ATMOSPHERIC DEPOSITION, AFFORESTATION AND WATER QUALITY AT LOCH DEE, S.W. SCOTLAND

Simon Johnathon Langan

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews

1986

Please use this identifier to cite or link to this item:
http://hdl.handle.net/10023/15210

ATMOSPHERIC DEPOSITION, AFFORESTATION AND WATER QUALITY AT LOCH DEE, S.W SCOTLAND.

BY

SIMON JOHNATHON LANGAN.

THE UNIVERSITY OF ST. ANDREWS 1985.

I Simon Johnathon Langan hereby certify that this thesis which is approximately 45,000 words in length has been written by me, that it is the record of work carried out by me, and that it has not been submitted in any previous application for a higher degree.

Date 26 Nov. 1985 Signature of candidate

We hereby certify that the candidate has fulfilled the conditions of the resolution and regulations appropriate to the degree of Ph.D of the University of St. Andrews and that he is qualified to submit this thesis in application for that degree.

Date 26 Nov 1985 Signature of supervisor

Date 26 NOV 1985 Signature of supervisor

I was admitted as a research student under Ordinance No. 12 on the 1st. October 1982 and as a candidate for the degree of Ph.D in January 1984; the higher study for which this is a record was carried out between 1982 and 1985.

Date 26 Nov 1985 Signature of candidate

In submitting this thesis to the University of St. Andrews I understand that I am giving permission for it to be made available for use in accordance with the regulations of the University Library for the time being in force, subject to any copyright vested in the work not being affected thereby. I also understand that the title and abstract will be published, and that a copy of the work may be made and supplied to any bona fide library or research worker.

ACKNOWLEDGEMENT.

I am grateful for this opportunity to thank all those who have helped in making this piece of work possible:

My two supervisors Dr.A.Werritty and Mr. W.T.Welsh
The Loch Dee Project.
Dr.P.G.Whitehead.
Mr. A Kite.

All my friends and colleagues at both the Solway River Purification Board and the University; Particularly the Hydrologists and Chemists at the SRPB without whose assistance this work would have been impossible.

This work was carried out under a NERC (CASE) award between the University and the Solway River Purification Board, Dumfries.

A special vote of thanks must go to all of my family for supporting me both morally and financially throughout my student career. My final thanks go to Jonquil and Charlie who keep life on the tracks.

SJL 1985.

ABSTRACT.

This work describes an investigation of the factors governing the water quality in three upland streams at Loch Dee, S.W Scotland. Particular emphasis is placed on the factors affecting streamwater acidification in the short and medium time scales. The streams are differentiated from one another by the land-use employed in each of the stream catchments. The details of both the site and methods of data collection are described. Variations in both bulk precipitation and streamwater chemistry are examined at the weekly scale in order to determine the factors regulating streamwater chemistry. The 5 factors are ; atmospheric deposition, weathering rates, biological production and consumption, ion-exchange and catchment hydrology. A more detailed examination of one of the processes (ion- exchange) is undertaken at both the catchment and laboratory scale. The data show that short-term streamwater acidification can be induced by ion-exchange of H^+ for Na^+ in the catchment soils following precipitation inputs heavily laden with sea-salts. The role of hydrology in determining streamwater acidity over storm periods is also considered using a time-series model. The model indicates that significant differences exist between the 3 catchments hydrology in terms of the duration and timing of acidic episodes in the streams.

CONTENTS.

CHAPTER 4 DATA COLLECTION AND QUALITY CONTROL

CHAPTER 5 ATMOSPHERIC AND STREAMWATER CHEMISTRY VARIATION IN THE THREE CATCHMENTS AT LOCH DEE

CHAPTER 6 EPISODIC ACIDITY IN THE STREAMS AT LOCH DEE

CHAPTER 7 MODELLING STREAMWATER ACIDITY IN THE THREE CATCHMENTS

LIST OF PLATES.

LIST OF TABLES.

LIST OF FIGURES.

CHAPTER 1 : INTRODUCTION.

1:1 INTRODUCTION.

In recent years there has been a growing concern as to the effects various anthropogenic activities may be having on the natural environment. One of the major areas of interest has been the effects of pollutants on water bodies.

In the past water pollution studies have concentrated on point-source pollution such as industrial or sewerage outfalls into large rivers surrounding areas of high population concentrations. However as society has expanded so has its pollution, until the present situation, in which attention has been focused on the somewhat delicately balanced water bodies and ecosystems of remote upland areas. It is now suggested that such water bodies are under threat from a non-point source of pollution, that of acid deposition.

The problem however is a complex one; and the question arises; how does the production of acid forming gases from industrial conurbations lead to changes in the water chemistry of surface waters hundreds and often thousands of kilometres away ? This process is particularly complex after the pollutant has infiltrated a mosaic of vegetational surfaces, and taken one of a multitude of hydrological routeways through a variety of soil and geology types in any one catchment area.

In addition to non-point sources of atmospheric pollution many upland catchment areas in the twentieth century have also seen a dramatic land-use change from areas of upland heath and moor to extensive programmes of coniferous afforestation. These are thought to affect the value of upland areas as water resources. The public concern aroused by these two issues has not until very recently lead, in Britain, to an integrated research effort aimed at evaluating these factors which may lead to the deterioration in the quality of upland waters and the effect this may have on the aquatic ecosystem.

The aim of this piece of work is to provide an integrated baseline study using tried and tested techniques to evaluate the different factors (both natural and anthropogenic) which may affect water quality of upland streams in the medium (seasonal/yearly) and short-term (storms). Specifically this dissertation sets out to answer the following questions:

i. What are the processes and factors governing water quality in upland catchments in S.W Scotland ?

ii. Do the factors and processes governing streamwater quality vary through time and space according to atmospheric inputs and land-use ?

iii. Having identified the major controls on water quality in such environments can they be mathematically modelled and thus provide a basis for predicting water quality response to storm inputs ?

To answer these questions a multiple catchment study has been employed in which the catchments are considered to be homogenous in all aspects except land-use and land management. Using this method attempts may be made to try and isolate and thereby evaluate the various factors by comparing and contrasting catchment results. The study focuses on part of a wider project being undertaken in the south west of Scotland by several cooperating bodies under the auspicies of the Solway River Purification Board (SRPB).

