AL	-0.639	-0.369	0.?44	0.1?0	0.044	-0.427	0.772	-0.406
PB	0.197	0.127	0.956	0.343	-0.213	0.167	-0.415	-0.160
MN	0.357	0.599	-0.990	0.466	-0.177	0.696	-0.127	0.604
FE	-0.074	0.074	-0.112	0.?09	-0.010	0.187	0.420	0.227
NI	-0.224	-0.451	0.901	0.127	-0.087	-0.407	-0.108	-0.338
HUMIC	-0.163	-0.256	0.9?6	0.?65	0.22?	0.006	0.450	0.251
P_SOLID	0.077	0.552	*	0.?6?	*	0.480	-0.104	-0.010
DOC	-0.115	0.294	-0.994	0.170	-0.008	0.142	0.243	0.034

	CL	OPO4	SIO2	SO4	NA	K	CU	MG
OPO4	?.4??							
SIO2	0.270	0.373						
SO4	0.?34	0.021	-0.057					
NA	0.?16	0.?94	0.471	0.662				
K	0.58?	*	0.[illegible]	0.?43	0.473			
CU	0.367	0.736	-0.167	0.121	0.170	-0.35?		
MG	0.726	0.532	0.560	0.205	0.834	0.063	0.146	
CA	0.552	0.?99	0.506	0.005	0.552	-0.039	0.103	0.943
ZN	-0.15?	0.079	-0.344	0.?49	-0.017	0.179	0.478	-0.228
CD	-0.?04	-0.014	-0.?11	0.025	-0.272	-0.106	0.199	-0.347
AL	-0.167	0.13?	0.0?0	-0.320	-0.406	0.004	-0.182	-0.398
PB	-0.174	0.275	-0.530	0.5?6	0.406	0.012	0.504	0.199
MN	0.439	0.582	0.691	-0.140	0.477	-0.148	-0.001	0.698
FE	0.166	0.336	0.545	-0.620	-0.122	-0.122	-0.189	0.168
NI	-0.437	-0.097	-0.303	-0.214	-0.493	-0.104	0.212	-0.448
HUMIC	-0.541	0.235	0.129	-0.767	-0.419	-0.441	-0.194	-0.062
P_SOLID	0.50?	0.?62	0.376	0.009	0.740	-0.245	0.908	0.685
DOC	0.477	0.257	0.771	-0.464	-0.018	0.062	-0.359	0.165

	CA	ZN	CD	AL	PB	MN	FE	NI	HUMIC	P_SOLID
ZN	-0.1??									
CD	-0.234	0.392								
AL	-0.415	0.071	0.010							
PB	0.135	0.519	0.307	-0.319						
MN	0.69?	-0.157	-0.247	0.13?	-0.155					
FE	0.243	-0.170	-0.201	0.59?	-0.555	0.568				
NI	-0.306	0.328	0.576	0.148	0.054	-0.276	-0.056			
HUMIC	0.039	-0.031	-0.003	0.623	-0.339	0.476	0.796	0.196		
P_SOLID	0.395	0.695	*	0.193	0.962	0.574	0.391	*	0.447	
DOC	0.152	-0.335	-0.196	0.312	-0.740	0.465	0.639	-0.179	0.322	0.016

(ii) logarithmic

	C1	C2	C3	C4	C5	C6	C7	C8
C2	0.1?7							
C3	0.11?	0.?7?						
C4	-0.42?	0.4?6	-?.???					
C5	-0.01?	-0.173	-?.1?2	?.377				
C6	-0.43?	0.661	0.?47	0.?4?	0.040			
C7	-0.44?	?.46?	?.2?2	0.?74	-0.054	0.?43		
C8	-0.2?1	0.41?	0.[illegible]	0.77?	0.496	0.742	0.573	
C9	0.?21	-0.030	0.442	-0.71?	-0.200	-0.55?	-0.574	-0.261
C10	0.17?	0.613	0.?02	0.?31	0.222	0.434	0.343	0.692
C11	-0.?13	-?.311	-0.675	0.712	0.456	0.290	0.096	0.414
C12	0.13?	0.?10	0.?91	0.?41	0.022	0.27?	0.234	0.240
C13	0.0??	-?.2??	0.?4?	-0.4??	-0.140	-0.422	-0.418	-0.328
C14	-0.40?	0.5??	?.2??	0.4?2	-0.513	0.768	0.356	0.171
C15	-0.45?	0.6?7	[illegible]	0.7?0	0.002	0.9?0	0.961	0.658
C16	-0.417	0.57?	?.?02	?.?79	?.351	0.2?5	0.801	0.839
C17	0.60?	?.4?7	[illegible]	-?.???	-?.?95	-0.344	0.032	-0.416
C18	[illegible]	[illegible]	[illegible]	[illegible]	0.13?	-0.77?	-0.865	-0.302

	C9	C10	C11	C12	C13	C14	C15	C16	C17
C10	-0.2??								
C11	-0.46?	?.014							
C12	-0.0?1	0.14?	0.?36						
C13	*	-0.1??	-0.425	-0.073					
C14	-?.45	[illegible]	-0.?75	-0.073	*				
C15	-0.??6	[illegible]	0.1?5	0.?35	-?.372	?.?24			
C16	-0.5??	?.?94	0.435	0.?76	-0.253	0.377	0.272		
C17	?.6?9	[illegible]	-0.775	0.?72	?.?15	?.2??	-0.040	-0.314	
C18	?.7??	-?.0??	-?.1?4	?.?94	?.?11	-0.7?4	-0.329	-0.514	?.171

substantially lower than those recorded for bulk precipitation indicating the continuation of nutrient uptake at the CI sites. NH_4 levels are similarly low.

The marine salts are all present at much lower concentrations than were found in the LI catchments, especially Na and Cl. Indeed, concentrations of the latter two average about 140 ueq l^{-1} and 150 ueq l^{-1} respectively in the Camddwr sites. These can be compared to an average of 114 ueq l^{-1} for Na and 142 ueq l^{-1} for Cl in bulk precipitation samples taken at C7 in 1984. Thus the reduction in evapotranspiration losses and sea-salt scavenging capacity has resulted in a major reduction in the marine salt concentrations. Hence, chloride probably behaves almost as a conservative element, although some enrichment of sodium seems to occur. More specifically, the slightly higher mean Na and Cl concentrations recorded in CI5 may reflect the effects of road salting since the site is below the access road. The above however, requires confirmation in the field.

Mg concentrations average 54 ueq l^{-1} at all sites in the Camddwr and are even lower than those found at LI1 and LI3, although they are still almost twice that found in bulk precipitaion at C7. Thus, although additional Mg is present within the catchment soils, the amounts only allow for a limited buffering capacity during acid events. Indeed, Ca concentrations are also low, averaging 43 ueq l^{-1} in CI3, CI4 and CI5. These levels are again lower than those recorded at the LI sites and further support the suggestion that there is still only a limited buffering capacity available in these catchments. CI6 however, exhibits a slightly higher mean Ca concentration (53 ueq l^{-1}) supporting the suggestion that it is somewhat atypical due to its soils, hydrology and topography and hence less acid. Likewise, total hardness concentrations average

4.6 mg l^{-1}, 4.6 mg l^{-1}, 4.8 mg l^{-1} and 5.1 mg l^{-1} at CI3, CI4, CI5 and CI6 respectively. Hence, the catchment soils, geology, hydrology and topography at each site combine to produce moderately acid waters without the added problems associated with afforestation demonstrated in the previous section.

Not surprisingly, dissolved aluminium levels are moderately high averaging 0.12 mg l^{-1}, 0.13 mg l^{-1}, 0.16 mg l^{-1} and 0.11 mg l^{-1} at CI3, CI4, CI5 and CI6 respectively. While, not as high as those found in the LI streams, the levels still represent a major increase on those found in bulk precipitation (averaging 0.027 mg l^{-1} Al at C7). In addition, the maximum concentrations recorded at each site all exceed the average levels found at LI8. Hence, although Al levels are not as severe in these moorland catchments, intermittent problems of high Al still occur at all of the sites principally during the more acid storm events.

Also, most CI sites exhibit very low dissolved Fe and Mn concentrations of less than 0.2 mg l^{-1} and 0.1 mg l^{-1} respectively. CI4 however exhibits a mean concentration of 0.26 mg l^{-1} and 0.14 mg l^{-1} for Fe and Mn respectively. Hence there appears to be an unusual source of these two metals in CI4.

Lastly, Table 15 presents a comparison of selected streamwater chemistry for the acidified moorland catchments. These can be compared directly to Tables 9 and 4. Clearly, CI3, CI4 and CI5 are slightly more acid than CI6, while sulphate concentrations in the latter are lower than in the other three. In addition, Ca concentrations are slightly higher at CI6, further supporting the suggestion that the stream has a slightly improved buffering capacity perhaps due to its atypical valley bottom soils and low slopes.

Examination of the correlation matrices for each acidified moorland catchment reveals several common and significant

Tables 15. A comparison of acidic moorland chemistry (ueq l^{-1})

	CI3	CI4	CI5	CI6	UC4[3]
[1] pH					
[2] $\bar{x}$	5.3	5.2	5.2	5.6	5.9
max	6.2	7.0	6.0	6.8	6.8
min	4.1	4.2	4.6	4.5	4.8
H^+					
$\bar{x}$	9	12	8	5	2.4
max	79	63	25	32	16
min	0.6	0.1	1	0.1	0.2
SO_4^{2-}					
$\bar{x}$	95	90	102	88	67
max	132	150	150	132	96
min	63	46	60	33	43
NO_3^-					
$\bar{x}$	15	10	15	14	8
max	100	21.4	86	43	29
min	7	7	7	7	7
[5] NH_4^+					
$\bar{x}$	1.5	1.5	1.5	1.5	1.5
max	2.9	2.9	5	2.9	2.1
min	1.4	1.4	1.4	1.4	1.4
Na^+					
$\bar{x}$	139	130	149	137	137
max	278	191	283	266	183
min	78	62	90	77	86
Cl^-					
$\bar{x}$	146	141	168	146	138
max	226	226	226	226	226
min	77	56	85	56	85
Mg^{2+}					
$\bar{x}$	54	53	56	54	64
max	95	114	91	98	98
min	34	4	33	26	42
Ca^{2+}					
$\bar{x}$	43	42	44	53	54
max	73	101	71	102	85
min	29	11	20	25	34
K^+					
$\bar{x}$	5.2	4.9	6.6	5.9	4.8
max	21.8	12	21	26	13
min	1.8	0.5	0.5	0.3	0.5
[4] Al					
$\bar{x}$	0.12	0.13	0.16	0.11	0.07
max	0.38	0.25	0.63	0.22	0.09
min	0.022	0.025	0.005	0.013	0.04

1. pH units. 2. $\bar{x}$ - arithmetic mean 3. $n < 21$
4. Dissolved Al. (mg l^{-1}) 5. mg l^{-1} as ammoniacal nitrogen

correlations (Tables 10b, 11b, 12b, 13b and 14b). First, CI3 indicates a significant negative correlation between pH and dissolved aluminium (r = -0.563) as at the LI sites. It also exhibits the expected positive correlation between pH and alkalinity (r = 0.968). Hence, acid events are accompanied by high aluminium levels during poorly buffered situations. Meanwhile SO_4 shows little correlation with any other parameter, as was also the case in the afforested catchments. The marine salts however, are more highly correlated at this site than was the case at LI1. For example, Na and Cl (r = 0.598); Mg and Cl (r = 0.695) and Na and Mg (r = 0.645) all reflect the major influence of sea-salts on rainfall chemistry with the reduced vegetation interference. Ca and Mg are also positively correlated (r = 0.813), although they do not exhibit any relationship with H^+ or Al concentrations, unlike LI1. Hence, at CI3 acid events accompanied by high aluminium concentrations do not necessarily correspond to periods of lowest buffering. As a result, aluminium concentrations and pH conditions are not as severe as those found in afforested catchments. Other notable correlations with H^+ include that with conductivity (r = 0.93), NO_3 (r = 0.933), free CO_2 r = 0.67) and total alkalinity (r = -0.84). Logarithmic transformation also suggests a high correlation between H^+ and Al (r = 0.66) which was not in evidence prior to transformation and probably reflects the curvilinear and scattered nature of the relationship. The high positive correlation with conductivity has not been demonstrated elsewhere and is difficult to explain since one would expect a negative correlation if any, as a result of the rapid runoff and reduced residence times associated with acid storm events.

At CI4 the relationships between pH and dissolved aluminium, and total alkalinity are repeated. The relationships between the marine salts however are less significant, perhaps suggesting some interference present within the catchment affecting the chemistry of marine salt inputs. On the other hand, Ca and Mg continue to exhibit a high correlation ($r = 0.84$), but with little correlation with H^+ concentrations, as at CI3. More specifically, the high correlation between H^+ and conductivity is not apparent at this site ($r = 0.43$), perhaps indicating a slightly different hydrochemical response during acid storm events. Lastly, H^+ and Al exhibit the familiar positive correlation ($r = 0.67$) associated with a stream subject to acid and aluminium pulses.

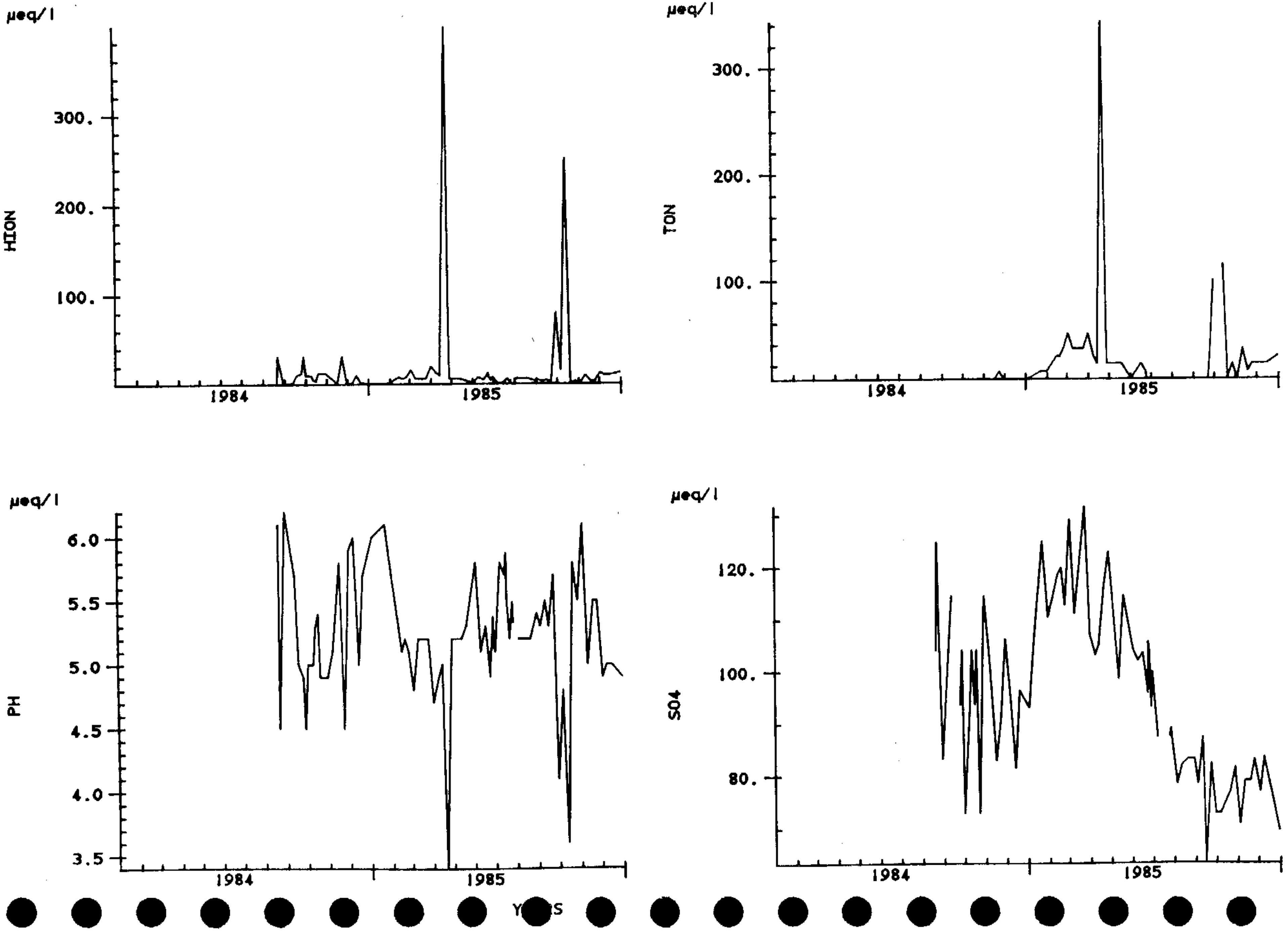
Similarly, CI5 exhibits a clear relationship between pH and dissolved aluminium ($r = -0.762$) and the existence of similar relationships to all those found at CI4, with no correlation between H^+ and conductivity. CI6 also indicates a clear negative correlation between pH and dissolved aluminium ($r = -0.85$). In addition, lower correlations between the marine salts are also demonstrated at this site. More importantly, CI6 does not indicate a good correlation between H^+ and conductivity as was the case at CI4 and CI5, but not CI3. Hence, the chemical interrelationships appear similar for each CI site, with the possible exception of CI3; a feature which requires more detailed investigation with regard to the catchments soils and hydrochemistry. Finally, correlation matrices for UC4 (Table 14b) are merely provided for information and are of limited applicability due to the small sample size.

Temporal patterns

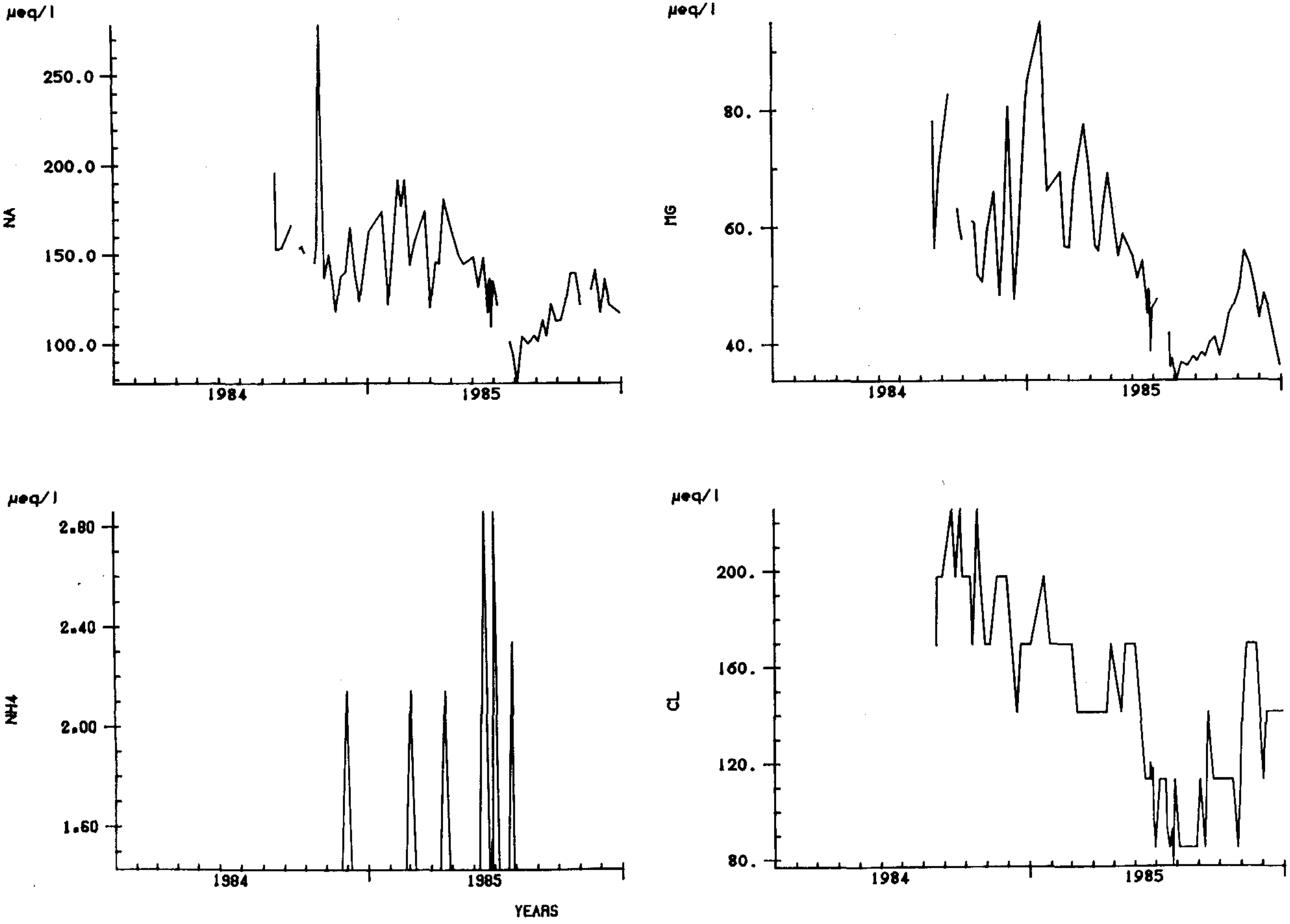
Figure 12 indicates that pH generally varies between 6.0 and 4.5 at CI3, but with two isolated peaks in acidity; these however correspond to two sample contamination incidences. Confirmation

Figure 12

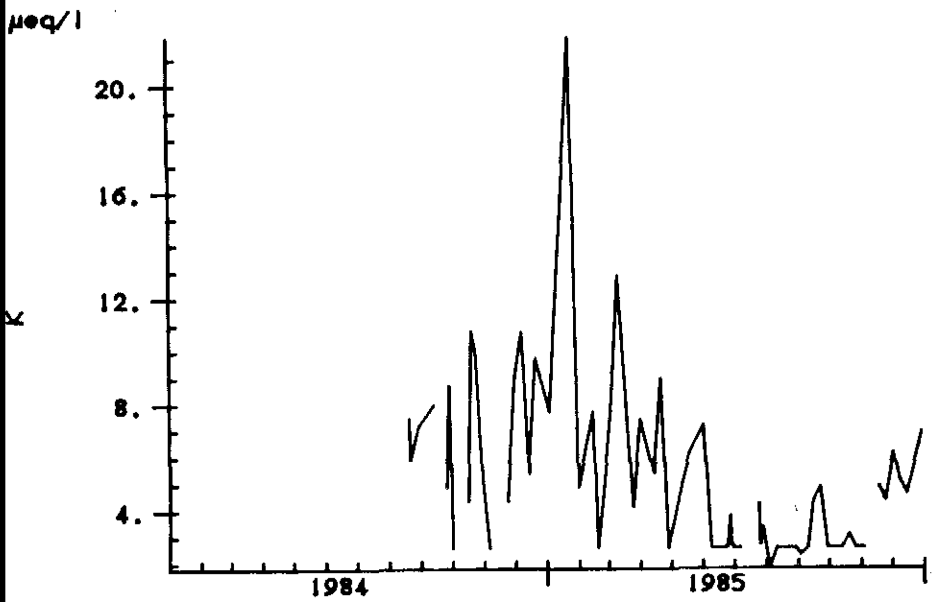
LLYN BRIANNE (CI3)

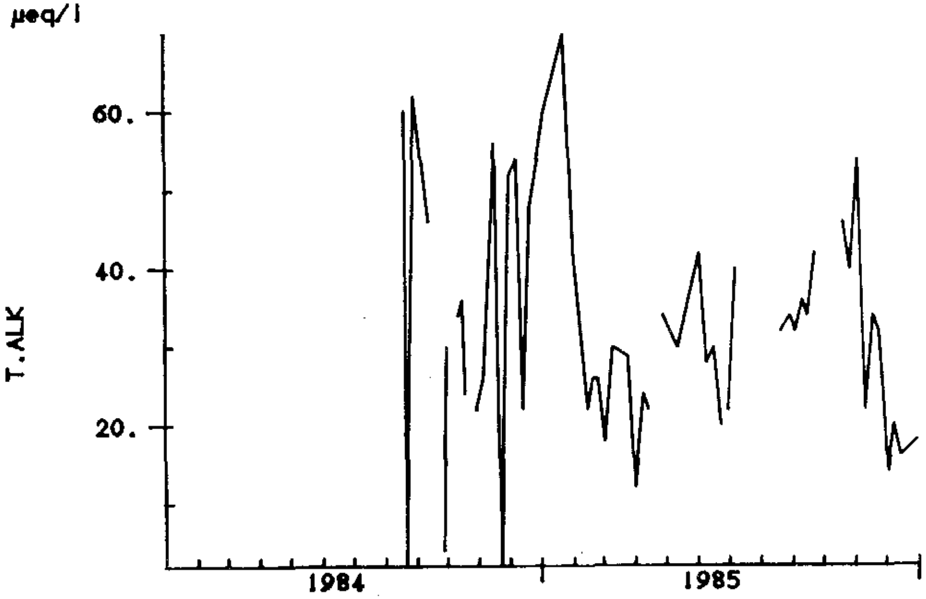


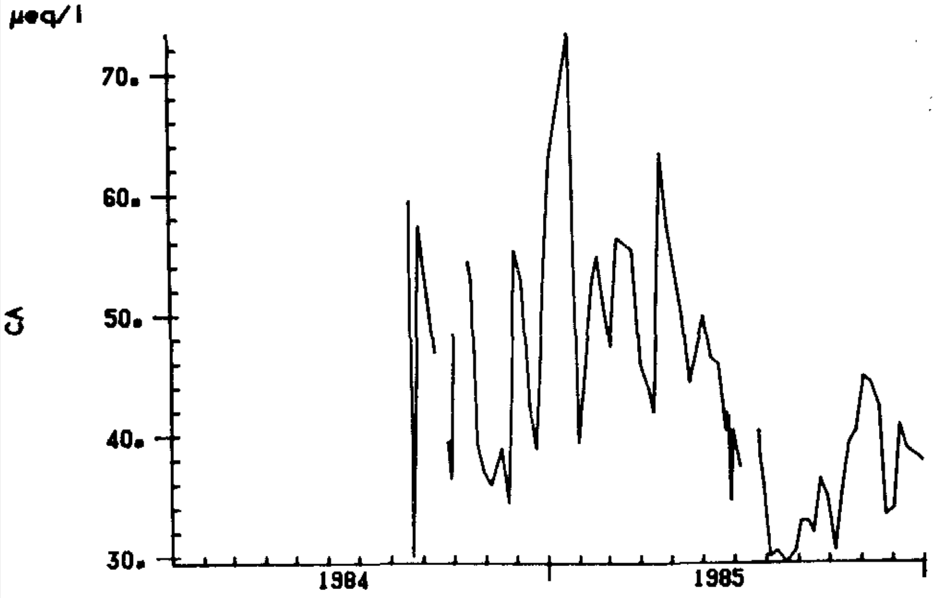
LLYN BRIANNE (CI3)

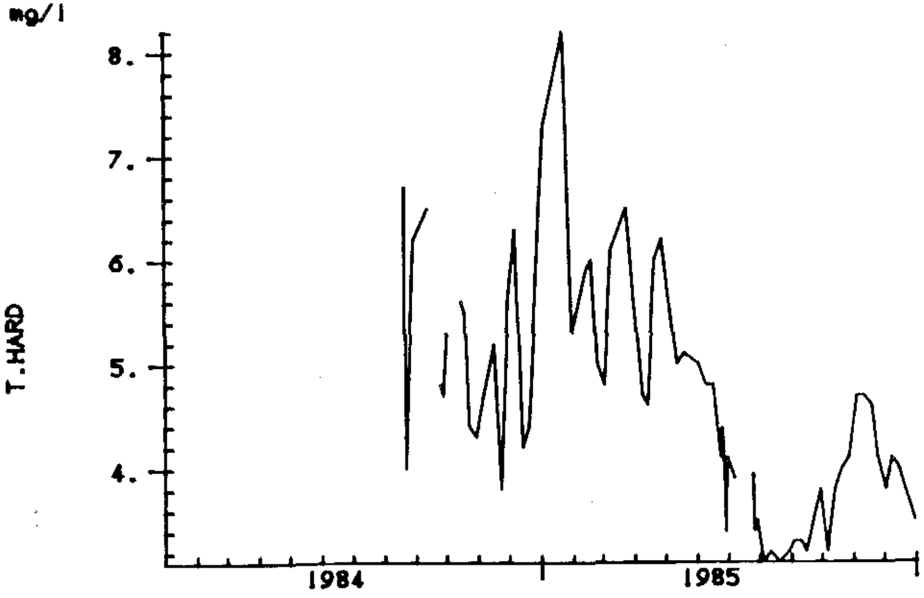


LLYN BRIANNE (CI3)









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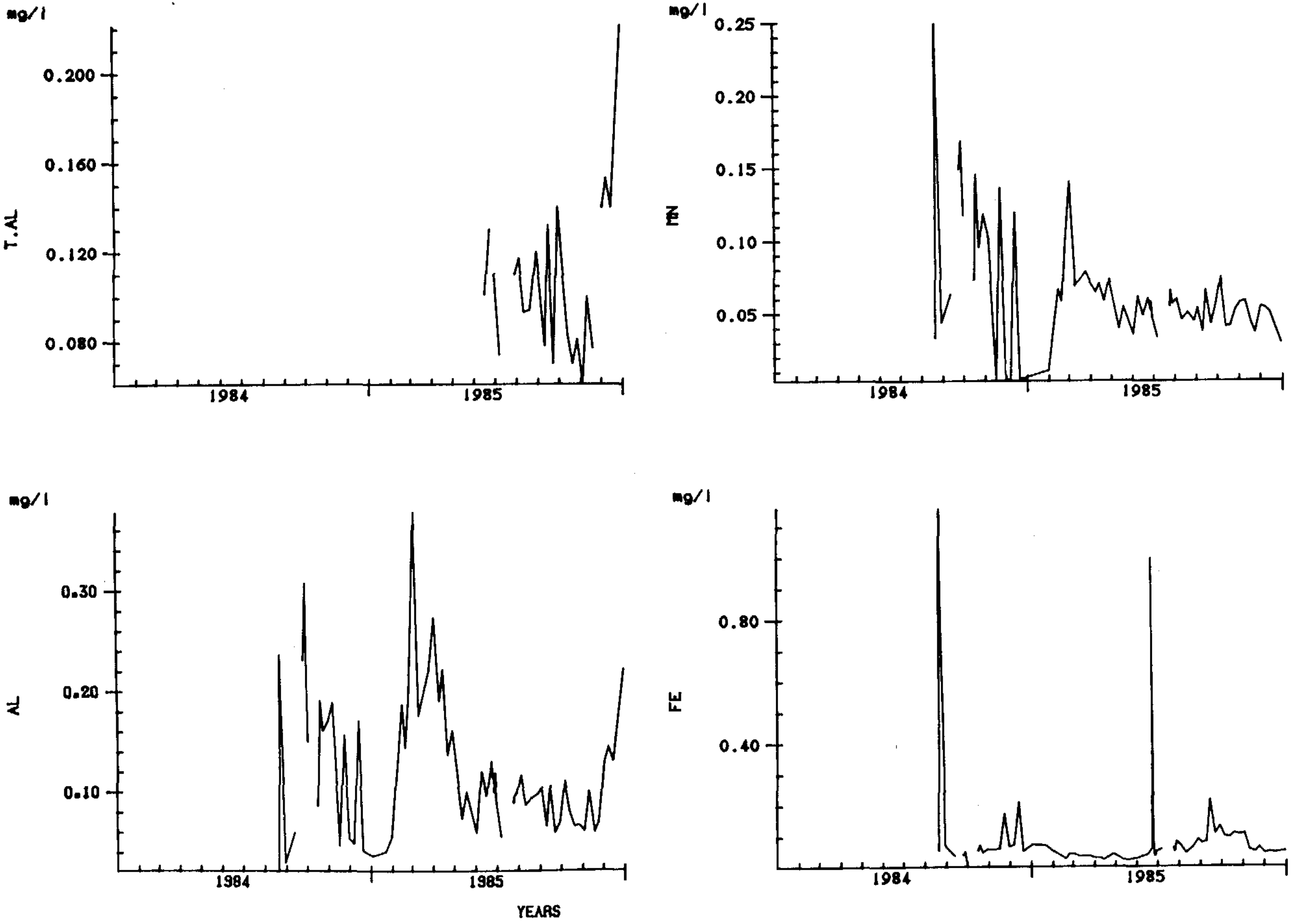

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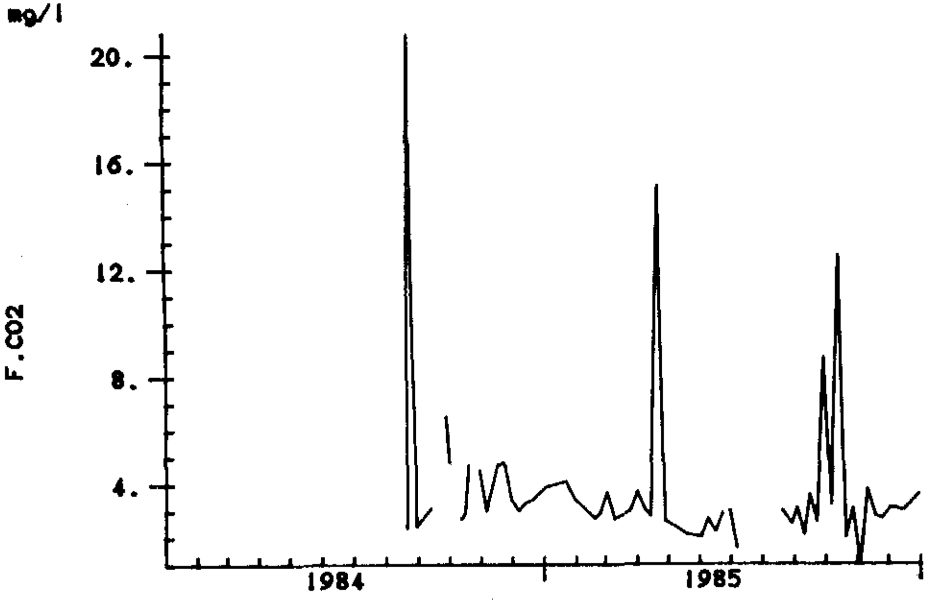
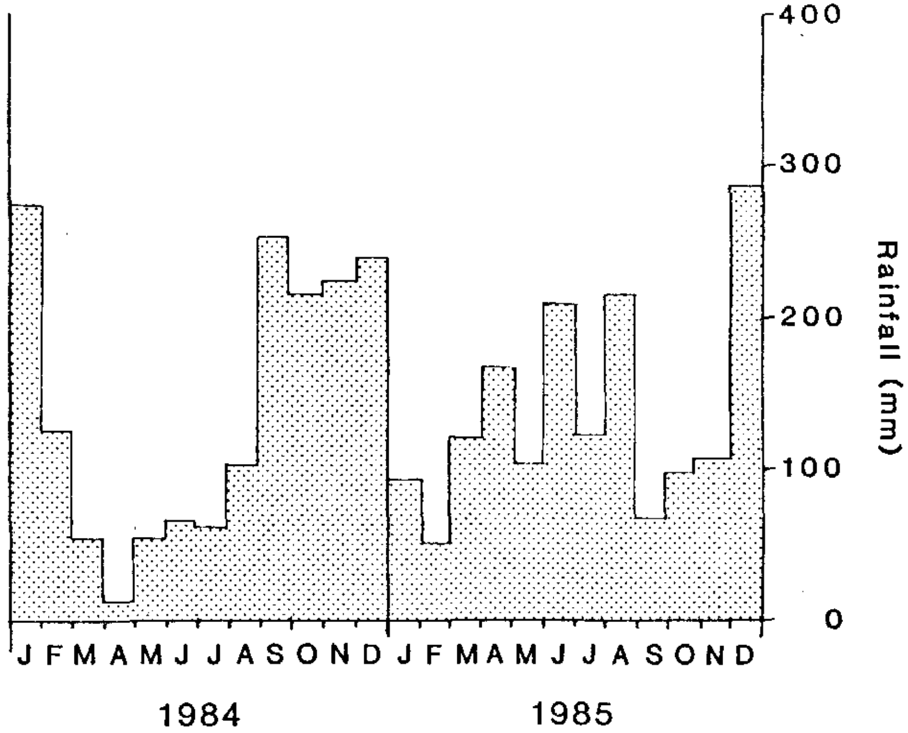
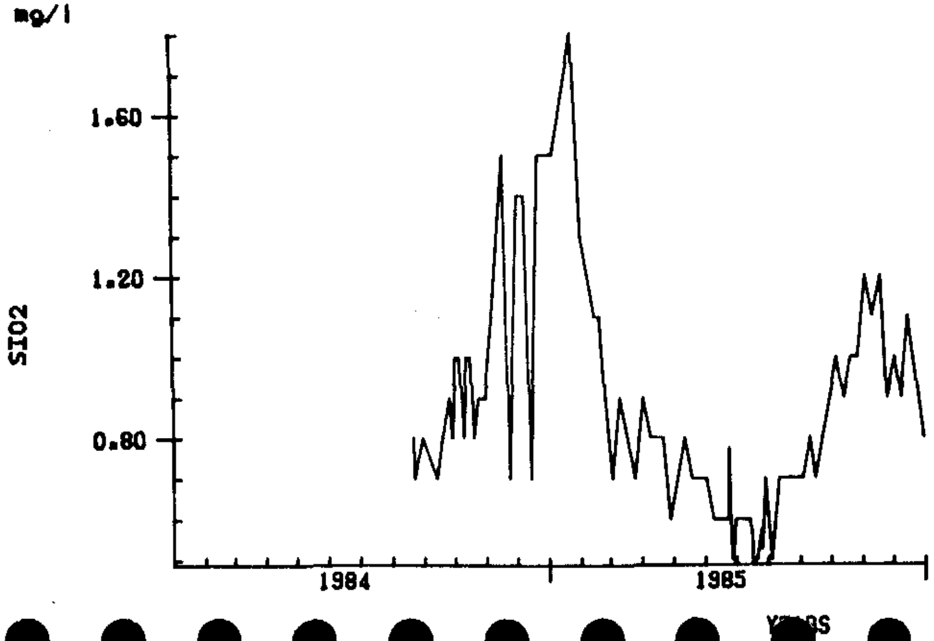
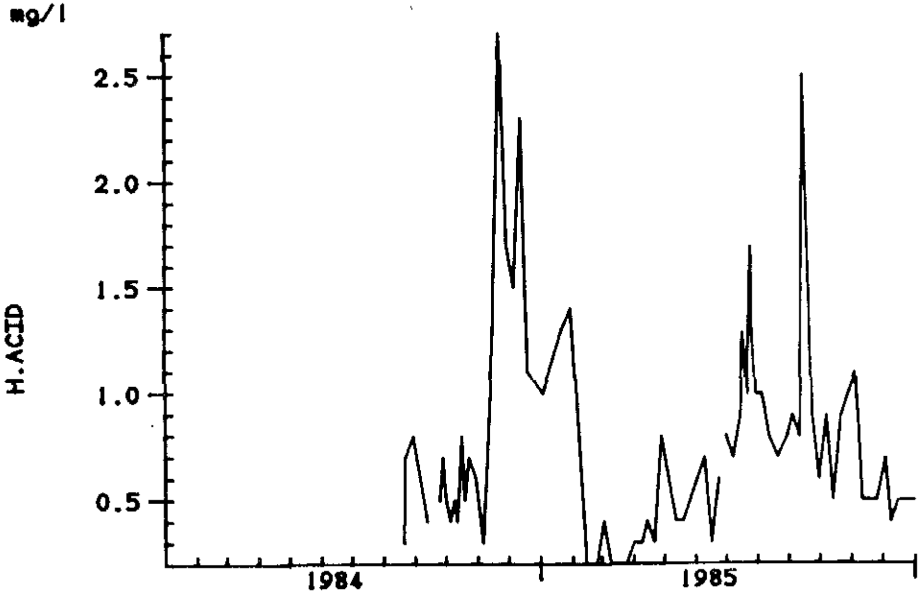








of the contamination is afforded by the correspondingly high levels of conductivity and NO_3. In normal circumstances as was the case with the statistics in Table 10a such samples will be removed from the record. Their inclusion is merely used to illustrate the need for careful sampling. Moreover, the above probably explains the spuriously high positive correlation between H^+ and conductivity at CI3. More generally then, pH and H^+ are seen to vary with rainfall inputs as at previous sites. In addition, some evidence of an Autumn flush is apparent in 1984.

SO_4 concentrations, while much lower than at LI1 for example, also show evidence of a flushing effect in August 1984, as well as late winter/ early Spring maximum during the low rainfall period of 1985. NO_3 levels indicate the usual Winter maximum caused by reduced plant uptake, the anomalous peaks being caused by nitric acid contamination.

The marine salts exhibit widely fluctuating patterns similar to those found in the forested streams. Levels are elevated following the Summer low flows of 1984, presumably reflecting concentration and flushing effects caused by the long dry spell. The reduced concentration in the Summer of 1985 probably reflects reduced flows when higher evapotranspiration losses countered moderately high catchment rainfall.

Ca, total hardness and total alkalinity levels also fluctuate widely, but show higher concentrations both following the dry Summer of 1984 and during the low rainfall period at the beginning of 1985. The latter probably occurred as a result of the larger baseflow contribution to streamflow at the time as well as the reduced evapotranspirational losses evident in Winter.

Dissolved aluminium at CI3 also exhibits a flushing effect in 1984 while in 1985 peaks correspond to individual acid events triggered by isolated rainfall inputs. Lastly, SiO_2 concentrations indicate a seasonal pattern of increased levels during the Winter high flow months. Certain diatoms may act as a sink for silica during Spring/ early Summer, perhaps accounting for the decline at such times.

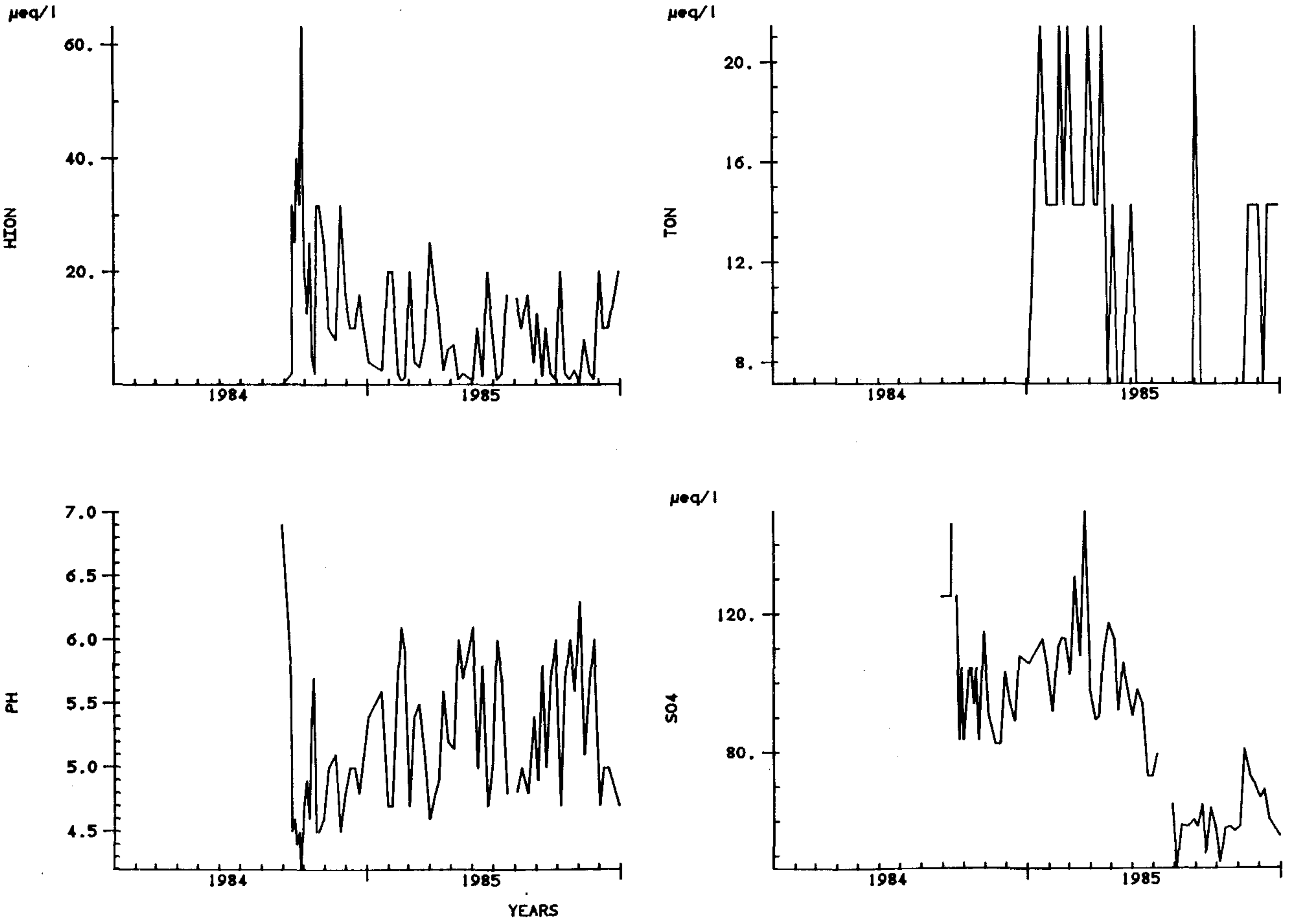
At CI4, pH and H^+ patterns again indicate the presence of an Autumn flush in September 1984 (Figure 13). In addition, high rainfall and high runoff months consistently exhibit elevated acidity levels, as at CI3. Furthermore, most of the other parameters exhibit very similar patterns to those found in CI3 although at slightly different concentrations in some cases.

CI5 also exhibits similar patterns, (Figure 14) more importantly the records available for the whole of 1984 also highlight the clear flushing effect recorded in September 1984. In addition, SO_4 and NO_3 patterns are similar and confirm the seasonal nature of both, moreover SO_4 peaks correspond with Winter periods. The marine salt and terrestrial cation patterns are also similar to those of CI3 and CI4. Aluminium concentrations again vary according to the incidence of acid events and exhibit a major flush following the reduced flows of Summer 1984. Lastly, SiO_2 also exhibits a clear seasonal pattern as at the previous site.