This dissertation is structured so as to familiarise the reader with the work dealing with water quality in upland areas, and surface water acidification, already covered in the literature (chapter 2). From here a description of the selection and site of the investigation is given in chapter 3 including the catchment details. The various methods and types of data collection, following the different needs of each part of of the investigation are given in chapter 4. In order to determine the systems regulating streamwater chemistry, chapter 5 investigates the temporal variation over a 4 year period (at the weekly scale) of both atmospheric input and streamwater chemistry in terms of their major ions. Chapter 6 takes a more detailed look at one of the mechanisms by which short-lived stream acidification may occur, using both field and laboratory data. In chapter 7 a time series model is developed using the continuous records of stream discharge and acidity in order to compare and contrast the catchments' land-use. Finally chapter 8 provides an overall discussion and evaluation of the various factors influencing water quality within the study and the implications of these results in a wider context.

The term water-quality is used throughout this work essentially as a descriptive and comparative term with no strict definition as to the chemical constituency implied, although emphasis is placed on a water's acidity measured by its pH. Throughout the dissertationthe term 'water quality' is variously ascribed to water in terms of its acidity, electrical conductivity (or "conductivity") or frequently dissolved ionic load.

CHAPTER 2: LITERATURE REVIEW.

2:1 INTRODUCTION.

The intention of this chapter is to provide an overview of the environmental factors and processes which act to determine water quality. Particular emphasis is placed on the acidification of surface water in upland Britian.

Watershed acidification is a natural process in areas of hard bedrock where base nutrients are leached and lost from a catchment faster than they are replaced by chemical weathering. More recently much attention has been given to the role played by acid deposition in accelerating and enhancing the rate of natural acidification. However in considering water quality and acidification of upland waters it is pertinent to consider all the factors which may influence its composition.

In order to structure such a review consider the flow path of a fictional water droplet from an unknown source to its deposition following a variety of modifying routes to its ultimate destination as part of a surface water body. It is possible to consider such a system as a series of cascading compartments (after Chorley and Kennedy 1971); where the output of one compartment is the input to the next. This is diagramatically presented in fig.2:1 which represents the structure of this review chapter.

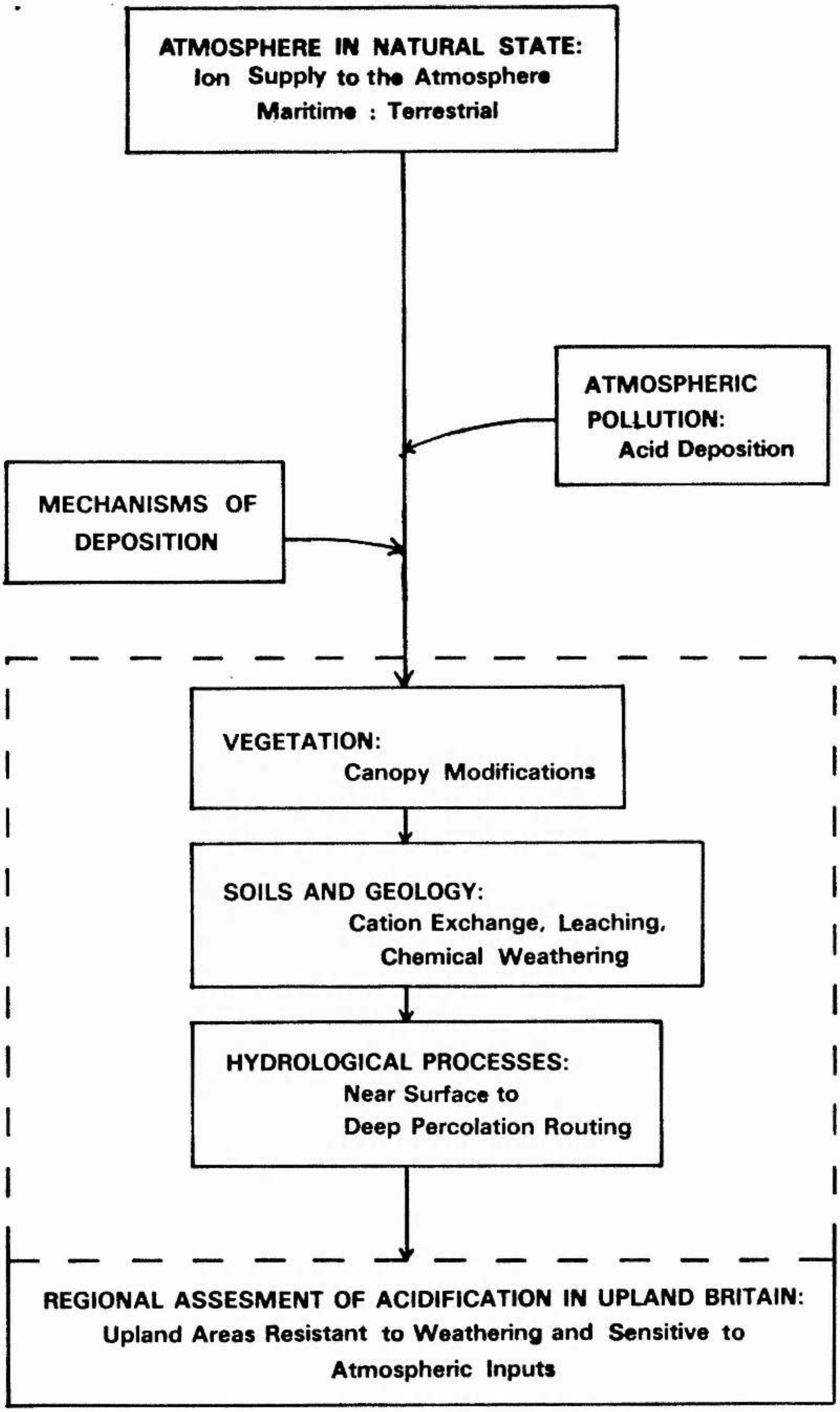


FIG 2:1 Fictional Path Of A Water Droplet, Through A Series Of Cascading Compartments.

2:2:1 Atmospheric Inputs.

The amount and quality of atmospheric deposition will be determined by 2 sets of factors:

i. The supply of ions to the atmosphere, both natural and anthropogenic and

ii. the mechanism of deposition.

In this review these 2 sets of factors are considered separately.

2:2:1:1 Ionic supply to the atmosphere.

The important contribution of atmospheric ionic supply to both terrestrial ecosystems and the water quality of inland areas has been considered by numerous authors, for example Gorham (1961), Crisp (1966), White et al (1971), Likens et al (1977) and Cryer (1976). Likens et al (1977, p.15) describe atmospheric inputs as " the major vehicle of nutrient input to the ecosystem " and Cryer (1976) suggests atmospheric inputs should be considered as "external credit factors". Ionic constituents in the atmosphere are derived from several sources. Thus Gorham (1961) identifies 5 sources of supply for ions in the atmosphere : sea-salts, soil fragments, volcanoes, organic matter and air pollution. Wright et al (1980) further indicate that atmospheric inputs of sea-salts supply Na^+, Mg^{2+}, K^+, Cl^- and SO^{2-}_4 whilst terrestrial inputs of weathering products provide Ca^{2+}, Mg^{2+}, K^+ and HCO^-_3 and atmospheric pollutants constitute H^+, NH^+_4, NO^-_3 and SO^{2-}_4.

Sea-salts are entrained into the atmosphere in large quantities by breaking waves and sea-spray, these sea-salts being transported in the atmosphere as raindrop nuclei by surface winds. The work of Junge and Werby (1958), Eriksson (1960), Stevenson (1968) and Skartveit (1981) demonstrate that the amount of sea-salt entrained in the atmosphere decreases with an increasing distance from the sea. The work by Eaton et al (1973) distinguishes between precipitation from maritime sources with a high sodium content and a calcium/magnesium ratio close to that of seawater, and continental precipitation with a high calcium/magnesium ratio where the maritime influence on composition is minimal. The extensive work reported by Eriksson (1960) shows a chloride gradient with a decreasing concentration across Scandinavia and continental Europe. Work by Stevenson (1968) indicates that precipitation over Britain has a similar chloride gradient, this is shown in fig 2:2. The figure shows a steep gradient along the north and west coasts of Scotland and Ireland in which chloride concentrations rapidly decreases inland. Such a gradient indicates the dominant role of the west to east Atlantic air mass movement over Britain. However it is unlikely that this concentration gradient is constant through time, with the amount of sea-salt entrained in the prevailing air stream depending on the meterologic conditions. Work by Sutcliffe and Carrick (1983) in the English Lake District documents the maritime component of precipitation as having a seasonal component in which maximum concentrations occur during midwinter and minimum concentrations during midsummer. Allen et al (1968) also indicate that the extent to which maritime influences extend inland will be greatly affected by local topography.

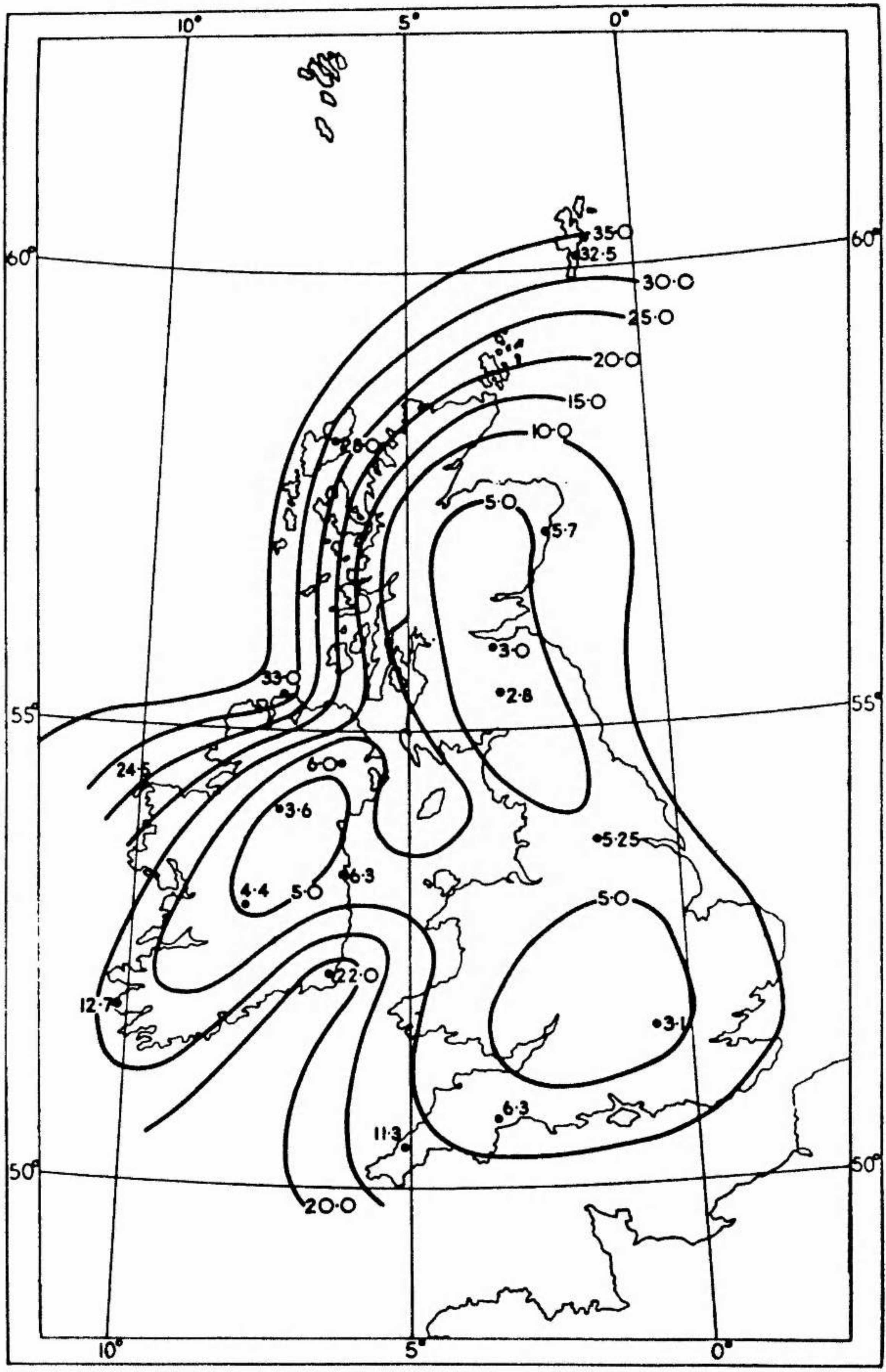


FIG 2:2 Annual Chloride Medians in Mg.l–1. Isopleths Drawn at 0.5 mg. l–1 Intervals. (Source Stevenson 1968)

Likens et al (1977) attribute only part of the Ca^{2+} and K^+ in precipitation to marine salts and the 'excess' of these elements being assigned to unknown "continental sources". Such ions may also be transported in a dry state. From work undertaken in northern Britain, Allen et al (1968) indicate areal differences in calcium which reflect agricultural liming activities. Cryer (1976) also reports for a site in mid-Wales calcium concentrations in excess of maritime precipitation inputs, although the inputs of all other major ions are closely related to seawater composition.