At CI6, pH and H^+ yield similar patterns, although their overall levels are slightly less acid (Figure 15). Hence, acid events continue to occur in conjunction with high rainfall and runoff, but the acidity is slightly dampened. All the other parameters again display almost identical patterns to those found at the other CI sites. The data for UC4 are included merely for

Figure 13

LLYN BRIANNE (CI4)



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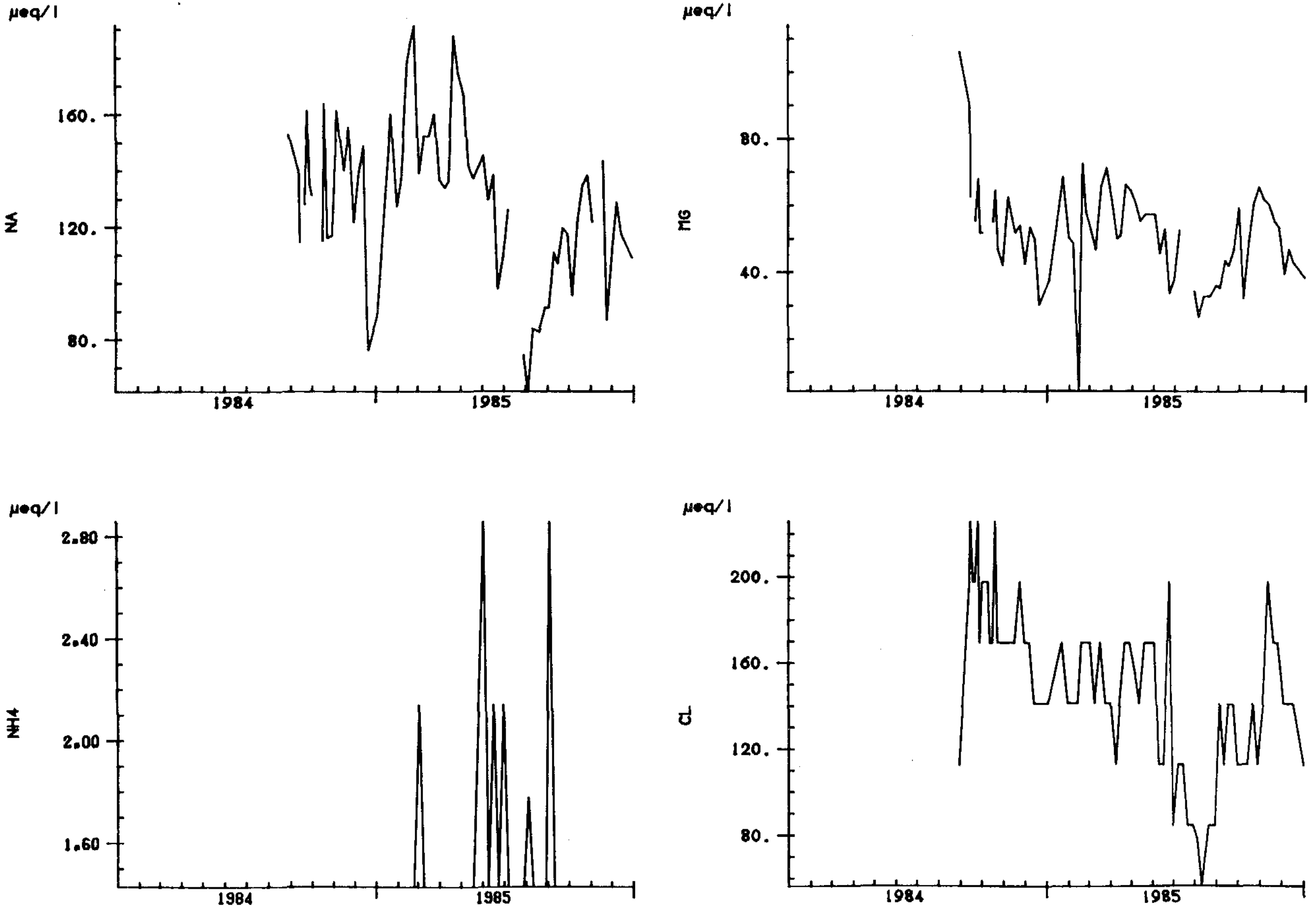

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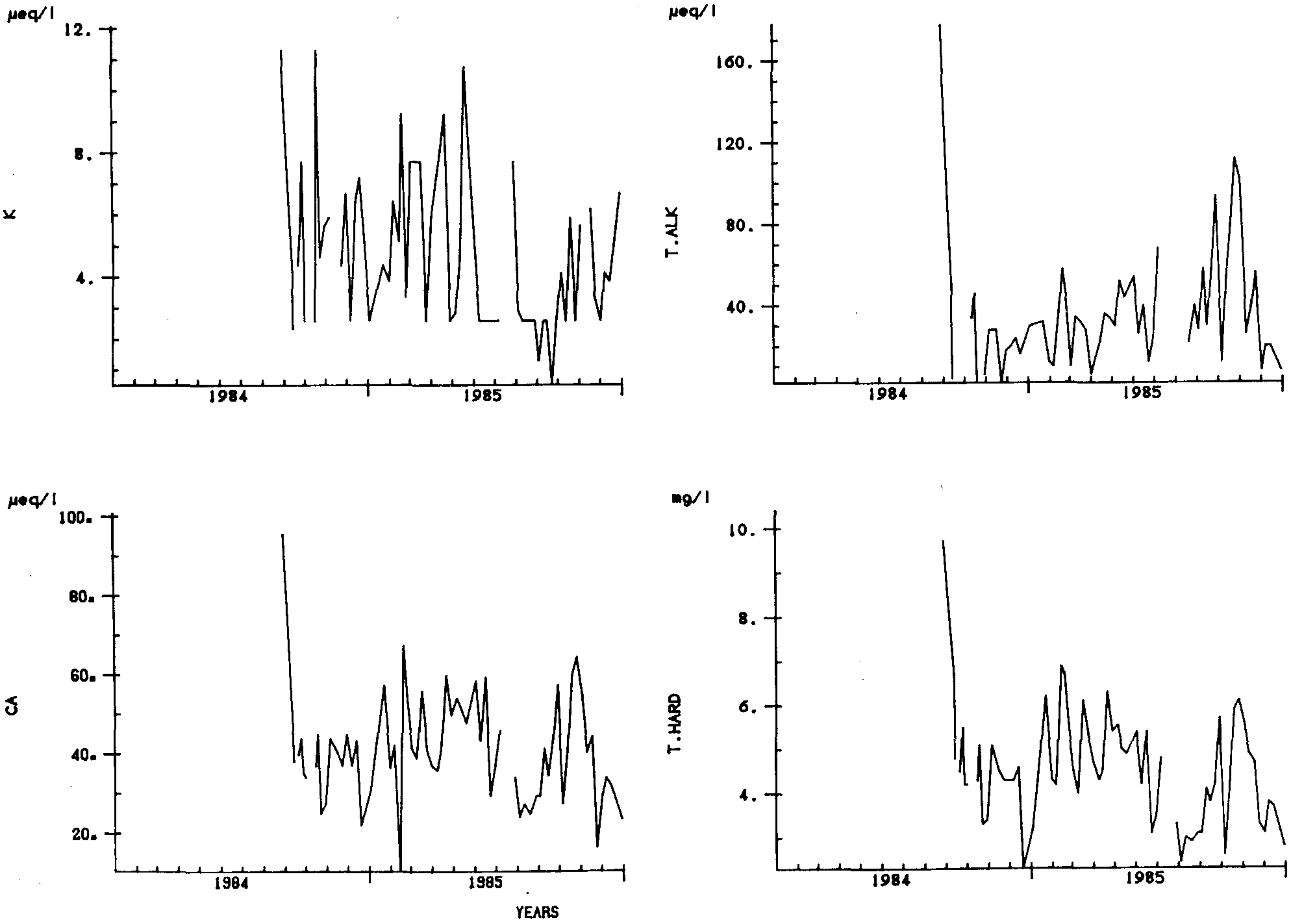

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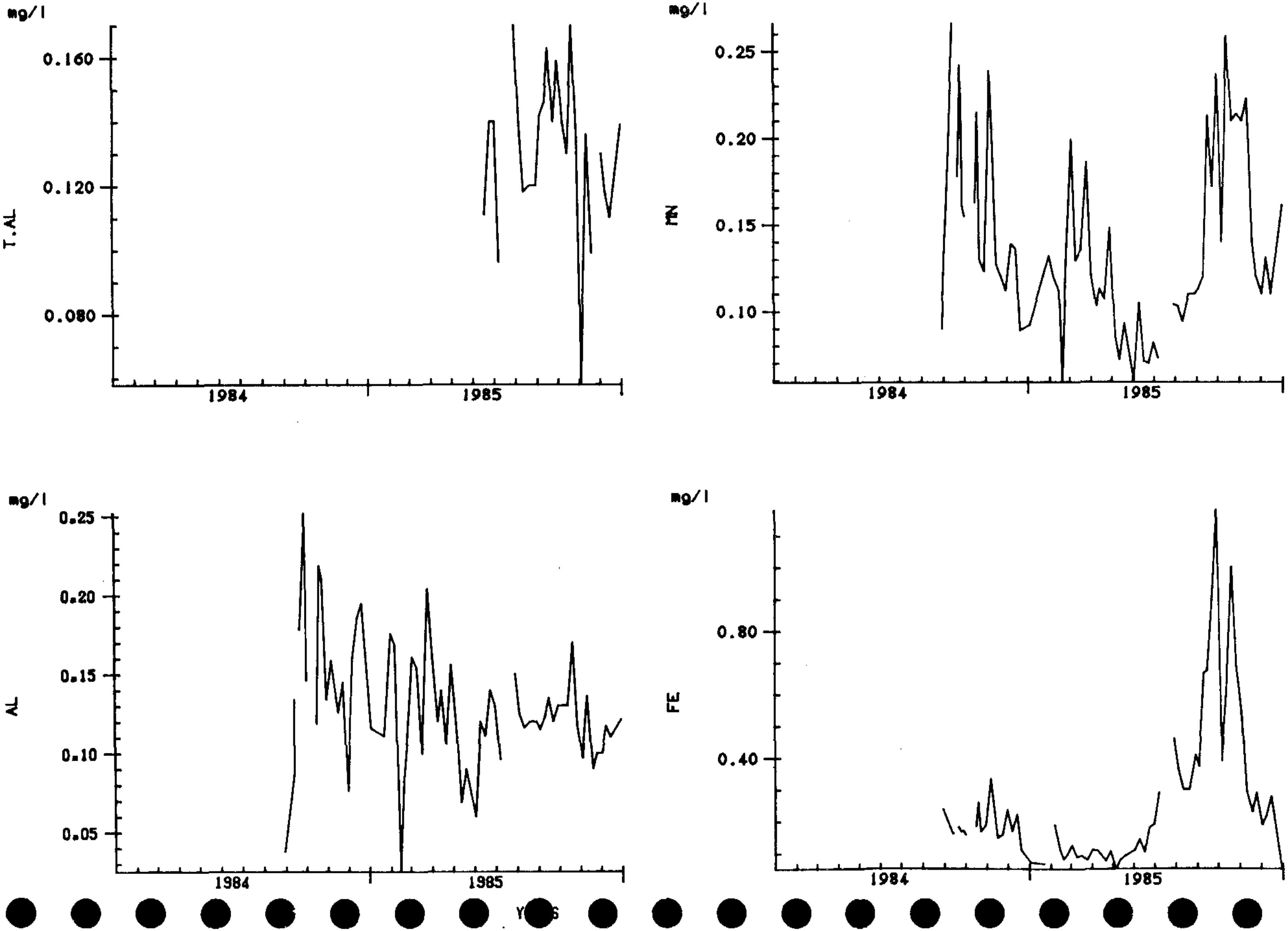

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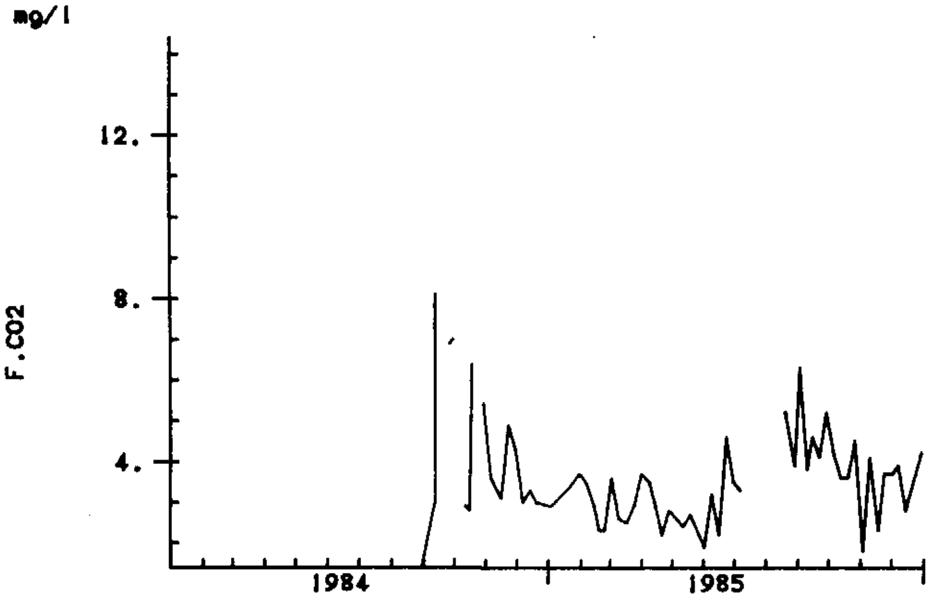
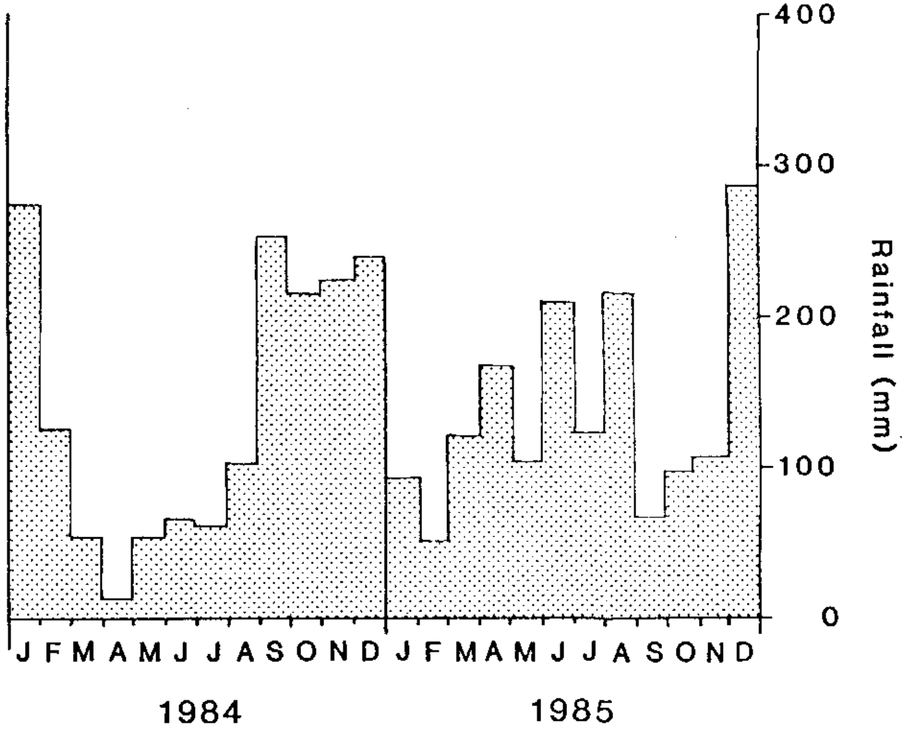
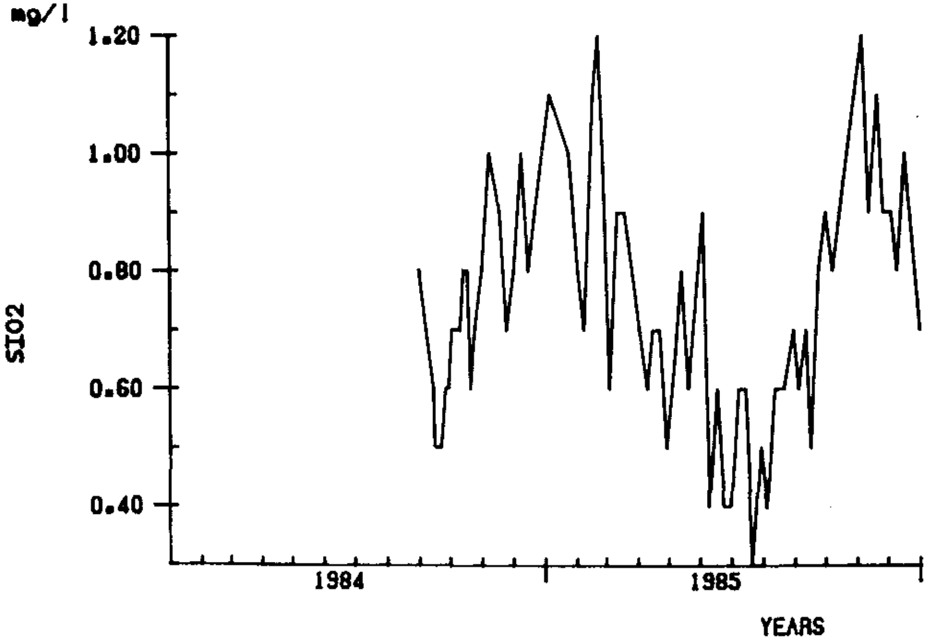






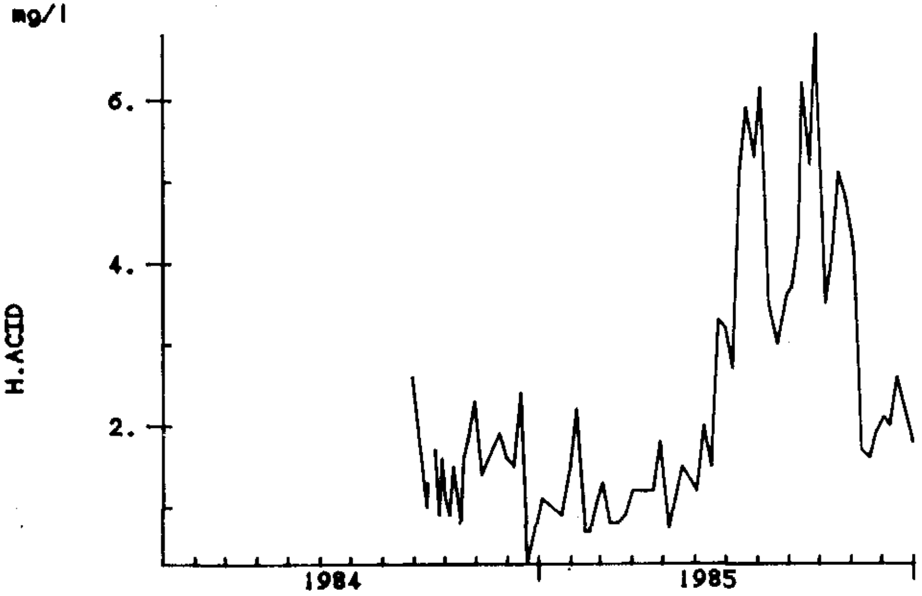
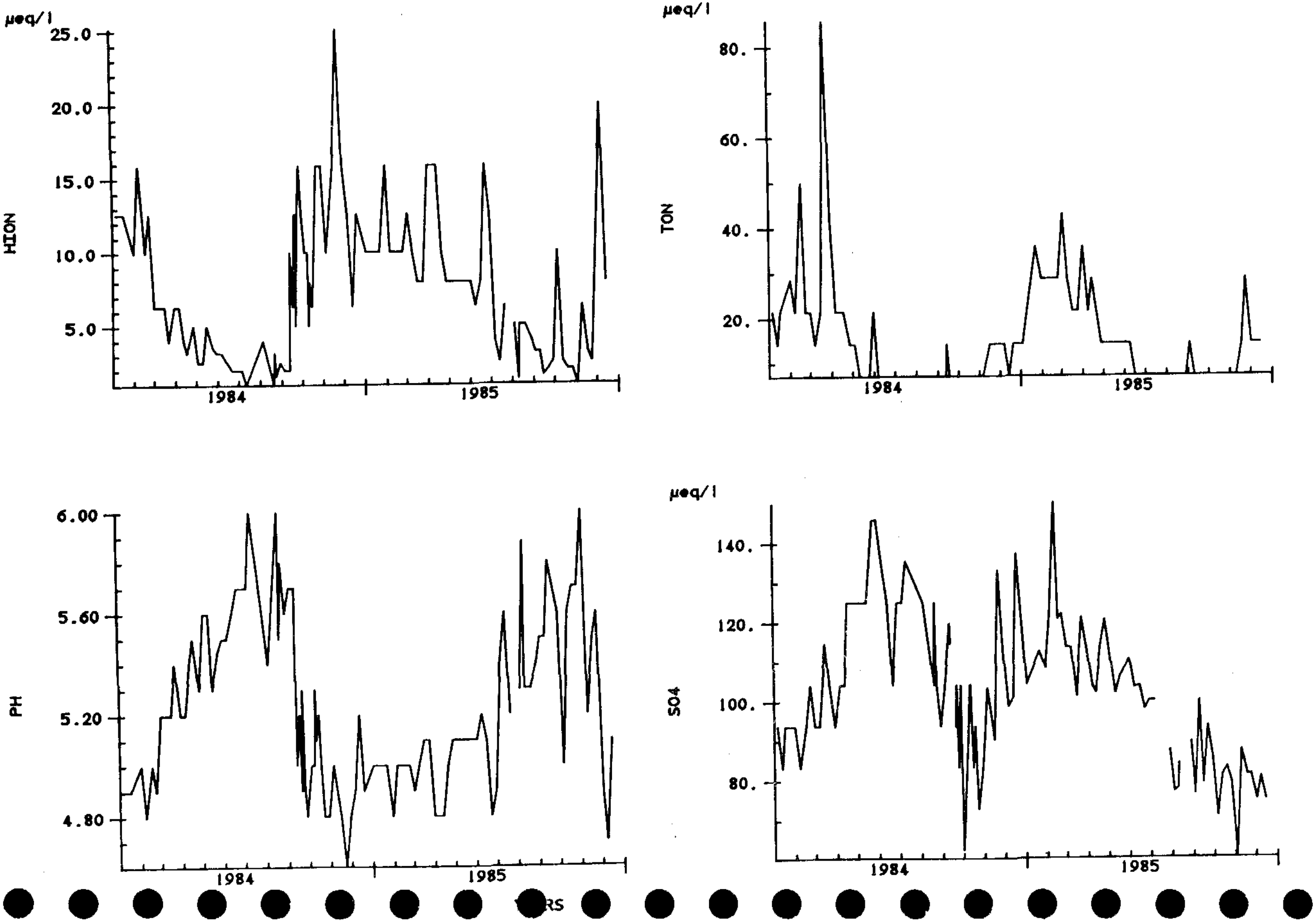


Figure 14

LLYN BRIANNE (CI5)



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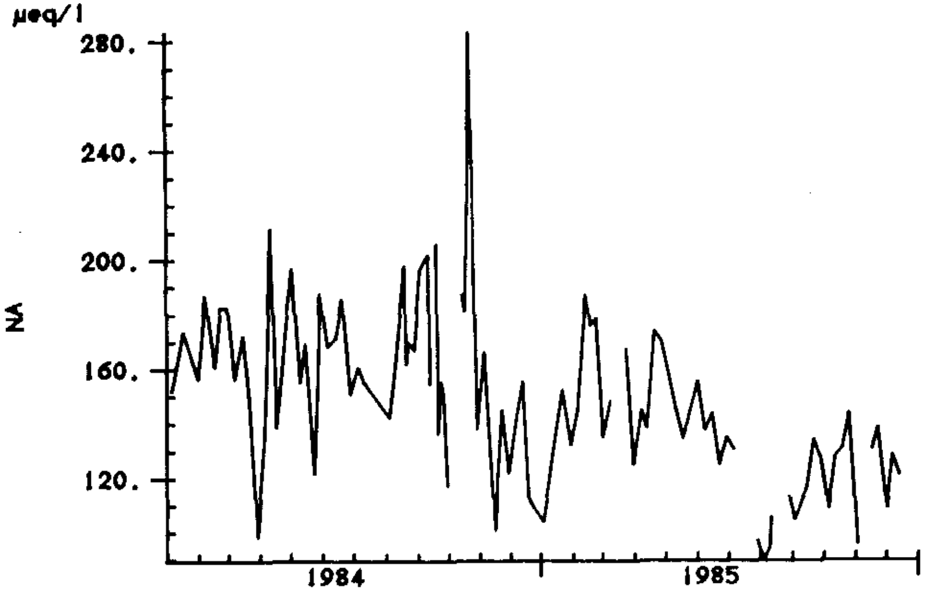

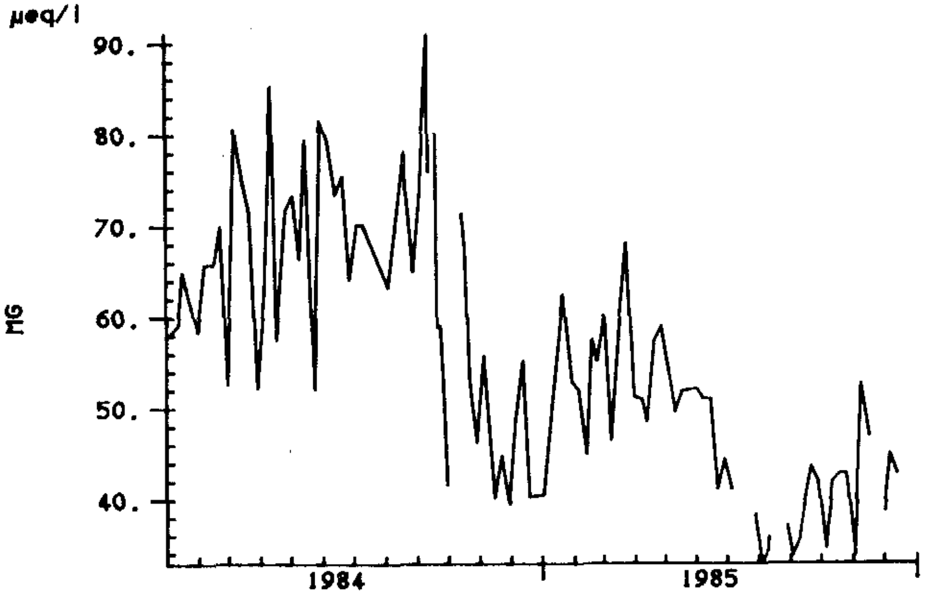

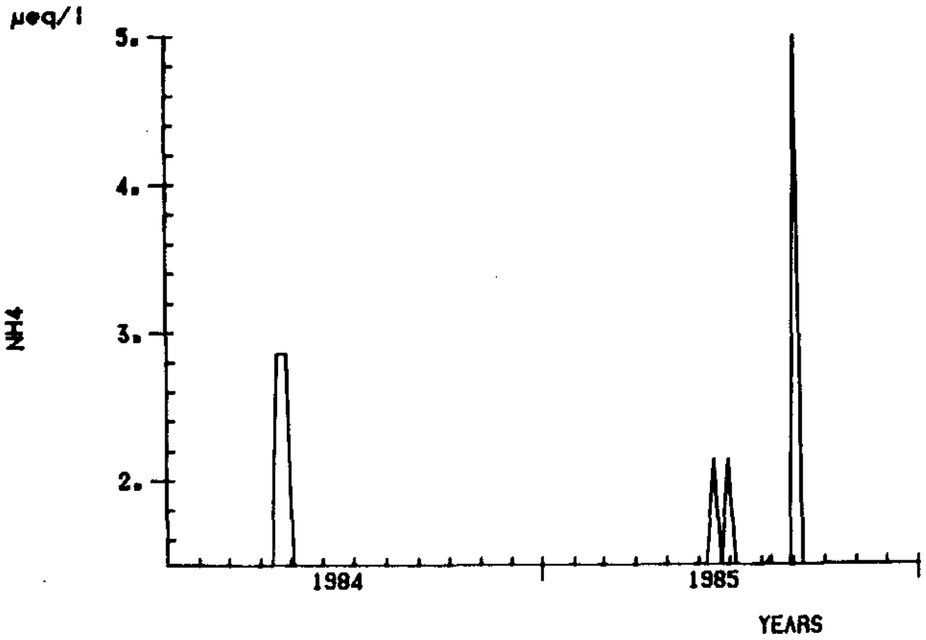

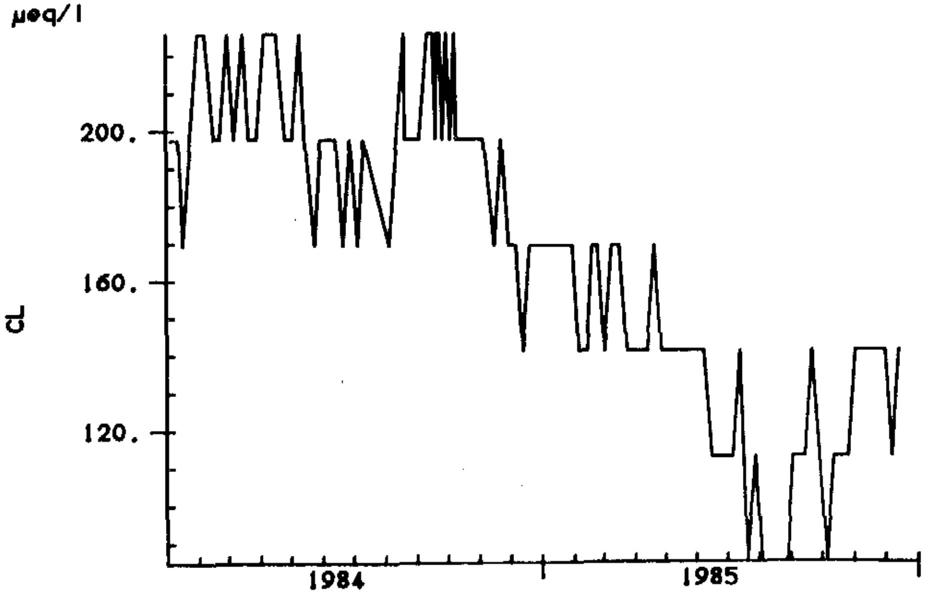

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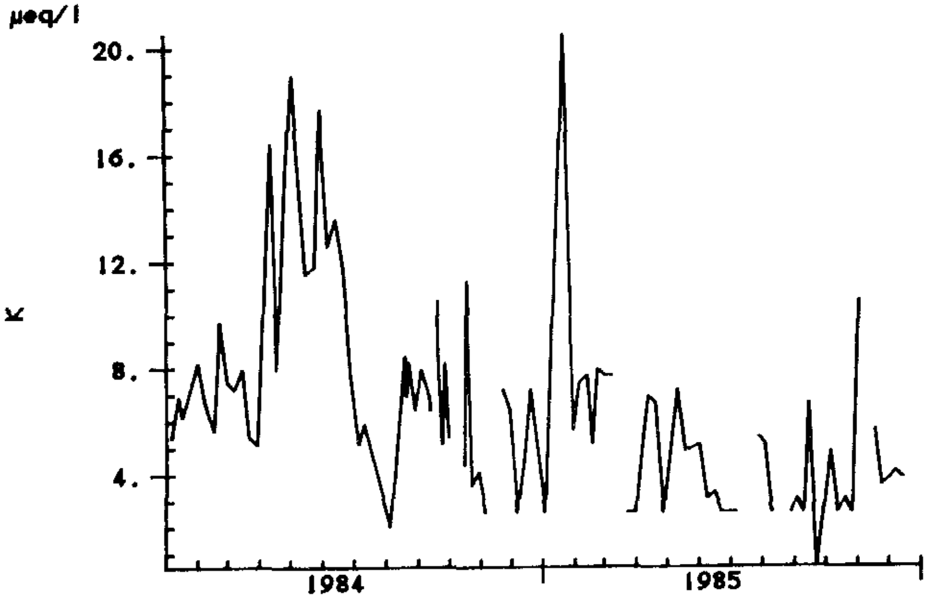

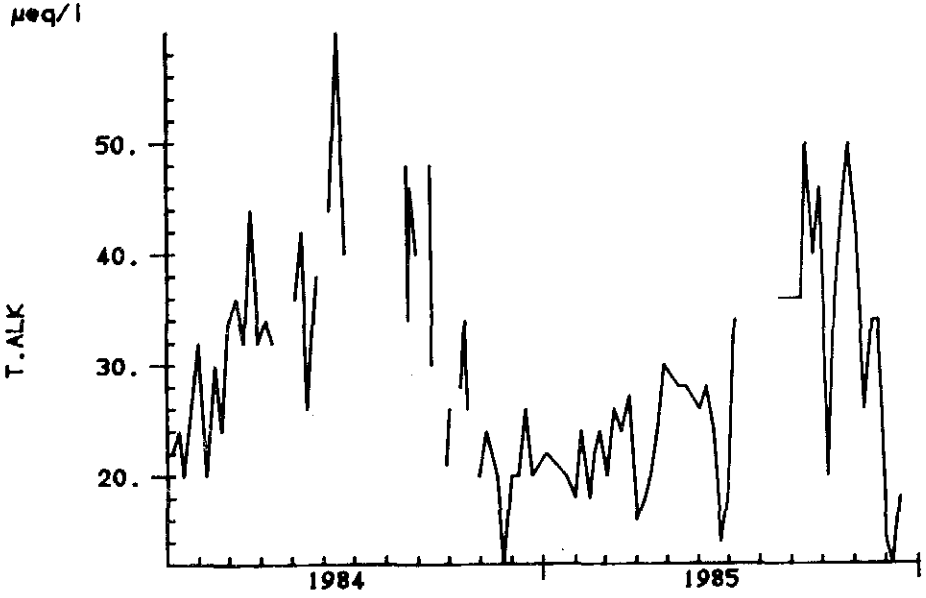

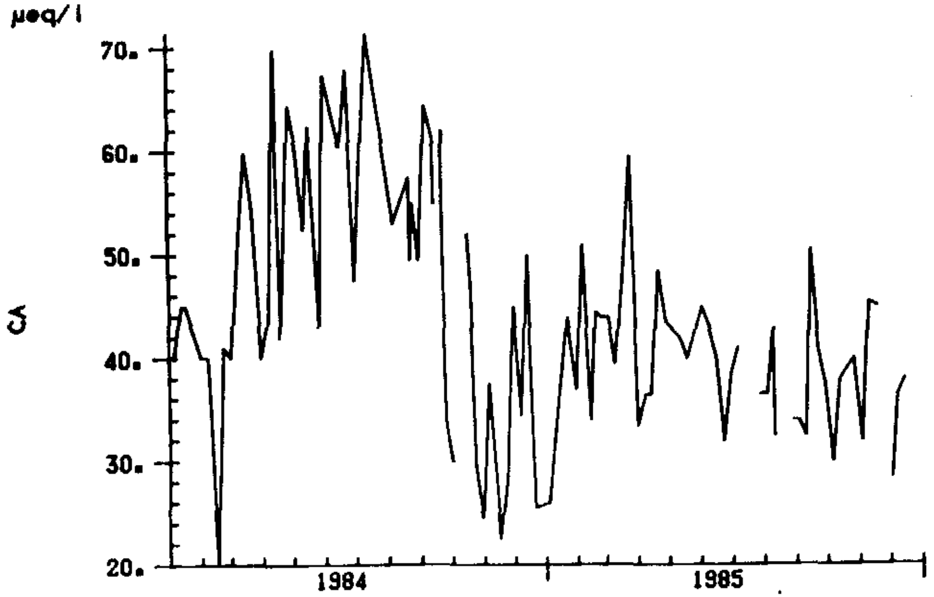

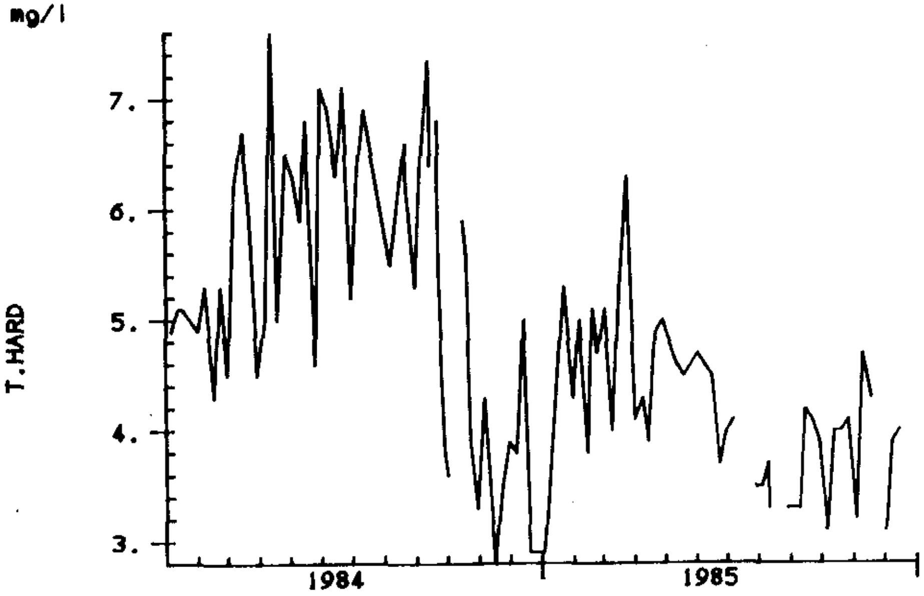

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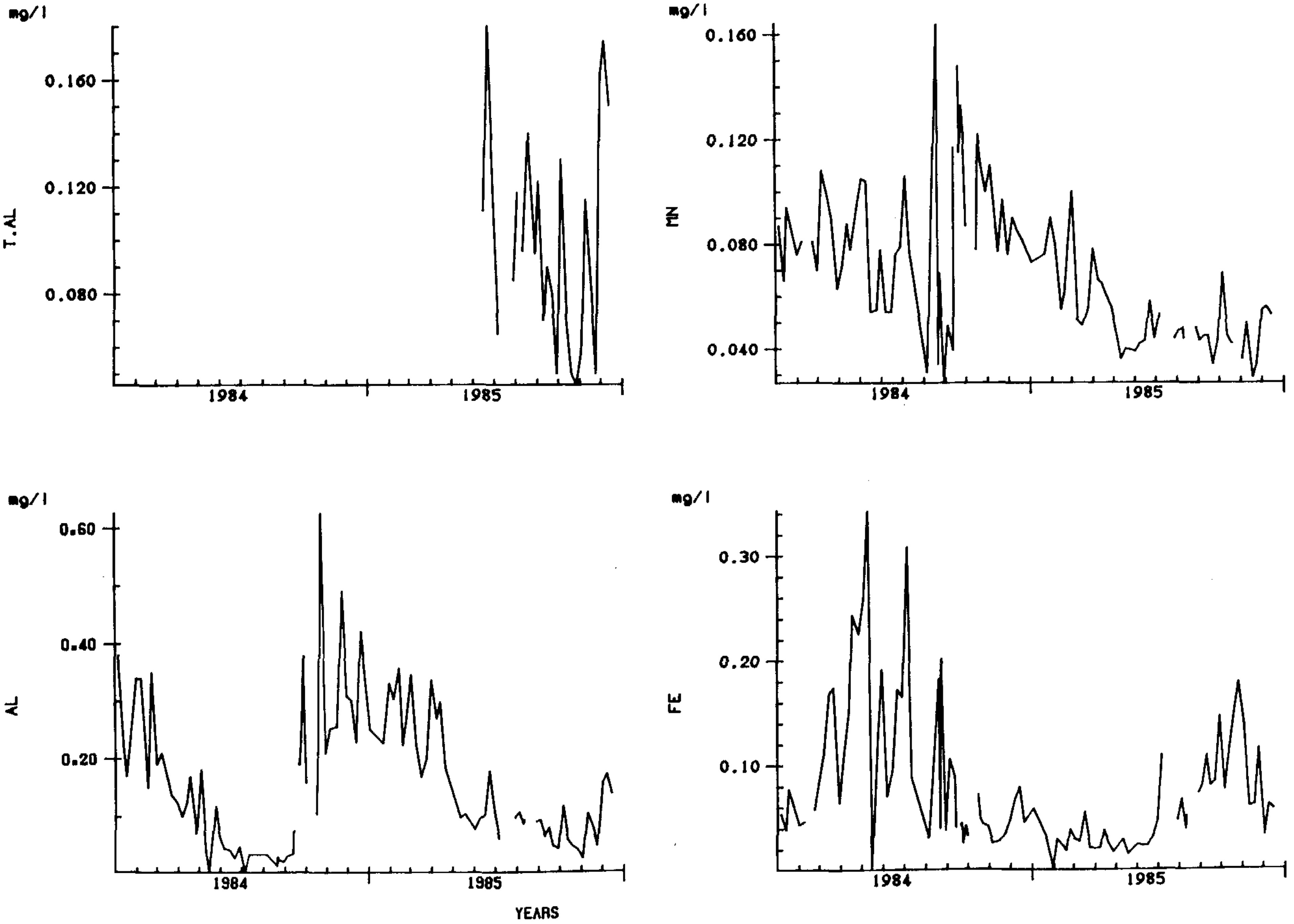

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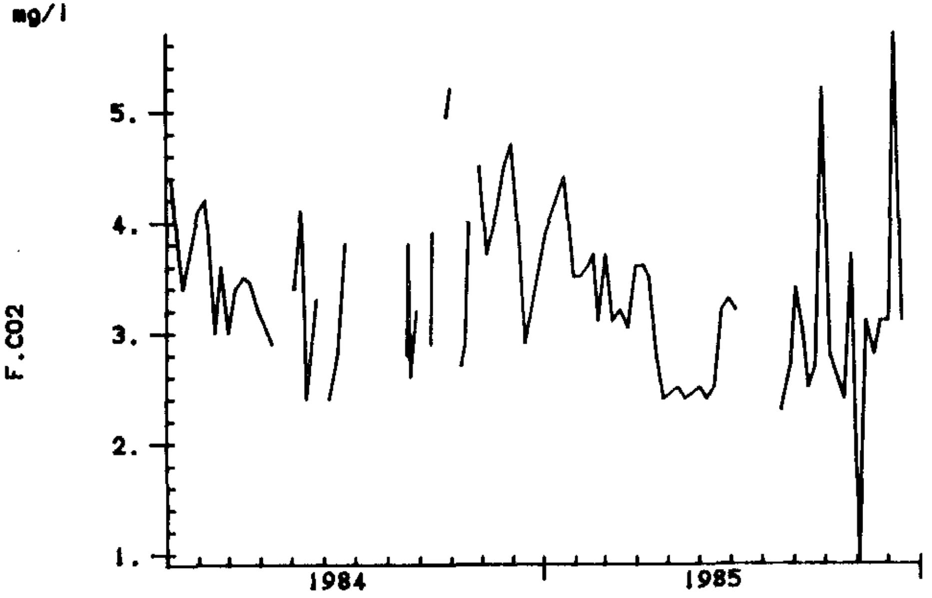
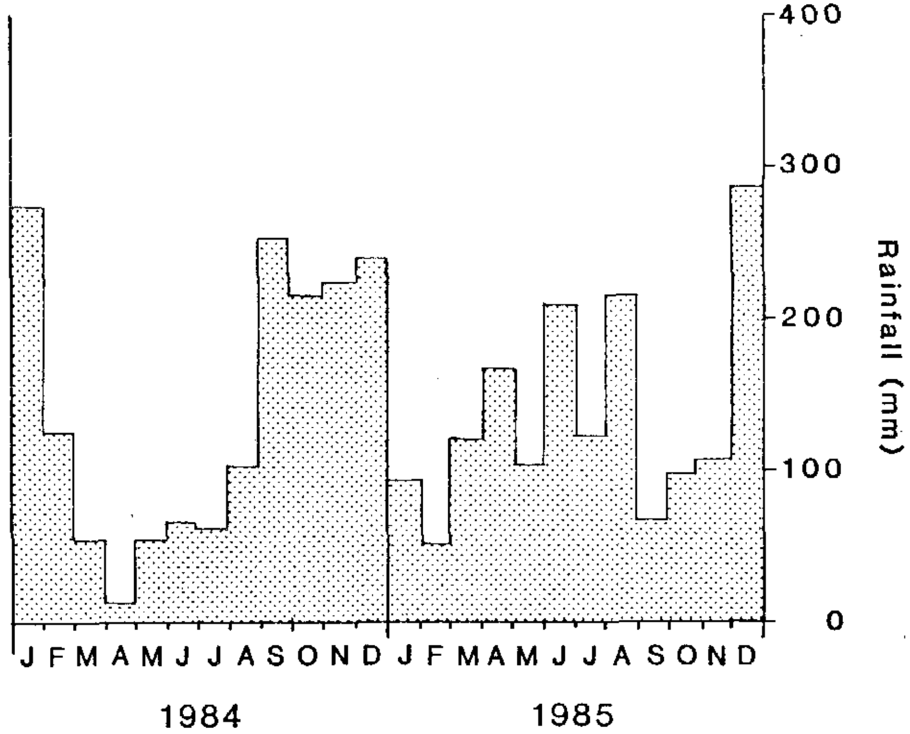
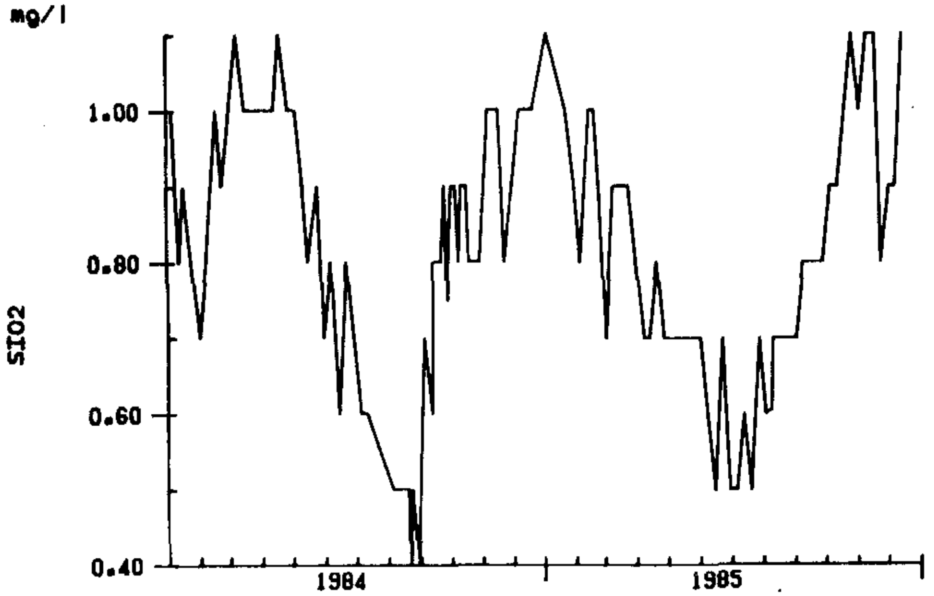






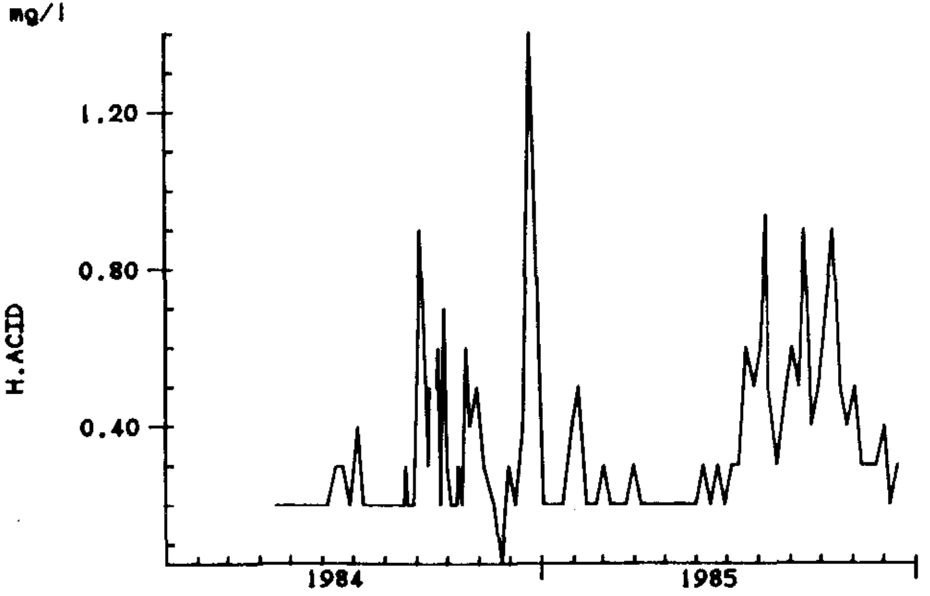
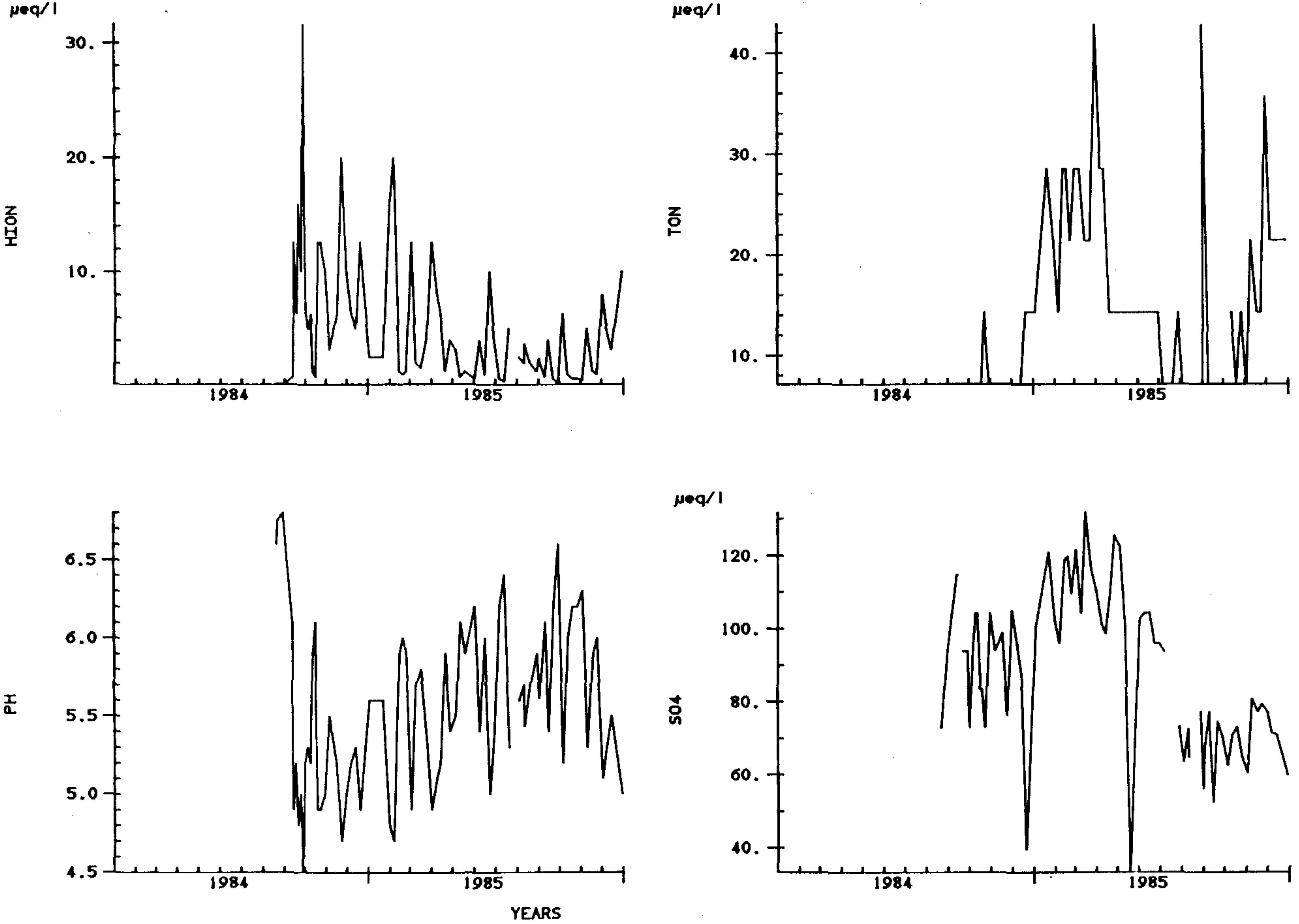