The influence of organic matter and volcanic emissions on atmospheric ions has received little attention in the literature and is relatively difficult to assess. The major component of organic input is likely to represent a local recycling of nutrients. Crisp (1966) argues that the loss of animal material such as insects carried out of the area by wind are balanced by a similar movement into the area from adjacent areas, the implication being that this input is in a steady state. The influence of volcanic emissions on the atmospheric supply of ions will be somewhat spasmodic. Gorham (1961) proposes that volcanoes represent the major source of volatile elements of carbon, chlorine, sulphur and hydrochloric acid, hydrogen sulphide and sulphur oxides.

More recently the emphasis of atmospheric studies has been towards atmospheric pollution and its role with regards to harmful effects on ecosystems. From a factorial analysis of 4 years data, Mohn et al (1980) report that seawater spray, the rate of chemical weathering and the rate of deposition of strong-acids (of anthropogenic origin) determine the composition of lakes in Norway. The major atmospheric pollutants of concern are those which lead to the formation of acid deposition.

Water evaporated from water bodies and plants (evapotranspiration) condenses on hygroscopic nuclei in higher levels of the atmosphere. Atmospheric CO_2, being slightly soluble, combines with this water to form carbonic acid; which in turn dissocites yielding H^+ and HCO^-_3. This process gives a natural atmospheric background acidity of 2.5 μeq. $H^+ \ l^{-1}$ (pH 5.6). Acid deposition is then considered to be precipitation with a higher acidity than 2.5 $H^+ \ l^{-1}$. However Charleson and Rodhe (1982) argue that rainwater acidities greater than this could be due to naturally occurring acids from the air caused by natural variability in the cycling of sulphur. Invoking these processes the authors argue that rainwater acidities can range by a factor of 5 regardless of man's activities. An extreme example of this is provided by Havas and Hutchinsons' (1983) work where the spontaneous burning of bituminous shales in the Canadian high Arctic produces high levels of SO_2 and rainstorms of 10000 μeq. $H^+ \ l^{-1}$ (pH 2.0) have been recorded. Consequently a 'natural' acidity of 2.5 μeq. $H^+ \ l^{-1}$ may not be a totally appropriate reference value. Vermeulen (1980) has shown from work on the atmospheric composition over the Netherlands that 80-100% of the acids in precipitation are attributable to sulphuric and nitric acids. Similarly Likens et al (1979), Likens and Bormann (1974), Fowler et al (1982) and Galloway et al (1980) attribute precipitation acidity to a combination of sulphuric and nitric acids. Overrein et al (1981), Fowler et al (1982) and Barrett et al (1984) have also suggested that the relative contribution to precipitation acidity is 30% and 70% for nitric and sulphuric acids respectively. Inevitably these authors suggest there is a close association between a region's energy consumption and atmospheric levels of these pollutants, in areas where fossil fuels are an important energy source. Vermeulen (1980) uses regression analysis to determine the effects of SO_2 and NO_x emissions on precipitation quality. Whilst there are various limiting assumptions, the tentative results show that for the Netherlands a pronounced relationship exists between total national emissions of SO_2 and acidification. Likens et al (1976) similarly suggest that during the period 1964-1974 all cations except H^+ in the precipitation at Hubbard Brook (New England) decreased, implying a loss of neutralising capacity within the precipitation.

Whilst the highest concentrations of acid in precipitation still exist around regional anthropogenic sources, there is an increasingly large area remote from these sources which are recipients of acid precipitation. The OECD findings on the long-range transport of air pollutants (reported by Ottar 1976) confirm the existence of large scale transport of SO_2 and indicates that the high concentrations observed with southerly winds over Scandinavia are not due to local sources. These levels, whilst not as high as concentrations in industrialised areas, are 10 times average concentrations and substantially influence precipitation chemistry. A similar situation is reported by Likens and Bormann (1974) for the U.S.A where remote rural sites have consistently high acidity precipitation due to the presence of these acids.

Stensland (1980) proposes that the building of higher chimney stacks has lead to a larger area being affected by atmospheric pollutants. Similarly Likens et al (1979) cite the increasing height of chimney stacks as relieving local problems but in turn creating larger regional scale problems. This situation has lead to rain over the eastern U.S.A and western Europe changing from a neutral like solution to the present solution of dilute sulphuric and nitric acids.

Hornbeck et al (1976) describe a seasonal variation in the precipitation quantity and quality of Hubbard Brook, in which summer precipitation is more acidic than that in winter (summer 102 µeq. $H^+ l^{-1}$ compared to winter concentrations of 40 µeq. $H^+ l^{-1}$). These seasonal differences are ascribed by the authors to changes in circulation and emissions of SO_2 affecting sulphur depositions. Barrett et al (1983) show sulphate levels and acidity in precipitation over northern Britain to have a clear Spring maxima and acidity of similar magnitude reported elsewhere, (Granat 1978, Joranger et al 1980 cited by Barrett et al 1983).

The report by Barrett et al (1983) is the most comprehensive assessment of the acidity of precipitation in the United Kingdom. The report shows that for northern Britain the weighted mean acidity of precipitation is least in the N.W. of Scotland (c.20 µeq. $H^+ l^{-1}$) and greatest in S.E. Scotland/N.E England (c.60 µeq. $H^+ l^{-1}$). The 'acidity' gradient is better illustrated and is reproduced in fig. 2:3. This gradient has also been described by Fowler et al (1982), in which the gradient is described by an empirical relationship of the form:

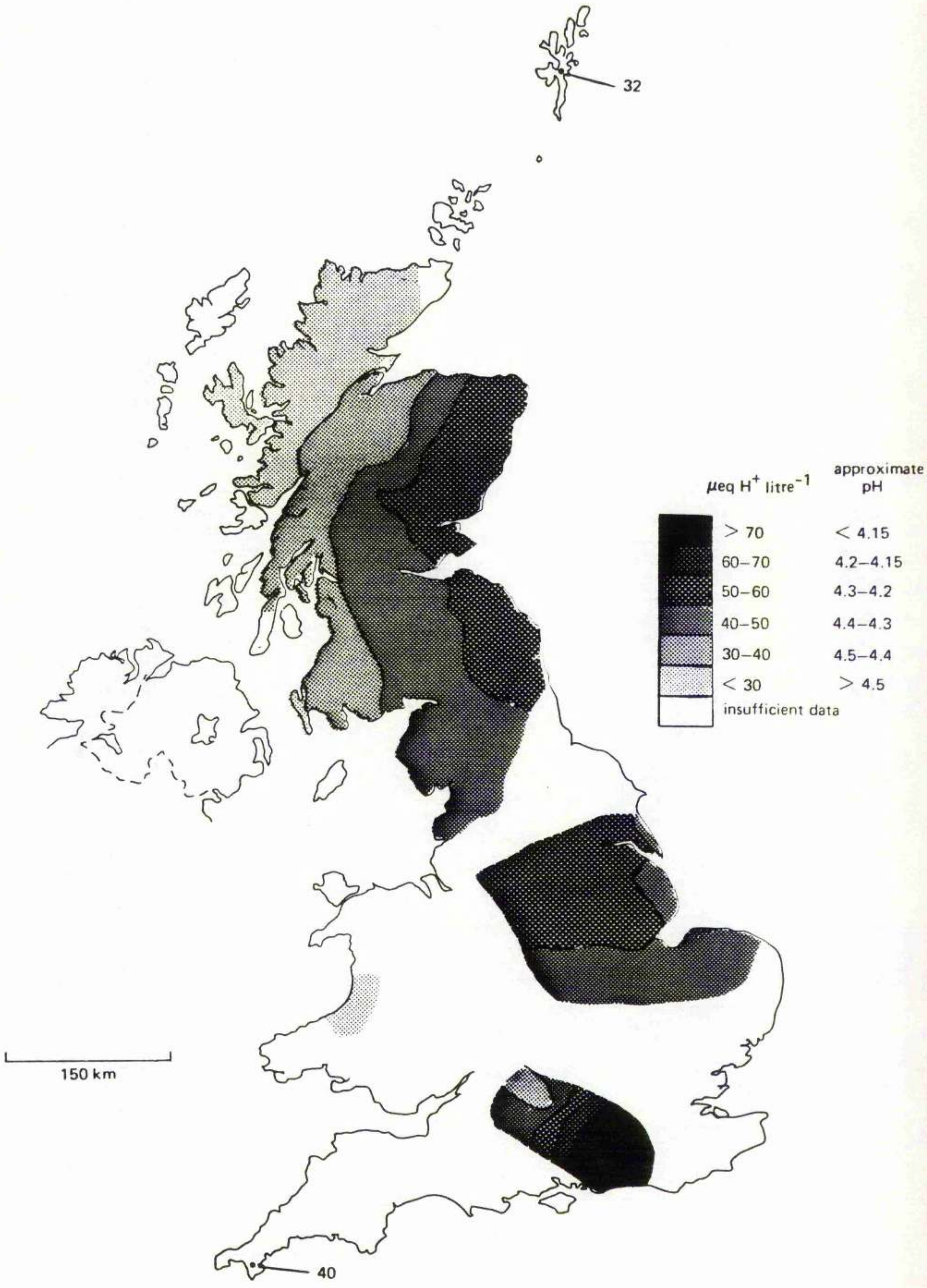


FIG 2:3 Rainfall Weighted Annual Average Hydrogen Ion Concentrations.

(Source Barrett et al 1983)

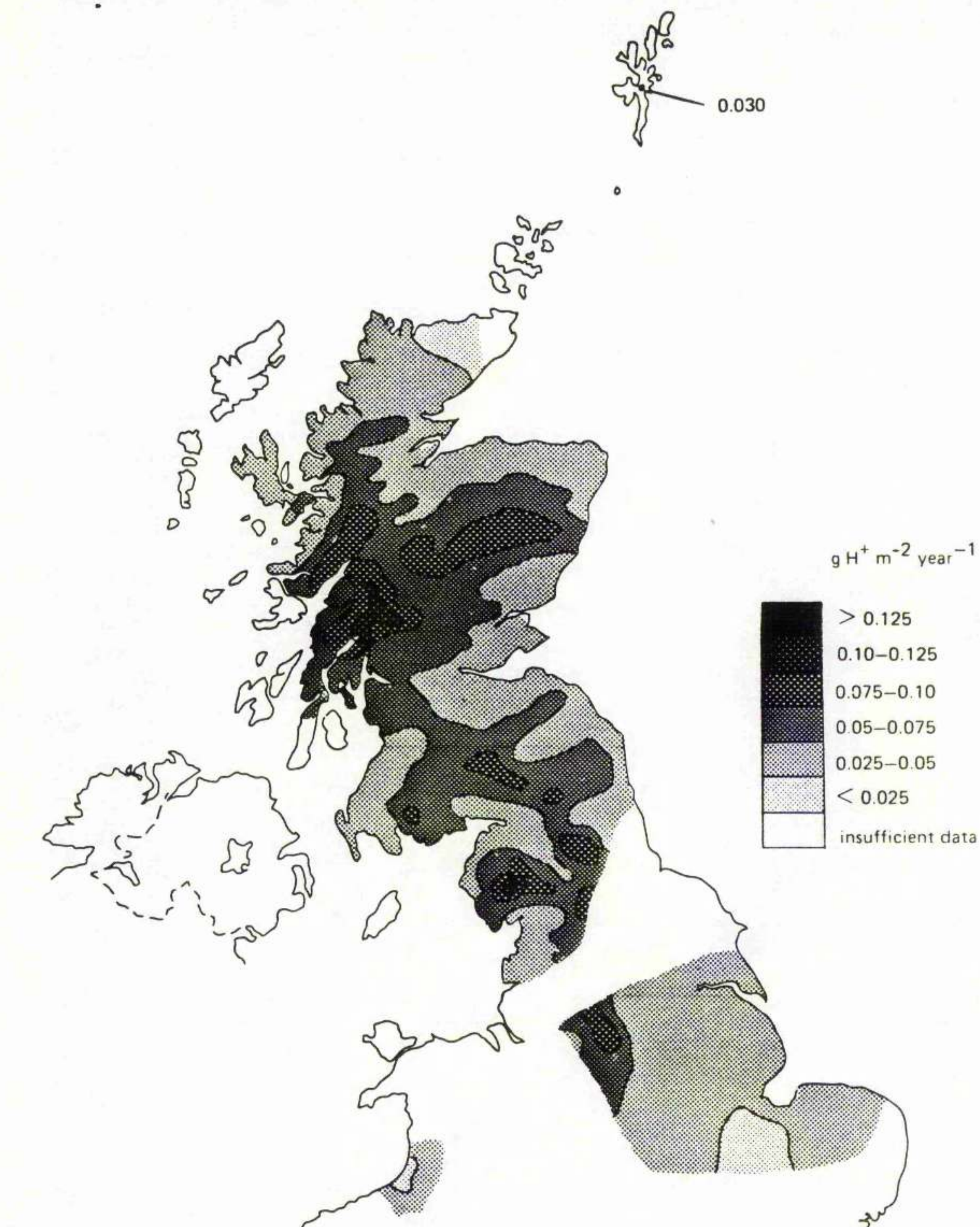


FIG 2:4 Deposited Acidity

(Source Barrett et al 1983)

$$H^{+}\mu eq.l^{-1} = 3.8\times10^{-6}\ E^{2}+7.05\times10^{-7}E.N$$
$$-3.16\times10^{-6}N^{2}-1.06\times10^{-2}E$$
$$+4.32\times10^{-2}N-118.$$

Where N and E are four figure northings and eastings from United Kingdom Ordnance Survey maps. This equation accounts for 94% of the variability in acidity over northern Britain (Fowler et al 1982).