Figure 15

LLYN BRIANNE (CI6)



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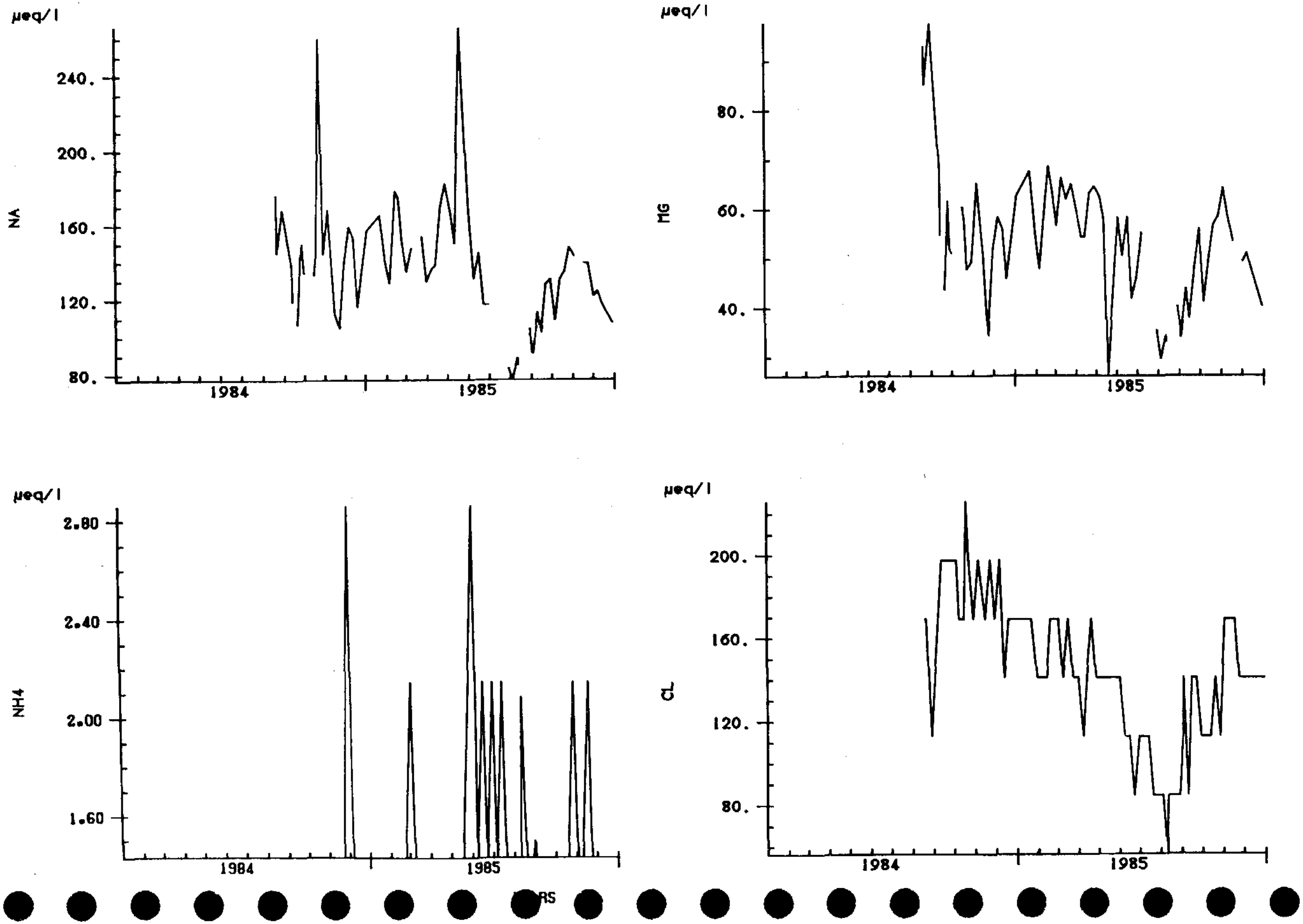

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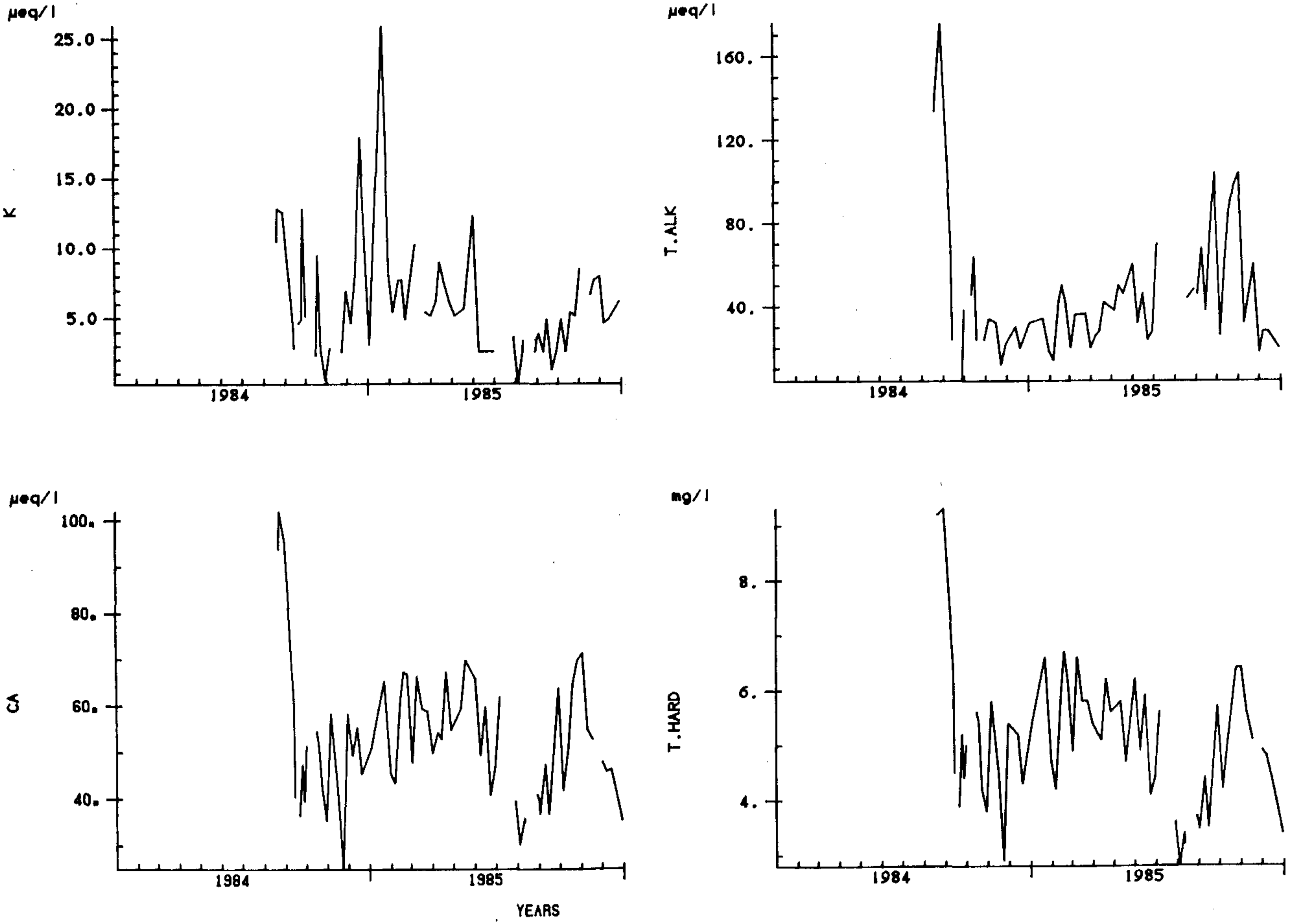

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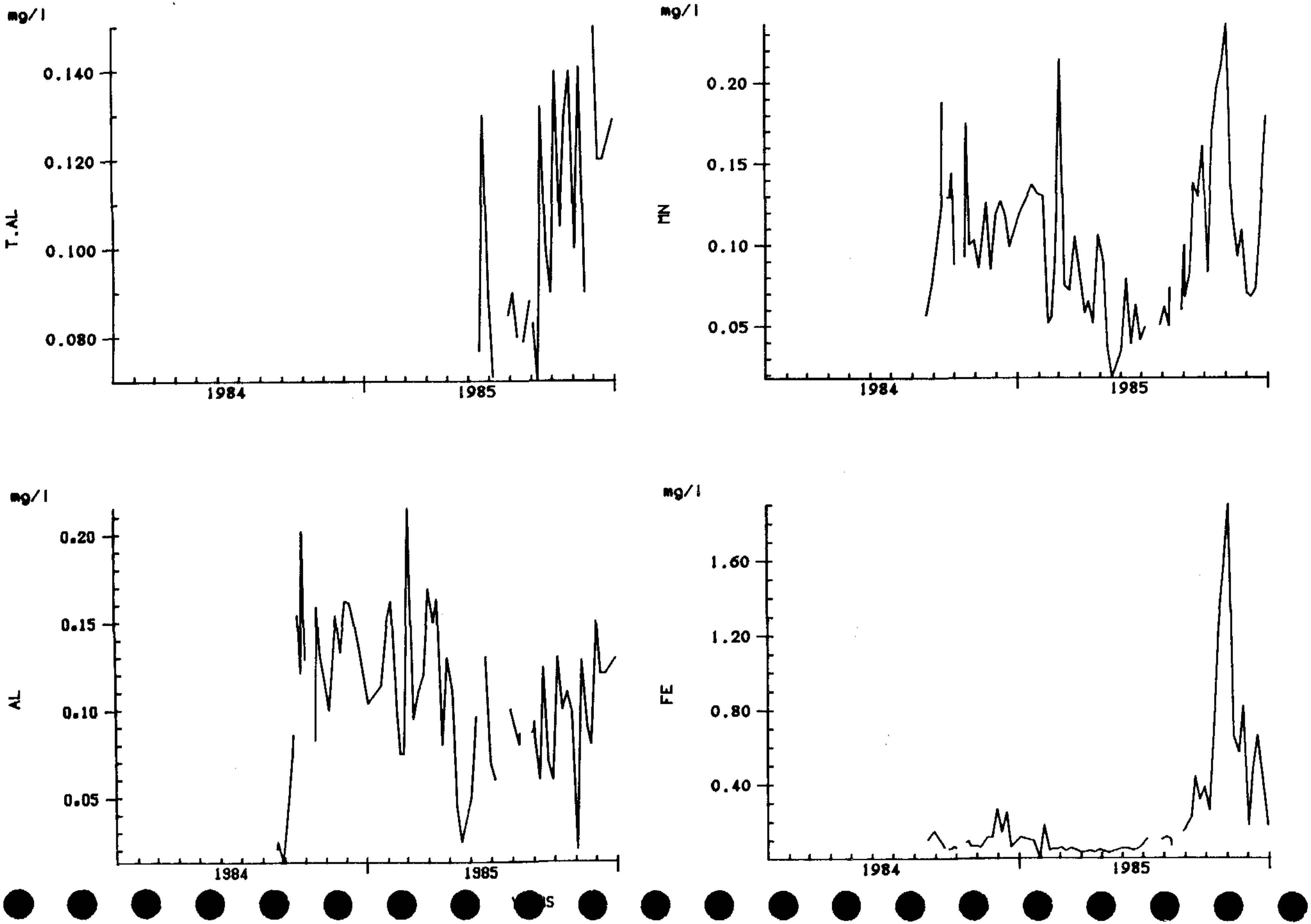

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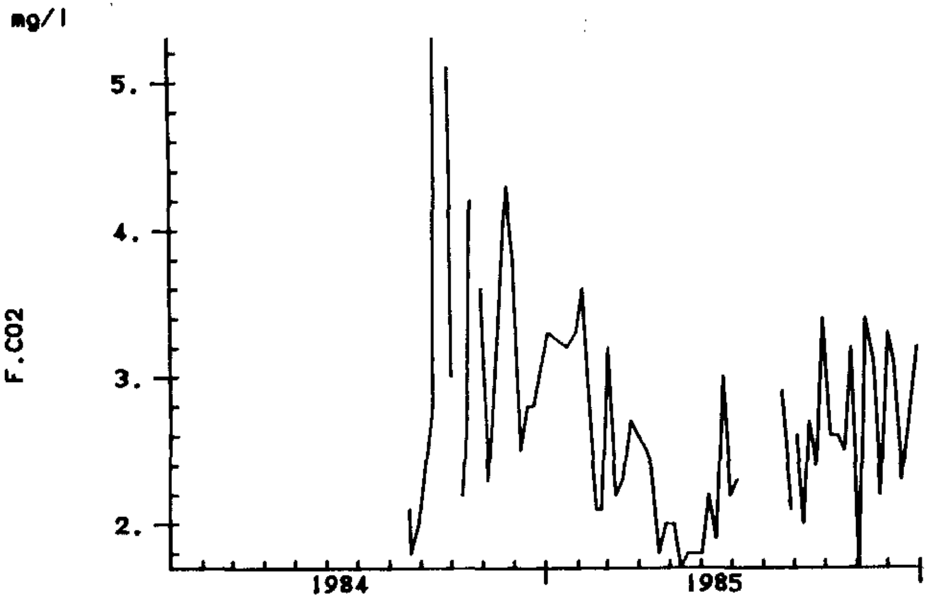
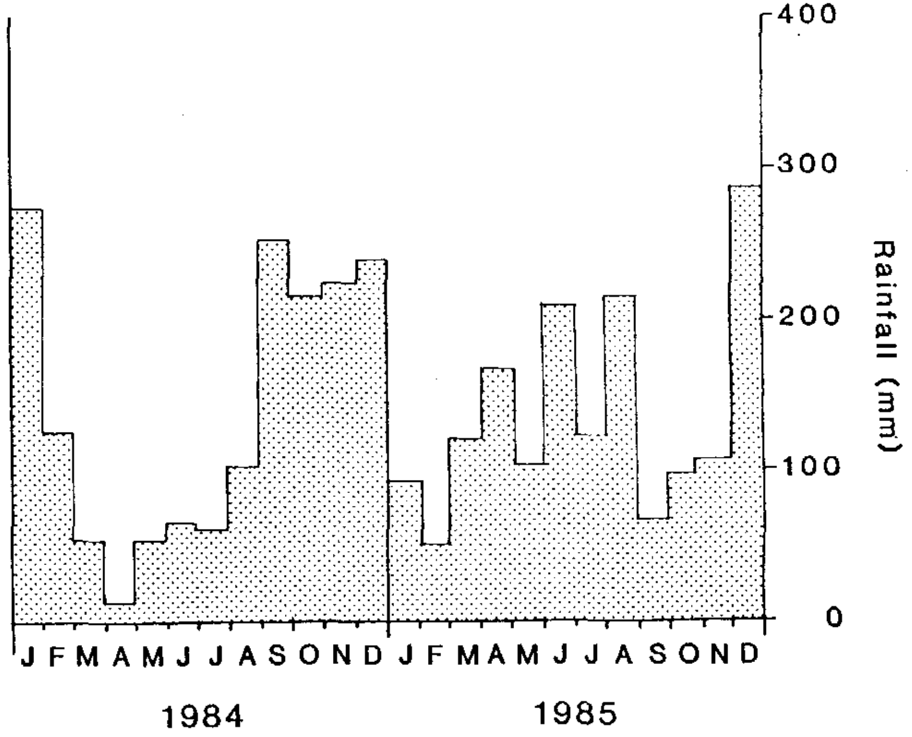
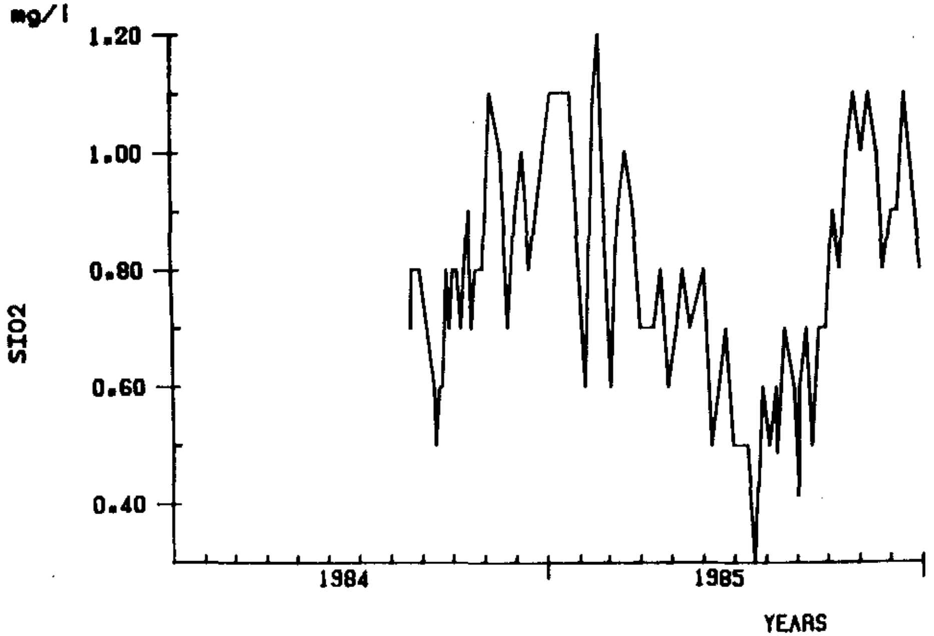






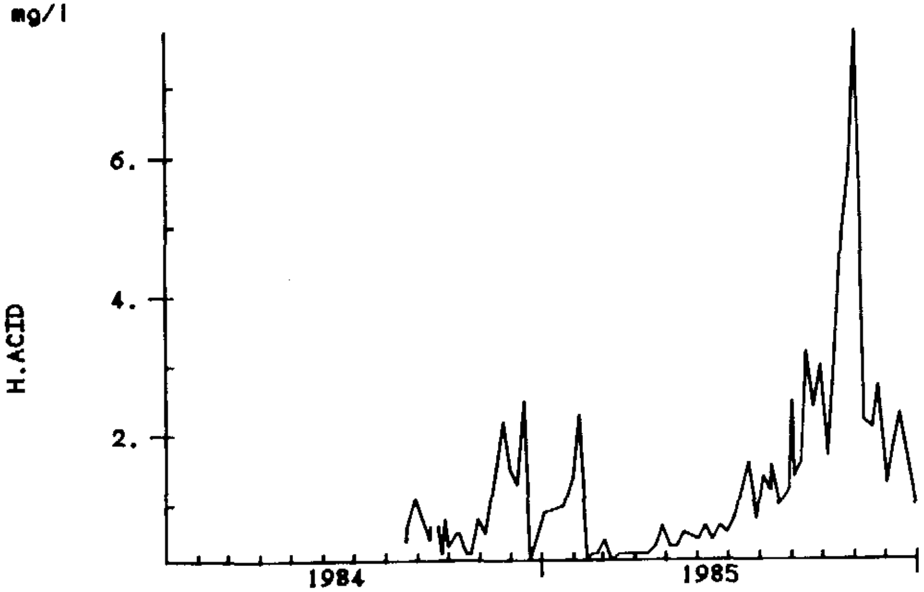
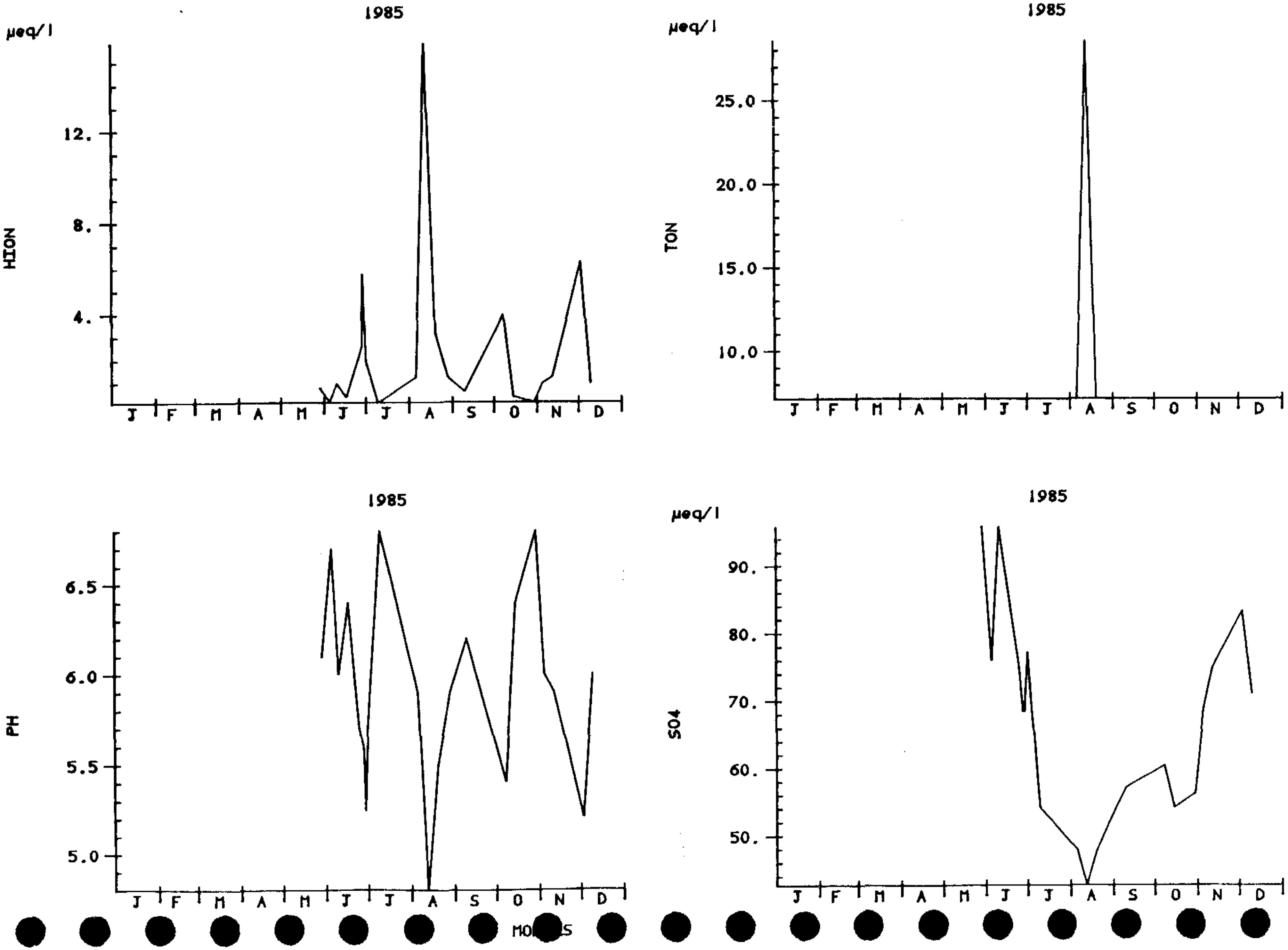


Figure 16

LLYN BRIANNE (UC4)



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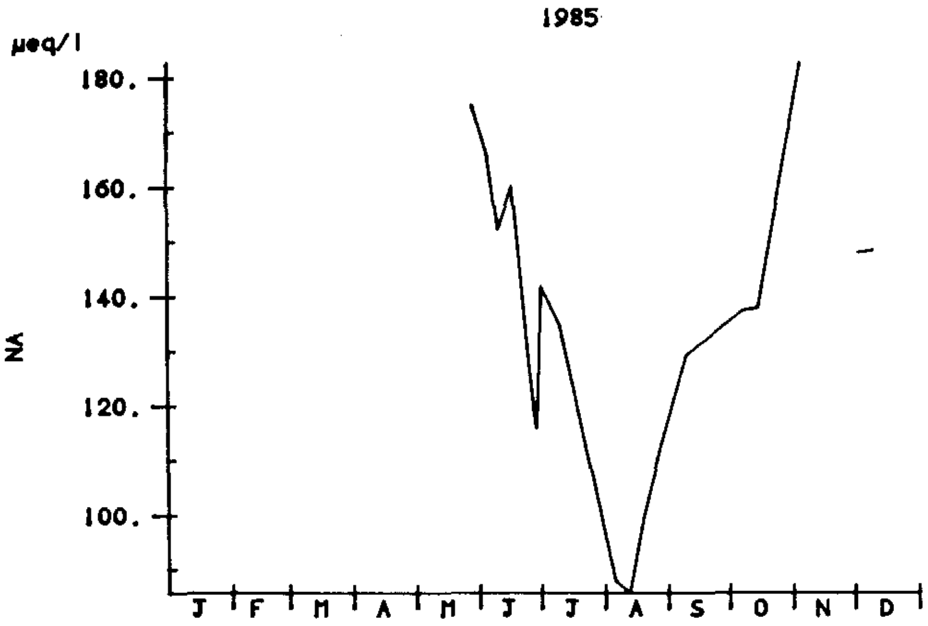

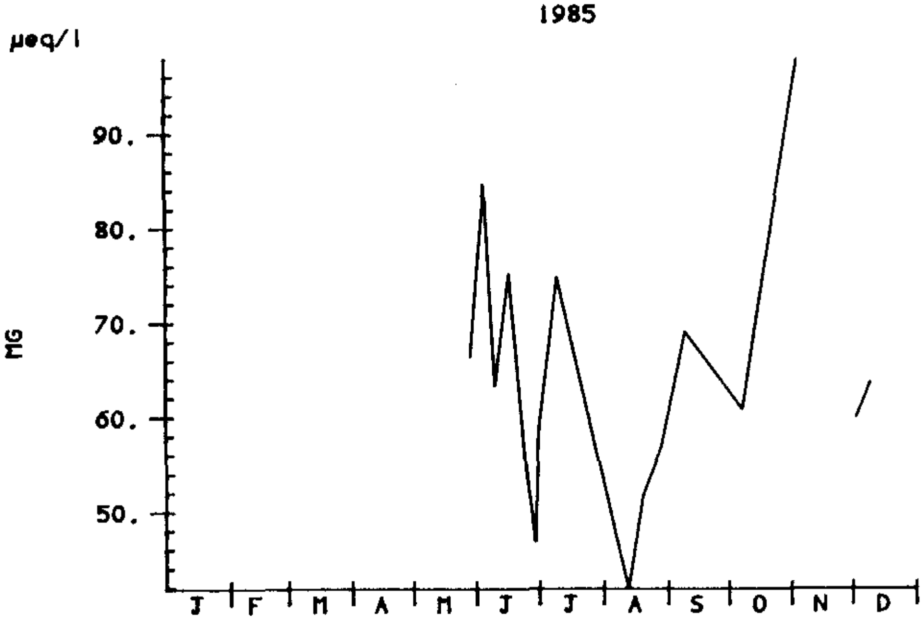

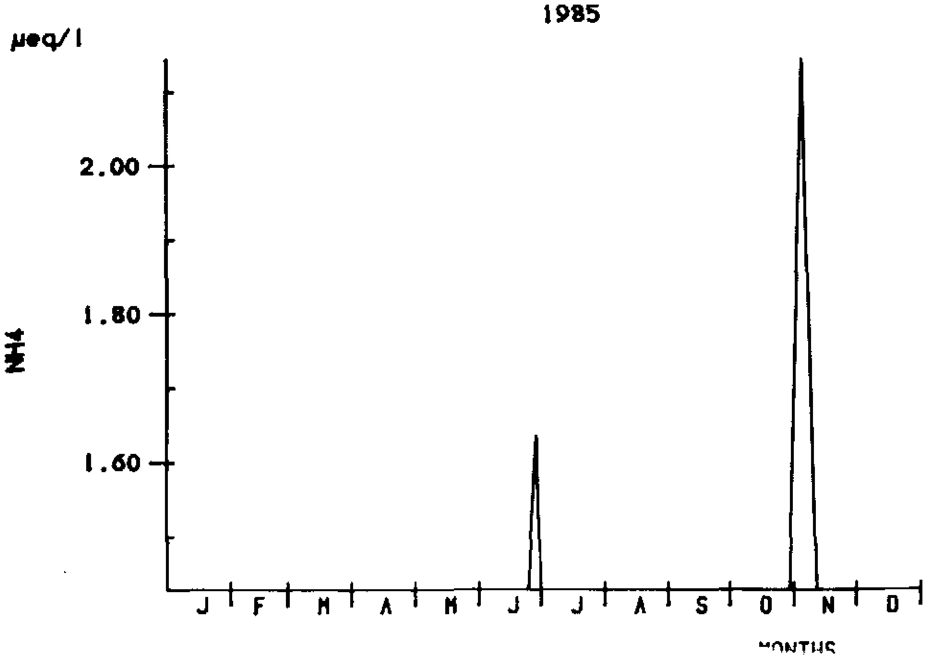

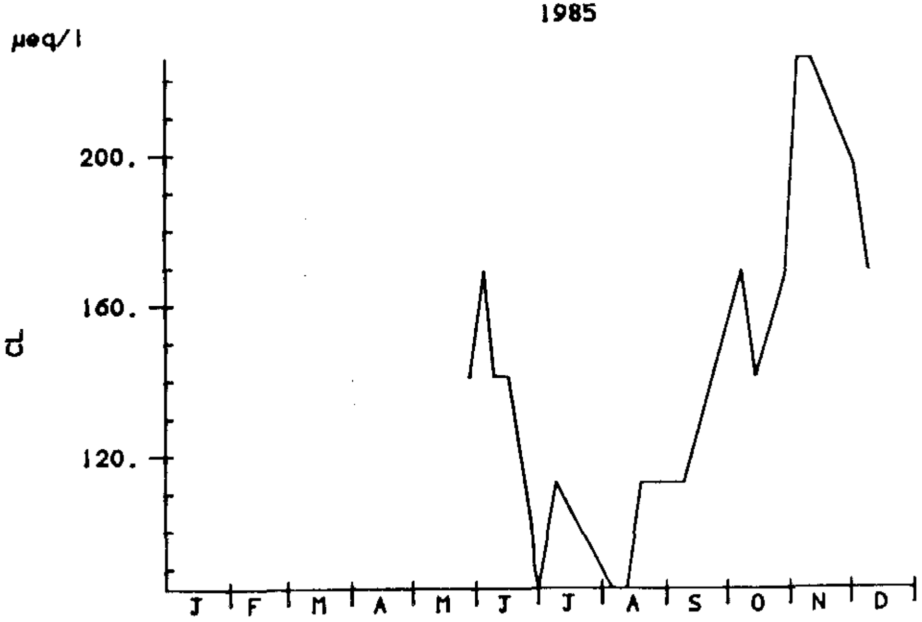

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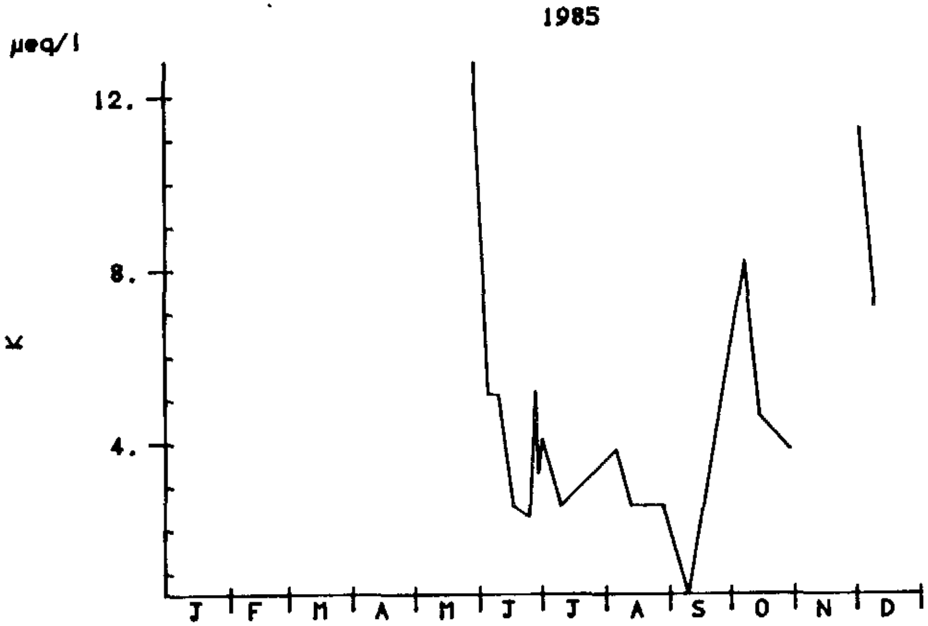

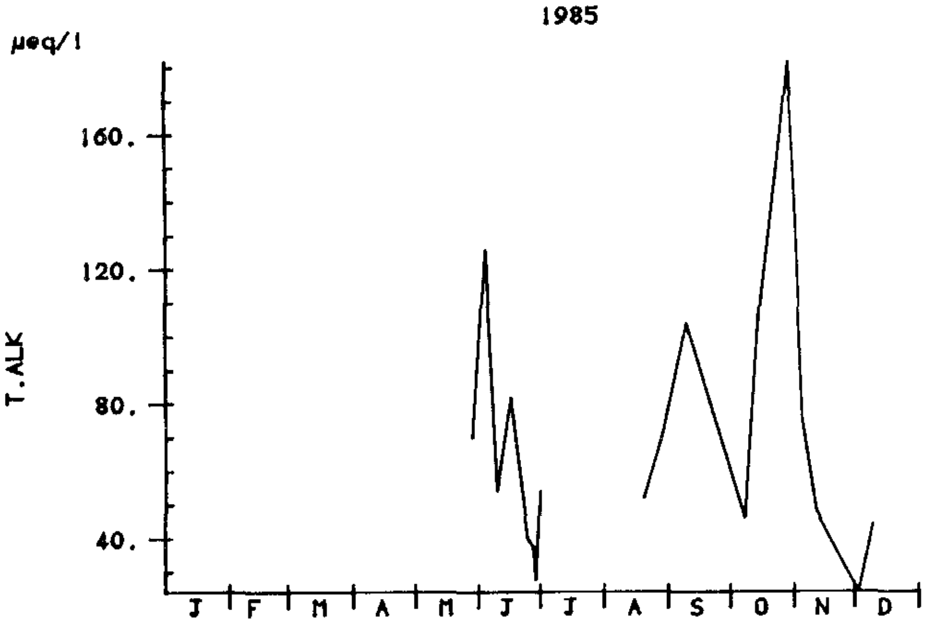

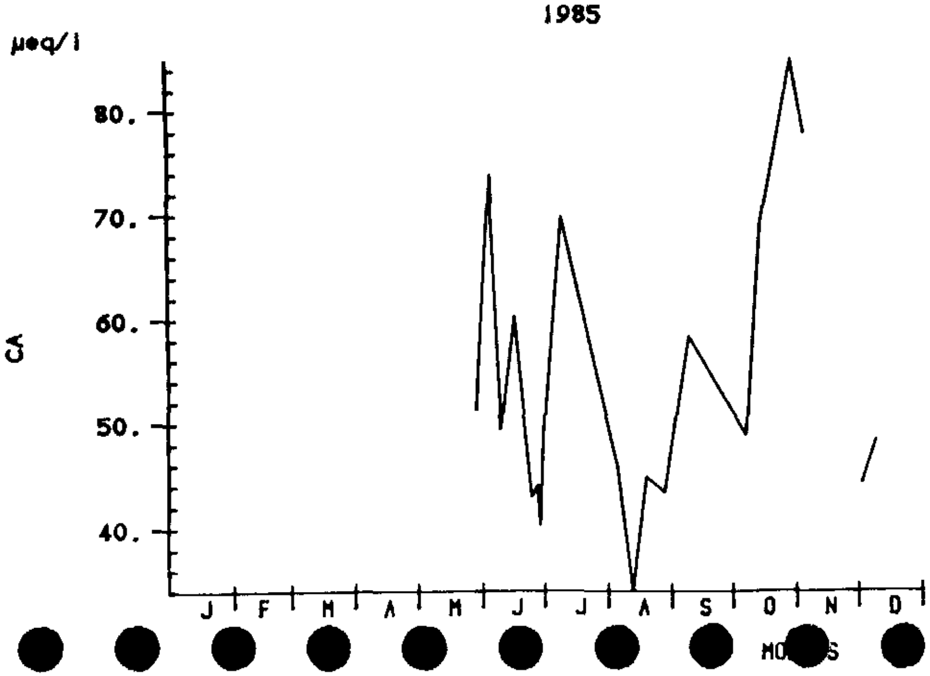

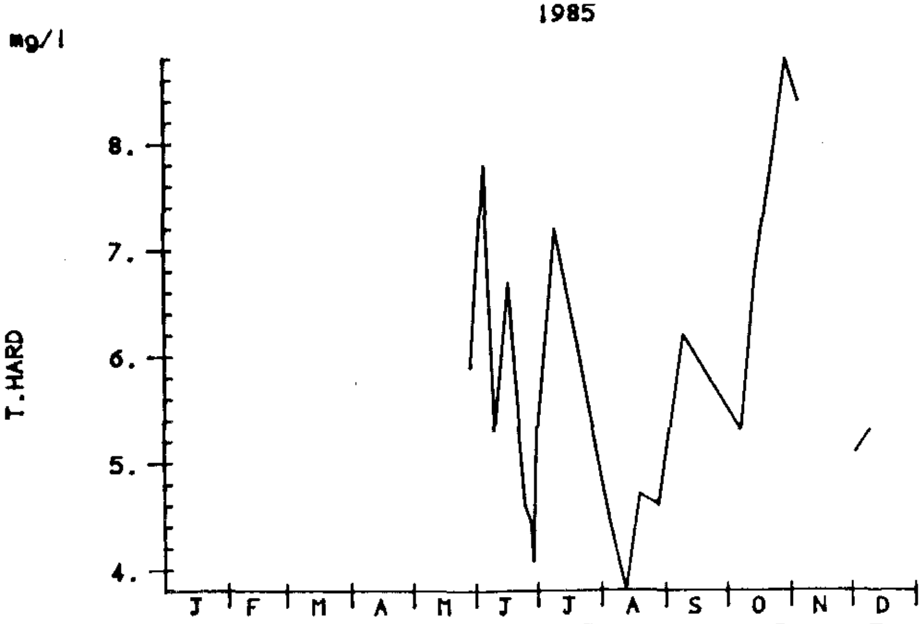

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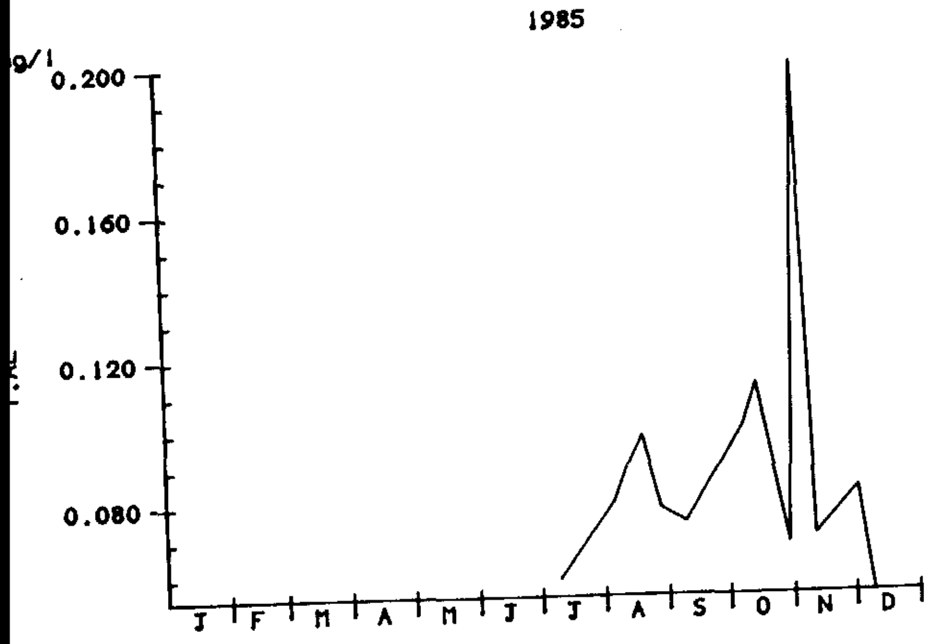

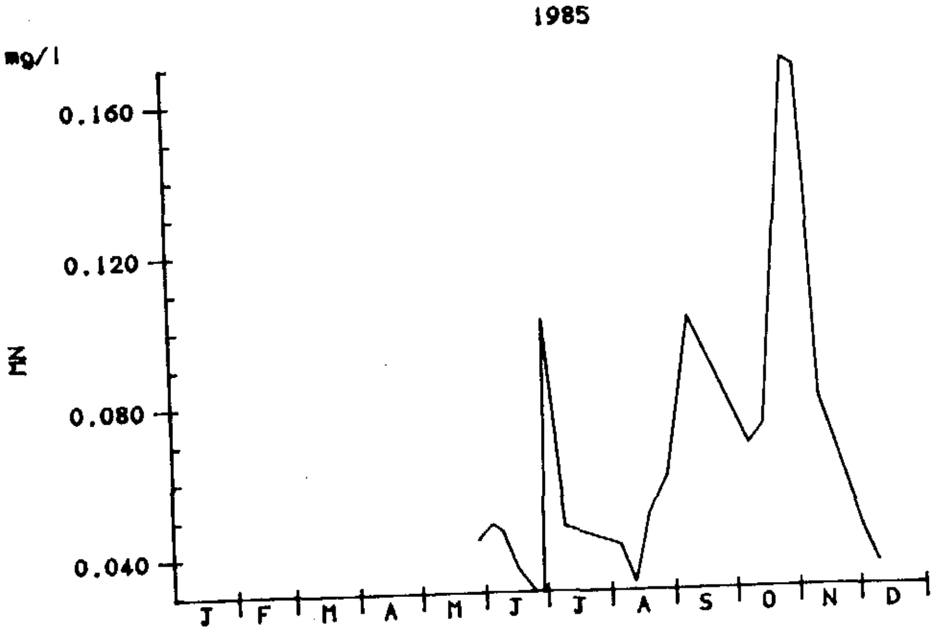

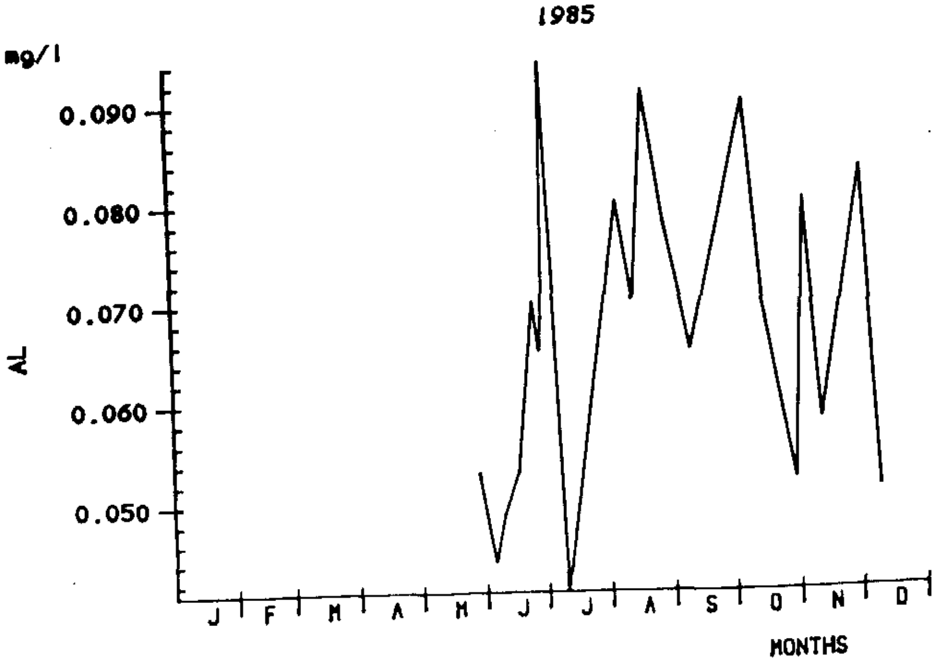

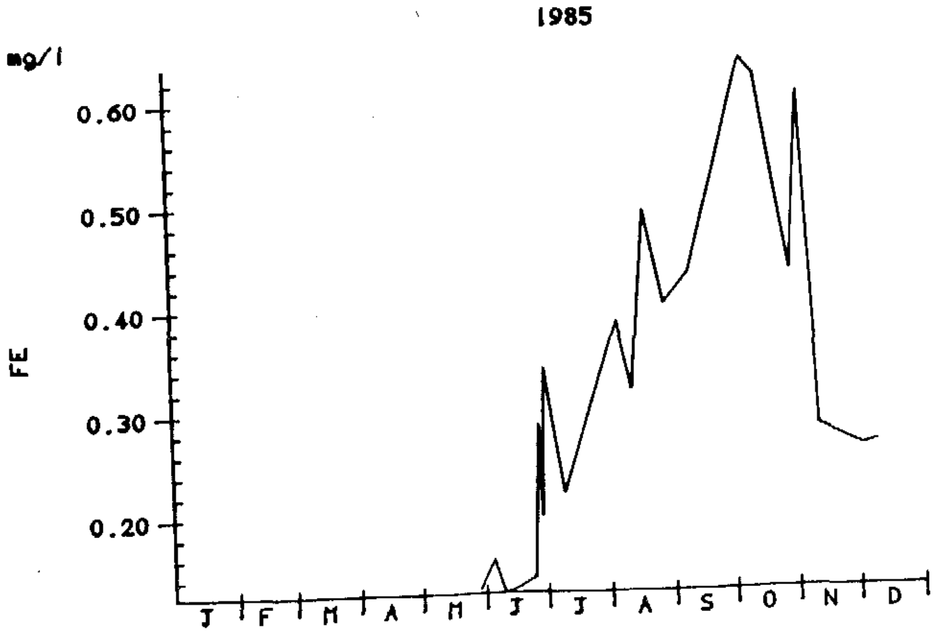

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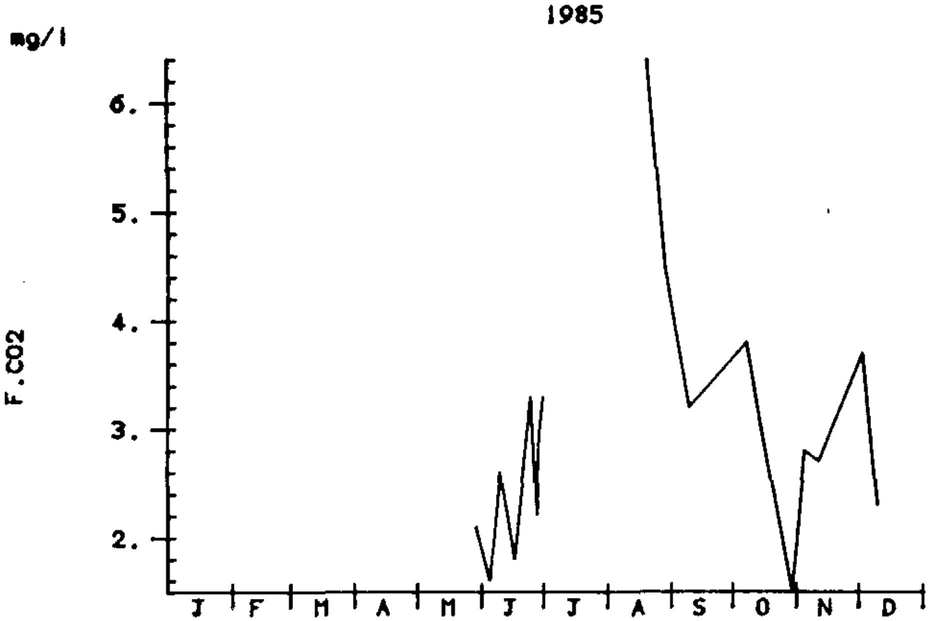

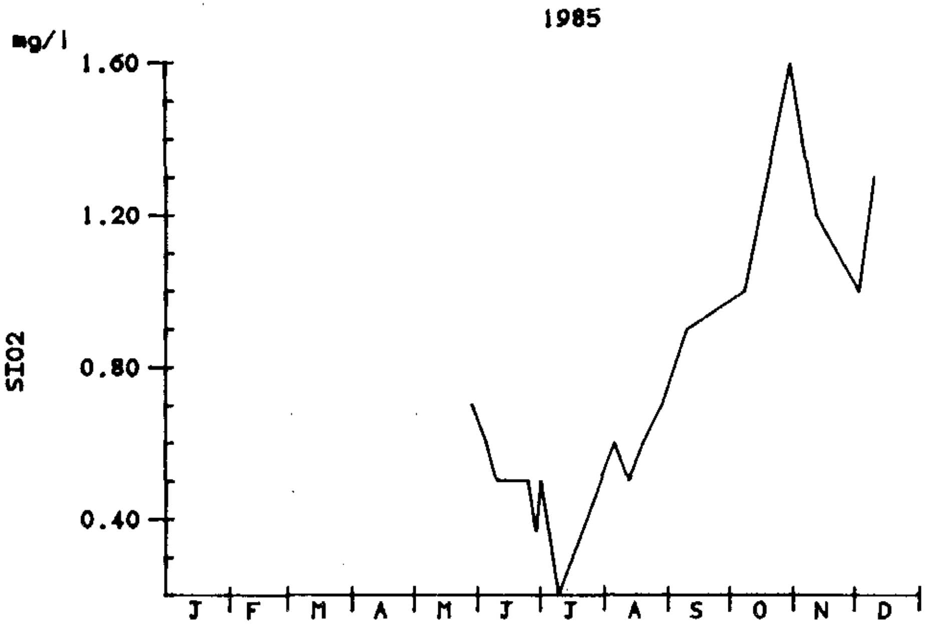

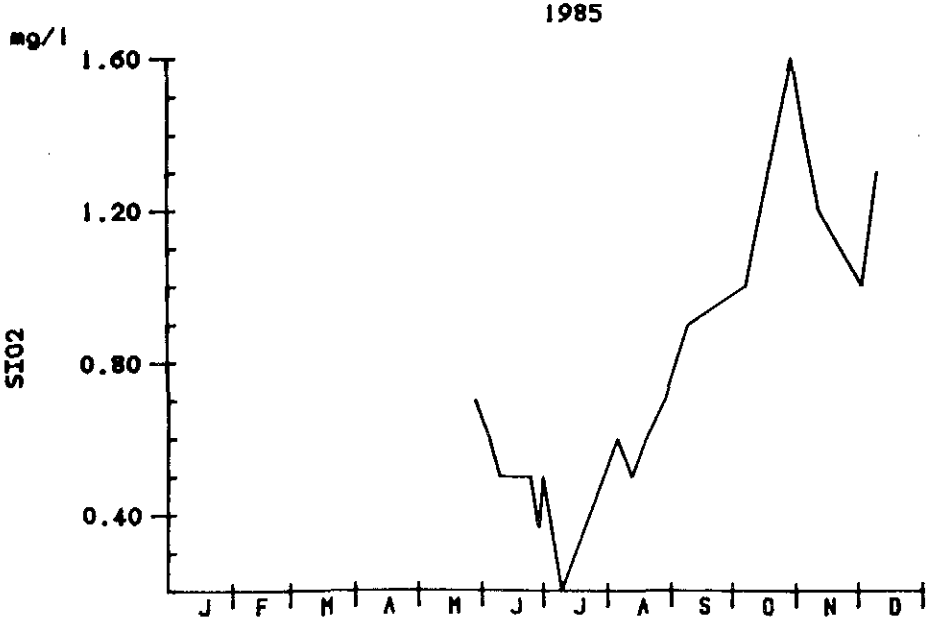

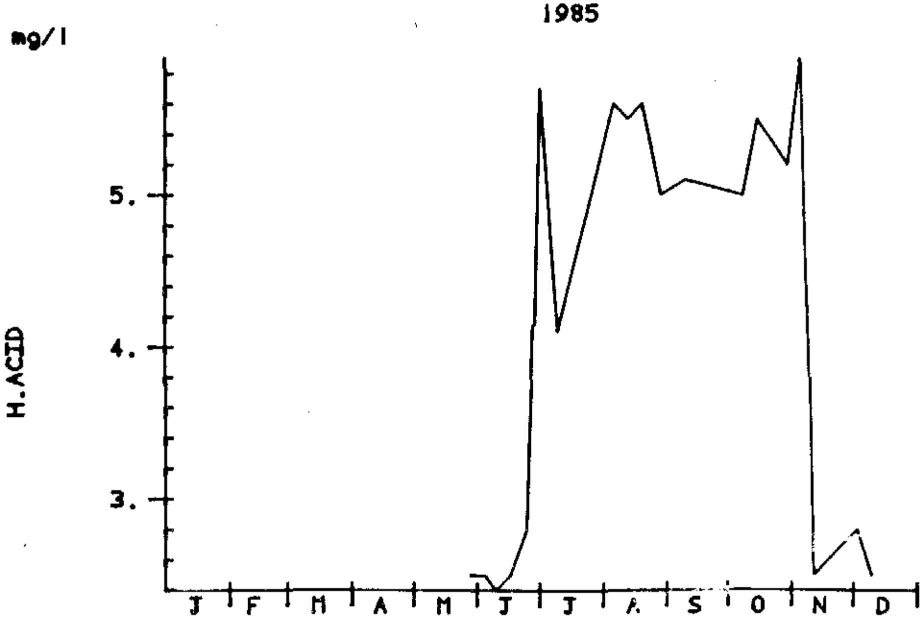

information, since too few samples are available for any meaningful analysis (Figure 16).