Barrett et al (1983) further describe wet deposited acidity obtained by multiplying the regional acidity by the average (yearly) rainfall amount. The result, shown in fig. 2:4, shows wet deposition to be in the range 0.025 to 0.075 g m^{-2} $yr.^{-1}$ for central and eastern areas; whilst deposition on the high ground in the west is larger by a factor of 2 to 3. The areas of highest acidity inputs are the Lake District, S.W Scotland and the west Central Highlands. Due to the fewer measurements the results presented for dry deposition are rather more speculative but they provide a provisional base-line. For the remote sites of northern Britain the authors indicate that a contribution to total acidity by SO_2 up to 40% may be appropriate; whilst in the dryer south and east of England dry deposited acidity may exceed wet deposited acidity by a factor of 3.

Having identified the various sources of ions in the atmosphere it is necessary to review the processes governing their precipitation and removal.

2:2:1:2 Mechanisms of deposition.

The mechanisms of removing ions from the atmosphere are of three basic types: (i) Wet deposition which includes the ions reaching the earth's surface in precipitation; (ii) Dry deposition which is the term used to encompass the processes of absorption and impaction of gaseous and particulate matter and (iii) Occult deposition. The distinction between the first two mechanisms is based on collection procedures. Whitehead and Feth (1964) distinguish samples which are collected between rainfall events (representing dry deposition) from precipitation where ions are in solution (wet deposition). The third deposition, that of occult precipitation, is caused by the interception of water droplets from wind driven cloud on exposed vegetation (Dolland et al 1983).

The processes of dry deposition are described in detail by Fowler (1980). They are most significant in terms of total deposition close to their source and tend to decrease in importance with distance away from their source as an increasing contribution is supplied by wet deposition. The individual mechanisms of dry deposition are dominated by gaseous absorption and particulate impact on natural surfaces. Fowler (1980) also identifies the role of surface resistance and chemical affinity. In an earlier paper by Fox (1976) the rate of dry deposition is viewed as a function of the sorbing capacity of the recipient surface, the amount of particulate matter and concentration gradient of the gas. Barrett et al (1983) indicate that annual dry depositions can be estimated considering 2 stages (i) atmospheric transport and (ii) uptake at the surface. The rates of atmospheric transport will be governed by particle roughness, wind velocity and vertical gradients in the air temperature; Whilst the rate of uptake at a surface will depend on the deposition velocity which in turn will depend on the land-use of an area and its associated canopy resistance (Fowler 1984).

The processes of wet deposition have also been described by Fowler (1980). He distinguishes between those ions reaching the earth's surface in solution which may have been collected by rain droplets before they begin their descent (collectively called 'rainout') from those processes that remove gaseous and particulate matter by falling raindrops (collectively known as 'washout'). The processes of wet deposition are common to the various types of hydrometeor, however there are variations between the chemistries of these, attributable to the mechanism of their formation.

Gorham (1976) indicates that snow has a lower scavenging efficiency than rain and therefore the concentration of ions in snow will be less than rain. Contradictory to this is the occurrence of black acidic snow reported by Davies et al (1984) in the Cairngorm mountains. These authors attribute the high concentrations of deposited fly ash as a function of the efficient atmospheric scavenging of the snow. Vermeulen (1980) reports differences in acidities between drizzles (highly acidic) and rains (less acidic) and attributes this to contrasts in surface-area and wash-out efficiency. Similarly Skartveit (1981) reports a negative correlation between precipitation amount and concentration of ions.

Because of the difficulties in the separate collection of wet and dry deposition, total deposition is often collected and measured together by continuously open collectors. This bulking of wet and dry deposition is justified "as being the most significant fluid to study in evaluating contributions of atmospheric mineralisation to the chemical quality of natural water." (Whitehead and Feth 1964, p.3320). The problem of collecting bulk precipitation is one of representativeness. A continuously open collector, of the type used to collect bulk precipitation, collects both dry and wet deposition in unknown proportions (Likens et al 1977). Futhermore the amount of dry deposition may vary according to the type and shape of the precipitation collector. Sutcliffe et al (1982) report elevated levels of calcium and potassium on collectors fitted with a gauze plastic cover, this difference being attributed to increased dry deposition. Tervet (1976) working in the southern Grampians has also shown an increase in the ionic content of bulk precipitation following the addition of a filter to the collecting funnel. The author attributes this increase to dry fallout.

The significance of the proportion of dry deposition to total deposition will vary according to the amount of annual precipitation and the distance from the source of the dry deposition. Whitehead and Feth (1964) report that bulk precipitation (in California) is 4 to nearly 10 times higher in ionic concentration than in the rainwater. Junge and Gustatson (1957, cited in Whitehead and Feth 1964) also report from the more humid climate of Massachussetts that chloride concentrations were 25% higher in open collectors compared to 'wet-only' collectors.

Barrett and Irwin (1984) have shown that in large parts of England dry depositions of sulphur exceed inputs of wet deposition by a factor of 2 and only in the remote high rainfall areas of the north and west does wet deposition exceed dry deposition.

In upland areas occult deposition is likely to play a dominant role in atmospheric precipitation, particularly where vegetation is exposed to high wind speeds and substantial cloud immersion. Lovett et al (1982) and Barrett and Irwin (1984) cite the significant role of coniferous vegetation in the capture of occult precipitation in upland areas. The composition of occult precipitation has been found by Lovett et al (1982) to be highly variable both within and between cloud events. This variability reflects the stage of raindrop development at the time of impaction. Dolland et al (1983) suggest that as water vapour condenses on hygroscopic nuclei within clouds, the ionic concentrations are higher than in raindrops where water droplet growth and dilution have taken place. A major obstacle in the assessment of the contribution of occult precipitation to total atmospheric deposition is the inability of conventional rain collectors to capture it. Dolland et al (1983, p.241) tentatively conclude that "the inclusion of occult deposition in assessing annual chemical deposition in areas prone to low cloud cover could increase wet deposition by up to 20%."