Conclusion

Thus, analysis of the acidified moorland sites seems to confirm that the reduction in evapotranspirational losses and scavenging capacity coupled with the change in catchment land use and its effects on catchment hydrology and hydrochemistry has resulted in a slightly improved and less acid streamwater chemistry. However, Table 15 still suggests that intermittently, moderately acid events do occur especially in CI3, CI4 and CI5, causing aluminium levels to rise significantly during storms and thus presumably making the re-establishment of fisheries difficult.

Unacidified catchments (LI6, GI1).

LI6 drains an area of 0.68 km^2 and is the steepest of all the catchments monitored, hence runoff rates and residence times are likely to be affected accordingly. Table 16a shows that LI6 experiences few problems of acidity or aluminium contamination. pH averages 6.9, while H^+ and dissolved aluminium concentrations average only 0.15 ueq l^{-1} and 0.06 mg l^{-1} respectively. SO_4 concentrations average 103 ueq l^{-1} similar to those found at the CI sites and reflect the scavenging capability and evapotranspirational losses associated with a grassland vegetation. The marine salt concentrations are also similar for the same reasons. Major differences are only in evidence for the terrestrially derived Ca, Mg and K concentrations which are all elevated; suggesting that LI6 is well buffered against acidity due to the presence of larger amounts of these base cations in the catchment's soils and perhaps geology.

Table 16a LI6 streamwater quality (1984-5)

	N	N*	MEAN	MEDIAN	TRMEAN	STDEV	SEMEAN		MIN	MAX	Q1	Q3
T_CU	25	73	0.00252	0.00200	0.00226	0.00063	0.00013	T_CU	0.00200	0.00400	0.00200	0.00250
T_ZN	25	73	0.01052	0.00700	0.00943	0.00826	0.00165	T_ZN	0.00500	0.04000	0.00550	0.01350
T_CD	25	73	0.00102	0.00100	0.00101	0.00007	0.00001	T_CD	0.00100	0.00150	0.00100	0.00100
T_AL	25	73	0.0827	0.0550	0.0673	0.0835	0.0177	T_AL	0.0220	0.4100	0.0405	0.0875
T_PB	25	73	0.00356	0.00200	0.00317	0.00303	0.00061	T_PB	0.00100	0.01400	0.00200	0.00500
T_CR	25	73	0.00300	0.00300	0.00300	0.00029	0.00006	T_CR	0.00200	0.00400	0.00300	0.00300
T_MN	25	73	0.02254	0.01800	0.01900	0.02087	0.00418	T_MN	0.00900	0.12000	0.01600	0.02100
T_FE	25	73	0.1653	0.1500	0.1617	0.0821	0.0164	T_FE	0.0510	0.3600	0.0975	0.2125
T_NI	25	73	0.00323	0.00300	0.00313	0.00098	0.00020	T_NI	0.00200	0.00700	0.00300	0.00300
PH	97	1	6.9320	6.9000	6.9282	0.2982	0.0303	PH	6.2000	7.9000	6.7500	7.1000
COND	98	0	52.21	49.50	50.51	15.04	1.52	COND	32.00	109.50	43.00	55.00
TURB	1	97	0.00E+00	0.00E+00	0.00E+00	*	*	TURB	0.00E+00	0.00E+00	*	*
AMM_N	98	0	1.539	1.429	1.429	1.073	0.108	AMM_N	1.429	11.429	1.429	1.429
TON	98	0	10.058	7.143	9.091	6.474	0.654	TON	7.143	50.000	7.143	8.929
NO2	98	0	0.28643	0.28570	0.28570	0.00721	0.00073	NO2	0.28570	0.35710	0.28570	0.28570
TH	96	2	14.436	12.300	13.405	7.715	0.787	TH	4.500	43.750	9.925	16.175
FCO2	76	22	1.6330	1.5000	1.5943	0.4469	0.0513	FCO2	1.0000	3.5000	1.3025	1.8000
TA	76	22	269.0	228.8	248.3	169.7	19.5	TA	73.7	831.3	153.4	309.7
CL	98	0	155.29	169.25	155.95	23.66	2.39	CL	84.53	197.46	141.04	169.25
OPO4	98	0	0.02010	0.02000	0.02000	0.00101	0.00010	OPO4	0.02000	0.03000	0.02000	0.02000
SIO2	98	0	1.2051	1.2000	1.2040	0.2571	0.0260	SIO2	0.6000	1.9500	1.0000	1.4000
SO4	93	5	102.62	101.23	101.57	26.21	2.72	SO4	22.91	197.33	85.19	115.09
NA	95	3	138.17	138.71	137.62	29.33	3.01	NA	36.09	266.99	118.28	152.19
K	94	4	10.808	7.692	9.624	8.762	0.904	K	2.564	43.332	5.641	12.115
CU	96	2	0.00235	0.00200	0.00203	0.00209	0.00021	CU	0.00100	0.01800	0.00200	0.00200
MG	96	2	145.76	120.44	135.94	76.91	7.85	MG	43.59	420.07	98.85	163.94
CA	96	2	146.43	127.99	136.50	80.98	8.27	CA	22.95	456.34	100.30	168.91
ZN	96	2	0.01271	0.01100	0.01133	0.01068	0.00109	ZN	0.00200	0.09100	0.00725	0.01375
CD	96	2	0.00125	0.00100	0.00096	0.00266	0.00027	CD	0.00030	0.02700	0.00085	0.00100
AL	96	2	0.06173	0.05000	0.05420	0.05875	0.00600	AL	0.00500	0.48000	0.03550	0.07325
PB	96	2	0.00868	0.00500	0.00803	0.00676	0.00069	PB	0.00100	0.03900	0.00500	0.01300
CR	96	2	0.00241	0.00300	0.00245	0.00091	0.00009	CR	0.00100	0.00300	0.00100	0.00300
MN	96	2	0.02191	0.01800	0.01866	0.01999	0.00204	MN	0.00450	0.15300	0.01500	0.02300
FE	96	2	0.07943	0.06350	0.07315	0.05296	0.00541	FE	0.00300	0.33000	0.04825	0.09300
NI	95	3	0.00302	0.00300	0.00289	0.00145	0.00015	NI	0.00100	0.01000	0.00300	0.00300
HUMIC	95	3	1.232	0.900	1.098	1.025	0.105	HUMIC	0.200	5.500	0.600	1.400
IG	1	97	0.00E+00	0.00E+00	0.00E+00	*	*	IG	0.00E+00	0.00E+00	*	*
TEMP	9	89	10.57	11.20	10.57	4.57	1.52	TEMP	0.00	16.00	9.30	13.45
T_NA	1	97	0.00E+00	0.00E+00	0.00E+00	*	*	T_NA	0.00E+00	0.00E+00	*	*
T_K	1	97	0.00E+00	0.00E+00	0.00E+00	*	*	T_K	0.00E+00	0.00E+00	*	*
T_MG	1	97	0.00E+00	0.00E+00	0.00E+00	*	*	T_MG	0.00E+00	0.00E+00	*	*
T_CA	1	97	0.00E+00	0.00E+00	0.00E+00	*	*	T_CA	0.00E+00	0.00E+00	*	*
ACID	1	97	0.00E+00	0.00E+00	0.00E+00	*	*	ACID	0.00E+00	0.00E+00	*	*
UV	1	97	0.00E+00	0.00E+00	0.00E+00	*	*	UV	0.00E+00	0.00E+00	*	*
F_PH	10	88	6.910	7.550	7.612	2.454	0.777	F_PH	0.000	8.200	7.500	8.125
STAGE	2	96	0.255	0.255	0.255	0.361	0.255	STAGE	0.000	0.510	*	*
P_SOLID	13	85	2.154	2.000	1.818	1.676	0.465	P_SOLID	1.000	7.000	1.000	3.000
DOC	1	97	0.00E+00	0.00E+00	0.00E+00	*	*	DOC	0.00E+00	0.00E+00	*	*
HICN	97	1	0.1465	0.1259	0.1328	0.1090	0.0111	HICN	0.0136	0.5510	0.0774	0.1790

Table 16b Correlation matrices

(i) normal

	T_NI	PH	COND	AMM_N	TON	NO2	TH	FCO2	TA	CL	CPO4	SIO2	SO4	NA	K	CU
PH	-0.113															
COND	-0.225	0.635														
AMM_N	-0.071	-0.051	0.017													
TON	-0.160	-0.222	-0.137	0.575												
NO2	-0.060	-0.045	-0.062	-0.015	0.292											
TH	-0.081	0.577	0.337	0.014	-0.189	-0.110										
FCO2	-0.005	-0.503	-0.325	0.201	0.128	0.017	-0.371									
TA	0.055	0.535	0.927	-0.031	-0.351	-0.062	0.950	-0.358								
CL	-0.100	0.088	0.146	0.032	0.079	0.060	0.175	0.051	0.137							
CPO4	*	-0.090	0.019	0.935	0.630	-0.010	-0.002	0.043	-0.095	0.060						
SIO2	-0.371	0.333	0.549	-0.064	-0.106	0.117	0.568	-0.010	0.627	0.472	-0.031					
SO4	-0.125	-0.042	0.189	0.142	0.142	0.106	0.205	-0.006	0.054	0.442	0.131	0.015				
NA	-0.189	0.147	0.314	0.038	0.107	0.142	0.492	-0.307	0.457	0.369	0.057	0.234	0.545			
K	0.092	0.303	0.713	0.091	-0.042	-0.083	0.819	-0.160	0.792	0.424	0.128	0.542	0.580	0.535		
CU	0.351	-0.125	-0.118	-0.022	0.094	0.032	-0.187	-0.019	-0.219	-0.046	-0.017	-0.237	0.224	-0.068	-0.161	
MG	-0.080	0.557	0.314	-0.021	-0.221	-0.126	0.976	-0.352	0.942	0.233	-0.023	0.573	0.215	0.480	0.822	-0.205
CA	-0.073	0.567	0.322	0.041	-0.152	-0.091	0.980	-0.332	0.940	0.113	0.021	0.534	0.191	0.480	0.786	-0.159
ZN	0.215	-0.190	-0.114	-0.044	0.090	0.061	-0.145	0.109	-0.181	0.025	-0.016	-0.223	0.136	0.115	0.009	0.018
CD	-0.060	0.011	0.018	-0.015	-0.041	-0.010	-0.078	0.176	-0.061	0.051	-0.010	0.053	-0.091	-0.111	-0.037	-0.066
AL	0.011	-0.357	-0.272	-0.007	0.233	0.734	-0.394	0.111	-0.390	-0.042	0.014	-0.206	0.081	0.116	-0.236	0.129
PB	0.611	-0.224	-0.134	-0.156	-0.095	-0.102	-0.151	0.027	-0.123	0.404	-0.117	0.009	0.271	0.293	0.111	0.053
CR	-0.000	-0.297	-0.404	0.099	0.300	0.067	-0.384	-0.019	-0.453	-0.472	0.057	-0.416	-0.326	-0.165	-0.537	0.085
MN	-0.057	-0.396	-0.237	-0.007	0.141	0.455	-0.252	0.229	-0.239	0.112	0.005	-0.109	0.135	0.169	-0.034	0.015
FE	0.371	-0.145	0.077	0.029	-0.242	-0.022	-0.043	0.127	0.026	-0.425	-0.018	-0.195	-0.193	-0.207	-0.094	0.178
NI	0.577	-0.330	-0.369	-0.012	0.162	-0.002	-0.428	0.063	-0.456	-0.030	-0.002	-0.302	-0.002	0.123	-0.363	0.226
HUMIC	0.422	-0.325	-0.127	0.131	-0.122	-0.084	-0.228	0.369	-0.174	-0.380	0.128	-0.490	-0.075	-0.236	-0.108	0.245
TEMP	*	0.515	0.492	*	-0.867	*	0.602	-0.709	0.762	0.502	*	0.134	0.268	0.762	0.655	-0.300
STAGE	*	1.000	1.000	0.000	-1.000	*	1.000	-1.000	1.000	1.000	*	1.000	1.000	1.000	1.000	-1.000
P_SOLID	*	0.191	-0.112	*	0.519	0.869	-0.280	-0.014	-0.047	0.331	*	0.194	0.798	0.720	-0.303	0.329
HICN	0.036	-0.884	-0.371	0.023	0.143	0.011	-0.311	0.445	-0.355	-0.074	0.050	-0.264	0.067	-0.058	-0.044	0.062

	MG	CA	ZN	CD	AL	PB	CR	MN	FE	NI	HUMIC	TEMP	STAGE	P_SOLID
CA	0.913													
ZN	-0.148	-0.138												
CD	-0.073	-0.084	-0.000											
AL	-0.404	-0.369	0.276	-0.037										
PB	-0.109	-0.179	0.293	-0.033	0.225									
CR	-0.424	-0.333	0.022	-0.133	0.333	-0.068								
MN	-0.243	-0.248	0.344	-0.024	0.689	0.312	0.056							
FE	-0.070	-0.018	-0.060	-0.034	0.138	-0.209	0.083	0.064						
NI	-0.443	-0.393	0.189	-0.106	0.308	0.557	0.391	0.132	0.024					
HUMIC	-0.218	-0.227	0.075	0.121	0.179	-0.009	0.016	0.213	0.707	0.061				
TEMP	0.625	0.578	-0.078	-0.157	-0.150	0.348	-0.630	-0.141	-0.113	-0.299	0.133			
STAGE	1.000	1.000	-1.000	-1.000	-1.000	1.000	-1.000	-1.000	-1.000	-1.000	-1.000	1.000		
P_SOLID	-0.331	-0.227	0.563	*	0.857	-0.000	0.000	0.879	-0.119	*	-0.068	*	*	
HICN	-0.300	-0.303	0.229	-0.039	0.276	0.237	0.168	0.482	0.147	0.181	0.306	-0.650	-1.000	-0.263

(ii) logarithmic

	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17
C2	0.541																
C3	0.061	0.180															
C4	0.036	0.153	-0.151														
C5	-0.396	0.075	-0.139	0.561													
C6	-0.627	-0.342	-0.241	0.526	0.627												
C7	-0.542	-0.373	0.013	0.495	0.480	0.776											
C8	-0.158	0.222	-0.355	0.369	0.570	0.266	0.069										
C9	0.202	0.435	0.037	-0.257	-0.057	-0.401	-0.466	0.047									
C10	-0.470	-0.049	-0.129	0.200	0.448	0.497	0.391	0.488	-0.095								
C11	0.025	0.247	-0.135	0.090	0.479	0.233	0.219	0.428	0.024	0.017							
C12	0.020	0.002	0.075	0.035	0.075	0.016	0.094	0.014	0.230	-0.057	0.071						
C13	0.326	0.110	-0.342	0.115	-0.037	-0.283	-0.150	0.088	0.172	-0.104	0.103	0.315					
C14	-0.743	-0.455	0.021	0.303	0.492	0.326	0.857	0.134	-0.461	0.415	0.015	-0.075	-0.431				
C15	-0.519	[illegible]	-0.015	0.552	0.591	0.965	0.903	0.175	-0.444	0.470	0.256	0.063	-0.236	0.261			
C16	-0.596	-0.354	-0.034	0.295	0.571	0.783	0.728	0.199	-0.192	0.547	0.170	0.030	-0.173	0.475	0.308		
C17	0.095	0.235	0.477	-0.263	-0.100	-0.215	-0.247	-0.310	0.319	-0.435	-0.130	0.145	-0.259	-0.172	-0.243	-0.239	
C18	[illegible]	[illegible]	0.104	-0.151	-0.196	[illegible]	-0.570	-0.091	0.556	-0.334	0.227	[illegible]	0.252	-0.715	-0.627	-0.663	[illegible]

GI1 is similarly unacidified (Table 17a) with an average pH of 6.3. Conditions in the catchment again show few signs of any quality problems. SO_4, Na and Cl levels are all slightly higher than at LI6 reflecting its acid oak woodland vegetation cover which scavenges the above more effectively than grass and is characterised by greater evapotranspiration losses. Levels however, do not approach those found in the conifer afforested catchments. NO_3 concentrations are also occasionally higher than at LI6, presumably as a result of Autumn leaf deposits contributing nutrients via runoff. Ca and Mg concentrations however, are much lower than at LI6, averaging 66 ueq l^{-1} and 88 ueq l^{-1} respectively. Nevertheless, the concentrations are an average still higher than those recorded at any of the other sites and clearly offer a sufficient buffering capacity for most of the time. Table 18 summarises the general differences in stream chemistry between the two sites and can be compared with tables 4, 9 and 15.

The correlation matrix for LI6 (Table 16b) confirms the existence of the expected correlations such as those between pH, total alkalinity and total hardness; pH, free CO_2 and H^+; total hardness, total alkalinity, Ca and Mg. As at many previous sites the marine salts are not highly correlated suggesting that hydrochemical processes continue to greatly modify the inputs even in an unacidified moorland. Few other significant parameter correlations exist in LI6. Similarly, the matrix for GI1 (Table 17b) reveals few notable correlations other than those expected.

Temporal patterns

Figure 17 indicates that although H^+ levels are always low at LI6, they still fluctuate in accordance with rainfall and runoff patterns. Likewise, SO_4 concentrations also indicate some

Table 17a GI1 streamwater quality (1984-5)

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              N    N*      MEAN    MEDIAN    TRMEAN     STDEV    SEMEAN                 MIN       MAX        Q1        Q3
T_CU         22    36   0.00250   0.00200   0.00245   0.00080   0.00017    T_CU     0.00200   0.00400   0.00200   0.00300
T_ZN         22    36   0.01122   0.00700   0.01080   0.01060   0.00226    T_ZN     0.00300   0.04100   0.00500   0.01600
T_CD         22    36   0.00104   0.00100   0.00100   0.00015   0.00003    T_CD     0.00100   0.00170   0.00100   0.00100
T_AL         22    36   0.03423   0.03350   0.03330   0.01037   0.00221    T_AL     0.02000   0.05700   0.02700   0.04250
T_PB         22    36   0.00450   0.00300   0.00375   0.00484   0.00103    T_PB     0.00200   0.02200   0.00200   0.00500
T_CR         22    36   0.00300   0.00300   0.00300   0.00000   0.00000    T_CR     0.00300   0.00300   0.00300   0.00300
T_MN         22    36   0.00341   0.00300   0.00315   0.00197   0.00042    T_MN     0.00200   0.01000   0.00200   0.00300
T_FE         22    36   0.02995   0.03000   0.02870   0.01359   0.00290    T_FE     0.00900   0.07600   0.02175   0.03525
T_NI         22    36   0.00309   0.00300   0.00300   0.00043   0.00009    T_NI     0.00300   0.00500   0.00300   0.00300
PH           57     1    6.2532    6.3000    6.2538    0.1654    0.0219    PH        6.0000    6.7000    6.1000    6.4000
CONC         58     0     43.31     43.00     42.92      7.93      1.04    CONC       34.00     67.00     40.00     46.25
TURB          1    57  0.00E+00  0.00E+00  0.00E+00         *         *    TURB     0.00E+00  0.00E+00         *         *
AMM_N        58     0     1.564     1.429     1.442     0.762     0.100    AMM_N       1.429     7.143     1.429     1.429
TON          58     0     11.58      7.14      8.52     16.35      2.19    TON          7.14    121.43      7.14      7.14
NO2          58     0   0.28570   0.28570   0.28570   0.00000   0.00000    NO2       0.28570   0.28570   0.28570   0.28570
TH           55     3     7.437     7.400     7.349     1.541     0.208    TH          5.100    14.300     6.600     8.000
FCO2         53     5     1.848     1.650     1.707     0.957     0.132    FCO2        1.100     6.200     1.500     1.900
TA           52     6     66.03     64.94     64.75     17.29      2.40    TA          41.96    127.39     51.96     75.44
CL           58     0    177.52    169.25    176.31     48.14      6.32    CL          84.63    517.50    141.04    225.67
OPO4         58     0   0.02052   0.02000   0.02000   0.00292   0.00038    OPO4      0.02000   0.04000   0.02000   0.02000
SIO2         58     0    1.3948    1.4000    1.4019    0.1538    0.0202    SIO2       1.0000    1.7000    1.3000    1.5000
SO4          56     2    130.55    128.33    130.59     24.43      3.26    SO4         62.49    183.30    115.92    141.67
NA           53     5    179.93    176.11    176.20     40.05      5.50    NA         125.67    403.53    150.02    193.27
K            52     6     6.395     5.897     6.081     3.354     0.465    K           2.564    15.384     3.910     7.884
CU           56     2   0.00286   0.00200   0.00252   0.00203   0.00027    CU        0.00100   0.01400   0.00200   0.00300
MG           55     3     65.72     65.38     65.31     10.86      1.46    MG          46.38    103.45     53.59     71.96
CA           55     3     87.77     84.33     85.34     21.52      2.90    CA          50.40    138.12     79.34     92.31
ZN           56     2   0.01516   0.01050   0.01264   0.02038   0.00272    ZN        0.00200   0.13200   0.00700   0.01700
CD           56     2   0.00104   0.00100   0.00100   0.00019   0.00003    CD        0.00100   0.00240   0.00100   0.00100
AL           56     2   0.04961   0.03200   0.03508   0.07053   0.00943    AL        0.00400   0.35000   0.02425   0.04000
PB           56     2   0.01118   0.00500   0.00772   0.02029   0.00271    PB        0.00200   0.14000   0.00200   0.01300
CR           55     3   0.00316   0.00300   0.00300   0.00121   0.00016    CR        0.00300   0.01200   0.00300   0.00300
MN           56     2   0.01330   0.00200   0.00638   0.03358   0.00449    MN        0.00200   0.17500   0.00200   0.00500
FE           56     2   0.03301   0.01700   0.02231   0.06165   0.00824    FE        0.00300   0.44100   0.01300   0.02775
NI           56     2   0.00336   0.00300   0.00318   0.00105   0.00014    NI        0.00200   0.00800   0.00300   0.00300
HUMIC        58     0    0.7190    0.5500    0.6250    0.7015    0.0921    HUMIC      0.2000    5.4000    0.4000    0.8000
IG            1    57  0.00E+00  0.00E+00  0.00E+00         *         *    IG       0.00E+00  0.00E+00         *         *
TEMP          1    57  0.00E+00  0.00E+00  0.00E+00         *         *    TEMP     0.00E+00  0.00E+00         *         *
T_NA          1    57  0.00E+00  0.00E+00  0.00E+00         *         *    T_NA     0.00E+00  0.00E+00         *         *

T_K           1    57  0.00E+00  0.00E+00  0.00E+00         *         *    T_K      0.00E+00  0.00E+00         *         *
T_MG          1    57  0.00E+00  0.00E+00  0.00E+00         *         *    T_MG     0.00E+00  0.00E+00         *         *
T_CA          1    57  0.00E+00  0.00E+00  0.00E+00         *         *    T_CA     0.00E+00  0.00E+00         *         *
ACID          1    57  0.00E+00  0.00E+00  0.00E+00         *         *    ACID     0.00E+00  0.00E+00         *         *
UV            1    57  0.00E+00  0.00E+00  0.00E+00         *         *    UV       0.00E+00  0.00E+00         *         *
F_PH          1    57  0.00E+00  0.00E+00  0.00E+00         *         *    F_PH     0.00E+00  0.00E+00         *         *
STAGE         1    57  0.00E+00  0.00E+00  0.00E+00         *         *    STAGE    0.00E+00  0.00E+00         *         *
P_SOLID      11    47     2.727     2.000     2.222     2.573     0.776    P_SOLID     1.000     9.000     1.000     3.000
DOC           1    57  0.00E+00  0.00E+00  0.00E+00         *         *    DOC      0.00E+00  0.00E+00         *         *
HICN         57     1    0.5841    0.5012    0.5789    0.2127    0.0282    HICN       0.1995    1.0000    0.3921    0.7943
```

Table 17b Correlation matrices

(i) normal

	pH	COND	AMM_N	TON	TP	PCO2	TA	CL
COND	-0.177							
AMM_N	0.211	0.427						
TON	[illegible]	[illegible]	0.557					
TP	-0.244	0.502	[illegible]	0.231				
PCO2	-0.072	0.903	[illegible]	0.234	0.127			
TA	0.755	0.137	0.476	0.370	0.141	0.332		
CL	-0.443	0.497	[illegible]	0.323	0.475	-0.031	-0.243	
OPO4	[illegible]	-0.037	[illegible]	-0.248	-0.028	-0.075	0.016	-0.066
SIO2	0.015	0.151	[illegible]	[illegible]	-0.056	0.174	0.172	0.066
SO4	0.249	0.131	[illegible]	[illegible]	0.343	-0.010	0.070	0.109
NA	-0.006	0.303	0.199	[illegible]	0.574	0.023	-0.006	0.424
K	-0.282	0.557	0.241	0.282	0.595	0.326	-0.136	0.588
CU	-0.117	0.077	-0.075	0.017	0.350	0.025	-0.232	0.075
MG	[illegible]	0.572	0.475	0.234	0.379	0.192	0.002	0.662
CA	0.056	0.407	0.697	0.256	0.966	0.158	0.211	0.344
ZN	-0.055	0.048	0.127	0.208	0.304	-0.005	-0.183	0.080
CD	-0.135	0.741	-0.034	0.143	0.070	0.903	-0.097	-0.057
AL	-0.145	0.106	[illegible]	0.161	0.345	0.033	-0.206	0.060
PB	-0.149	0.119	-0.053	0.245	0.438	0.010	-0.259	0.235
CR	0.030	-0.068	-0.025	-0.038	0.414	-0.064	-0.136	-0.024
MN	-0.132	0.213	0.269	0.244	0.408	0.067	-0.083	0.156
FE	-0.031	0.126	0.034	0.177	0.491	0.158	-0.142	-0.026
NI	-0.261	0.034	-0.075	-0.094	-0.059	-0.049	-0.311	0.226
HUMIC	0.219	-0.041	0.017	-0.016	0.177	0.071	0.254	-0.077
P_SOLID	0.049	0.077	*	0.146	0.004	0.006	-0.161	0.425
HION	-0.976	0.211	-0.146	-0.067	0.066	0.110	-0.743	0.443

	OPO4	SIO2	SO4	NA	K	CU	MG	CA
SIO2	-0.111							
SO4	[illegible]	[illegible]						
NA	[illegible]	0.035	-0.011					
K	[illegible]	0.023	0.156	0.575				
CU	-0.057	-0.177	0.107	[illegible]	[illegible]			
MG	-0.021	0.025	0.343	[illegible]	[illegible]	[illegible]		
CA	-0.006	-0.105	0.313	[illegible]	[illegible]	0.406	0.739	
ZN	-0.034	-0.319	0.227	0.145	0.451	0.590	0.267	0.573
CD	-0.025	0.129	-0.036	0.074	0.122	0.060	0.109	0.022
AL	[illegible]	-0.454	0.121	0.076	[illegible]	[illegible]	0.140	0.404
PB	-0.041	[illegible]	[illegible]	0.151	0.417	[illegible]	0.240	0.460
CR	-0.019	-0.179	0.259	0.103	0.347	0.747	0.129	0.508
MN	-0.046	-0.484	0.173	0.090	0.335	0.256	0.232	0.449
FE	-0.033	-0.216	0.233	[illegible]	0.411	0.700	0.186	0.564
NI	-0.046	0.069	-0.066	0.050	0.137	0.220	-0.004	-0.071
HUMIC	0.132	-0.162	0.047	0.112	0.052	-0.111	0.123	0.198
P_SOLID	*	-0.273	-0.080	-0.301	0.078	-0.011	-0.159	0.208
HION	-0.214	0.011	-0.046	0.072	[illegible]	0.133	0.242	-0.032

	ZN	CD	AL	PB	CR	MN	FE	NI	HUMIC	P_SOLID
CD	0.013									
AL	0.629	-0.012								
PB	0.701	0.093	0.543							
CR	0.773	-0.026	0.586	[illegible]						
MN	0.521	-0.029	0.915	0.362	0.351					
FE	0.785	0.149	0.717	[illegible]	0.925	0.527				
NI	-0.105	0.044	-0.106	0.062	-0.047	-0.100	-0.084			
HUMIC	-0.066	-0.014	0.119	-0.198	-0.148	0.196	0.030	-0.231		
P_SOLID	-0.066	0.035	0.349	0.101	*	-0.107	0.179	*	0.016	
HION	0.034	0.127	0.149	0.127	-0.053	0.150	0.037	0.290	-0.206	-0.122

(ii) logarithmic

	C1	C2	C3	C4	C5	C6	C7	C8
C2	[illegible]							
C3	[illegible]	0.471						
C4	[illegible]	[illegible]	[illegible]					
C5	0.214	[illegible]	[illegible]	[illegible]				
C6	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			
C7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.753		
C8	[illegible]	0.277	[illegible]	[illegible]	[illegible]	0.661	0.292	
C9	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.177	0.024
C10	[illegible]	[illegible]	[illegible]	[illegible]	0.110	0.010	-0.045	0.033
C11	0.257	[illegible]	[illegible]	-0.014	[illegible]	[illegible]	0.292	0.076
C12	0.166	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.482	0.295
C13	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.166	0.239	0.037
C14	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-0.124	0.077	-0.373
C15	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.960	0.453
C16	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.644	[illegible]	0.576
C17	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.207	-0.131
C18	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-0.035	0.486

	C9	C10	C11	C12	C13	C14	C15	C16	C17
C10	[illegible]								
C11	[illegible]	-0.246							
C12	[illegible]	[illegible]	[illegible]						
C13	[illegible]	[illegible]	[illegible]	[illegible]					
C14	[illegible]	[illegible]	[illegible]	[illegible]	0.179				
C15	[illegible]	[illegible]	[illegible]	0.450	0.234	[illegible]			
C16	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		
C17	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.157	-0.055	
C18	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.231	[illegible]

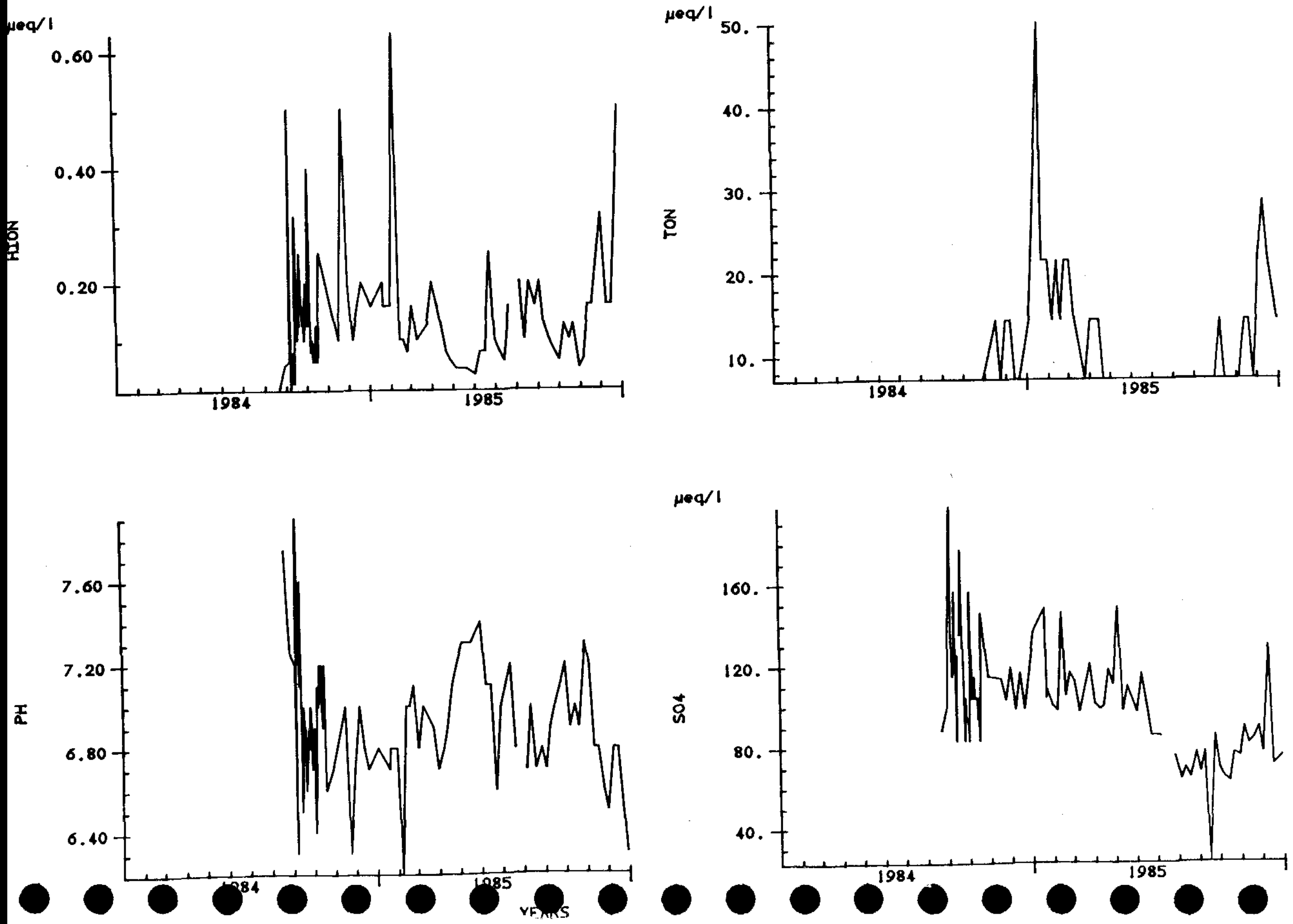
Table 18. A comparison of unacidified streamwater chemistry (ueq l^{-1}).

	LI6	GI1
1. pH		
2. $\bar{x}$	6.9	6.3
max	7.9	6.7
min	6.2	6.0
H^+		
$\bar{x}$	0.15	0.6
max	0.63	1
min	0.01	0.2
SO_4^{2-}		
$\bar{x}$	103	131
max	198	188
min	23	62
NO_3^-		
$\bar{x}$	10	11.6
max	50	121
min	7	7
4. NH_4^+		
$\bar{x}$	1.6	16
max	11.4	7.1
min	1.4	1.4
Na^+		
$\bar{x}$	138	180
max	267	404
min	36	126
Cl^-		
$\bar{x}$	155	178
max	197	310
min	85	85
Mg^{2+}		
$\bar{x}$	146	66
max	420	103
min	44	47
Ca^{2+}		
$\bar{x}$	146	88
max	456	188
min	23	50
K^+		
$\bar{x}$	11	6.4
max	43	15.4
min	2.6	2.6
3. Al		
$\bar{x}$	0.06	0.05
max	0.48	0.35
min	0.005	0.004

1. pH units
2. arithmetic mean
3. dissolved (mg l^{-1})
4. mg l^{-1} as ammoniacal nitrogen

Figure 17

LLYN BRIANNE (LI6)



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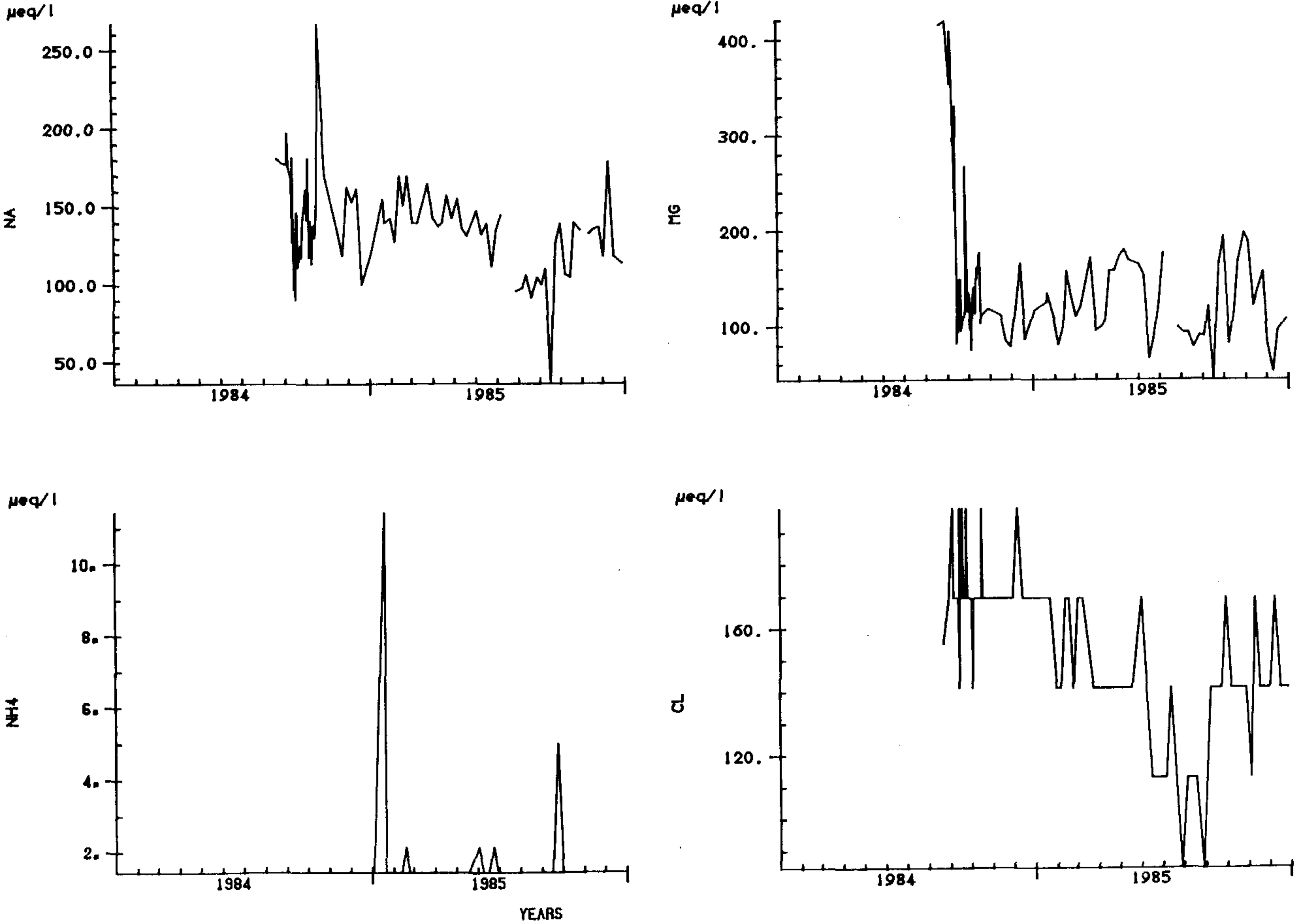

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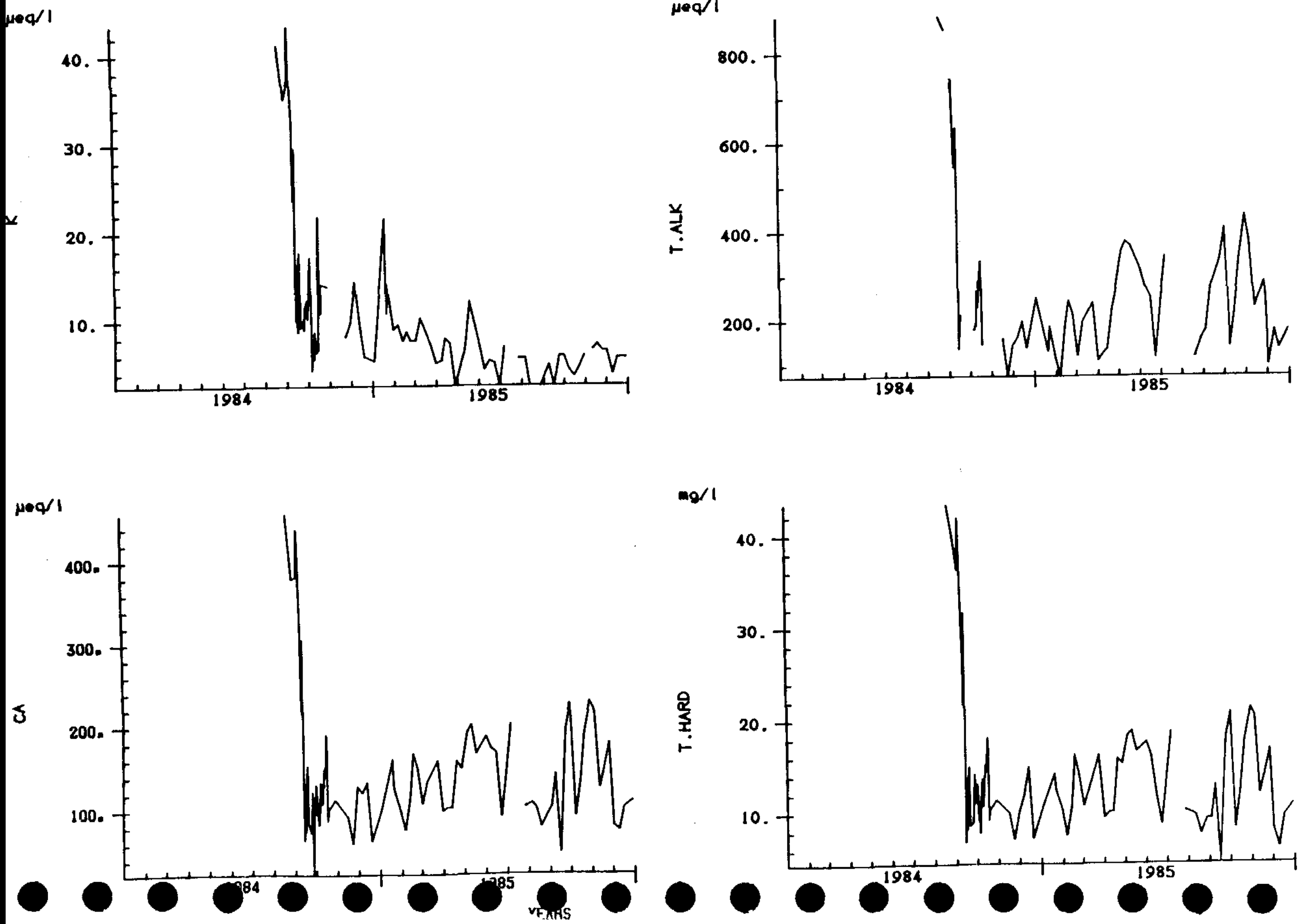

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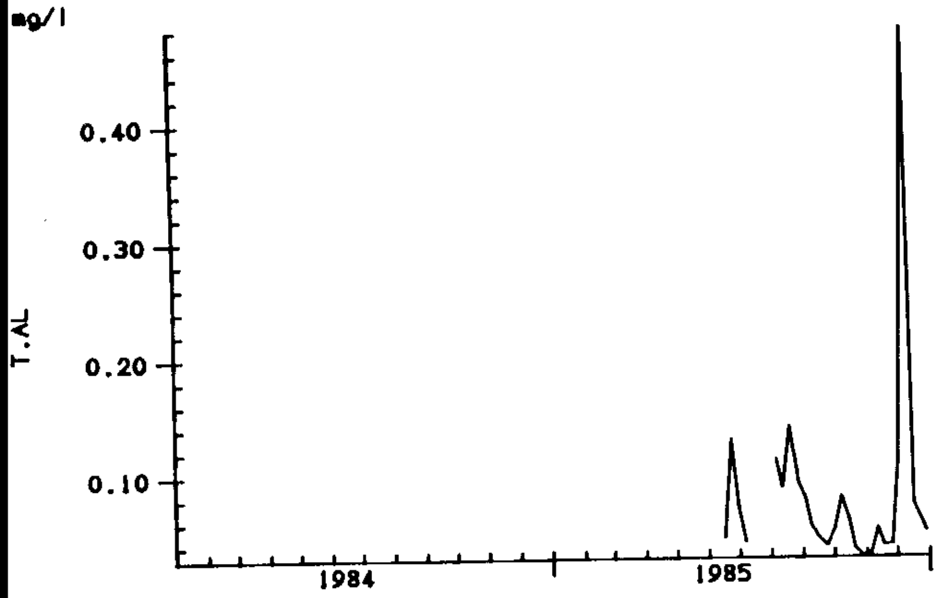
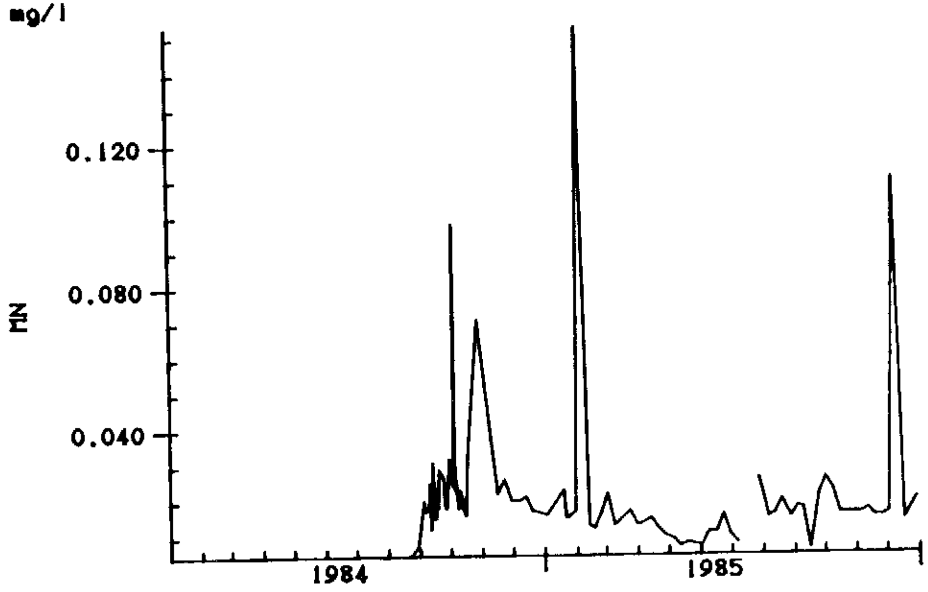
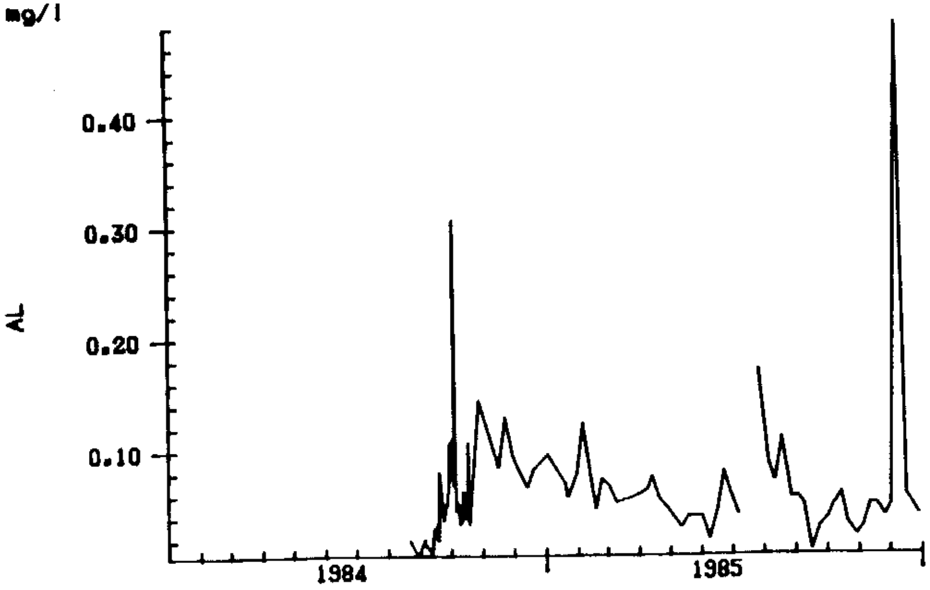
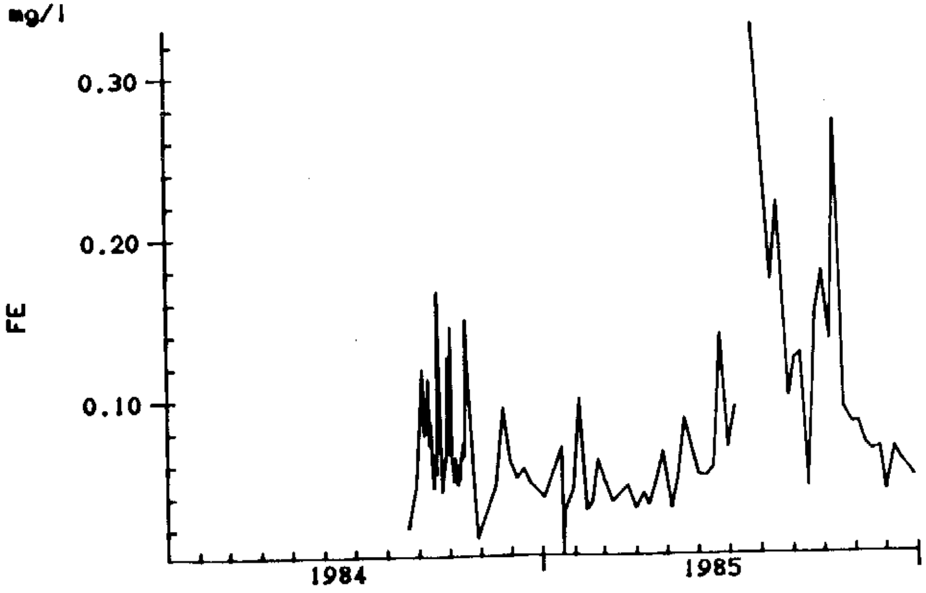
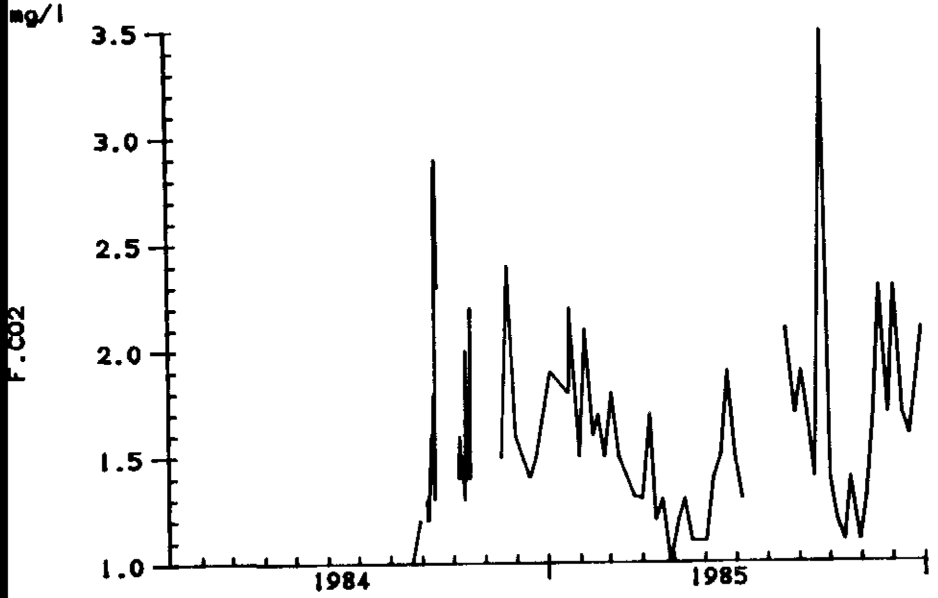


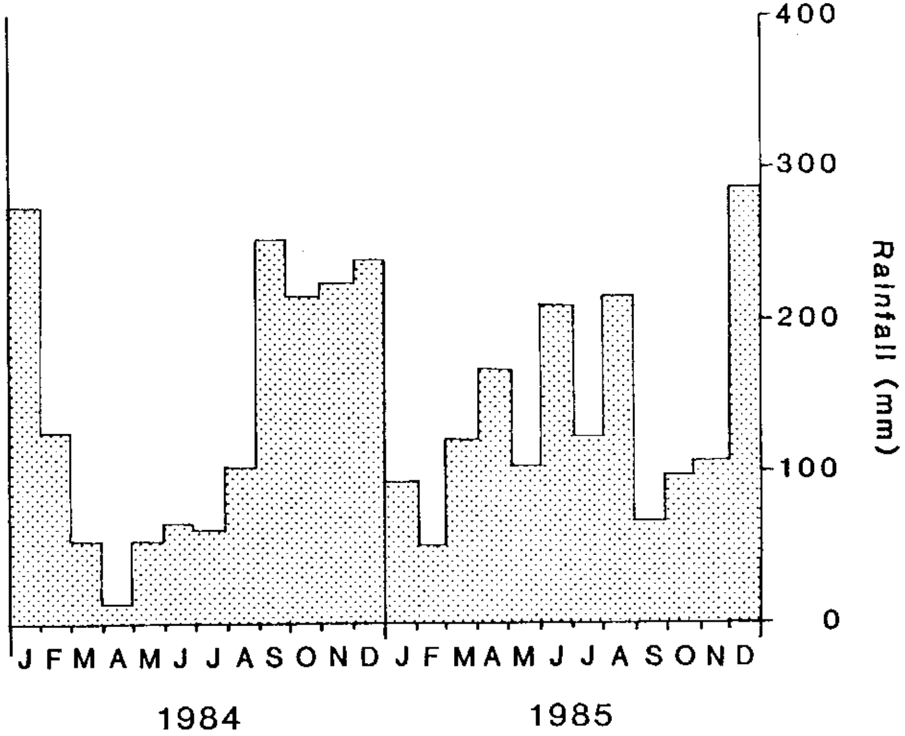


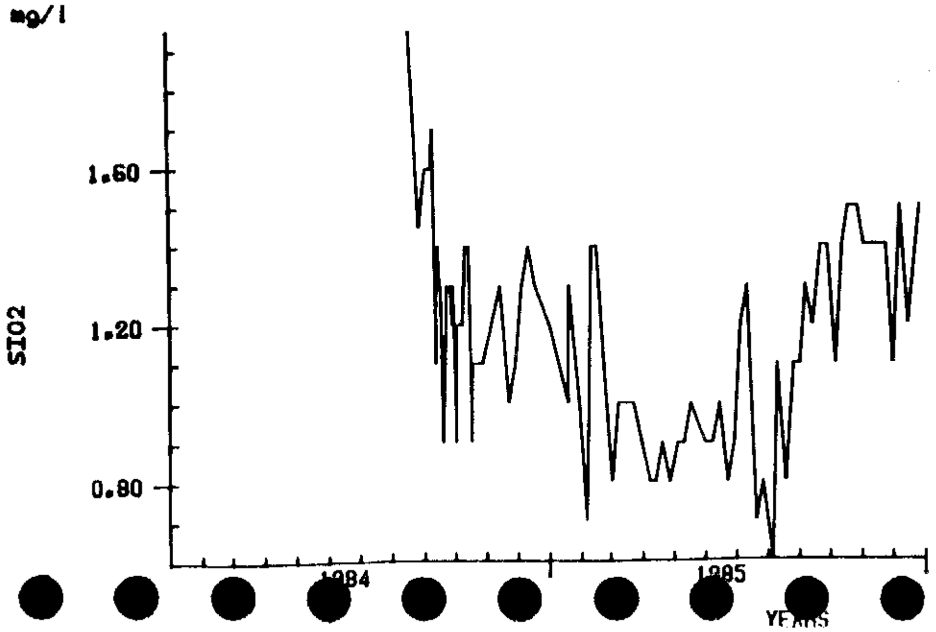


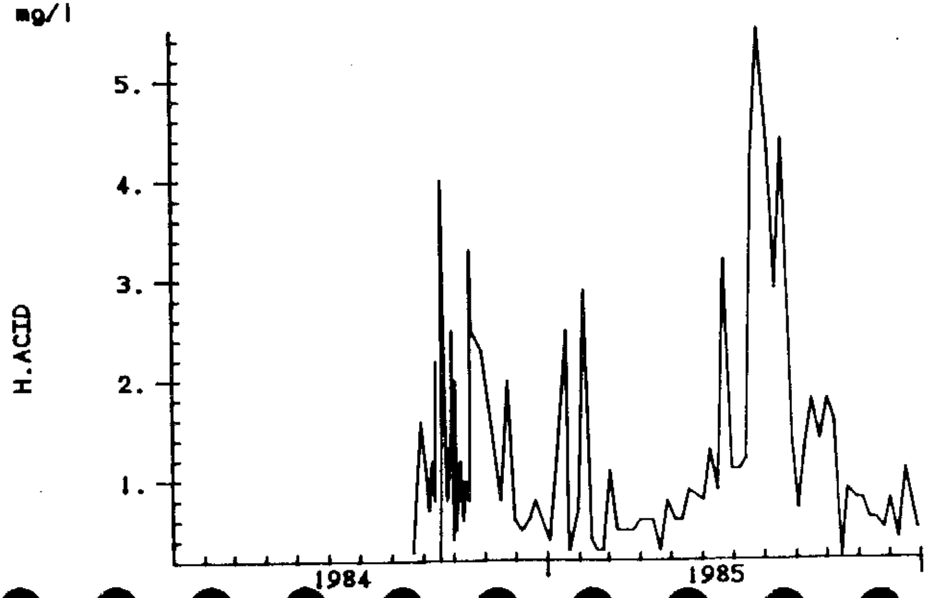


LLYN BRIANNE(LI6)







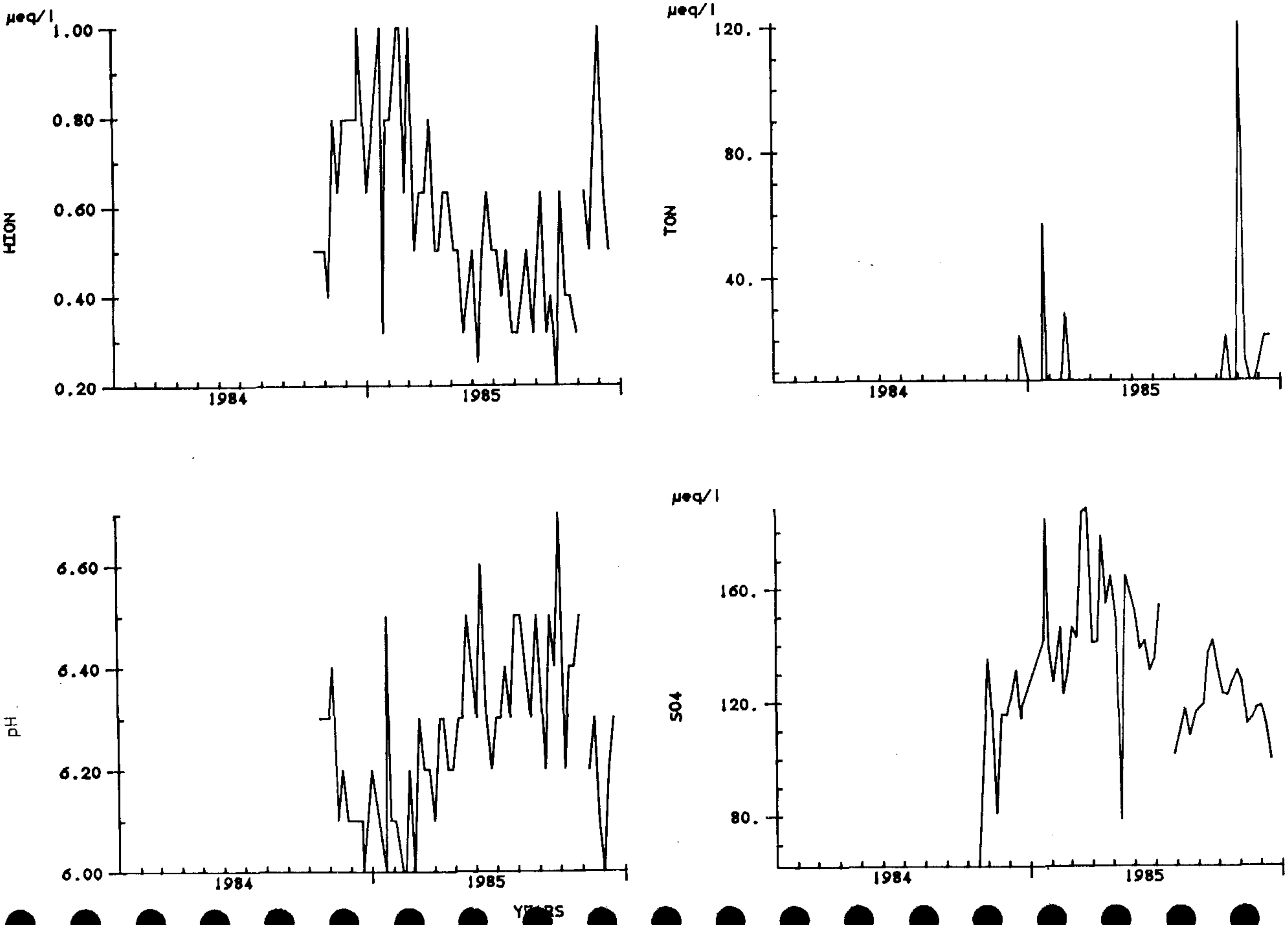


evidence of flushing in September 1984 and NO_3 also exhibits a seasonal pattern with a Winter maxima. Similarly, the marine salts (Na, Cl and Mg) all indicate the presence of an Autumn flush in 1984 and variations similar to those recorded at all of the other sites. Terrestrially derived cations and total hardness also indicate the occurence of flushing at the end of the 1984 dry period. In addition, hardness fluctuates, presumably in response to individual rainfall and runoff events, throughout the period. Lastly, dissolved aluminium concentrations indicate a tendency to rise sharply during occassional events, reaching concentrations of up to 0.48 mg l^{-1} in December 1985 during one very large storm. Hence, even in this catchment aluminium levels can reach levels approaching the highest recorded in the CI catchments, despite its "unacidified" nature. Clearly in these instances the catchments hydrological and chemical response is crucial in determining the level of acidity and aluminium contamination.

Lastly, at GI1 (Figure 18) there is a clear seasonal pattern of pH and H^+, with pH levels reaching a maximum during the Summer low flow periods. This presumably results from the larger baseflow component in streamflow during the Summer months. SO_4 concentrations also show a tendency to peak during the months receiving low rainfall. NO_3 concentrations meanwhile, continue to exhibit Winter peaks in response to reductions in nutrient uptake. The marine salts exhibit little seasonal pattern, although Cl does indicate a major reduction in concentration in August/ September 1985 when flows are reduced by evapotranspirationl losses occuring during the Summer months, as at various other sites. In general, the total hardness and alkalinity levels however, show some indication of increased concentrations during low rainfall and low runnoff

Figure 18

LLYN BRIANNE (GI1)



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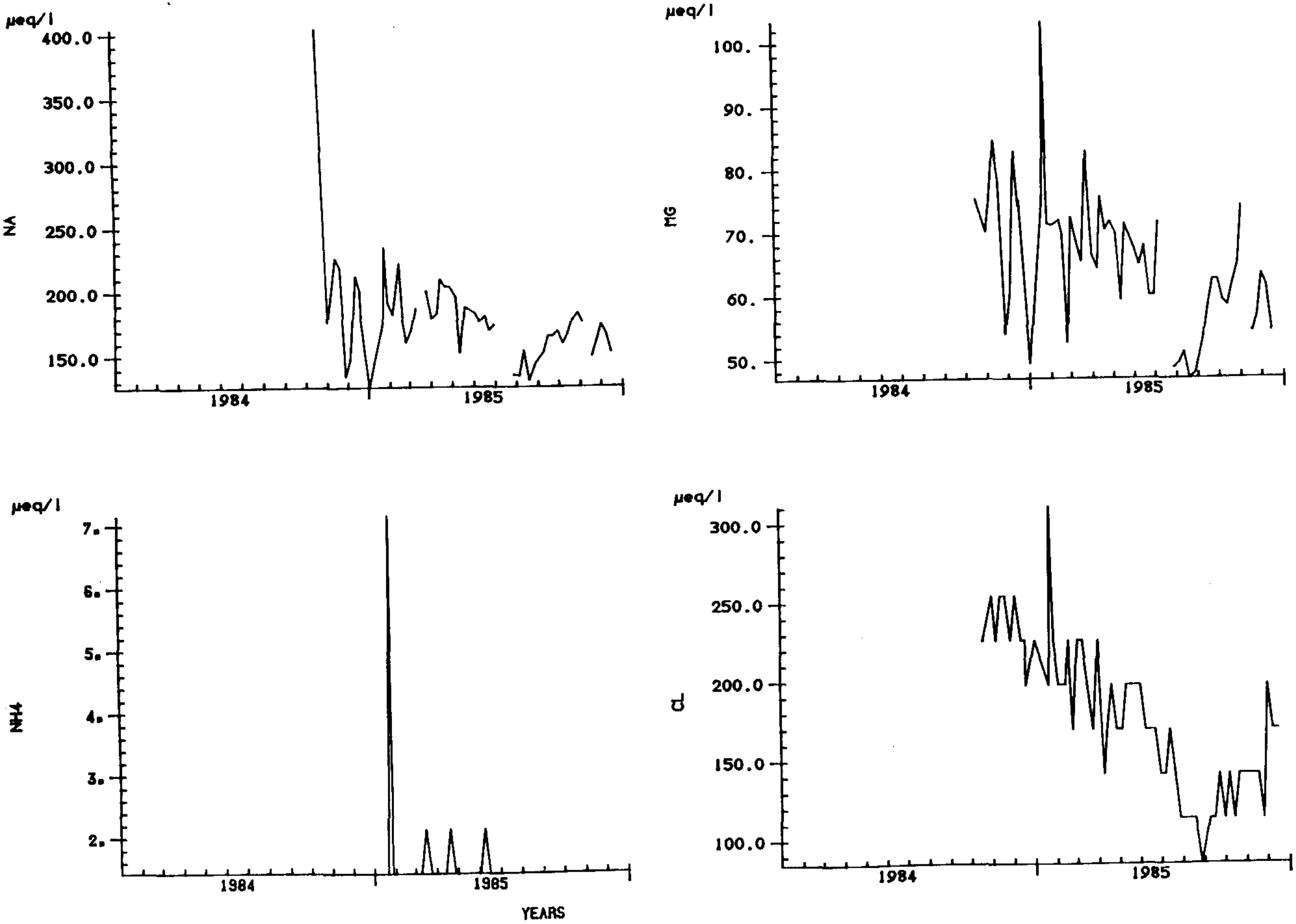

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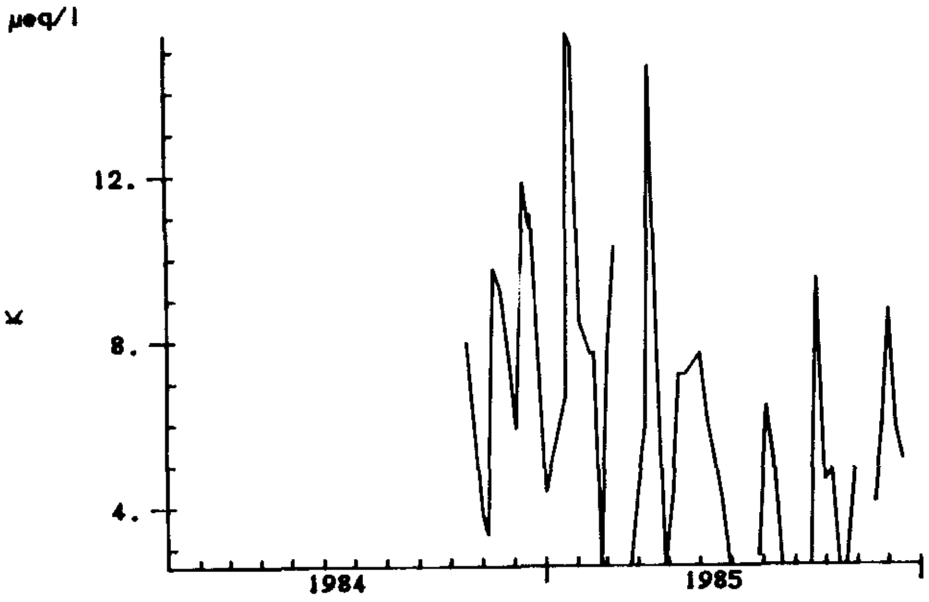

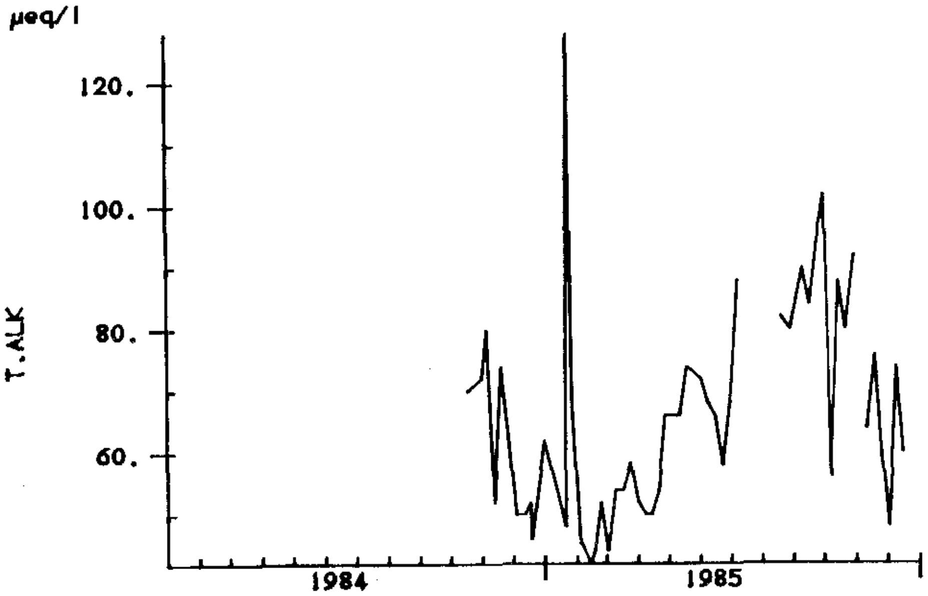

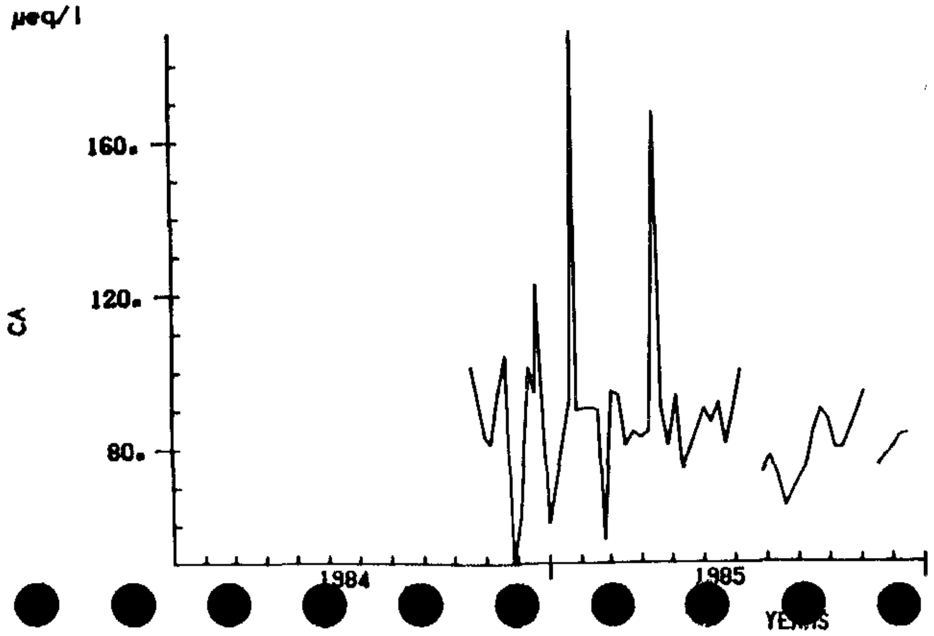

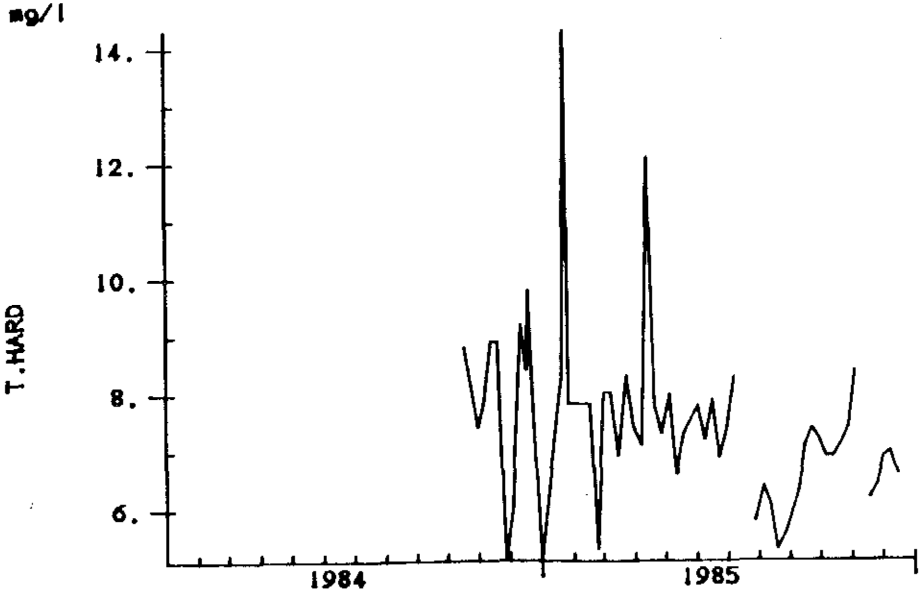

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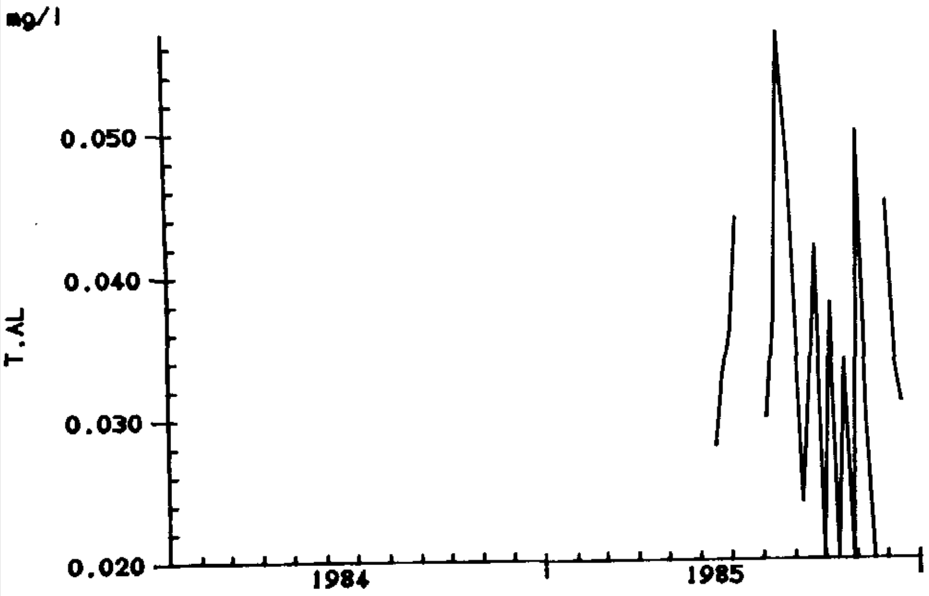
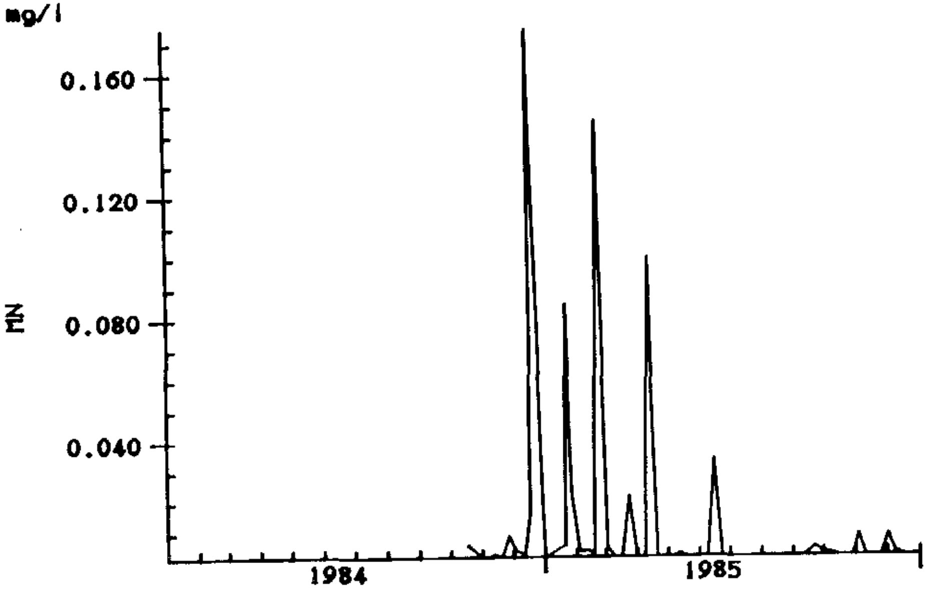
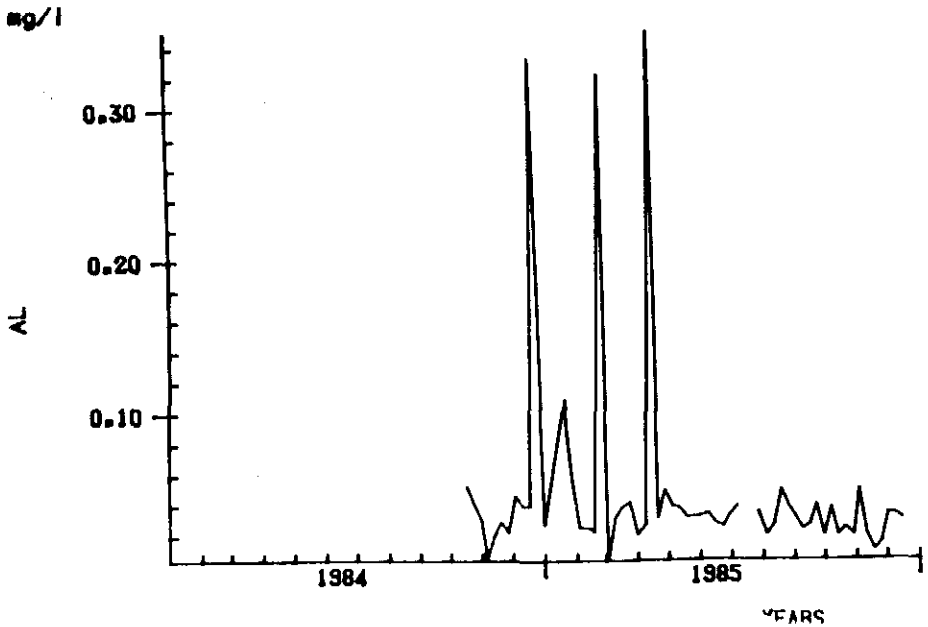
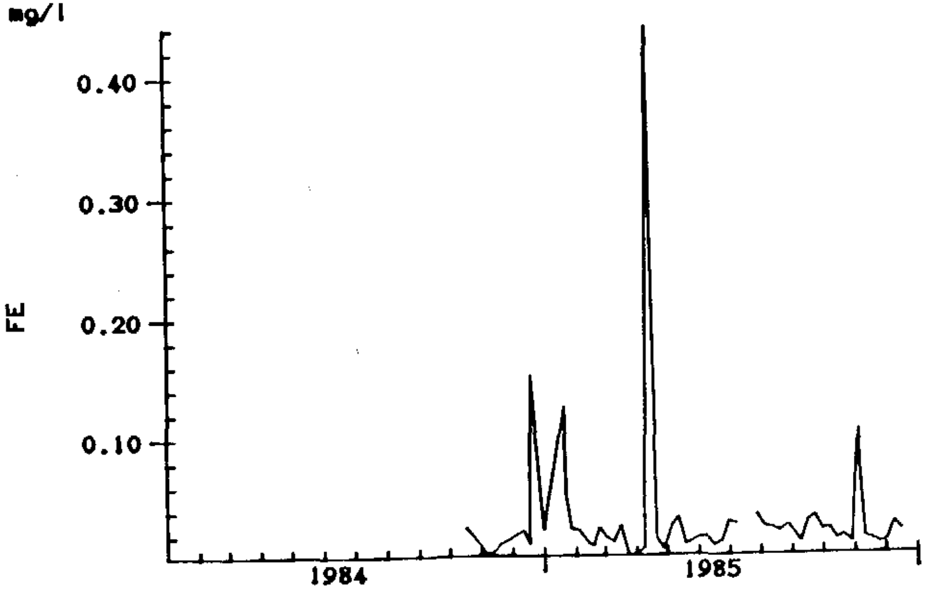
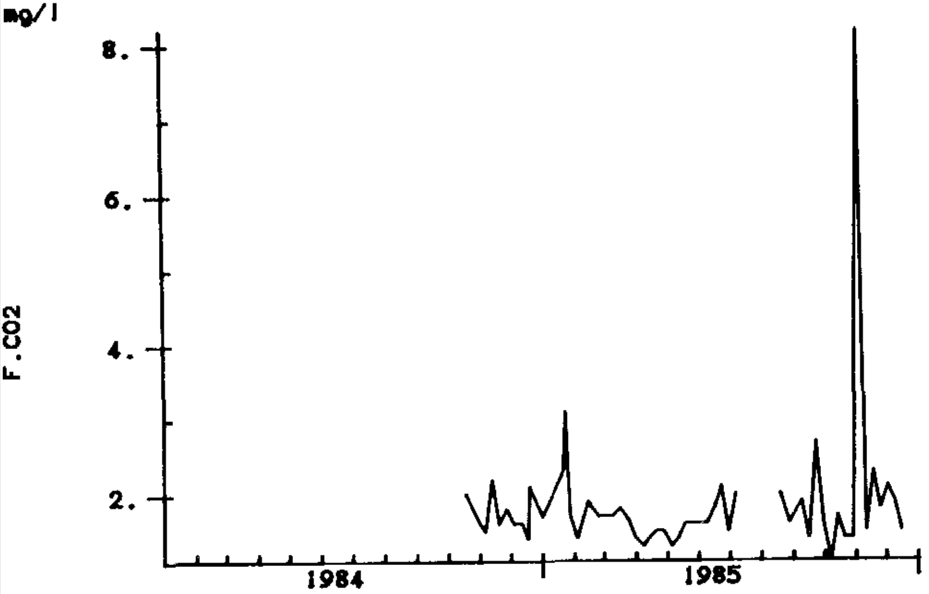


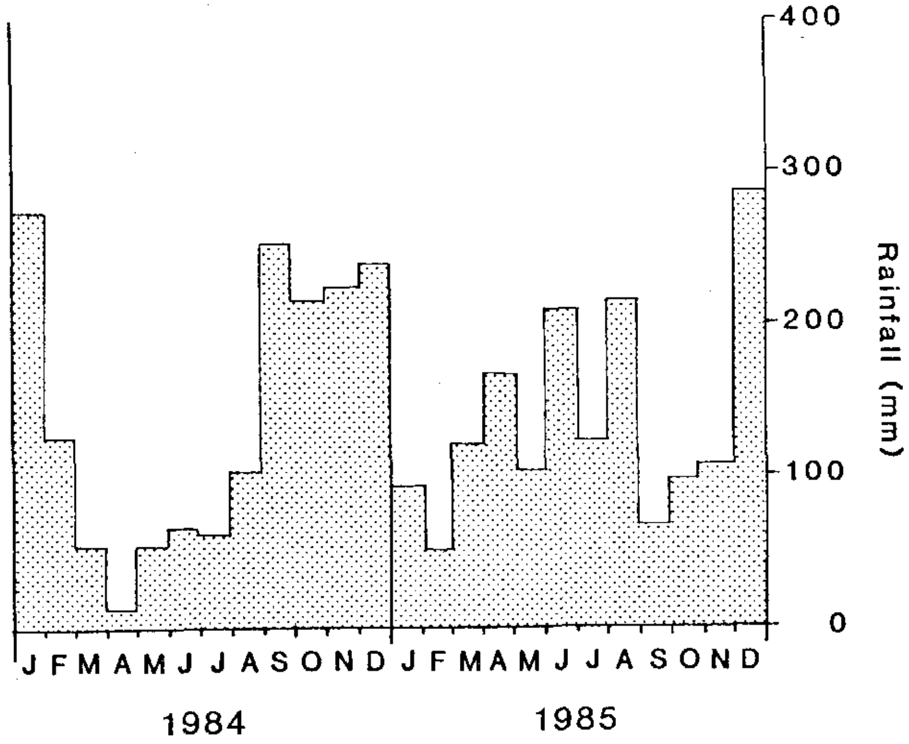


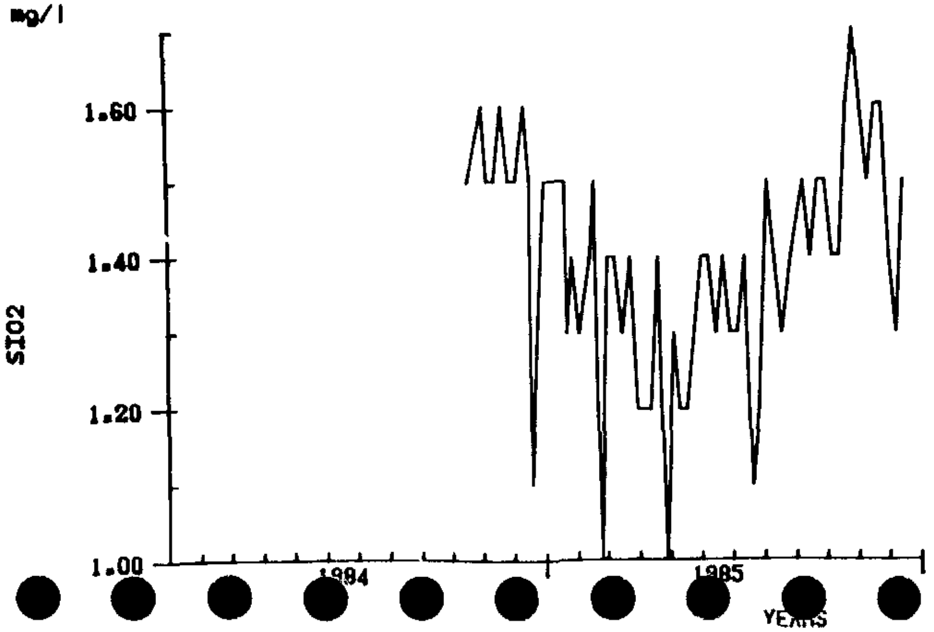


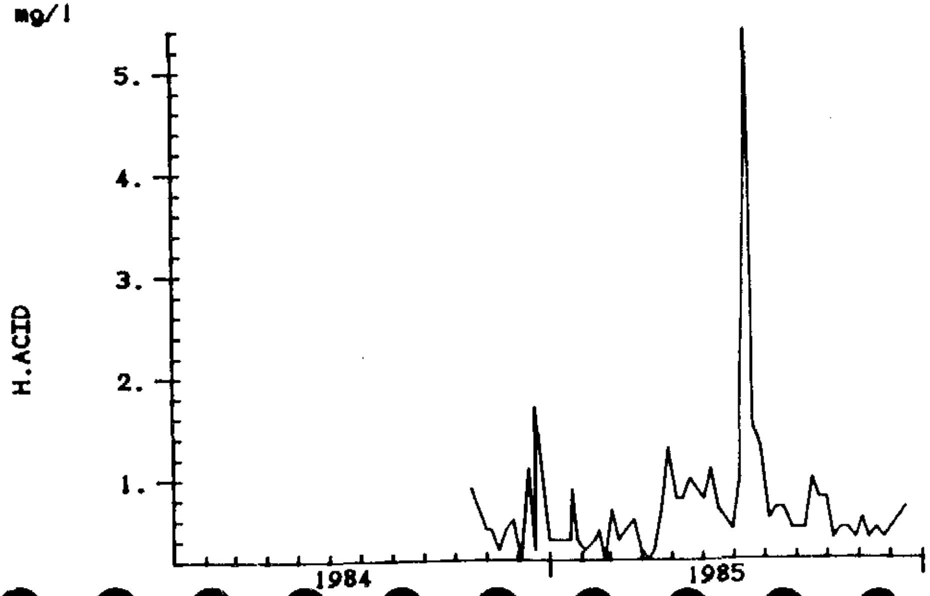


LLYN BRIANNE (GI1)









months, presumably reflecting the increased baseflow component and residence times prevalent at such times. Lastly, dissolved aluminium and manganese concentrations, while generally low, exhibit several major peaks which correspond to major rainfall and runoff events. Again then, even in an apparently unacidified oak woodland catchment, exteme conditions can give rise to significant levels of aluminium contamination. Analysis of the data for the two unacidified catchments confirms that few problems exist with regard to streamwater chemistry irrespective of whether the land use is oak woodland or rough grassland. Nevertheless, there still remains the intermittent occurrence of elevated aluminium concentrations during extreme hydrological events. However, in general the two catchments are clearly sufficiently well buffered with pH and calcium concentrations well above those levels considered problematical (i.e. $pH < 5.5$ and $Ca < 100$ ueq l^{-1}).

Conclusion

In conclusion, while bulk precipitation quality in the area is dominated by marine salts and terrestrially derived anions, moderately acidic events do occasionally occur. Moreover, the area receives a large volume of mildly acidic precipitation, although as has been seen both its volume and acidity are subject to variations. Furthermore, within the study area those catchments dominated by conifer forest land use clearly exhibit the most acid streamwater and highest aluminium concentrations due to the limited buffering available. In addition, factors such as the enhanced evapotranspiration, enhanced scavenging capability, stemflow contamination, increased base cation uptake and the encouragement of more rapid runoff processes, contribute to the above. Conditions within the acidified moorland catchments are also by no means satisfactory despite their reduced scavenging capacity and evapotranspirational losses, since only limited buffering is available from the catchment soils. As a result pH, Calcium and aluminium levels during storm events combine to create conditions unsuitable for the re-establishment of fisheries. Only in catchments GI1 and LI6 are conditions totally satisfactory.

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4. STORM EVENT CHEMISTRY

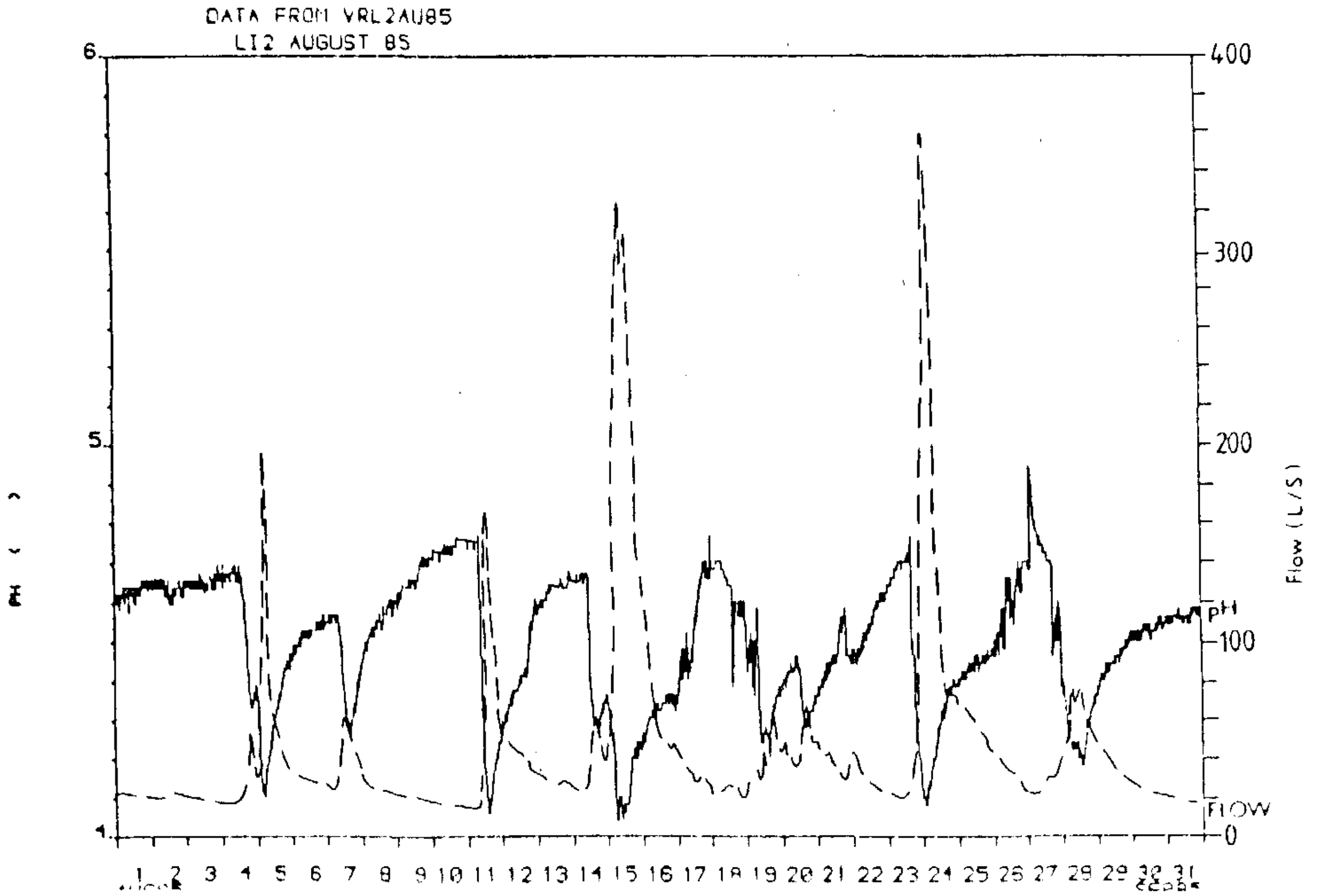
1. Monitoring Strategy

Previous work in the Llyn Brianne area (Stoner and Gee 1985) and elsewhere has demonstrated the importance of monitoring episodic events in stream water quality. Short duration flushes in response to storm or snow melt events may be of ecological significance and it is essential that detailed information on these events is obtained. Monitoring frequency also needs to be sufficient to provide data for mathematical modelling of stream chemistry responses to changes in flow.

Arising from these needs continuous monitoring systems for pH, conductivity, temperature, flow and rainfall intensity have been installed at all the study catchment stream monitoring sites in the Llyn Brianne study area. Measurements of these parameters are logged at 15 minute intervals, monitoring being continuous throughout the year. These systems of measurement have provided detailed information on individual catchment responses and this information is currently being used for modelling purposes. The value of the continuous monitoring systems in describing episodic events is illustrated by Fig.19. This example summary plot shows the pH response of stream LI2 to a series of summer storm events.

Automatic sampling to provide discrete samples for detailed analysis from episodic events is effected by a rainfall activated trigger system. This system, developed by the Institute of Terrestrial Ecology, is based on a standard tipping bucket raingauge which, as well as providing a rainfall record for each monitoring station, triggers the autosampler to commence sampling when a pre-set rainfall intensity is exceeded. Sampling times are automatically recorded on the site data logger. The trigger threshold value may be varied depending on the type of storm event which needs to be monitored. The

Fig.19 The PH response of Stream LI2 to a series of Summer Storm Episodes.



systems installed at Llyn Brianne were initially set to activate automatic sampling when rainfall exceeds 3mm/hour. This method of triggering is more effective in ensuring that the "first flush" is sampled than flow or pH triggers which depend on significant responses in stream flow or quality to activate sampling. An example of this effective triggering is shown by the plot of stream CI3 for 26th July 1985 (Fig. 20).

Several operational constraints of this system have been identified which have necessitated modifications to the sampling strategy:

(1) The setting of the trigger threshold value is important. It has been found that triggering at rainfall intensities of 3mm/hour and above may lead to autosampling of insignificant events. An example of this problem is shown by Fig 21. In this case, a short duration rainfall event led to activation of the autosampler on 21st August 1985. The system was subsequently unavailable to sample a significant episode which occurred on 23rd and 24th August. Resetting of the system would not then have occurred until the next fortnightly service visit. The trigger threshold value has now been raised to a rainfall intensity of 4mm/hour but the possibility remains that autosampling of significant storm events may be missed if preceeded by less significant events which are however sufficient to trigger the system.

Further increases in the trigger threshold value would possibly delay triggered sampling until later in the episodes possibly leading to failure to pick up the first flush conditions. Also extended duration storms with relatively low rainfall intensity but which are still sufficient to lead to a significant stream response may be missed.

Fig 20 Catchment CI 3 Storm Episode to show Effectiveness of Rainfall Trigger.

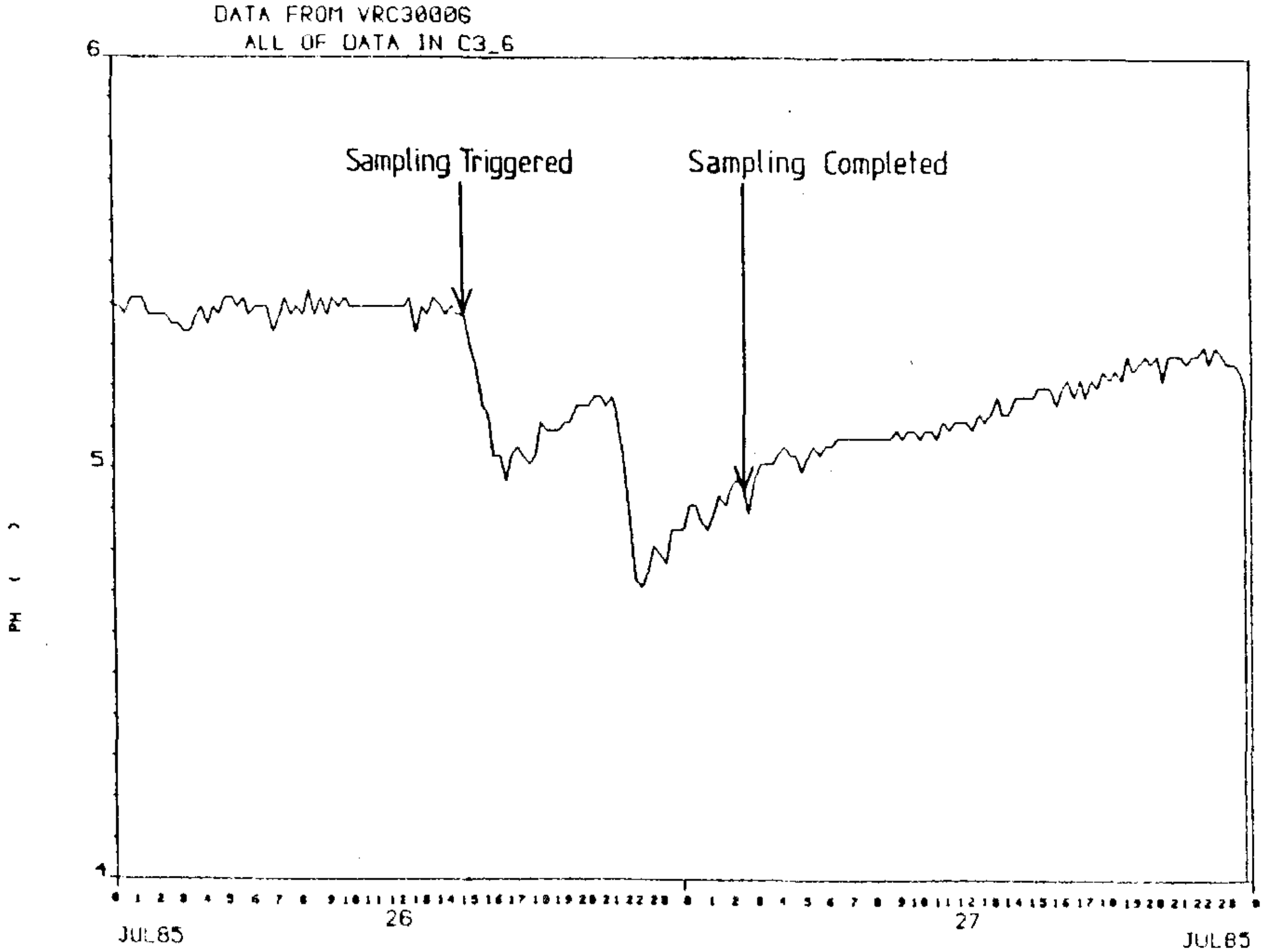
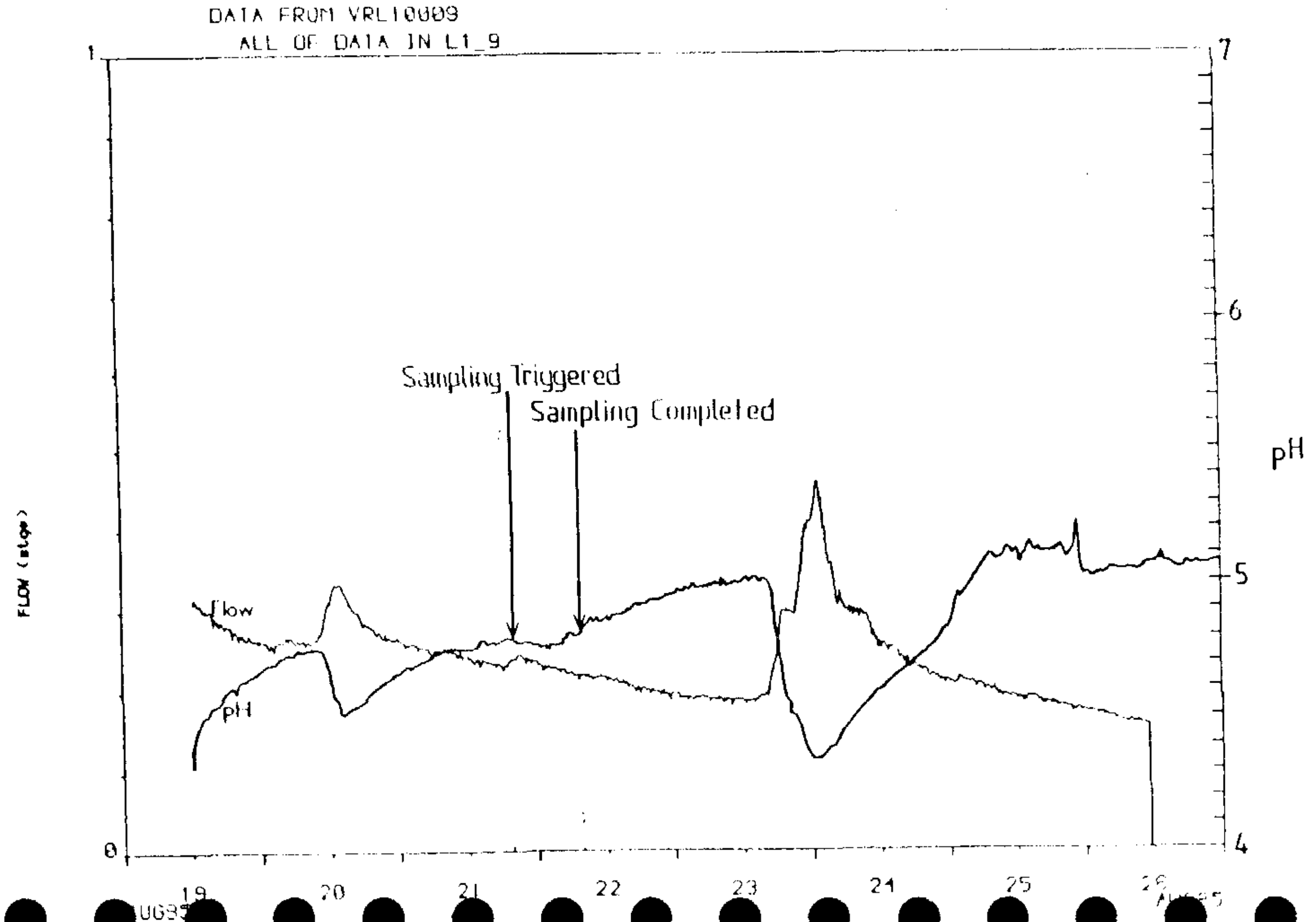


Fig. 21 Premature Triggering of Autosampling.



(2) Prior to February 1986 only a single prototype trigger was available to cover all the sites. The number of episodes for which sampling was completed prior to that date are therefore limited and data for that period are only available for selected catchments.

(3) Invariably and ideally triggered autosampling will be synchronous in all catchments for high rainfall episodes. Under these circumstances the sample numbers generated exceed the capacity within the laboratory facilities at Llanelli. (13 catchments would generate a maximum of 624 samples under these conditions). The Modelling sub-group have therefore made the decision to select 12 samples from each set of 48 samples generated per site per event. The requirement for 15 minute interval sampling during the early part of the episode remains. Selection of samples for subsequent analysis is made by reference to the continuous monitoring records for the period of the episode.

(4) The requirement for 15 minute interval sampling throughout the period of increasing and peak flows has restricted the sampling period to a maximum of 12 hours. This frequency prevents sampling throughout the full recession limbs of the episode. To overcome this problem the autosampler timers are currently being replaced with dual interval timers which will allow pre-setting of two sampling periods at different sampling frequencies. For example, it will now be possible to sample at a frequency of 15 minutes for the first 6 hours of an episode followed by hourly sampling for a further 24 hours. Both periods and frequencies may be varied as required.

The revised autosampling strategy will lead to a reduction in the sample loading on the analytical facilities without significant loss of information together with increased information on the recovery of water quality following episodes. The decision to be selective in analysis of samples will allow those samples not required to be used for other purposes such as the Lampeter College sediment studies.

2. Results

A number of important episodes have been identified from the continuous monitoring records for each catchment. Information on those periods for which detailed water quality data from autosamples are available is summarised in Table 19.

Detailed processing of data from episodes is pending. Considerable progress in preliminary processing of the back log of continuous monitoring data by Welsh Water has been achieved for most sites but difficulties in transferring data to IH have led to some delays.

Continuous data for sites LI1, LI6 and CI6 for August 1985 are currently being run through the CAPTAIN model at IH and flow /H^+ ion response characteristics for single events are being examined.

An important episode occurred during March 1986 when a high rainfall event following a prolonged cold period led to rapid run-off and snow melt resulting in substantial effect on the water quality of the streams in the study area. Because of its apparent importance this particular episode has been reported in detail as an example of episodic effects on stream water quality.

Table 19

Summary of Episodes for which detailed Water Quality Information is available

Site	Date	No. Samples	pH range	Comments
LI1	21/22.8.85	48	4.8-4.7	Insignifiant Event.
"	4.3.86	48	5.4-4.1	SNOW MELT. Very Important
"	20.3.86	48	4.8-4.3	Diss. Al. 0.38 ---> 0.58
LI2	14.7.85	48		Not significant
"	4.3.86	48	4.4-3.9	SNOW MELT. Early part of event missed - manual triggering of autosampler required.
"	19/20.4.86	48	4.3-4.1	
LI3	4.3.86	12	6.3-5.0	SNOW MELT. Early part of episode only sampled by autosampler.
	30.7.86	12	5.8-5.1	No continuous records
LI4	None			
LI6	4.3.86	8	5.5-5.7	Samples taken at peak of SNOW MELT event
	20.3.86	48	-	Insignificant
	19/20.4.86	48	6.8-5.7	Significant
LI8	5.11.85	48	6.4-5.2	Significant event.
	2. 8.86	12	5.6-5.1	Significant. No continuous records available.
CI3	17/18.7.86	48	5.9-5.4	Significant. No Al data.
	26/27.7.86	48	6.1-5.3	Significant.
	17/18.5.86	48	5.4-4.9	Significant.
	10.6.86	12	5.1-4.9	

Site	Date	No. Samples	pH range	Comments
CI4	5.8.85	48	5.1--> 4.7	Significant.
	4.3.86	48	4.5-4.7	SNOW MELT. Samples taken during peak episode.
	20.3.86	48	5.0-4.8	Small episode.
	17.5.86	48	5.1-4.7	Small episode.
	10.6.86	12	5.5-4.0	Worst case conditions of significant episode.
	22/23.8.86	13	5.6-5.2	No continuous monitoring record
CI5	11.8.85	48	6.3-5.7	Significant.
	4.3.86	48	5.9-4.6	SNOW MELT. Very important event
	28.7.86	13	6.6-6.2	No continuous monitoring record
CI6	13.8.85	48	6.3-5.2	Significant event.
	2/3.9.85	48	6.5-5.5	Signifiant event.
	4/5.3.86	48	4.6-4.8	Peak episode conditions during SNOW MELT.
UC4	28/29.6.85	48	6.0--> 5.0	Significant event.
	22.1.86	48	5.1-5.3	Not significant? Possible worst state conditions.
	24.3.86	48	5.1-5.3	" "
	29/30.3.86	12		V.small event under peak episode conditions.
	19/20.4.86	48	5.2-4.8	Significant event.
	9.6.86	13	6.5-5.2	" "
	28.7.86	12	7.0-6.0	" "
GI1	4.3.86	48	5.2-5.9	SNOW MELT. Sampled at peak episode?
	25.8.86	13	6.3-5.6	Major episode

5. SNOW MELT EVENT CHEMISTRY

1. Preceeding Weather Conditions