2:2:2 The Atmosphere-Vegetation Interface.

Only a small fraction of the total atmospheric deposition will fall directly on 'open' land surfaces and water bodies. The majority of ions deposited from the atmosphere will be deposited on a vegetational canopy. This canopy will modify the atmospheric inputs in a variety of ways according to the type of vegetation. This has already been noted in the factors affecting both dry and occult deposition (section 2:2:1:2).

Nutrients deposited on a forest canopy will be removed and transferred to the forest floor by throughfall and stemflow, the chemistries of which will be determined by the leachate of the vegetation and the incident precipitation. Hornung (1984) indicates precipitation chemistry will be modified by 3 main processes as it passes through vegetation:

(i) Increased concentration due to evaporation from the canopy.

(ii) The washing off of substances which have been deposited by dry and occult deposition.

(iii) The leaching of elements from the canopy.

Voigt (1980) comments that the degree of modification of atmospheric inputs will vary with the nature of the forest stand and storm intensity.

In upland areas exposed to strong winds the evaporation of water from vegetated surfaces can be quite significant. Newson (1984) suggests up to 50% of rainfall is evaporated directly from forest canopies in central Wales. For shorter vegetation evaporation losses will be less, Hornung (1984) indicating this to be in the order of 10% for heath and moorland communities. Madgewick and Ovington (1959) present results from S.E England which show a significant increase in the ions in rainwater below trees. This the authors attribute to the concentration of ions through evapotranspiration and the increased capture of aerosols. The increase of ions by vegetation capture is referred to as the 'filtering-effect' (Mayer and Ulrich 1974, cited by Miller and Miller 1980 p.33). The ability or efficiency of vegetation to filter ions from the atmosphere is dependant on:

(i) The transfer mechanism from the atmosphere to the vegetational surface and

(ii) the aerodynamics and surface characteristics of the vegetation.

For these reasons Miller and Miller (1980) suggest that increased filtering is closely associated with very fine drizzle and dry deposition onto wet surfaces. In verification of a throughfall model Clesceri and Vesudeven (1980) report preliminary results in which there was an increase in the concentration of ions in throughfall as a consequence of greater interception by coniferous than under deciduous forest.

In a comparative study by Mayer and Ulrich (1980) in the Solling forest, Germany, collectors above and below a Spruce compared to a Beech canopy show the filtering of the Spruce to be on average 150% of that of the Beech, with even greater increases for the nitrogen family. The Spruce canopy also showed higher $SO^{2-}4$ and H^+ concentrations which the authors attribute to the adsorption of SO_2 on the film of water coating pine needles and resulting in the oxidation of SO_2 to H_2SO_4. Miller (1984) however reports a decrease in acidity with throughfall as a result of H^+ exchange on the vegetational surfaces. The only case where Miller finds an increase in acidity with throughfall occurs with conifers deficent in Nitrogen which, following fertilization, revert to a decrease in acidity with throughfall. Carlisle et al (1966) report that there is an increase in potassium in throughfall which has a seasonal distribution with the highest concentrations occurring during the vegetative season. This seasonal difference in concentrations is determined in part by the leaching of elements from the canopy, although as Miller et al (1976) have noted there are problems in separating and quantifying the processes of crown leaching and wash down. Miller et al (1976) however propose a linear regression relationship between the concentration in gross rainfall and in net rainfall. Where the intercept crosses the net rainfall axis the concentration below the line is taken to estimate the amount of crown leaching. Using this technique Miller et al (1976) interpret the washdown of aerosols beneath a Corsican Pine in northern Scotland as accounting for between 30-60% of ion gain (above gross rainfall). Comparing coniferous species in Scotland Miller (1984) suggests throughfall to be more acidic below Scotts Pine than under Sitka

Spruce. Both Miller (1984) and Hornung (1984) indicate that the acidity of throughfall will be dependent on the age of the crop, with young crops being the least acidic. In a further study Eaton et al (1973) suggest that the amount of leaching from a vegetational canopy will be a function of the residence time of the precipitation on the leaf, the time of year and the species involved.

A more detailed investigation of the processes contributing to vegetation modification indicates differences between the processes of stemflow and throughfall. Newson (1984) proportions the amount of water reaching the ground as comprising 15-30% stemflow and 40-60% by throughfall (both as % of gross precipitation). Whilst this indicates that stemflow only represents a small proportion of the water, it can be important in qualtity terms. Miller (1984) attributes >50% of acidity reaching forest floors to be derived from stemflow. The increase in acidity seen in stemflow above that in the precipitation is not seen in throughfall (see above). Hornung (1984) postulates the difference between the chemistry of stemflow and throughfall may be due to a greater contact time and longer path length of stemflow.

Research on the effect of non-forest vegetation in modifying atmospheric inputs is sparse. Hornung (1984) reports the throughfall chemistry for bracken, gorse, heather, cotton grass and mat grass dominated communities. These data show an increase in the concentration of solutes above those reported for precipitation. Hornung also indicates that for unpolluted regions generally these communities will serve to decrease acidity, the exception being cotton grass in which acidity increases following throughfall. Work by Clymo (1984) on sphagnum dominated peat-bogs in the Pennines indicates that such sites show an increase in acidity particularly following drought conditions during the growing season. In this work Clymo stresses the importance of cation exchange processes.

The role of vegetation in modifying atmospheric inputs has been shown in the preceding section to depend on 4 factors:

(i) The type of atmospheric deposition (intensity,duration and frequency)
(ii) characteristics of the canopy
(iii) pathway through the canopy
(iv) and the time of year.

Once the precipitation has reached the ground, vegetational factors will combine with soil and geological considerations to determine the chemistry of percolating waters.

2:2:3 Modification of Atmospheric Inputs by Soil and Bedrock.

The composition of precipitation is modified by vegetation interception, but more extensive alteration in terms of its chemical composition often takes place in the soil. With an acidic input to a soil Gorham and McFee (1980) suggest 3 possible reactions:

(i) Neutralised
(ii) Cation exchange
(iii) Reaction with silicates.