Throughout the whole of February and the beginning of March 1986 a stable weather system was established over the U.K. and extremely cold conditions prevailed.

Sub-zero daily mean air temperatures were recorded at the Llyn Brianne Automatic Weather Station (A.W.S.) from 4th February until 3rd March and during this period soil temperatures (10cm depth) fell progressively from 3.7°C on 1st February to a minimum of 0.3°C on 4th March. The coldest air temperature recorded was -11.1°C during the night of 21st/22nd February (Fig. 22).

Falls of snow occurred on 30th and 31st January (approx. 10cm) and 9th and 10th February (approx 5cm) although the precise times and quantities of snowfall for Llyn Brianne are not available.

Following the first and subsequent falls, snow covered the area until early March although the extent of this cover gradually reduced to approximately 50 per cent following each snowfall event as a result of drifting and very limited gradual daytime surface thaw. Air temperatures were only very infrequently above zero throughout the whole period and any surface thaw would only have occurred in direct sunshine in the early afternoon (Fig.22).

The surface winds throughout the period were predominantly easterly and north easterly although these moved around to the south in the early hours of 3rd March preceeding a sudden change in weather conditions (Fig.23).

Fig 22 Rainfall, Air and Soil Temperature Records for Llyn Brianne Automatic Weather Station. 29th January — 6th March 1986.

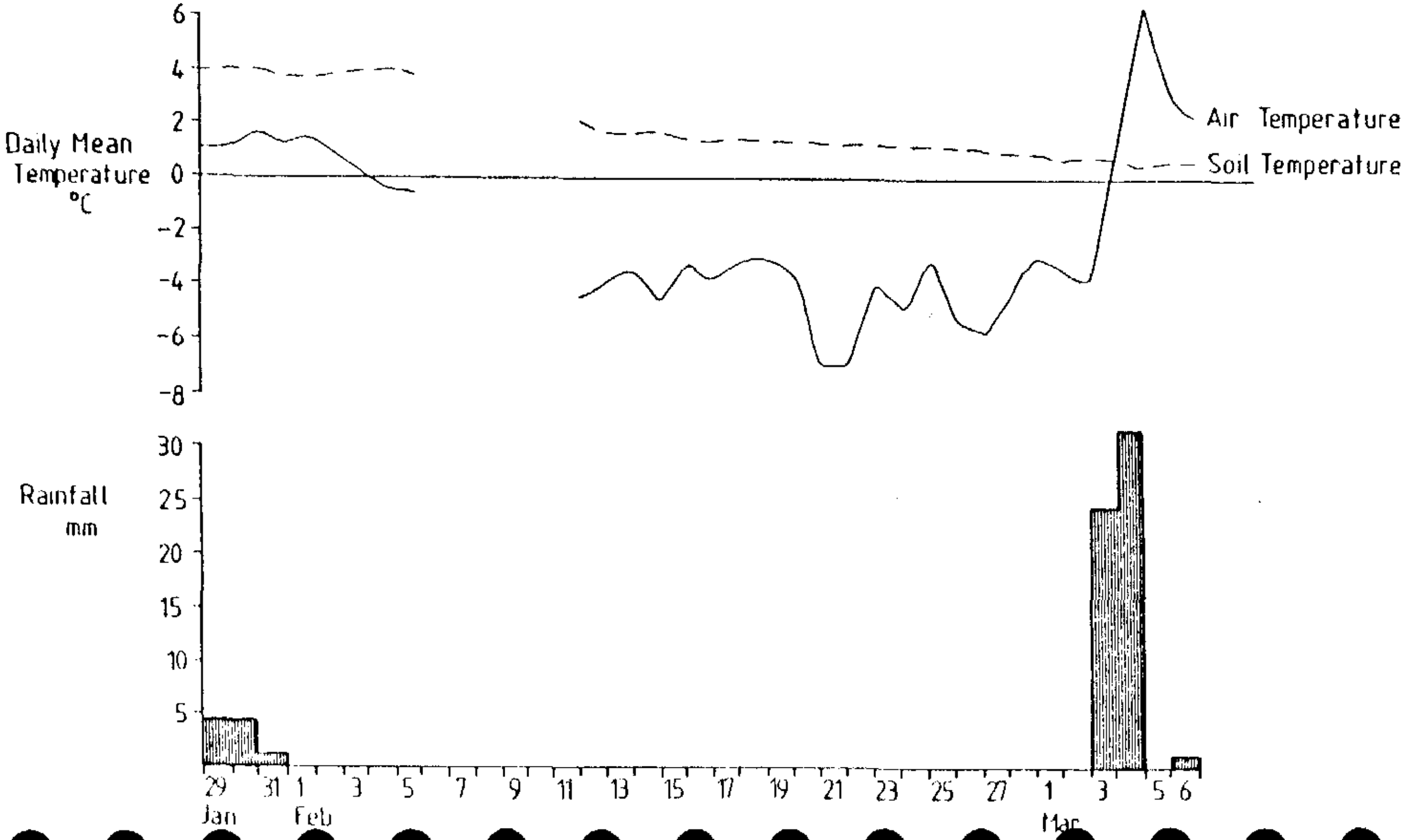
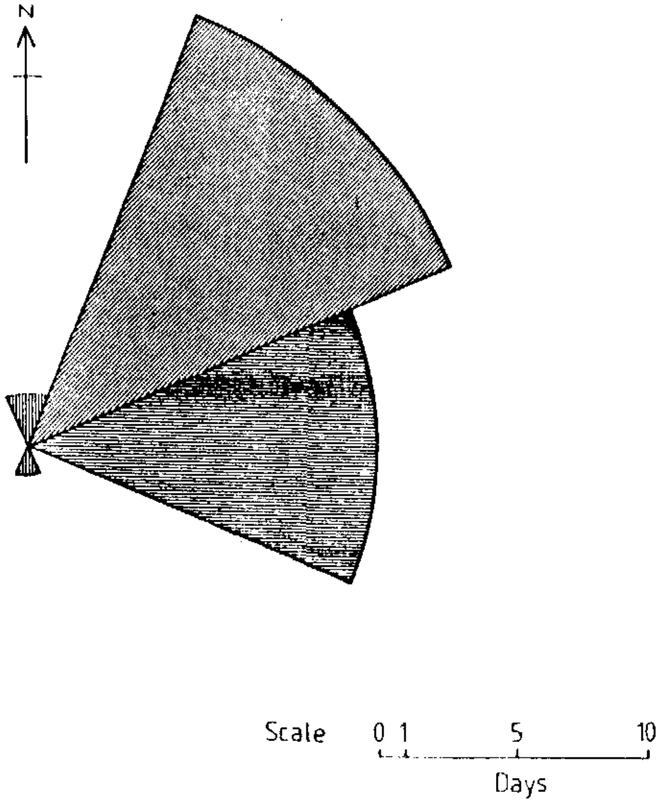


Fig 23 Summary Wind Rose for Llyn Brianne Automatic Weather Station 29th January – 2nd March 1986 *



* Data for period 6th – 10th February not logged. Information for this period substituted by records from U.C. Swansea, Geog. Dept.

2. Snow Quality

Following field observations of increasing accumulation of black smuts and the formation of a dirty surface layer on standing snow throughout the study area a series of snow samples were taken on 27th February.

Samples were collected in duplicate from three sites in the study area from both surface and sub-surface (mid-depth) layers. The resulting meltwater from all samples was grey in colour with black particulate matter in suspension. Subsequent analyses confirmed that the samples were significantly polluted compared to average bulk deposition quality for Llyn Brianne (Stoner et al 1984) and variation in snow quality was apparent between sites and snow depth (Table 20).

At both the automatic weather station and the conifer forest site LI2, the quality of the surface layer of snow was significantly poorer than the sub surface layer whereas at the moorland site CI3 the snow was of poor quality both at the surface and at depth. The surface layers at LI2 and the weather station and both levels at CI3 were found to have pH values considerably lower than typical Llyn Brianne bulk deposition. Levels of $SO_4{}^{2-}$, $NO_3{}^-$ and Cl^- were considerably elevated in the polluted layers compared to typical bulk deposition, as were "excess" or non-sea derived sulphate levels. Levels of NH_4N, Ca^{2+} were also substantially higher in comparison to typical deposition.

The levels of $NO_3{}^-$, Cl^- and $SO_4{}^{2-}$ in the polluted layers were equal or greater than those found in average East Midlands rain (Martin and Barber, 1984) and levels of excess $SO_4{}^{2-}$ comparable and considerably greater in the case of the weather station surface sample.

TABLE 20

Llyn Brianne Snow+ and Rainfall Quality. February/March 1986

+ samples taken 27th Feburary 1986

Site		Cond. uscm^{-1}	pH	H$^+$	K$^+$	Na$^+$	NH$_3$N	Ca^{2+}	Mg^{2+}	Al^{3+}	NO$_3^-$	Cl$^-$	SO$_4^{2-}$	Excess SO$_4^{2-}$
CI3 Moorland Snow	Surface	136	3.7	200	8	166	189	86	34	23	167	338	174	132
	Sub-Surface	183	3.5	316	11	201	210	79	52	36	228	380	230	179
A.W.S. Moorland Snow	Surface	206	3.65	225	15	286	357	130	63	44	300	422	361	289
	Sub-Surface	42	4.05	89	7	27	58	14	9	9	61	56	57	50
LI2 Conifer Forest Snow	Surface	110	3.85	142	10	119	171	69	27	22	143	225	161	131
	Sub-Surface	42	4.05	90	4	23	59	11	6	6	43	56	62	56
Bulk Deposition UC4 19th February - 4th March		29	7.1	0.1	26	57	27	143	13	-	10	85	40	21
Average Brianne Rain *1		ND	4.6	27	12	136	31	35	34	-	17	148	54	20
Average East Midlands Rain *2		ND	4.1	73	13	80	129	59	27	-	80	140	171	151
Cairngorms Black Snow 1984 *3		ND	3.0	1000	10	197	17	31	43	-	337	418	412	362

*1 Stoner and Gee (1985)
*2 Martin and Barber (1978)
*3 Davies et al (1984)

ND = No Data
Units uequiv.l^{-1} unless otherwise stated
Snow quality results pooled from duplicates at each site

The quality of the polluted layers was not as poor as that of the "black snow" reported from the Cairngorms (Davies et al 1984) although the surface sample from the weather station contained comparable levels of NO_3^-, Cl^- and SO_4^{2-} and excess SO_4^-. NH_4-N levels were considerably higher in the polluted Brianne snow samples than in the Cairngorms black snow or average East Midlands rainfall.

Similar observations to those at Llyn Brianne were made in the Maesnant, Plynlimon area during the same period (Hyatt, pers.comm.1986). Visible discoloration of the snow with considerable quantities of black smuts was reported with pH levels somewhat lower than those recorded at Brianne.

Whilst back trajectories to establish the sources of pollution have not been plotted, the dominant period of easterly and north easterly winds throughout February strongly suggests that dry deposition of industrial pollutants from the North West, the Midlands and South Wales may be responsible for the conditions observed. Snow scavenging of aerosols during precipitation seems unlikely due to the differences in snow quality observed at different depths.

Reasons for differences in snow quality at depth and between different sites at Brianne are not clear although the overall shallow snow depth, considerable drifting and a second snowfall event following approximately 10 days after the initial fall may have led to the earlier surface layer subsequently forming a sub-surface layer at CI3. The lower levels of pollutants in the surface layer at LI2 may suggest that scavenging of dry deposition by the tree canopy caused localised reduction in the quantity of deposited material reaching the ground level.

The chief source of Ca^{2+} in rainfall is thought to be terrestrial dust (Reynolds et al 1984) and the comparatively elevated levels observed for the Brianne snow samples may be attributable in part to this source, as may part of the NH_4-N.

3. Snow melt

From 0600 hours on 3rd March the wind direction became more variable and after 0900 hours moved around to the south. By 0100 hours on 4th March air temperatures were beginning to rise and it commenced raining. Throughout the next 18 hours, 50mm of rainfall fell in the Llyn Brianne area and whilst air temperatures progressively increased to a maximum of 6.6°C, soil temperatures remained very low and field observations during the day confirmed that the surface soils remained frozen (Figs.22 & 23).

The effects of the rainfall, which rapidly reached a peak intensity of 6mm/hour were dramatic. Rapid run-off occurred over the frozen ground and the snow cover was either melted or washed off leading to flood conditions in the study streams.

4. Effects on Stream Water Quality

4.1. Results

Despite the adverse conditions, continuous records of water quality were obtained from 8 of the 12 monitoring stations for the duration of the snow melt episode. Measurements of stage were more difficult to maintain in the sub-zero temperatures preceeding snow melt and as a result full flow records for the snow melt episodes were obtained for only 3 sites. Triggered autosampling was successful at two sites from the beginning and throughout the episode with manually triggered autosampling providing samples for a further 4 sites from later stages (Table 21).

Table 21 Summary of Snow melt Data obtained for Llyn Brianne Catchments 4th March 1986

Catchment	Continuous Record				Autosamples + Time started and finished	Spot Samples + time taken	Comments
	pH	Cond	Temp	Stage			
LI1	✓	✓	✓	✓	Full Set (48) 0451-1636		Full data set for continuous monitoring and autosampling
LI2	✓	✓	✓	✓	Full Set (48) 1217-2347		Autosampler triggered manually during episode
LI3	✓	✓	✓	-	Full Set (12) 0509-0831		80PL Frozen up. Early part of event autosampled.
LI4	✓	✓	✓	-	None		80PL frozen up.
LI6	-	-	-	-	Part event only (8) 1300-1522	1300 hours 1352 hours	Probes iced up.
LI8	-	-	-	-	None	1605 hours 1652 hours 1700 hours	Recession period monitored - worst case picked up?
CI3	✓	✓	✓	-	None		80PL frozen up.
CI4	✓	✓	✓	-	Full set 1431-0116		Early part of event missed by autosampler-manually triggered
CI5	✓	✓	✓	✓	Full set 0449-1634		Full data set for continuous monitoring and autosampling
CI6	✓	-	✓	-	Full set 1348-0133		Early part of event missed - autosampler manually triggered 80PL frozen up.
GI1	-	-	-	-	Full set 1125-2310	1430 hours	Early part of event missed. No continuous monitoring record.
UC4	-	-	-	-	None	1653 hours 1656 hours	Similar to LI8. Recession period monitored from mid-day.
LI5	-	-	-	-		1200 hours	-
LI7	-	-	-	-		1400 hours	-

The effects of the combined rainfall and snow melt episode on stream water quality was virtually immediate despite the initial low intensity of rainfall. The pH levels in the streams commenced dropping between 0100 and 0200 hours following only 1mm of rainfall and were accompanied by large increases in conductivity. Minimum pH levels were reached by early afternoon in most streams coincidental with peak flows. Stream LI4 was atypical in that the response was much more rapid and the minimum pH was reached within 4 1/2 hours.

The fall in pH at all sites was considerable. Prior to the rainfall the flows in the streams were very low and in some cases virtually frozen solid. Stream pH values were also in most cases well above normal winter levels (Tables 22 & 23). However, during the snow melt episode minimum pH values fell to near or below the minima recorded from spot samples during the 1984-85 winter period and were comparable with the minimum levels recorded by the continuous monitoring systems during the exceptional storm events of 21st December 1985 and 25th August 1986 when considerably more rainfall and higher flows resulted (Table 23). The pH drops observed during the snow melt were amongst the largest which have been observed in the study streams for any single episode since continuous monitoring commenced.

The large increases in conductivity which also occurred during the early snow melt were atypical of the normal stream responses during storm episodes and appear to be peculiar to the conditions prevailing during the snow melt.

Complete records of continuously monitored water quality determinands and stage together with autosampling from the beginning of the episode was achieved for only 2 sites, CI5 and LI1 (Table 21). This does however provide the opportunity to compare the responses of both moorland (CI5) and forest catchments (LI1) over the full period of the episode.

Table 22

Comparison of Snow Melt Conditions in Study Streams with Normal Winter Conditions

Catchment	Normal Winter Conditions 1984/85 - spot sample data (December - March inclusive)									Snow Melt 4th March 1986 "Worst Case" Conditions		
	pH			Diss.Al mgl^{-1}			SO_4 $uequivl^{-1}$				Diss max Al mgl^{-1}	max SO_4 $uequivl^{-1}$
	min	$\bar{x}$	S.D.	max	$\bar{x}$	S.D	max	$\bar{x}$	S.D.	min pH		
LI1	4.3	4.75	0.2	0.84	0.50	0.18	198	161	21	4.0	1.04	259
LI2		N.D			N.D.			N.D		4.2	1.16	252
LI3	4.5	5.0	0.3	0.68	0.45	0.19	221	167	44	4.6	0.33*	212*
LI4		N.D			N.D.			N.D		4.5	-	-
LI6	6.2	6.8	0.2	0.12	0.07	0.02	148	114	18	5.4	0.15*	102*
LI8	4.7	5.1	0.2	0.40	0.30	0.06	119	140	15	4.15	-	-
CI3	4.8	5.4	0.1	0.38	0.14	0.10	132	110	16	4.75	-	-
CI4	4.7	5.3	0.5	0.20	0.14	0.05	150	109	16	4.5	0.16*	110*
CI5	4.8	5.0	0.1	0.42	0.28	0.07	150	115	14	4.75	0.43	228
CI6	4.7	5.4	0.4	0.21	0.13	0.04	132	104	23	4.25	0.17*	109*
UC4	+4.8	+5.9	+0.5	+0.09	+0.07	+0.02	+96	+67	+15	4.25	0.09*	243*
GI1	6.0	6.1	0.1	0.33	0.08	0.10	188	142	24	5.2	0.16	325

* Samples from incomplete sets of autosamples which may have missed worst state conditions

\+ Insufficient data to select winter conditons only. 1985 summary data used.

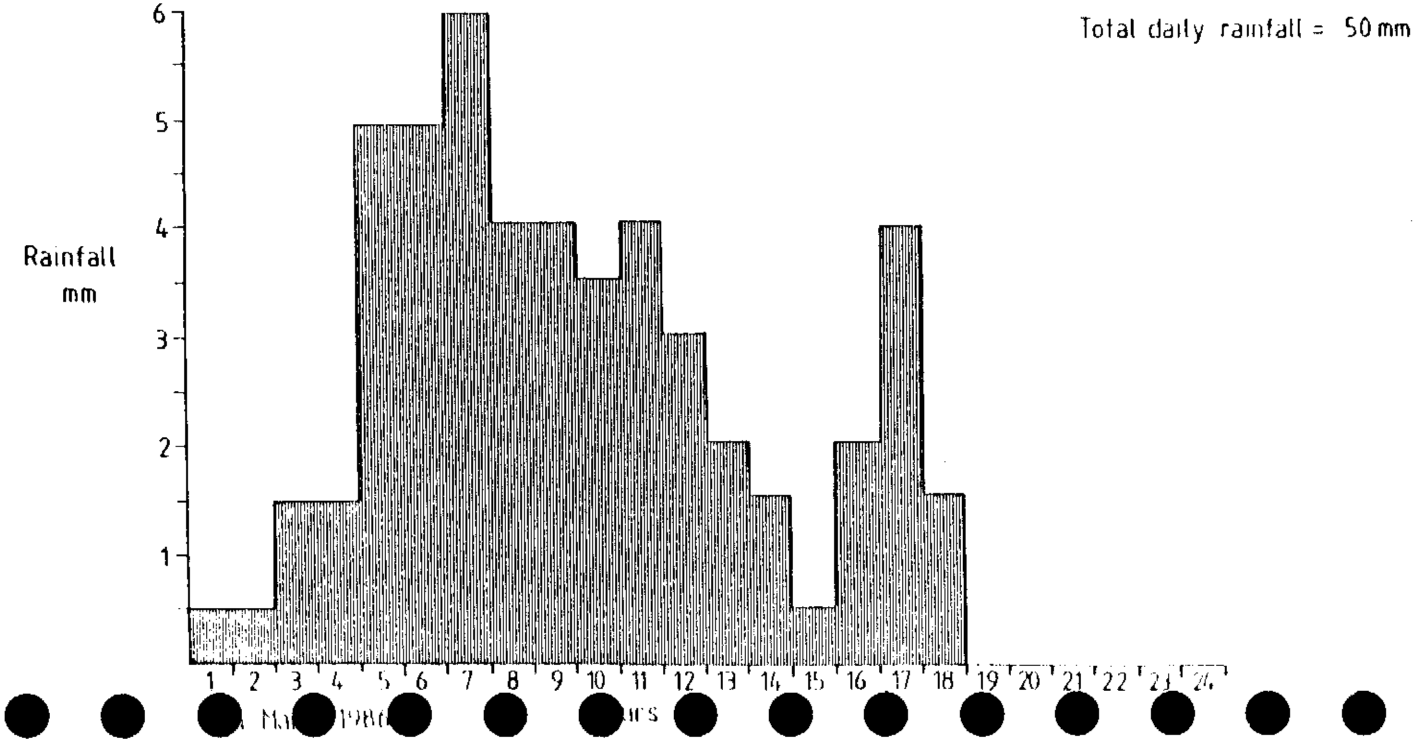
Table 23

pH Responses of Catchment Streams to Important Episodes

Catchment	Storm Episode 21.12.85 (Rainfall - 76mm)			Snow melt 4.3.86 (Rainfall 50mm)			Storm 25.8.86 (Rainfall 90.5mm)		
	Pre Event	Peak Event	Change	Pre Event	Peak Event	Change	Pre Event	Peak Event	Change
LI1	4.8	4.0	- 0.8	6.0	4.0	- 2.0	N.D.	N.D.	N.D.
LI2	4.6	4.15	-0.45	4.9	4.2	- 0.7	N.D.	N.D.	N.D.
LI3	5.35	4.35	- 1.0	6.2	4.6	- 1.6	N.D.	N.D.	N.D.
LI4	5.0	4.6	- 0.4	5.35	4.5	-0.85	N.D.	N.D.	N.D.
LI6	6.3	5.2	- 1.1	7.1	5.4	- 1.7	7.25	5.6	-1.65
LI8	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
CI3	5.0	4.4	- 0.6	5.8	4.75	-1.05	N.D.	N.D.	N.D.
CI4	5.5	4.6	- 0.9	6.2	4.5	- 1.7	5.9	4.25	-1.65
CI5	5.2	4.5	- 0.7	5.5	4.75	-0.75	5.3	4.4	- 0.9
CI6	5.45	4.2	-1.25	5.2	4.25	-1.05	N.D.	N.D.	N.D.
GI1	6.5	5.55	-0.95	-	5.2	-	6.1	5.4	- 0.7
UC4	5.7	4.4	- 1.3	-	4.25	-	6.1	4.1	

N.D. No Data

Fig. 24 Rainfall Record from Llyn Brianne Automatic Weather Station 4th March 1986



Whilst the catchment sizes of LI1 and LI5 are somewhat different, (LI1, 2.64 km^{-1}, CI5, 0.33 km^{-2}), responses in terms of time to peak flow during 4th March were similar and pH minima for the episode occurred in both cases approximately 12 hours after the onset of rainfall. The pH response in the streams differed in that for stream CI5 a slight increase in pH was initially recorded followed by a drop from 5.6 to 4.7 units. The response in catchment LI1 was much greater, dropping from 6.0 to 4.0 within 11 hours (Fig.25).

In both catchment streams large increases in conductivity occurred during the period of increasing flows although the peak for CI5 was much earlier than in LI1, of greater magnitude but of shorter duration. The conductivity had peaked and was falling in stream CI5 approximately 8 hours before peak flow was reached whereas in stream LI1 peak conductivity was of longer duration and more coincidental with peak flows. In both streams there was no evidence of a significant secondary peak in conductivity coincidental with the secondary peak in flow (Fig.26).

The dissolved calcium and alkalinity of moorland stream CI5 were initially substantially higher than in LI1 although these levels fell rapidly from an early stage in the episode. Although initially at a lower level in stream LI1, dissolved calcium levels were maintained at that level for approximately 3 hours longer than in stream CI5 and over the period of peak flows, although somewhat reduced, remained slightly higher than the levels in stream CI5 (Fig.27).

Similar levels of sulphate were recorded in both streams although the levels in stream CI5 were at peak when autosampling commenced. The highest levels in stream LI1 occurred some hours later during peak flows. In both cases the changes in levels followed the pattern described for conductivity. The concentrations of sulphate recorded were considerably greater than the maximum levels recorded by routine sampling during the

Fig.25 Snow Melt Episode 4thMarch 1986. Streams CI5 and LI1 — PH & Flow.

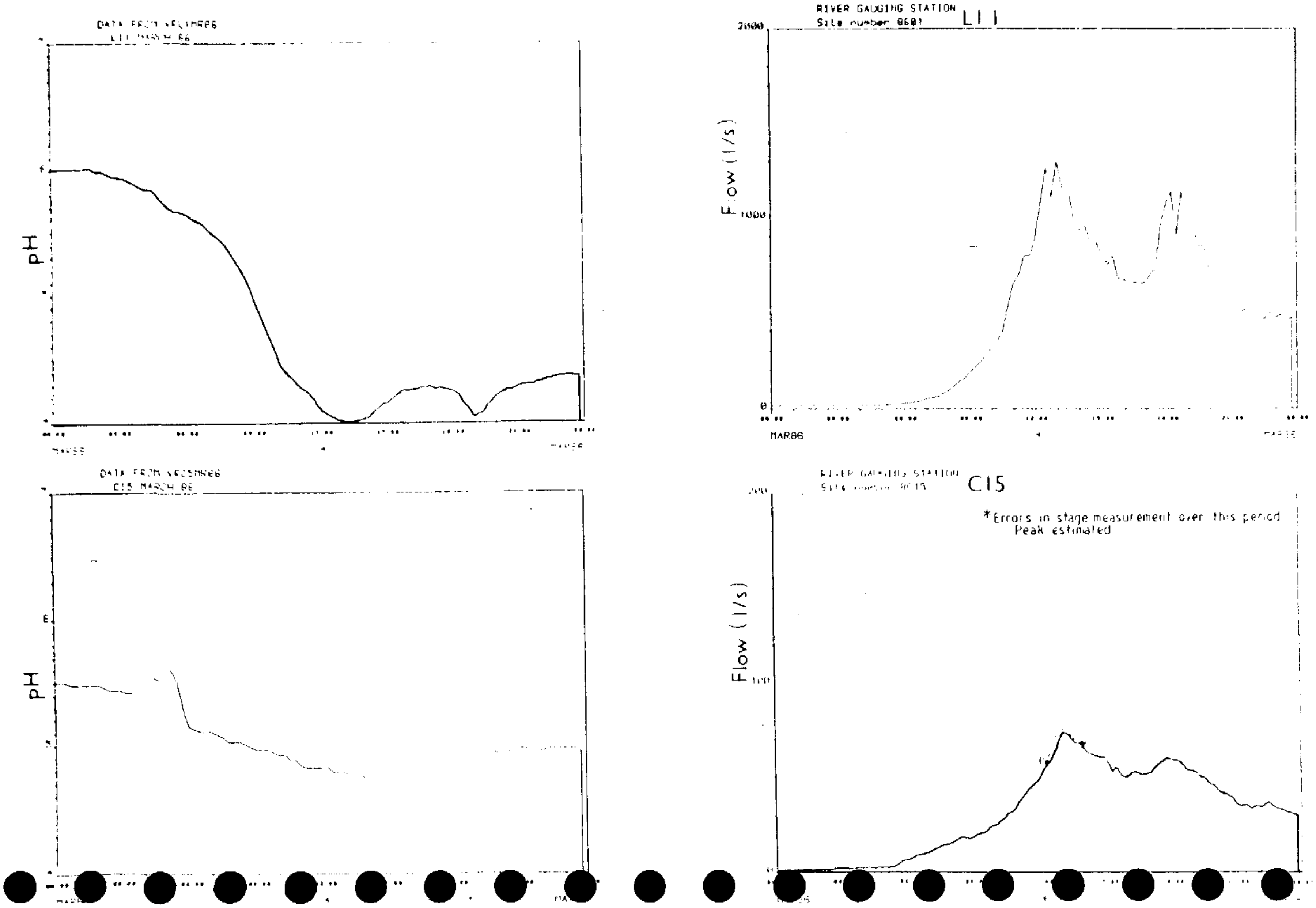


Fig. 26 Snow Melt Episode 4th March 1986. Streams CI5 and LI1 — Chloride & Conductivity.

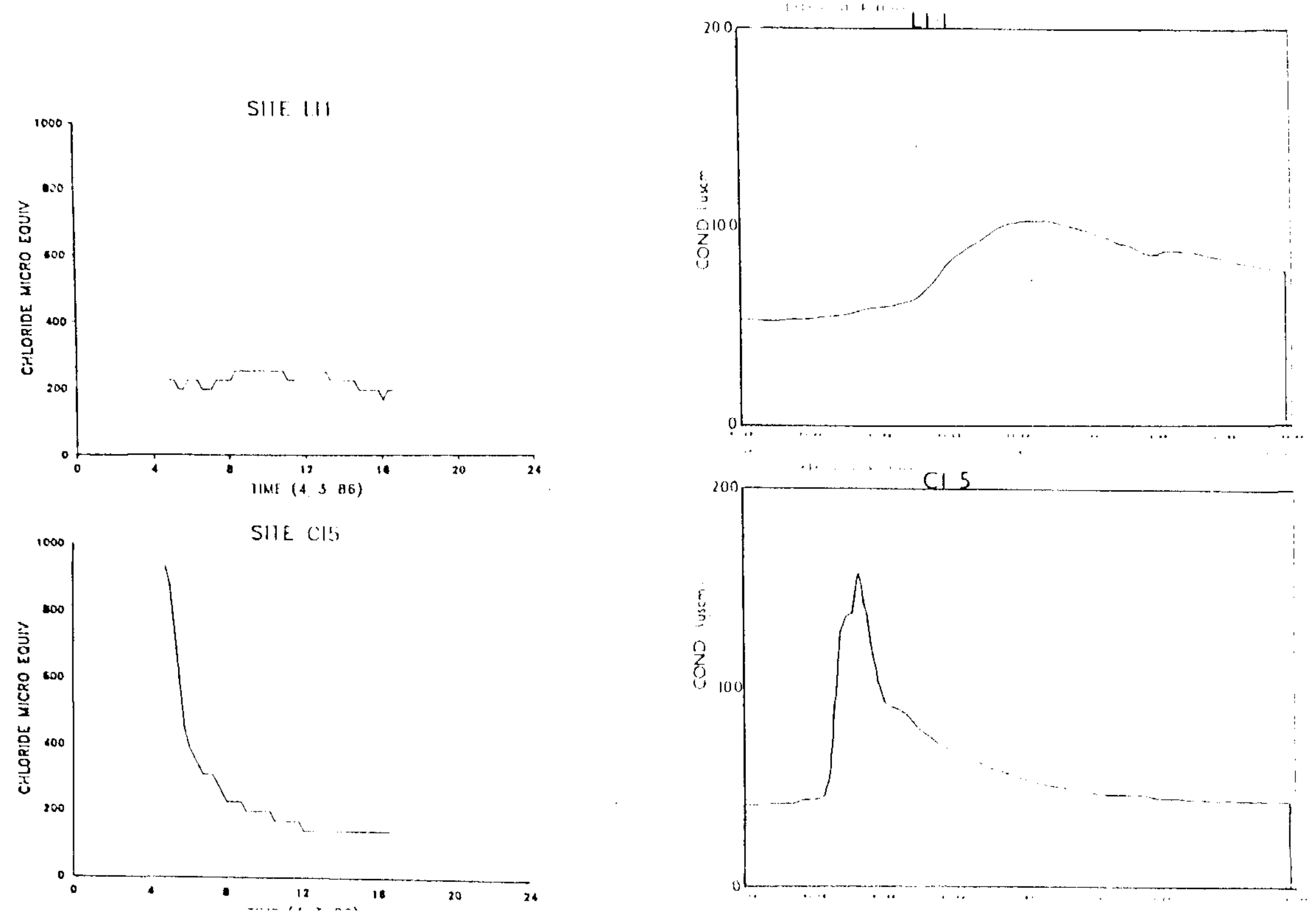
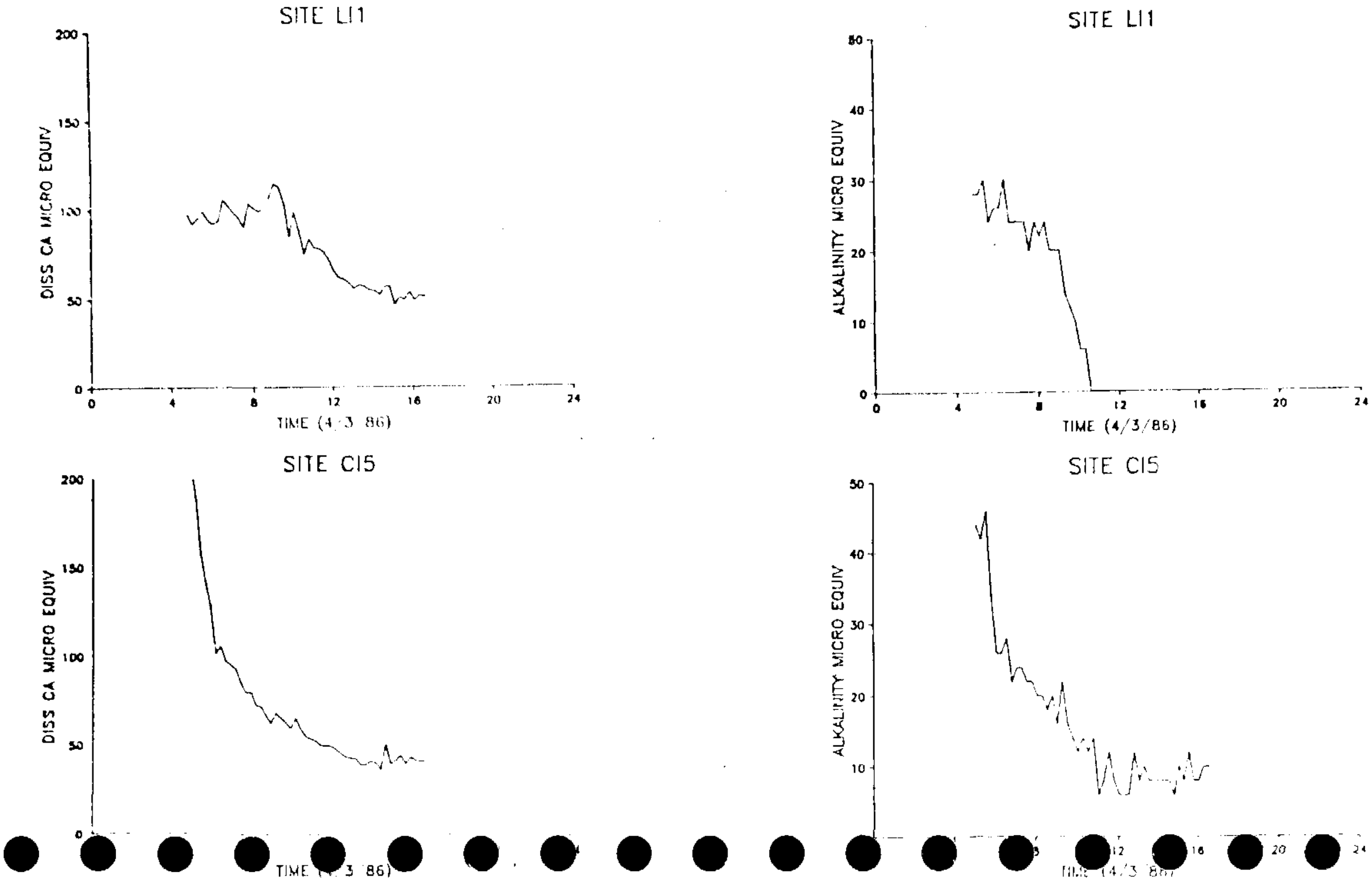


Fig.27 Snow Melt Episode 4th March 1986. Streams CI5 and LI1 — Dissolved Calcium & Alkalinity.



previous 1984-85 winter period (Fig.28).

Nitrate levels were comparatively much lower and not substantially elevated in either stream compared to data from 1984-85. However, levels in stream LI1 increased during the episode following a similar pattern to that of sulphate, being highest during peak flows.

Dissolved aluminium levels increased substantially in both streams and reached the highest levels during peak flows. In both streams increases in dissolved aluminium were closely associated with a fall in calcium although the dissolved aluminium in stream LI1 was already increasing prior to any reduction in calcium. The levels of dissolved aluminium in both streams were the highest recorded since the current monitoring programme commenced. In stream LI1 the levels peaked at 1.04 mgl^{-1} (Fig.29).

Other differences were observed between the two catchments. Elevated levels of ammoniacal nitrogen occurred in both streams although as with sulphate, the peak levels occurred earlier in stream CI5 than LI1 (Fig.29).

Chloride levels were elevated in stream CI5 during the early snow melt period but these dropped rapidly to levels comparable to those in stream LI1 which remained constant (Fig.26).

Turbidity levels in stream LI1 increased coincidentally with the period of highest flow whereas the turbidity in stream CI5 remained relatively low (Fig.30).

The levels of dissolved organic carbon again differed between the two streams during the episode, being highest in stream CI5 earlier on and before peak flows, whereas in stream LI1, the levels increased and peaked corresponding to the increasing flow (Fig.30).

Fig. 28 Snow Melt Episode 4th March 1986. Streams CI5 and LI1 — Dissolved SO_4 & NO_3

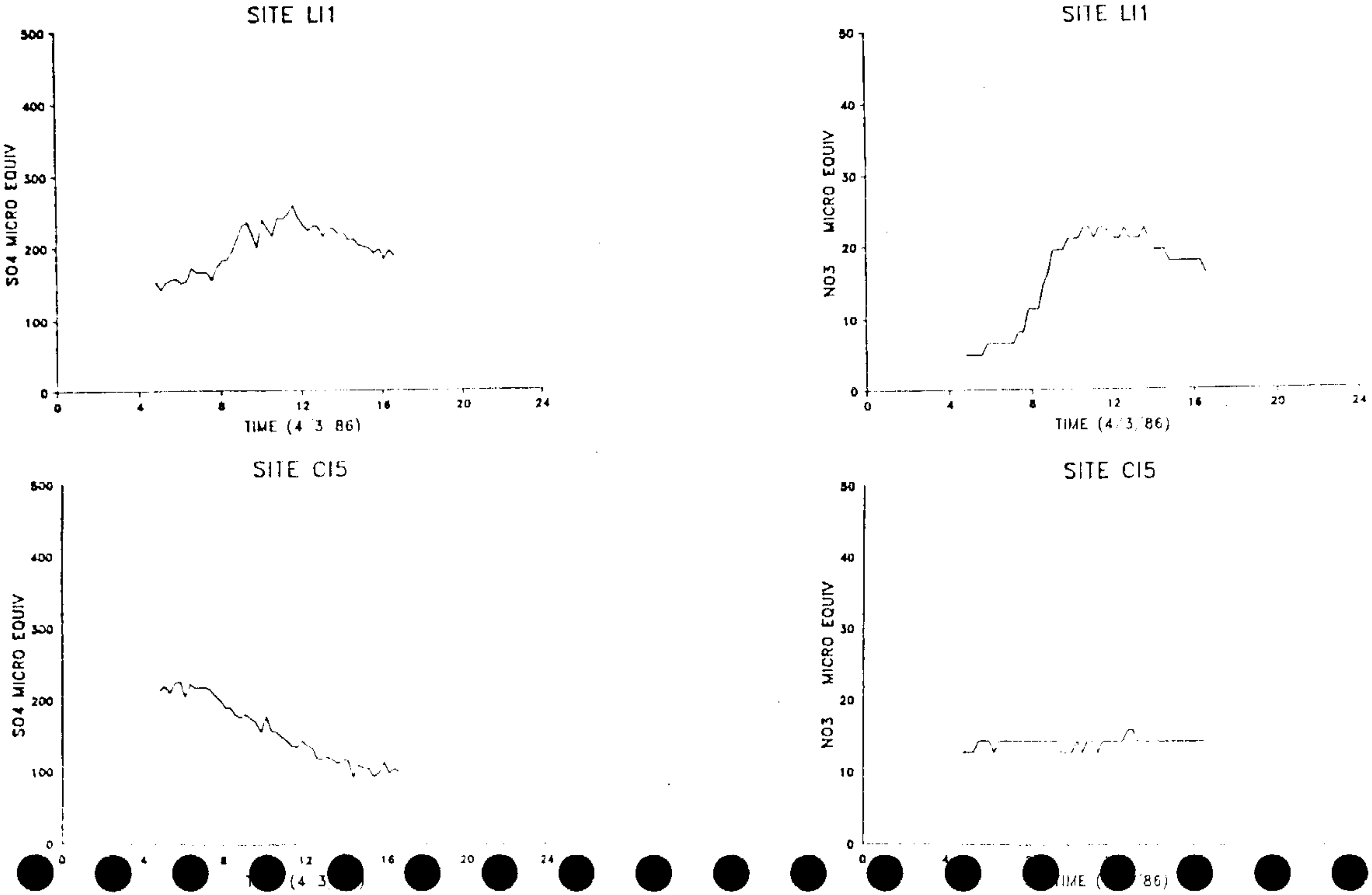


Fig. 29 Snow Melt Episode 4th March 1986. Streams CI5 and LI1 — NH_3-N & Dissolved Aluminium.

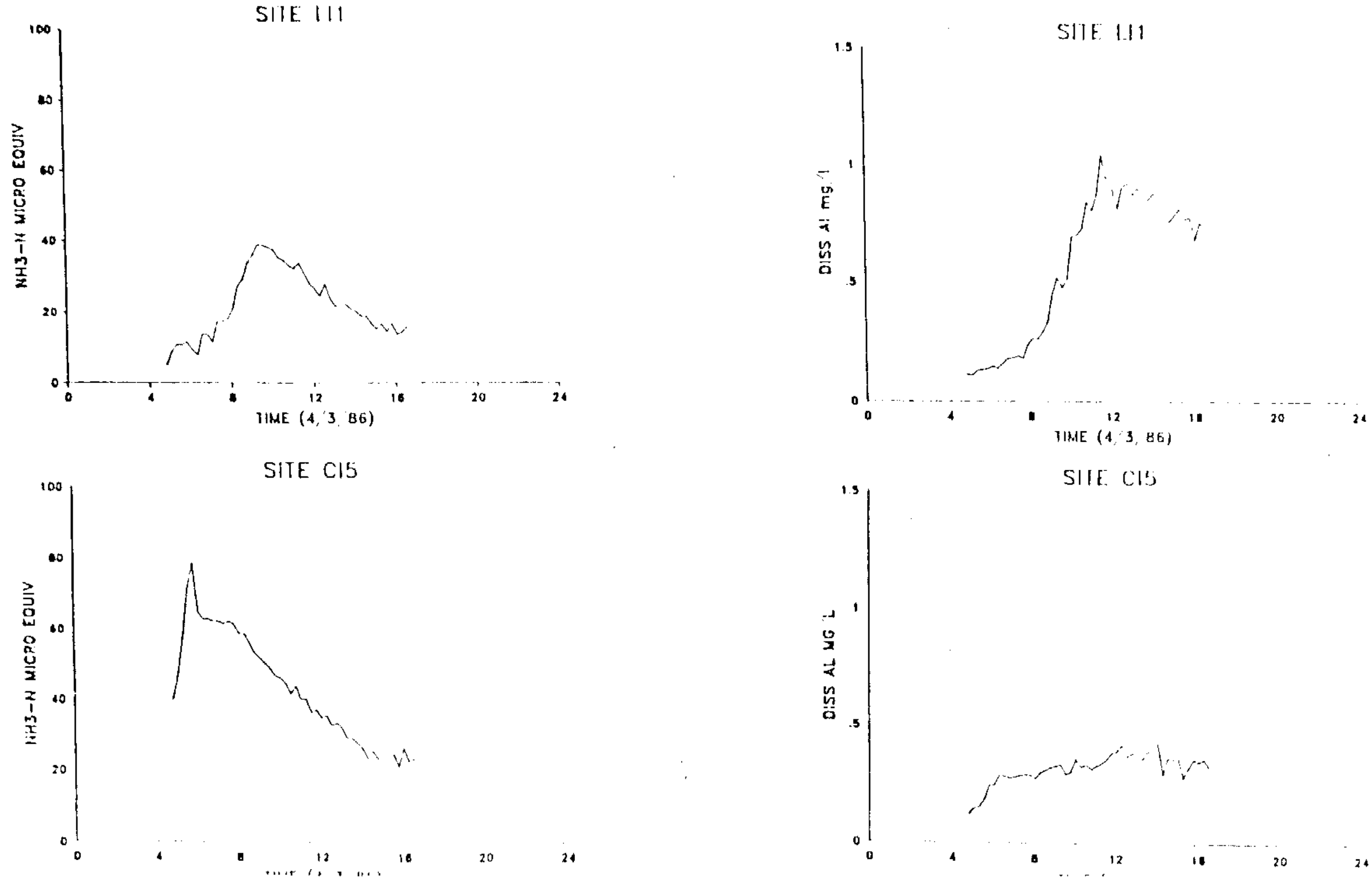
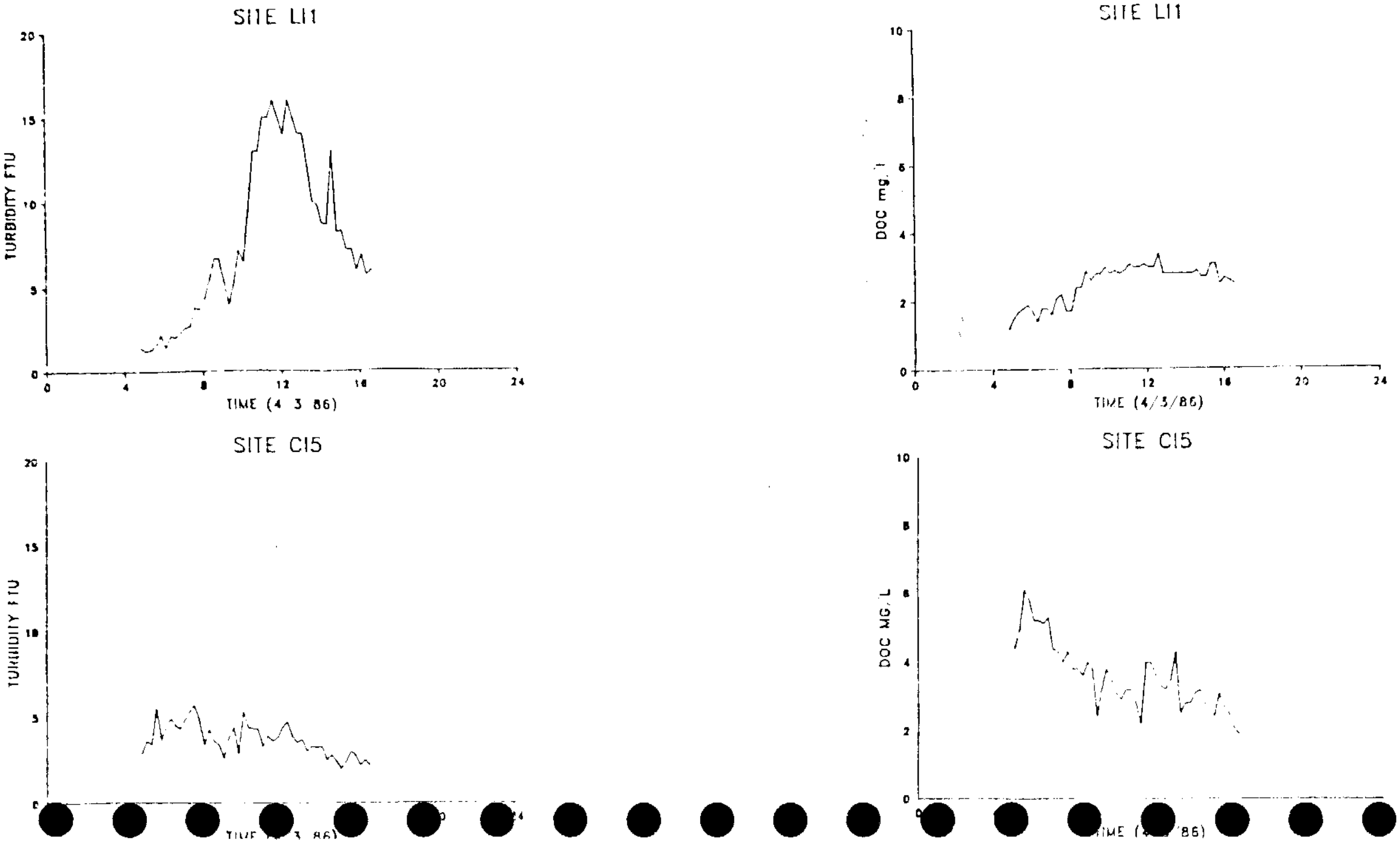


Fig. 30 Snow Melt Episode 4th March 1986. Streams CI5 and LI1 — Turbidity & D.O.C.



Whilst records for the other study catchments are incomplete the available data support the trends observed for streams CI5 and LI1. It does appear however that the quality of stream CI5 may have been somewhat lower than in the other comparable moorland sites. The dissolved aluminium levels in moorland streams CI4 and CI6 around the time of peak flows were lower than in CI5. Under the winter conditions of 1984-85 the mean levels of dissolved aluminium in CI5 were approximately twice those in CI3, CI4 and CI6 (Table 22).

Unfortunately no sampling occurred during the early stage of the episode in other moorland sites and no direct comparisons may be made between these catchments. However, the chemistry of these streams was otherwise not dissimilar to that of CI5 at the comparable times when sampling commenced.

The quality of forest catchment stream LI2 responded in a similar manner to stream LI1, with a minimum pH of 4.2 units and dissolved aluminium and sulphate levels similar to those in stream LI1 (Table 22).

The episode also appears to have had a substantial impact on normally relatively well buffered streams. The deciduous catchment stream GI1 experienced a drop in pH to 5.2 units accompanied by very high levels of sulphate and elevated dissolved aluminium. Similarly there is evidence to suggest that the stream draining catchment LI6, which is normally classified as unacidified, experienced atypically low pH and elevated dissolved aluminium levels during the episode.

4.2. Discussion

The changes in stream chemistry following this "rain on snow event" appear to be attributable to a combination of reduced buffering capacity resulting from frozen soils and reduced groundwater flows, combined with rapid run-off of material deposited from the atmosphere during the preceeding period.

The monitoring of snow quality, prior to the episode described, has confirmed that the surface layers of snow in particular contained high levels of deposited materials. It appears that pollutants in the snow cover and on the ground and vegetation surfaces were rapidly flushed into the streams leading to the observed responses. Other workers have shown that when snow melts, the first meltwater appearing at the bottom of the snow contains much of the dissolved load of pollutants (Morris and Thomas 1985; Gregory et al 1986). Whilst only limited information is available on bulk precipitation chemistry at the time of snow melt, the available data suggest that the rainfall associated with this episode was relatively unpolluted and was not responsible for the observed effects (Table 20).

The observed increases in conductivity confirm the "first flush" of solutes typically observed during snow melt conditions. The different response times in moorland catchment CI5 and conifer forest catchment LI1 may be a reflection of catchment size, LI1 being considerably larger than CI5. However, peak flows and lowest pH values occurred in both catchments at approximately the same time and this suggests that the delayed flush in catchment LI1 may result from the tree cover. In catchment CI5 preferential leaching of solutes from the snow and predominantly overland flow due to frozen surface soils may have led to rapid transport to the stream. In the afforested catchment LI1, leaching of pollutants through the tree canopy by stemflow and throughfall may have led to less rapid transport.

The rapid flush of sulphates and chlorides into stream CI5 may have been buffered initially by the calcium in the stream and from the snow, together with the elevated level of ammoniacal nitrogen which appears to be derived from the polluted snow layers. The high levels of chloride in the first flush in stream CI5 may have resulted from the snow cover although it is possible that run-off of road salt above the sampling point initially had a significant effect on stream chloride levels (Dissolved sodium levels were also elevated compared to catchment LI1 during the early part of the episode).

The absence of further peaks in conductivity corresponding to the observed secondary peaks in flow for the sites studied supports the conclusion that a flush of solutes occurred during the early part of the episode.

Nitrate levels in stream CI5 are generally higher than in LI1 under normal winter conditions (Mean values, LI1 15 $\mathrm{uequivl}^{-1}$; CI5 27 $\mathrm{uequivl}^{-1}$ during 1984-85). The observed increase in stream nitrate values during the episode for LI1, which did not occur in CI5, may indicate that the forest catchments had increased deposition of nitrogen oxides compared to the moorland as a result of scavenging by the tree canopy (similar increases were observed in conifer forest stream LI2 and in deciduous catchment GI1).

The elevated levels of ammoniacal nitrogen in both moorland and forest catchments were atypical and appear to be derived from the snow cover. The levels in stream CI5 may have been elevated by the effects of the concentration of sheep within certain areas of the catchment during the cold spell. However, the data from moorland catchments CI4 and CI6 suggest that similar levels of ammoniacal nitrogen also occurred in these streams during the episode.

The increases of dissolved aluminium observed in the streams for which data are available confirm the significance of the episode. It appears that peak levels have occurred closely associated with a fall in stream calcium levels. The levels recorded in both streams LI1 and CI5 were considerably elevated above those levels which are considered to have harmful ecological effects particularly as peak levels were also coincidental with periods of lowest pH and dissolved calcium values. The observed unusual increases in dissolved aluminium in those streams normally well buffered, such as streams LI6 and GI1 confirm that this particular type of episode may be of high importance even to those streams not normally considered to be vulnerable.

Recent evaluation of routine aluminium fractionation results has shown a very close correlation between the routine "filterable" or dissolved aluminium concentrations and labile species of aluminium determined by fractionation, for samples with pH values of less than 5.0. The labile species of aluminium are thought to be those of greatest toxicity. During this particular snow melt episode the pH values of all the study streams with the exception of LI6 and GI1 fell below 5. The source of aluminium during such events is not certain although given that the soils were frozen, some reduction in contribution of aluminium from surface soils may be expected. Under such circumstances it has been suggested that aluminium previously precipitated onto the stream bed under a higher pH regime may be mobilised by episodic flushes of higher acidity (Norton and Henricksen, 1983).

Information obtained during the snow melt episode is still being processed and that currently reported results from preliminary assessment only. Various aspects require further consideration, and this work is continuing. In particular ionic balances at various stages of the episode and further consideration of mechanisms leading to differences between catchments require further consideration.

It is suggested that "rain on snow" events of this nature may occur more frequently than pure snow melt events and that preparations should be made to monitor conditions in more detail should a similar set of circumstances arise during the forthcoming winter. Additional information needs include:-

1. Aluminium fractionation on samples taken at various stages of the episode for catchments with different land use should be arranged.

2. Attempts should be made to establish back trajectories to more accurately describe the origin of deposited material. This should be attempted for the 1986 data.

3. Samples of snow should be taken on a regular basis and changes in quality monitored. If possible, electron microscopic analysis of smuts should be carried out to identify possible sources.

4. It is essential that automatic sampling is triggered at the beginning of snow melt or rainfall to ensure that the "first flush" is sampled.

5. Vegetation and soil water data are of key importance and efforts should be made to ensure collection of sufficient data to cover the episode.

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6. TIME-SERIES MODELLING STUDIES

The main objective with the time-series modelling has been to derive preliminary statistical models of catchment rainfall-runoff responses in an attempt to gain an insight into the dominant dynamics which occur in control catchments LI1, LI6 and CI6. Hourly point rainfall from the Automatic Weather Station (AWS) at Trawsnant was taken to be the areal rainfall input for all three catchments (the shortcomings of this assumption became apparent during analysis). Other objectives of the preliminary statistical modelling exercise were to (a) examine the streamflow data for gross errors and inconsistencies, (b) relate different catchment responses (if detected) to catchment characteristics and (c) to become familiar with the many data handling and analysis options afforded by CAPTAIN (a time series analysis system on the GEC computer at the Institute of Hydrology). The CAPTAIN package has also been used to model flow-hydrogen ion response; an understanding of these dynamics will be particularly important in later modelling studies.

Rainfall-Runoff Dynamics

For each of the three catchments, a data set of hourly rainfall and stage t for the 180 hour period from 1300 GMT 10 August to the end of 17 August 1985 (referred to subsequently as the 7-day time series) was retrieved from the Llyn Brianne Acid Waters Study database held at the Institute of Hydrology. The data transformation facility of CAPTAIN was employed to convert stages into flows using appropriate stage-discharge relations.

The first step in any data analysis is to inspect the data for gross errors and inconsistencies. Figure 31a shows the 7-day hourly rainfall time series and Figures 31b, 31c and 31d show the corresponding hydrographs for LI1, LI6 and CI6 respectively. A most striking difference between the hydrograph for CI6 and the hydrographs for LI1 and LI6 is that there were three runoff events at CI6 but only two at LI1 and LI6. Approximate distances from the AWS site at Trawsnant to the centroids of catchments are 2.1, 4.7 and 7.8 km for LI6, LI1 and CI6 respectively. It was expected that the relevance of the hourly rainfall would decrease with increasing distance from Trawsnant and, indeed, there was a hydrologically significant rainfall event over catchment CI6 (corresponding to the second runoff event at CI6) during which there was only light rainfall at Trawsnant. This observation confirms the need for good records of rainfall from a network of recording raingauges in the Study area for measuring areal rainfall inputs to individual catchments.

During the 180 hour period 95.5 mm of rain was recorded at Trawsnant and the total runoff was computed to be 90.3, 103.8 and 70.9 mm from catchments LI1, LI6 and CI6 respectively, i.e. 95, 109 and 74% of Trawsnant rainfall. The very high apparent yields of catchments LI1 and LI6 and the inconsistency between the runoff from CI6 and the runoffs from LI1 and LI6 cannot be explained at the present time and there will have to be further investigations into catchment rainfall differences and the uncertainties involved in streamflow measurement (there are some comments on streamflow measurement at LI1, LI6 and CI6 in a later section of this report).

CAPTAIN

The CAPTAIN system was employed to identify the best structure and to estimate the parameters of transfer function models of the general form

$$(1+\delta_1 B+\delta_2 B^2+\ldots)Q_t = (\omega_0+\omega_1 B+\ldots)R_{t-b}$$

where δ_1,δ_2 etc. are autoregressive parameters
ω_0,ω_1 etc. are moving average parameters
b is the time delay (hours)
Q_t is the relevant streamflow at time t (l/s)
R_{t-b} is the rainfall in the hour ending at time $t-b$ (mm)
and B is the backward shift operator (i.e. $Bx_t = x_{t-1}$)

For each catchment, models were derived for the 7-day time series and for sub-time series corresponding to the two main runoff events at LI1 and LI6 (referred to subsequently as time series 1 and 3 respectively). In each case the best model was obtained when the means were subtracted from variables and the option for 1 iteration was selected in the CAPTAIN parameter estimation routine. With due regard to the standard errors of parameter estimates and to the principle of parsimony with respect to the number of parameters permitted in a model, the best model structure in each case, whatever the time delay (b), was one autoregressive parameter (δ_1) and one moving average parameter (ω_0). The general form of the transfer function models derived in the current exercise may be reduced, therefore, to

$$(1+\delta_1 B)\ (Q_t-\bar{Q}) = \omega_o(R_{t-6}-\bar{R})\ .$$

The CAPTAIN system can also provide (a) the system impulse response function, (b) the system step response function and (c) plots of the recursive estimates of the autoregressive and moving average parameters. These and many other output options of the CAPTAIN system are extremely useful in applications outside the scope of the preliminary analyses of the current exercise and they are not, therefore, discussed in detail here.

The systems theory background upon which CAPTAIN is based permits the system mean residence time (T) and the system gain (G) to be calculated from the autoregressive and moving average parameters as follows.

$$T = -\frac{1}{\ell n \delta_1}$$

$$G = \frac{\omega_o}{(1-\delta_1)} \times \text{(a factor to account for the units of the input and output)}$$

Interpretation of mean residence times in the context of catchment input and output is not straightforward if there is piston flow in a catchment. The gain (G) is the asymptote of the step response function referred to above, i.e. the steady state system output caused by a step input. Clearly, rainfall does not occur as a step input and catchments do not reach a steady state and so care should be exercised when interpreting gains calculated from CAPTAIN output. However, both T and G may be expected to vary with factors such as antecedent wetness and amount of rainfall: for summer events T would be expected to be higher and G lower than for winter events.

The variances of (a) the observed streamflow data, (b) the noise (the component of the observed streamflow data not explained by a transfer function model) and (c) the final residuals (the component of the observed streamflow data not explained by a transfer function-noise model) were selected for output by CAPTAIN. From these variances the percentage of observed streamflow variances explained by transfer function and transfer function-noise models were calculated.

Data Analysis

The 7-day rainfall is shown again in Figure 32a and the model outputs for LI1, LI6 and CI6 are shown in Figures 32b, 32c and 32d respectively. The model parameters (δ_1 and ω_0) mean residence times, gains and percentage variances explained for all the models derived (7-day time series and time series 1 and 3) are summarised in Table 24. The standard errors (shown in parentheses in Table 24) indicate that all the estimated parameters are very significantly different from zero. Figures 33a and 33b show the rainfall land model fit for CI6 time series 1. In general, simple transfer function models with one autoregressive parameter (δ_1) and one moving average parameter (ω_0) provide good fits to the time series of observed streamflow. As expected, however, there was a very poor model fit for the second runoff event at CI6, as shown in Figure 32d.

Some of the interesting points revealed in the summary of the models given in Table 24, and speculation on the hydrological processes which caused the particular catchment rainfall-runoff responses, are as follows. The models derived from the 7-day time series and from time series 3 have autoregressive parameters (δ_1) of decreasing magnitude in the order LI1, CI6 and LI6 (0.870 for both LI1 and CI6 for time series 3). This might have been expected since (a) catchment 'memory' increases with catchment size and (b) a value for δ_1 of unity would mean that streamflow in the absence of rainfall remained constant (catchment areas are 2.5, 0.72 and 0.68 km^2 for LI1, CI6 and LI6 respectively). However, although catchments LI6 and CI6 are about the same size, the autoregressive parameters derived from the 7-day time series and time series 3 for LI6 are considerably smaller than the corresponding parameters for CI6 (see Table 1). This could be due to the fact that the main stream slope is much greater for LI6 than for CI6 (194 and 67 m/km respectively), causing more rapid runoff in LI6 than in CI6.

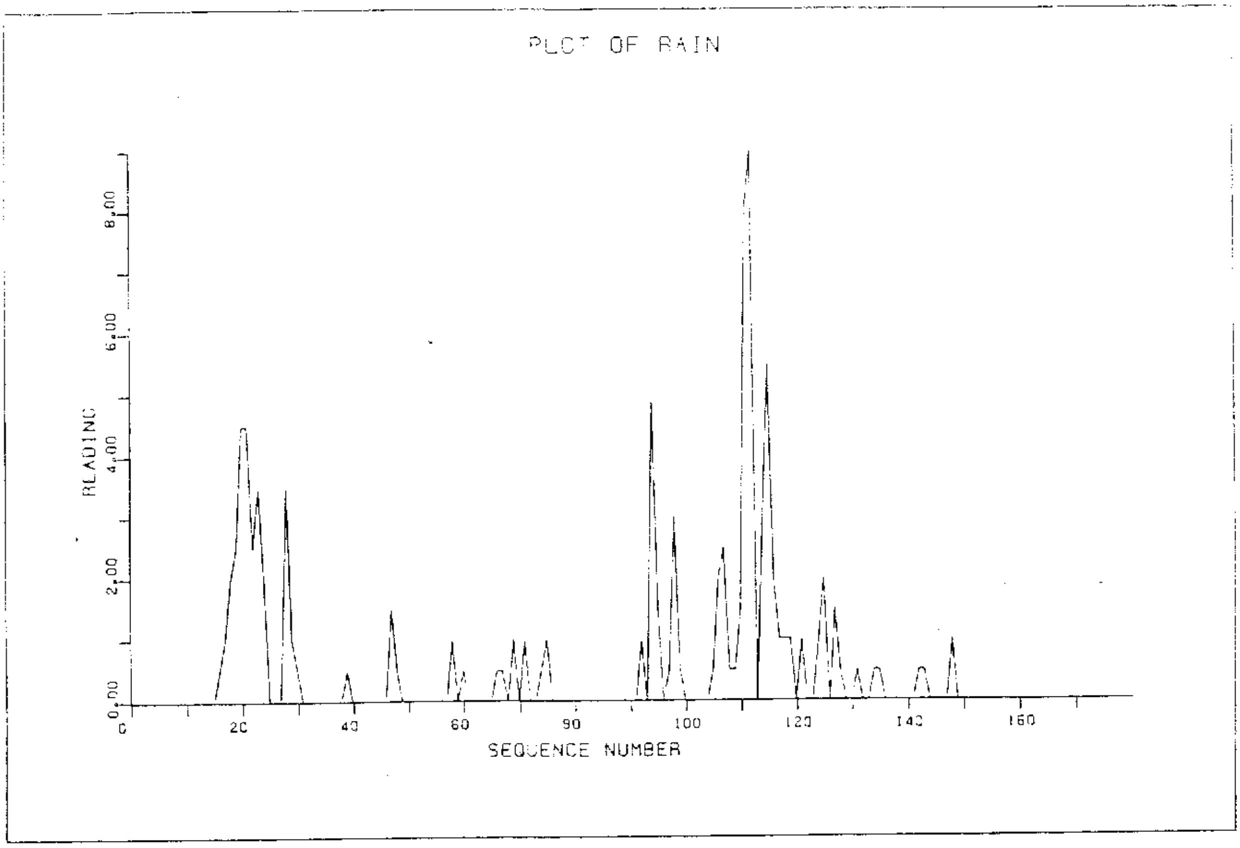
The reverse order of decreasing autoregressive parameter values from the CAPTAIN analyses of time series 1 is, on the basis of the preceding argument, anomalous. However, the differences between δ_1 values for different catchments from the analysis of a given time series are about the same as the standard errors of individual δ_1 values and so the anomaly

TABLE 24 **Summary of CAPTAIN models**

Catchment	Series	δ_1	ω_o	b (hours)	Mean residence time, T (hours)	Gain G	% variance explained	
							Transfer function	Transfer function-noise
LI1	7-day	0.883 (0.041)	65.2 (11.7)	0	8.0	0.76	70.1	88.7
LI6	7-day	0.837 (0.042)	20.1 (2.6)	0	5.6	0.54	69.7	88.4
CI6	7-day	0.870 (0.042)	10.1 (1.9)	0	7.2	0.47	72.4	91.2
LI1	1	0.741 (0.063)	44.1 (8.5)	2	5.3	0.23	85.0	94.0
LI6	1	0.843 (0.070)	12.8 (3.0)	0	5.9	0.36	73.2	89.0
CI6	1	0.809 (0.041)	8.95 (1.38)	1	5.7	0.28	93.3	96.3
LI1	3	0.870 (0.051)	80.2 (15.1)	0	7.2	0.84	77.1	86.6
LI6	3	0.808 (0.051)	23.3 (3.1)	0	4.7	0.53	78.3	85.8
CI6	3	0.870 (0.037)	11.2 (1.6)	0	7.2	0.52	89.0	92.7

Figure 31

(a)


PLOT OF RAIN
READING
0.00
2.00
4.00
6.00
8.00
0
20
40
60
80
100
120
140
160
SEQUENCE NUMBER

(b)

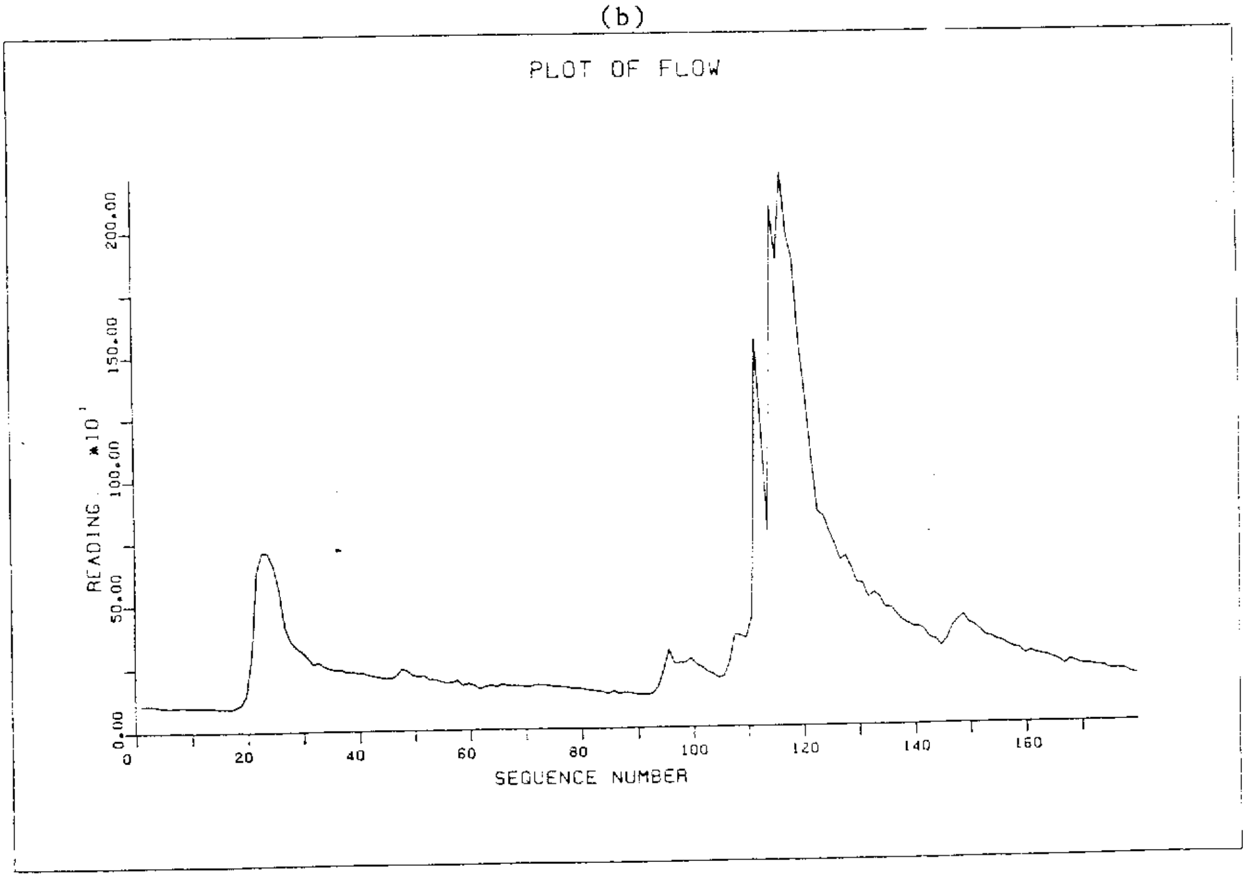

PLOT OF FLOW
READING *10¹
0.00
50.00
100.00
150.00
200.00
0
20
40
60
80
100
120
140
160
SEQUENCE NUMBER

Figure 31 (continued)

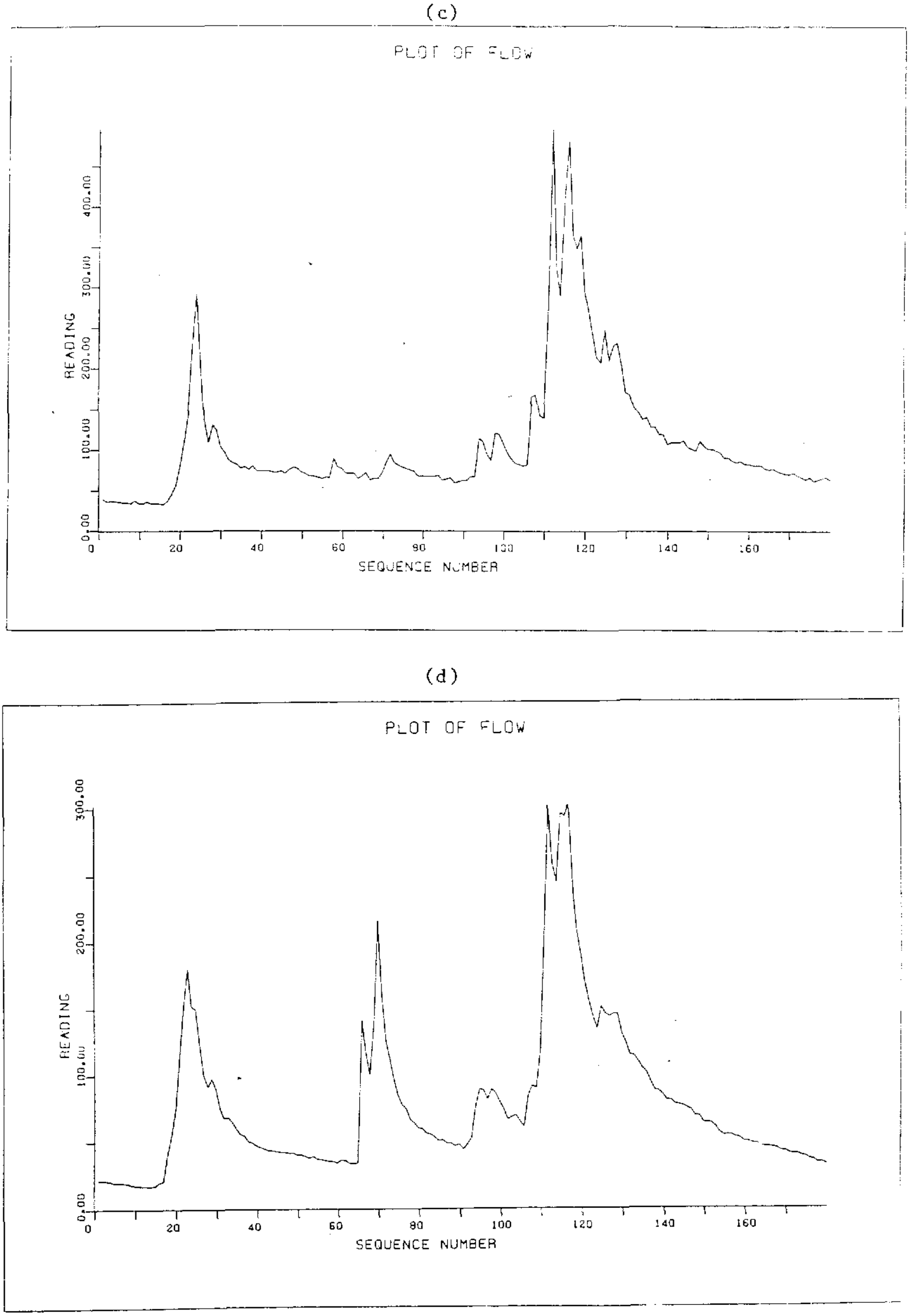
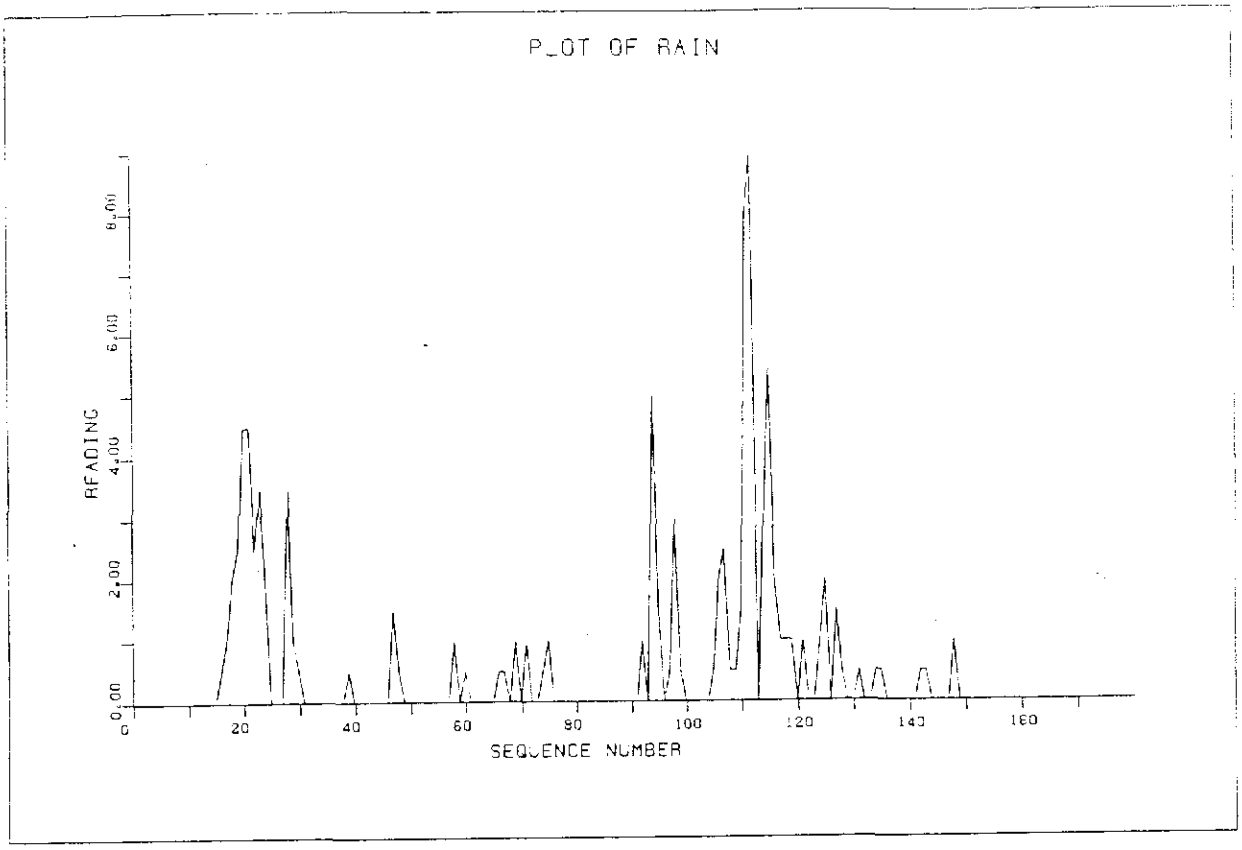


Figure 32

(a)


PLOT OF RAIN
READING
0.00
2.00
4.00
6.00
8.00
0
20
40
60
80
100
120
140
160
SEQUENCE NUMBER

(b)

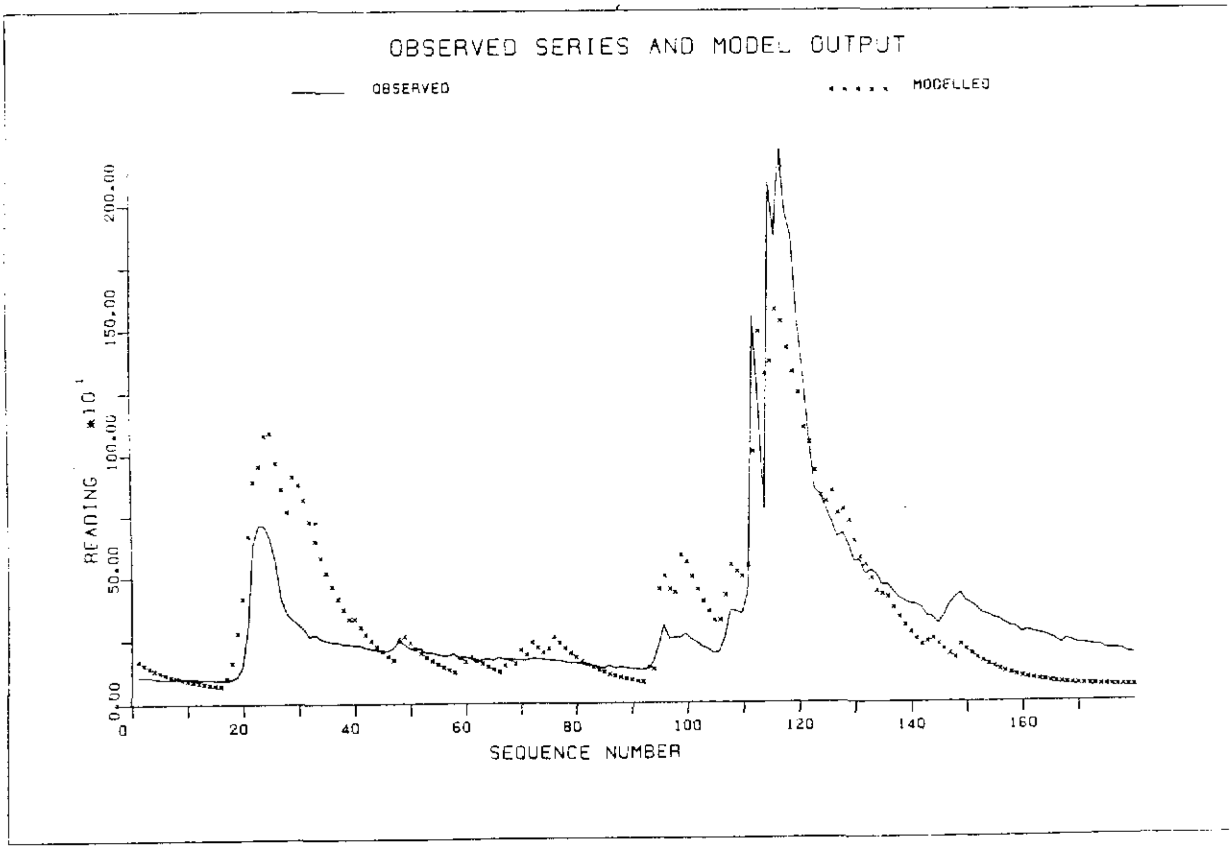
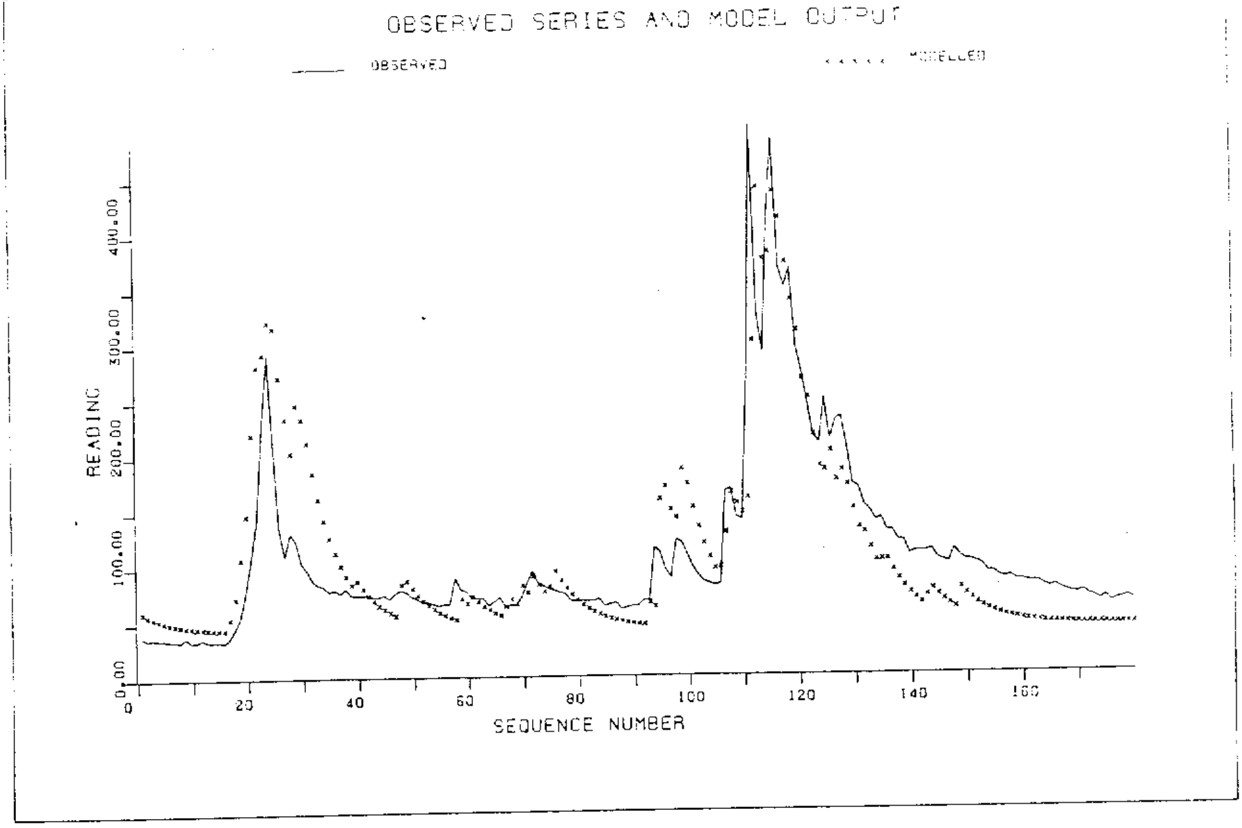

OBSERVED SERIES AND MODEL OUTPUT
OBSERVED
MODELLED
READING *10¹
0.00
50.00
100.00
150.00
200.00
0
20
40
60
80
100
120
140
160
SEQUENCE NUMBER

Figure 32 (continued)

(c)



(d)

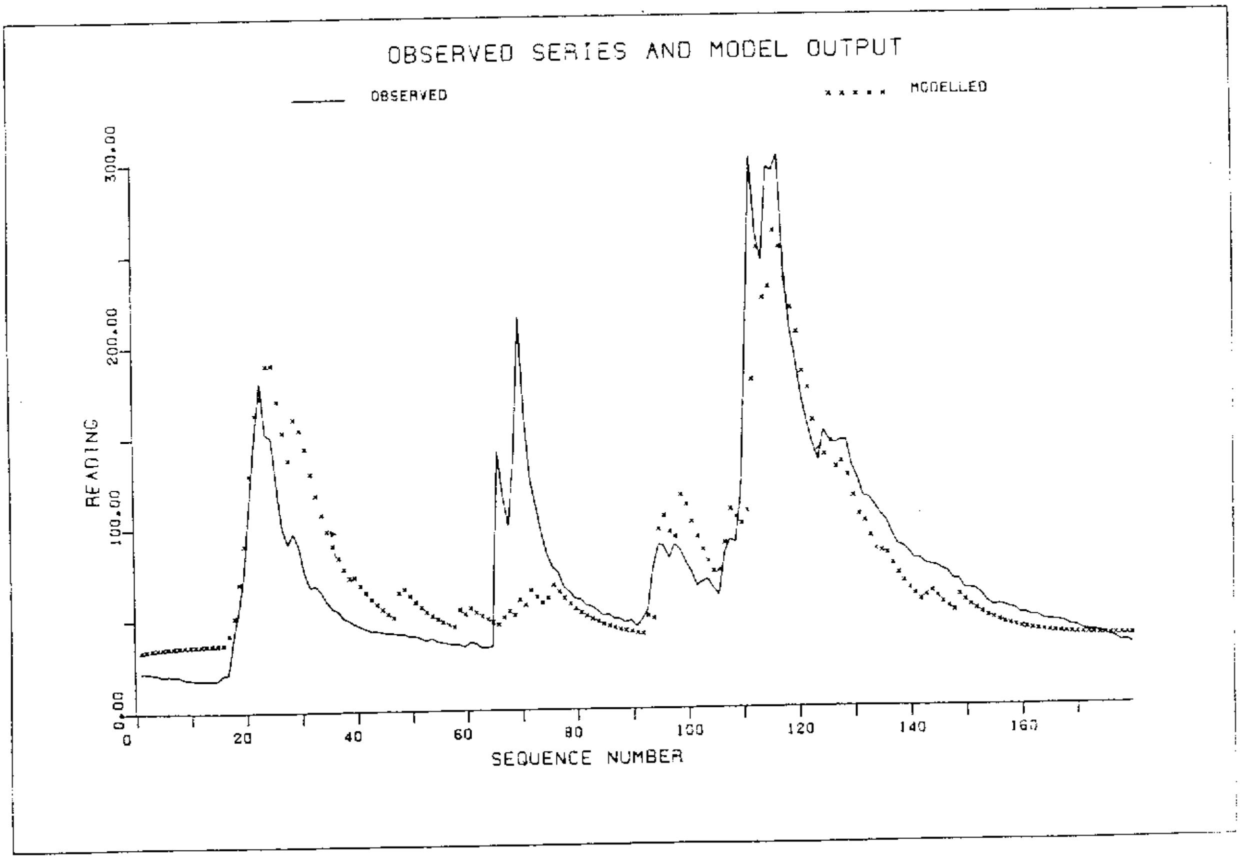
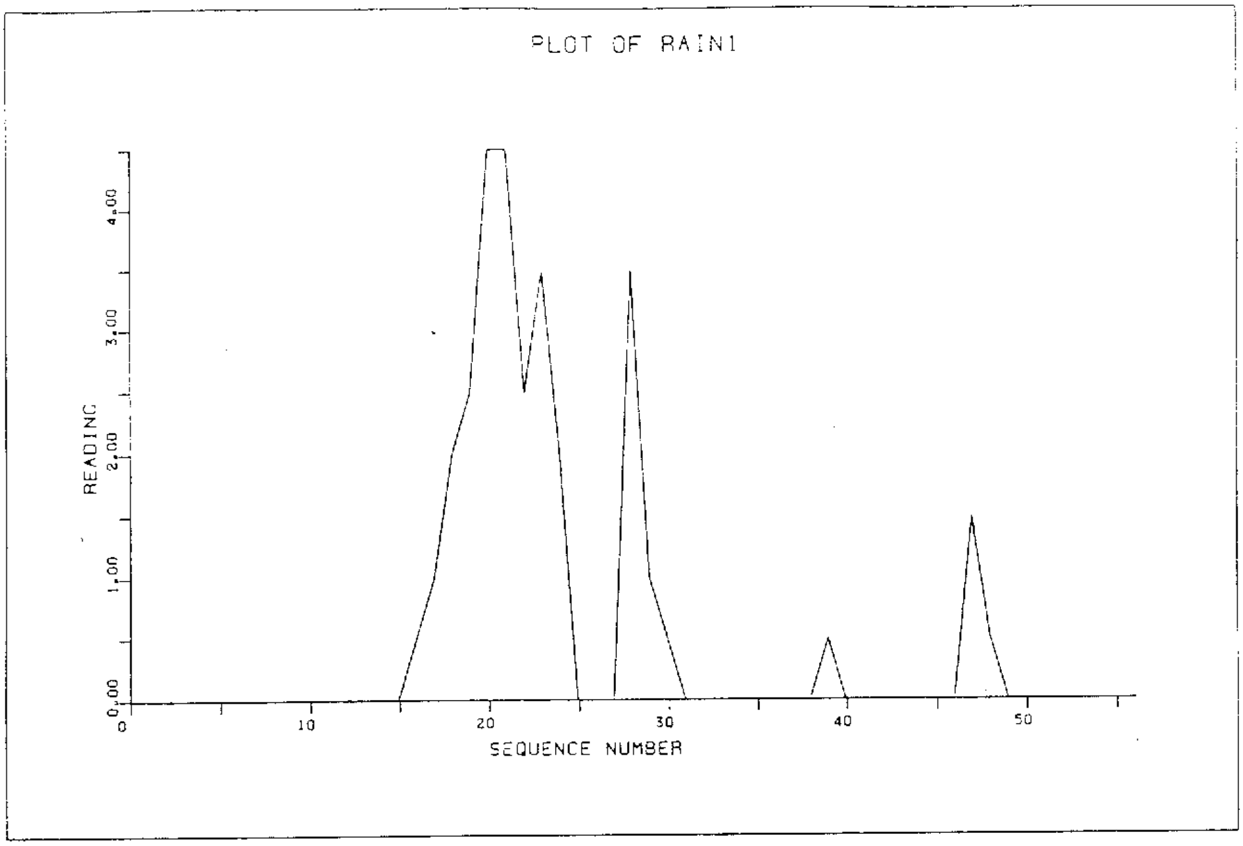
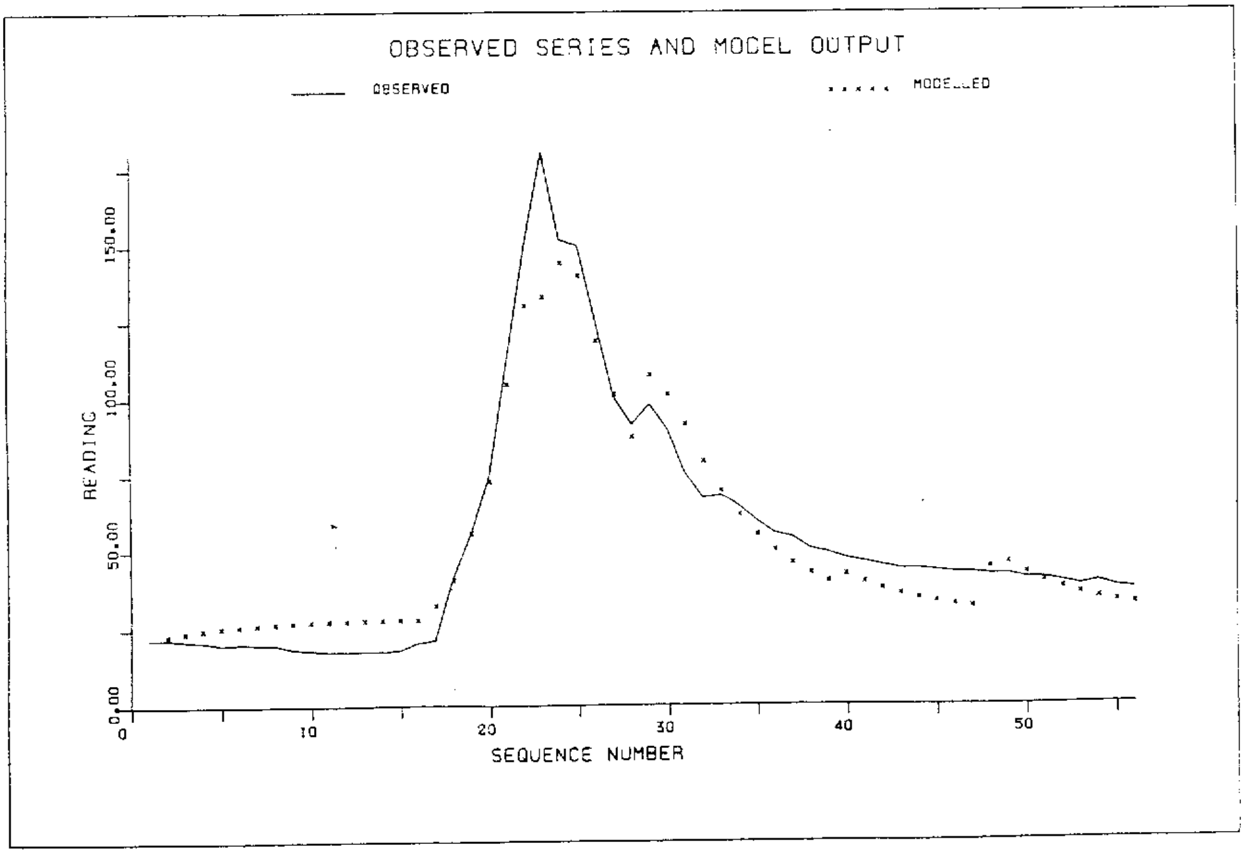


Figure 33

(a)


PLOT OF RAIN1
READING
0.00
1.00
2.00
3.00
4.00
0
10
20
30
40
50
SEQUENCE NUMBER

(b)


OBSERVED SERIES AND MODEL OUTPUT
OBSERVED
MODELLED
READING
0.00
50.00
100.00
150.00
0
10
20
30
40
50
SEQUENCE NUMBER

could have arisen by chance. Furthermore, it is possible to speculate about the very low δ_1 value for LI1 of 0.741 from time series 1 as follows. It should be noted that the time delay for the relevant model is 2 hours (probably due to the first rainfall going into canopy storage). Rainfall intensity increased in the early part of the storm so that by the time canopy storage was full, rainfall intensity was high. The forest ditches would then have quickly converted throughfall to runoff and also caused rapidly decreasing flows on the recession limb of the storm hydrograph, and hence the low value for δ_1 in this case.

As might be expected from a consideration of the effects of the wetting-up of a catchment due to successive storms, the time delays (b) are generally less for the models derived from time series 3 than they are for models derived from time series 1 (note that CAPTAIN only permits delay times of integer multiples of the time series sampling interval whilst the delay in catchment responses are not actually restricted in this way).

The moving average parameter (ω_0) in a transfer function model is largely a scaling factor for converting effective rainfall into stream flow and it is not surprising, therefore, that the magnitudes of ω_0 in Table 1 for catchment LI1 are much larger than the corresponding ω_0 values for catchments LI6 and CI6. The large differences between values for LI6 and CI6 cannot be accounted for at the present time.

From the viewpoints of catchment characterisation and of assessing the quality of rainfall and streamflow data, the percentage of variance in the observed streamflow data explained by a transfer function model is of more interest than the percentage of variance explained by the transfer function-noise model. In terms of the percentage of variance explained, Table 24 shows that the best models were invariably those derived for catchment CI6. This may seem surprising at first since CI6 is the furthest of the three catchments from Trawsnant and clearly, as discussed above, the catchment rainfall at CI6 is sometimes very different to the rainfall employed to derive the models. The reason better models were obtained for catchment CI6 than for the catchments closer to Trawsnant (LI1 and LI6) could be due to the relatively good quality data available from the thin-plate rectangular notch weir installed at CI6.

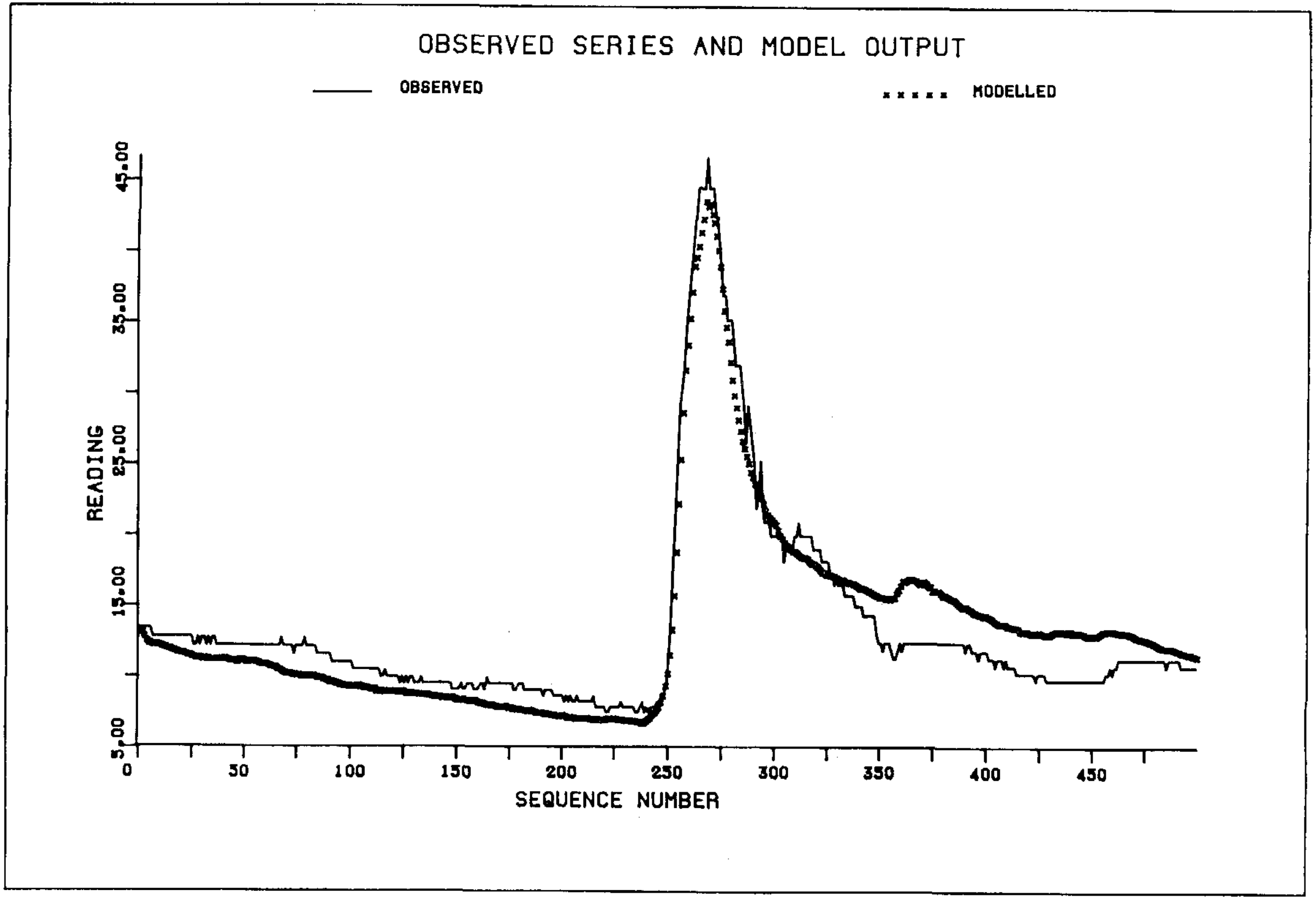


Figure 34 Simulated and Observed Hydrogen Ion concentration $\mu eq \ell^{-1}$

Flow-Hydrogen Ion Relationships

Another application of CAPTAIN is in the analysis of flow-hydrogen ion relationships. An essential requirement of any modelling study concerning acidification is the adequate prediction of hydrogen ion concentrations ($H^+ = 10^{(6-pH)}$ e.g. pH of 4 gives $H^+ = 100\ \mu eq\ell^{-1}$). The flow-hydrogen ion relationship has been investigated for LI1 and as in the case of the rainfall-runoff model a first order model has been obtained with $\delta_1 = -0.806\ (0.037)$ and $\omega_o = 0.0152\ (0.003)$ and zero time delay. The model produces a satisfactory simulation of hydrogen in concentration as shown in Figure 34 and indicates that the hydrology plays an extremely important role in determining catchment acidity.

7. MODELLING LONG TERM BEHAVIOUR USING MAGIC

An extremely important aspect of the Llyn Brianne study is the investigation of long term trends in acidification and the effects of land use change on stream chemistry. A modelling technique developed recently has been successfully applied to a range of catchments in Scotland, Norway, Sweden and USA. The model MAGIC (Model of Acidification of Groundwater In Catchments) 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 $Al(OH)_3$.

A sequence of atmospheric deposition and mineral weathering is assumed for MAGIC. Current deposition levels of base cations, sulphate, nitrate and chloride are needed along with some estimate of how these levels had 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. Nevertheless, it is the weathering process that controls the long term response and recovery of catchments to acidic deposition and MAGIC can be used to estimate these weathering rates.

A detailed description of MAGIC is given in Appendix 1. In the Llyn Brianne Study the model has been applied initially to the acidified moorland catchment CI5.

MAGIC requires a considerable input of data such as:

a) Physical and chemical properties of soil (mean depth, bulk density, porosity, cation exchange capacity, rate of sulphate uptake, temperature half saturation concentration for sulphate, equilibrium constants, base saturation levels and partial pressures of CO_2;

b) Hydrological factors (annual and monthly rainfall and runoff);

c) Dry deposition factor

d) Cation weathering rates and nitrate and ammonium uptake rates;

e) Background and present rainfall chemistry;

f) Historical patterns of sulphate emissions.

A typical set of data for CI5 is as follows with the model determining both background stream and soil chemistry and then simulating annual chemistry every year up to 1984. Only 1984 levels are presented here but Figure 35 gives a typical response of stream and soil pH over the period 1844-1984.

The following constants have been set for the Llyn Brianne CI5 MAGIC run

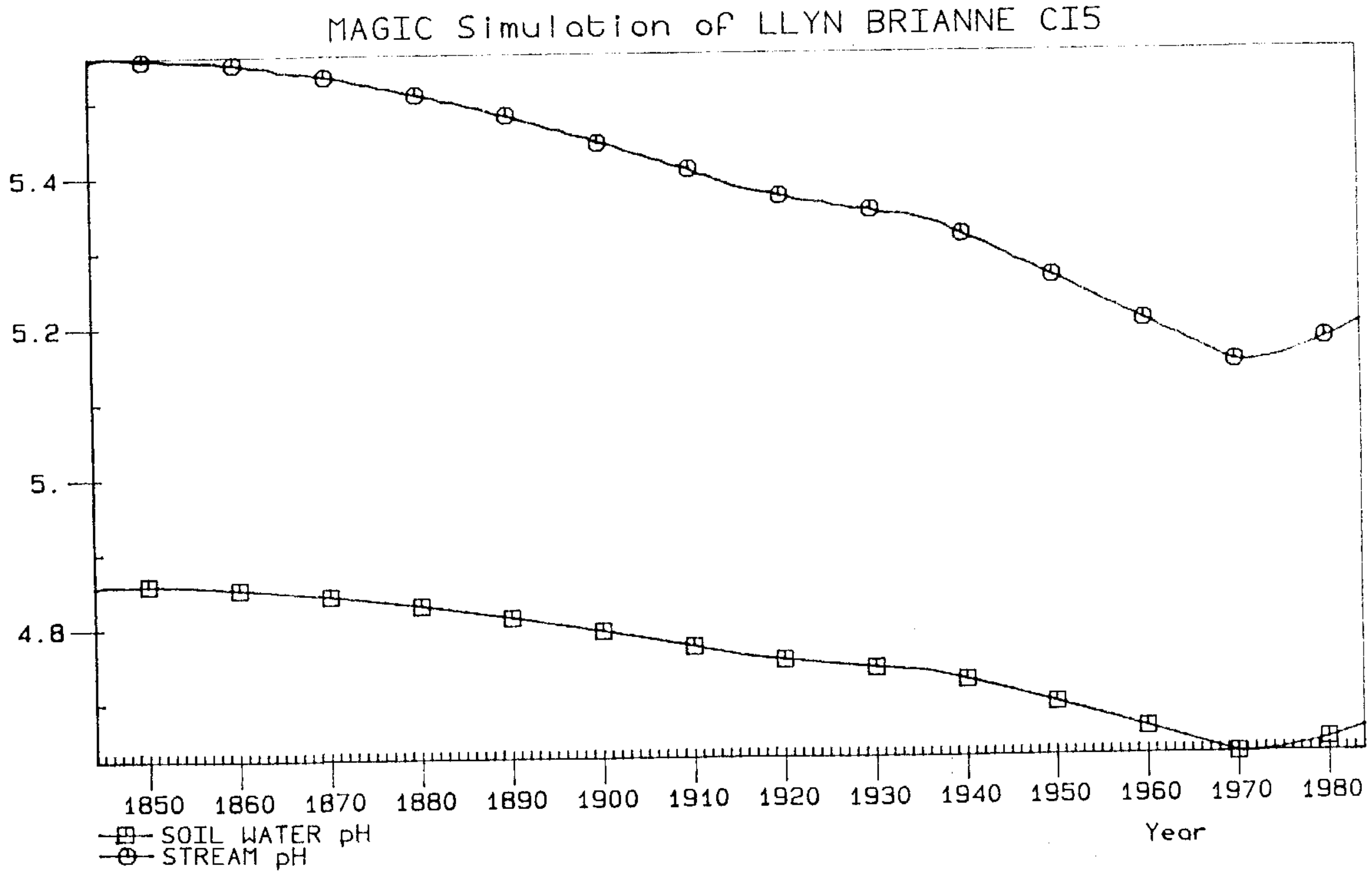


Figure 35 MAGIC Simulation of Llyn Brianne CI5

```
 1  DEPTH M      =      0.7500        2   POROSITY     =     0.4500
 3  BULK DEN     =   1060.0000        4   CEC          =    90.0000
 5  C MEQ/M3     =    150.0000        6   EMX MEQ/KG   =     0.4100
 7  DRYDEP S     =      1.3000        8   LOG(KAL)     =     9.0000
 9  LOG(KAL) S   =     10.3000       10   LOG(SALCA)   =     2.1233
11  LOG(SCANA)   =     -1.7878       12   LOG(SMGNA)   =    -1.8448
13  LOG(SKNA)    =      0.3129       14   Q            =     1.7400
15  QP           =      2.0000       16   DCO2         =     0.1500

The monthly variations of temperature and PCO2 are:

                MONTH     TEMP DEG C     PCO2 ATM
                  1          4.8         0.05000
                  2          4.5         0.05000
                  3          6.0         0.05000
                  4          7.8         0.05000
                  5         10.6         0.05000
                  6         13.1         0.05000
                  7         14.6         0.05000
                  8         14.9         0.05000
                  9         13.5         0.05000
                 10         11.1         0.05000
                 11          7.7         0.05000
                 12          6.1         0.05000

                MEAN         9.56        0.05000

The fractions of mean annual fluxes occuring in each month are:

           MONTH    STREAMFLOW    PRECIP    WEATHERING    UPTAKE
               1       0.141       0.112       0.083       0.083
               2       0.104       0.076       0.083       0.083
               3       0.084       0.070       0.083       0.083
               4       0.070       0.066       0.083       0.083
               5       0.054       0.062       0.083       0.083
               6       0.032       0.057       0.083       0.083
               7       0.030       0.064       0.083       0.083
               8       0.046       0.074       0.083       0.083
               9       0.055       0.083       0.083       0.083
              10       0.093       0.100       0.083       0.083
              11       0.134       0.116       0.083       0.083
              12       0.157       0.120       0.083       0.083
```

```
The following weathering rates will be used (MEQ/M2/YR)

                        BACKGROUND              (H) POWER
     CA         1         44.00000        10      0.00000
     MG         2         45.00000        11      0.00000
     NA         3         40.00000        12      0.00000
     K          4          0.00000        13      0.00000
     SO4        5          0.00000        14      0.00000
     CL         6          0.00000        15      0.00000
     NO3        7          0.00000        16      0.00000
     F          8          0.00000        17      0.00000
     NH4        9          0.00000        18      0.00000

The following are concentrations in precip (MEQ/M3)

                        BACKGROUND                PRESENT
                               5.40                  4.23
     PH         1              11.5       10         17.2
     CA         2              24.9       11         27.9
     MG         3             104.9       12        113.7
     NA         4               2.2       13          7.7
     K          5              13.6       14         69.9
     SO4        6             131.9       15        142.3
     CL         7               3.0       16         44.3
     NO3        8               0.0       17          0.0
     NH4        9               1.0       18         30.8

The following uptake rates will be used (MEQ/M2/YR)

                          BACKGROUND                PRESENT
       CA         1          0.00000       10       0.00000
       MG         2          0.00000       11       0.00000
       NA         3          0.00000       12       0.00000
       K          4          0.00000       13       0.00000
       SO4        5          0.00000       14       0.00000
       CL         6          0.00000       15       0.00000
       NO3        7          1.00000       16      55.00000
       F          8          0.00000       17       0.00000
       NH4        9          1.00000       18      55.00000
```

```
Historical deposition sequence:  south west Wales

                    BREAK        YEAR        SCALE FACTOR
                      1          1915           0.860
                      2          1935           0.860
                      3          1970           1.570


MODEL ESTIMATED 1844 CONDITIONS LLYN BRIANNE CI5

         SOIL  STREAM PRECIP    STREAM  ATMDEP  NTFLUX   WEATH UPTAKE   TOTAL
         ------MEQ/M3-------    --------------MEQ/M2/YR--------------  -MEQ/M2-
CA      32.0    32.0    11.5    49.8    23.0    26.8    44.0    0.0    1469.5
MG      45.3    45.3    25.0    70.6    50.0    20.6    45.0    0.0    1830.4
NA     130.8   130.8   105.0   216.1   210.0     6.1    40.0    0.0    3077.8
K        2.3     2.3     2.2     3.8     4.4   - 0.6     0.0    0.0     110.2
SO4     18.4    18.4    13.7    33.0    35.6   - 2.6     0.0    0.0      61.5
CL     145.8   145.8   132.0   212.6   264.0   -51.4     0.0    0.0      41.2
NO3      2.8     2.8     3.0     4.2     6.0   - 1.8     0.0    1.0       0.8
F        0.0     0.0     0.0     0.0     0.0     0.0     0.0    0.0       0.0
NH4      0.6     0.6     1.0     1.0     2.0   - 1.0     0.0    1.0       0.2
SBC    210.4   210.4   143.7   340.3   287.4    52.9   129.0    0.0    6488.0
SSA    166.9   166.9   148.7   249.8   305.6   -55.8     0.0    1.0     103.6

      MEQ/M3     SOIL  STREAM           MEQ/M3     SOIL  STREAM           EXCHAN %
PH                4.9     5.6       H              14.0     2.8      ES     10.90
ALK              44.2    44.1       HCO3           70.5    53.3      ECA     1.53
AL                8.3     1.4       TOTAQ F         0.0     0.0      EMG     1.90
TOTAQ AL         15.8    20.8       TOTAQ SO4      18.4    18.4      ENA     3.17
SUM PLUS        237.3   221.4                                        EK      0.11
SUM MINUS       237.4   222.8                                        BS      6.71
```

```
MODEL SIMULATED 1984 CONDITIONS LLYN BRIANNE CI5


         SOIL  STREAM PRECIP    STREAM  ATMDEP  NTFLUX   WEATH UPTAKE   TOTAL
         ------MEQ/M3-------    --------------MEQ/M2/YR--------------  -MEQ/M2-
CA       42.6    42.6    17.2    67.0    34.4    32.6    44.0   0.0    798.0
MG       53.3    53.3    27.9    84.0    55.9    28.1    45.0   0.0    879.3
NA      148.6   148.6   113.8   246.6   227.6    19.0    40.0   0.0   2237.1
K        10.3    10.3     7.8    17.0    15.6     1.4     0.0   0.0    313.3
SO4     104.9   105.5    70.0   182.8   182.0     0.8     0.0   0.0    249.0
CL      155.1   155.1   142.3   229.2   284.7   -55.4     0.0   0.0     44.5
NO3      33.6    33.6    44.4    55.1    88.8   -33.7     0.0  28.0     10.7
F         0.0     0.0     0.0     0.0     0.0     0.0     0.0   0.0      0.0
NH4      18.7    18.7    30.8    33.3    61.7   -28.4     0.0  28.0      6.5
SBC     254.8   254.8   166.8   414.6   333.5    81.1   129.0   0.0   4227.7
SSA     293.6   294.1   256.7   467.1   555.5   -88.4     0.0  28.0    304.2



     MEQ/M3     SOIL  STREAM           MEQ/M3    SOIL  STREAM         EXCHAN %
PH               4.7     5.2    H                22.1     6.4     ES     41.14
ALK            -21.0   -21.0    HCO3             44.9    23.4     ECA     0.82
AL              33.0    16.5    TOTAQ F           0.0     0.0     EMG     0.90
TOTAQ AL        50.5    63.8    TOTAQ SO4       106.0   106.0     ENA     2.29
SUM PLUS       338.3   317.9                                      EK      0.33
SUM MINUS      338.5   334.6                                      BS      4.34
```

The simulated 1984 chemistry is generally very close to the observed chemistry as indicated in Table 25.

TABLE 25

		Observed Chemistry	Simulated Chemistry
	CA	44.0	42.6
	MG	56.0	53.3
	NA	149.0	148.6
	K04	6.6	10.3
	S04	102.0	104.9
	CL3	167.6	155.1
	N03	14.8	33.6
	NH4	16.1	18.7
	PH	5.22	5.2
	H	7.7	6.4
*	ALKALINITY	-30.0	-21.0
	AL	18.0	16.5
	SOIL BASE SATURATION	6%	4.34%

ALKALINITY = $(HCO_3^-)-(H^+)-3(AL^{3+})$
(in MAGIC)

All chemistry units $\mu eq \ell^{-1}$

With exception of nitrate the simulation reproduces with reasonable accuracy the observed chemistry. The nitrate uptake in the catchment may be higher than that estimated and this may explain the discrepancy in the nitrate simulation. Alternatively the rainfall nitrate concentrations seem rather high (almost double the levels observed at Plynlimon and elsewhere in Wales - see Table 4) and nitrate rainfall chemistry should be rechecked. However, as a first run with MAGIC the model appears to perform adequately and the long term trends indicated in Figure 35 appear reasonable and follow similar trends obtained for catchments in Scotland and Wales. It would be extremely interesting to compare the simulated trends with results from paleoecological studies or fisheries data.

Significant features of the 1984 chemistry compared to the 1844 chemistry is the major decrease in alkalinity from 44.1 to -30 and increase in aluminium from 1.4 to 18 $\mu eq \ell^{-1}$. This indicates a major shift in catchment chemistry during the past 150 years.

Further applications of MAGIC will be undertaken for all catchments and land use change will be investigated as described in Appendix 1.

Appendix 1

PREDICTING LONG TERM TRENDS IN SOIL AND WATER ACIDIFICATION

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BACKGROUND

In sensitive areas receiving acidic deposition, paleolimnological data indicate changes in lake pH over 1-3 decades during the past century (Batterbee et al., 1985). Estimates of emissions and deposition of SOx and NOx over this same period suggest that deposition increases occurred (1) earlier and (2) more slowly than did the lake pH changes. Clearly chemical and biological processes in the terrestrial catchment and lake ecosystem damp, delay, and moderate the response of surface water pH to deposition of acidifying compounds. This response is controlled by key terrestrial processes that include chemical weathering, sulphate adsorption, cation exchange, dissolution and precipitation of aluminium compounds, and dissolution and disassociation of inorganic carbon. These various processes interact in a complex fashion and may exhibit marked spatial variability. Consequently, quantification of the mechanisms of freshwater acidification has proved to be difficult. Nevertheless, future trends in surface water acidification can only be predicted using mathematical models based on an understanding of these mechanisms.

To estimate surface water response to future reduction in deposition, mathematical models must (1) be based on physical, chemical and biological processes that control catchment response, (2) treat interacting processes simultaneously and (3) be capable of representing long-term responses. MAGIC (Model of Acidification of Groundwater In Catchments) provides a tool by which soil processes can be simultaneously and quantitatively linked to examine the impact of acid deposition on surface water chemistry over time scales of several years to several decades. The model was originally developed and tested for catchments in Shenandoah National Park, Virginia (USA) and has recently been adapted for catchments in Scotland (Loch Dee, Loch Grannoch) and in Norway (Lake Hovvatn, and the RAIN project catchments at Sogndal and Risdalsheia). MAGIC provides the ideal tool for investigating the regional aspects of acidification and for predicting the effects of reduced emission levels on soil and stream water quality. MAGIC is currently being applied to several UK catchments and an application to the Loch Dee catchment in Galloway is presented here.

APPLICATION OF MAGIC TO LOCH DEE

MAGIC (Model of Acidification of Groundwater In Catchments; Cosby et al, 1985) 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 had 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. Nevertheless, it is the weathering process that controls the long term response and recovery of catchments to acidic deposition, and MAGIC can be used to estimate these weathering rates.

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). The model has been calibrated using measured rainfall and stream chemistry data together with relevant hydrological and soils data. The model simulates long term behaviour and can be used to separate out different effects. For example sea salt acidity has a different effect to athropogenic sources of acidity and afforestation has another type of effect. In the application to Dargall Lane the factors considered are afforestation, dry and occult deposition, variations in sea salt and acidic oxide loading and deforestation.

LONG TERM ACIDIFICATION TRENDS FOR DARGALL LANE

Figure 1 shows a simulation of long term acidity for the Dargall Lane catchment. The sulphate deposition history is shown in Figure 1a and this 'drives' the MAGIC model. The historical simulation of pH shown in Figure 1b 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(Betterbee et al, 1985, Flower et al, 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 (Figure 1b). 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.

Afforestation

Afforested systems are more complex to model than grassland systems because the introduction of the forest pertubs a grassland ecosystem which in itself is difficult to 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 (see Whitehead et al., 1986). 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 precipitatation 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 atmospheric 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 whilst 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 40 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 2 shows the effects of increasing evapotranspiration from 16 to 30% over the forest growth period with varying levels of marine, pollutant and marine + 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% has a similar effect but the changes are much smaller. The important features of these results are the enhanced and 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.

Atmospheric acidic oxide inputs

An important factor in determining stream acidity in the upland UK 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 3 shows the effects of such variations for both moorland and forested catchments; the highest levels correspond to areas with high atmospheric acidic oxide rates (3 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.

Deforestation

Whilst afforestation increases stream acidity, as shown both by the model predictions and field evidence (Whitehead et al., 1986), then deforestation will possibly result in a reduction in stream water acidity. Figure 4 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 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.

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 UK, 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 UK cannot be gauged immediately because many unresolved factors remain. However, much of the British uplands have 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 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 appears highly significant. 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.

CONCLUSIONS

The MAGIC model has proved to be particularly useful yielding information on the catchment responses, processes and possible future behaviour. Whilst considerable doubt remains on the exact processes controlling stream acidification MAGIC does appear to describe the dominant mechanisms and can be considered a useful tool in assessing the relative importance of different sources of 'pollution' and land use change.

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Figure | (a) Sulphate deposition history used as input for the MAGIC reconstruction of pH in the Dargall Lane moorland catchment.

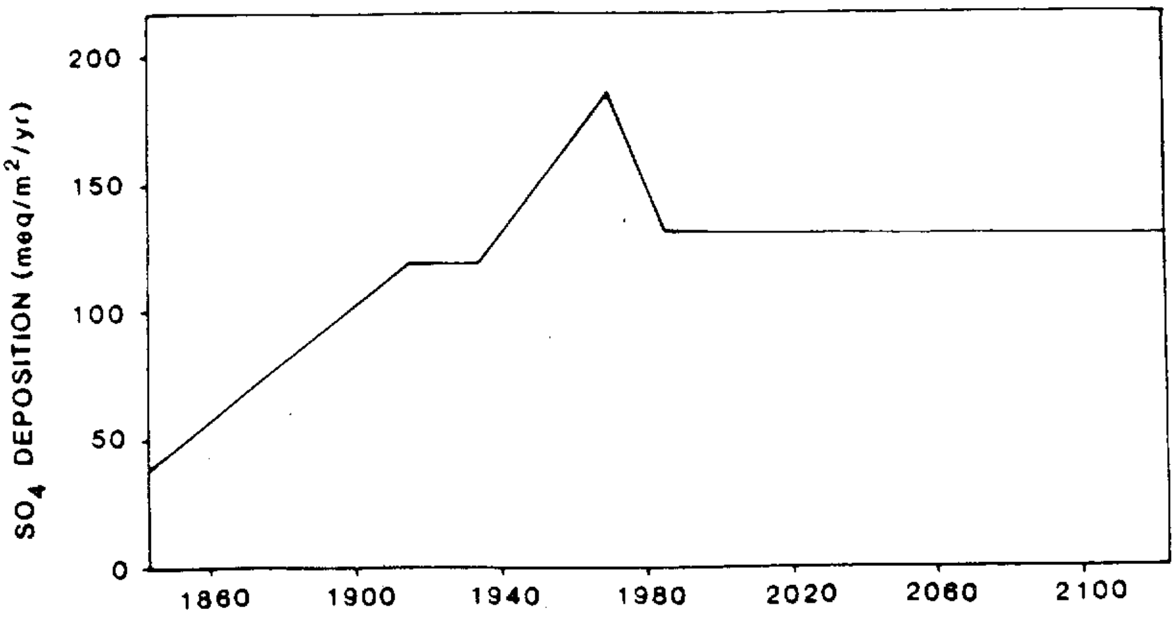


Figure | (b) Simulation of the pH of streamwater in the Dargall Lane moorland catchment assuming three sulphate deposition scenarios

—— Historical levels to 1984 and constant 1984 levels thereafter (see Figure |(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.

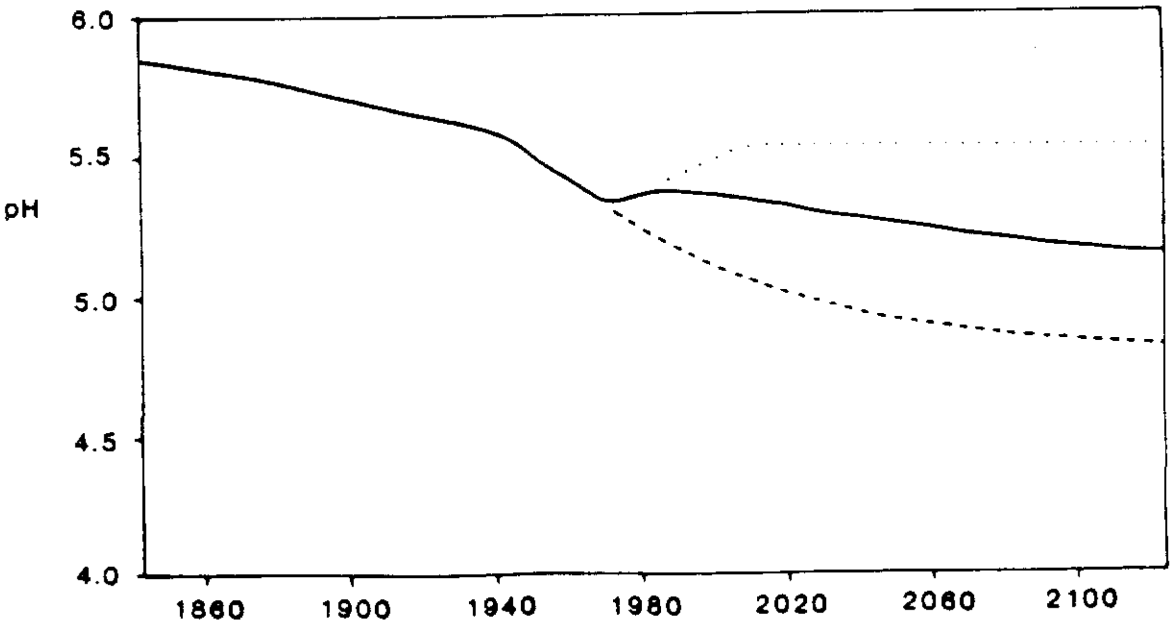


Figure 2(a) Simulation of the pH of the streamwater from the Dargall Lane catchment comparing the moorland catchment response assuming Figure 5(a) deposition rates (———), the effect of 14% additional evaporation following afforestation (······), the effect of 14% additional evaporation plus 15% additional input of natural sea salts following afforestation in 1985 (------), and the effect of 14% additional evaporation plus 30% additional input of natural sea salts following afforestation in 1985 (— — —).

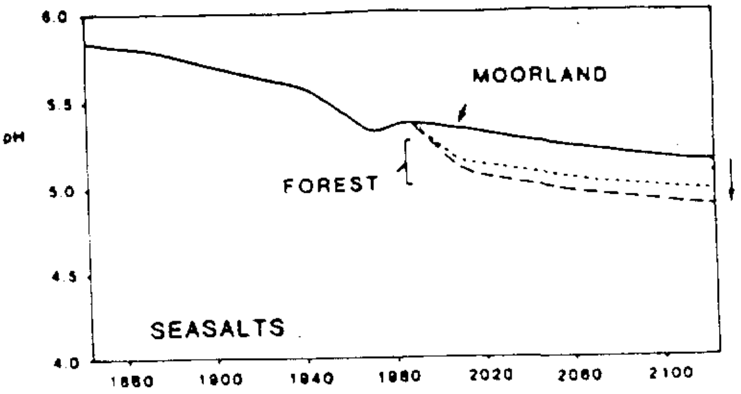


Figure 2(b) Simulation of the pH of streamwater from the Dargall Lane catchment comparing the moorland response (———) to the forested catchment response assuming increased evaporation (–––––) with different levels of pollutant scavenging (·······, 20% additional sulphate,-----; 40% additonal sulphate,— — —, 60% additional sulphate).

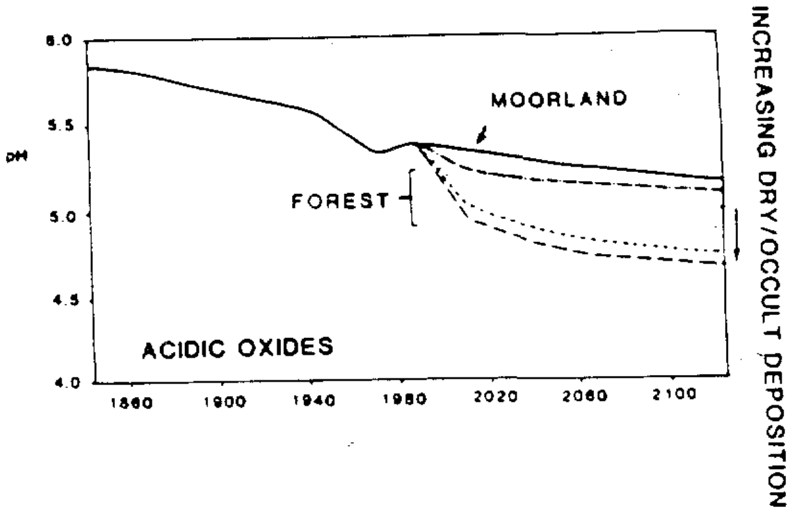


Figure 2(c) Simulation of the pH of streamwater from the Dargall Lane catchment showing the moorland response (———) and the combined effects on the forested catchment of increased evapotranspiration, increased scavenging of natural sea salts, and various levels of increased scavenging of pollutant inputs (–·–·– , zero additional pollutant scavenging, ······ , 20% pollutant scavenging,-----, 40% pollutant scavenging,— — , 60% pollutant scavenging).

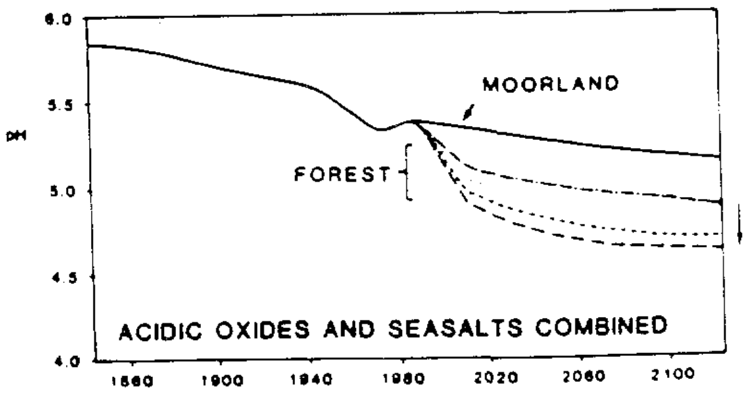


Figure 3 (a) Simulation of the pH of streamwater from the Dargall Lane moorland catchment assuming sulphate deposition patterns (shown in Figure 1(a)) modified by various factors to reproduce a range of loading conditions (ie from pristine to heavy pollution).

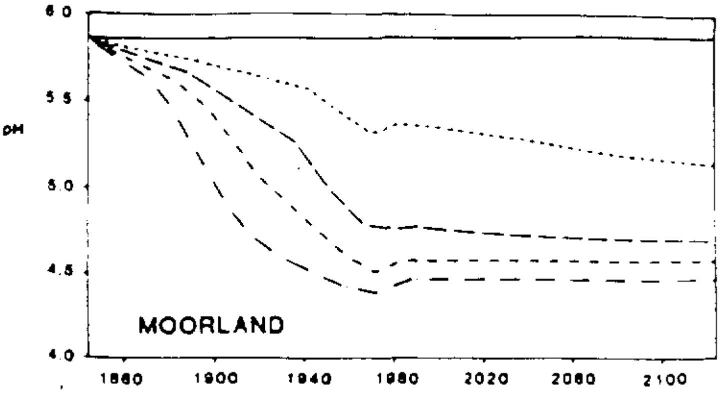


Figure 3 (b) Simulation of the pH of streamwater from the 'forested' Dargall Lane catchment assuming afforestation from 1884 onwards and sulphate deposition patterns (see Figure 1(a)) multiplied by various factors to reproduce a range of loading conditions from pristine to heavy pollution.

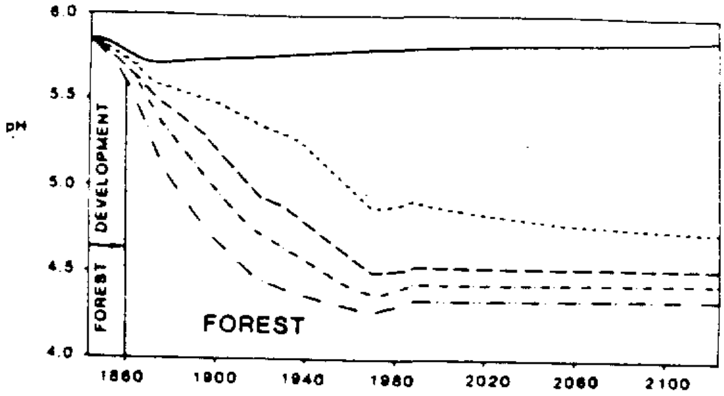
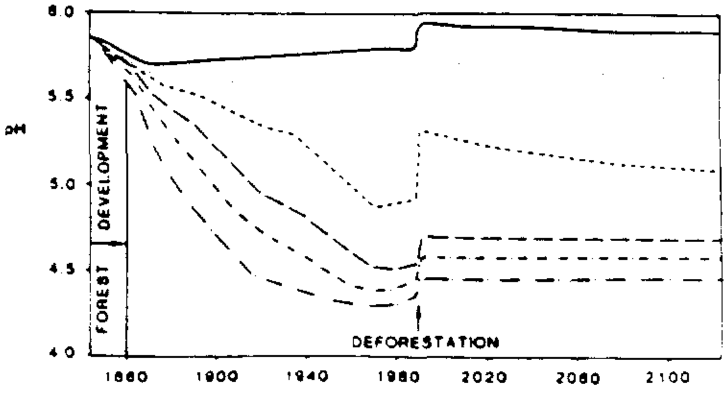


Figure 4 Simulation of the pH of streamwater for the Dargall Lane catchment assuming afforestation from 1844 and deforestation in 1990.



—— Background rates (pristine conditions)

······ 0.5 x Figure 1a deposition concentrations (low pollution)

------ 1 x " " " ")intermediate
— — 1.5 x " " " ")pollution

—·—·— 2 x " " " ")heavy
— — 3 x " " " ")pollution

Appendix 3

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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