The amount of alteration depends upon a soil's ability to buffer the inputs. Ulrich (1983) proposes that soils can be classified into 5 main groups each having a specific pH range:

(i)	Calcium Carbonate	pH> 8.0-6.2
(ii)	Silicate	6.2-5.0
(iii)	Cation Exchange	5.0-4.2
(iv)	Aluminium	4.2-2.8
(v)	Iron	3.8-2.4

Many upland catchments with soils in the silicate and cation exchange ranges have such slow weathering rates that the quantity and quality of precipitation can influence surface water quality (Harriman and Wells 1984). Both Seip (1980) and Hornung (1984) describe cation exchange as the most important influence on drainage water chemistry. The process of cation exchange involves an exchange of cations held on negatively charged sites on plant tissue and soil colloids, with cations in solution passing these sites. This process operates both rapidly and quantitatively according to the lime potential (Bache 1984). Webb (1980) suggests the process of cation exchange will tend to smooth and buffer short term changes in the concentration of particular cation species in surface waters. The major cations involved are Ca^{2+}, K^{+}, Na^{+}, NH^{+}_{4}, Mg^{2+}, Al^{3+}, and H^{+}. Wiklander (1975) emphasises the role of the sea-salt effect in creating an apparent acidification of the soil. This process operates when base cations percolate into the soil and come into contact with an ion exchange surface occupied by an H^{+} ion, exchange will occur releasing H^{+} and acidifying the drainage waters ('exchange acidity'). In the soil there is a corresponding adsorption of the salt cations, the net result being an increase in the base saturation of the soil. Wiklander further proposes that where there are high inputs of base cations such as sea-salts, the affect of acid deposition will be lessened. In strongly acid mineral soils Bache (1984) indicates Al^{3+} occupies a large proportion of the soil exchange sites in which case the exchanging cations are H^+ from solution for Al^{3+} from the exchange sites. Whilst this is a neutralising reaction it also releases potentially toxic Al^{3+} into solution. It is this mechanism which gives rise to increased Al^{3+} leaching reported from areas receiving acidic inputs (Cronan and Schofield 1979). Hornung (1984) reports the dominant exchange in this process (in areas subject to acid deposition) is the replacement of base cations, particularly calcium and magnesium held on clay and organic surfaces by H^+ from solution. This process neutralising some of the acidity in percolating waters commonly occurs in the British uplands.

Although cation exchange processes determine the relative proportion of each cation in the leaching solution, the amount of leaching is controlled by the availability of balancing anions. Harriman and Wells (1984) indicate the major inorganic anions in upland streams are Cl^-, NO^-_3 and SO^{2-}_4. In view of the role of these anions in governing the process of cation exchange it is necessary to review the factors governing their concentration within a catchment.

Chloride can be considered the most conservative anion derived from sea-salts and passing through soil profiles unchanged. The levels of chloride are thereby determined by atmospheric deposition of sea-salts. Skartveit (1981) describes episodes of sea-spray laden precipitation deposited on catchments in western Norway which have led through the process of cation exchange to acidification of runoff.

Sulphate is less conservative than the chloride ion being subject to adsorption and desorption processes. The two atmospheric sources of sulphate can be summarised as sea-salt and atmospheric pollution; whilst in the soil the oxidation of organic and inorganic sulphides can be leached during the first heavy autumnal rains. In Britain, Harriman and Wells (1984) indicate this process is infrequent and restricted to times of drought. Nevertheless the reduction in moisture associated with forest growth (Binns 1968) may increase this source of sulphate in areas of afforestation. The increased deposition of sulphate associated with acid deposition is often cited as the cause of the acidification of water bodies (eg. Seip 1980, Overrein et al 1981). This is the concept of a 'mobile anion' in which the importance of sulphate as a transporter of cations and the increased leaching of soil is emphasised.

Nitrate is the least conservative anion discussed here,this is due to its utilisation by vegetation. In upland areas nitrate is often in limited supply and thus plays a diminished role in terms of water quality during the growing season. However nitrate may play an important role in cation exchange throughout the year or during a storm in which it may be rapidly flushed from soils.

The second process governing soil-water chemistry is that of chemical weathering of the bedrock causing primary mineral decomposition. These reactions are much slower than those of cation exchange.

Chemical weathering results from the chemical reaction of minerals with air and water. The most important processes of chemical weathering are solution, oxidation and hydrolysis (Ollier 1984). Solution is usually the first stage of weathering its effectiveness being dependant on the amount of water passing and the solubility of the weathering surface. The oxidation of minerals in which atmospheric (or bacterial) oxygen reacts to produce oxides is most evident in iron which oxidise to give a characteristic red/yellow colour. Hydrolysis is the breaking down of minerals by H^+ and OH^- ions in percolating waters. This reaction will take place wherever a mineral is in contact with water. Ollier (1984) indicates that in all weathering reactions H^+ ions are of fundamental importance for 3 reasons:

(i) They are available from a large number of sources and increasing their concentration reduces the solubility of SiO_2 and Al_2O_3.

(ii) H^+ ions combine with OH^- ions (which increase during hydrolysis) thus removing them from the system allowing continued hydrolysis.

(iii) They readily replace other cations (cation exchange).

It is the products of these weathering reactions which give water with longer residence times (the baseflow component of streamflow, see section 2:2:4) a higher concentration of ions than the dilute storm runoff. Through these processes of weathering and reactions of mineral decomposition natural and anthropogenic acids are consumed so that even on granitic rocks calcium, magnesium and sodium salts are leached with bicarbonate in solutions of pH 6-7. However as Hornung (1984) notes the dissolution of aluminosilicates is very slow and frequently the contact time between drainage waters and mineral surfaces is not long enough for the reactions to reach equilibrium consequently not all the acid in percolating waters will be neutralised. The solution of carbonate minerals is much more rapid and may be important in offsetting the accelerated leaching from cation exchange sites as a result of acidic inputs.

As a soil develops and matures the more it will differ from its parent material. In humid temperate areas Krug and Frink (1983) argue that soils will be more acidic than their parent material. As weathering progresses the authors suggest that the rates of acid neutralisation, weathering and cation denudation decrease and acids accumulate giving rise to soil and water acidification. Krug and Frink (1983) also argue that the present day acidification of soils is a biological function generated from the biological oxidation of carbon, nitrogen and sulphur (see section 2:3).

2:2:4 Hydrological Processes Determining Stream Water Chemistry.

Vegetation, soil, geology and topography all interact to determine the routing of water through a catchment which in turn affects the chemistry of the effluent waters. the degree to which different routing produces different hydrochemistries in the streams will be determined by two factors:

(i) The contact time with the soil or rock and
(ii) the proportion of flow that takes different routes through the catchment.

(After Bache 1984 p.401)

If runoff reaches a stream channel within 24 hours, it causes a high rate of discharge in the stream and is usually classified as 'storm runoff' or 'direct runoff'. Water that percolates to groundwater at much lower velocities by longer paths and reaches the stream slowly over longer periods is usually termed 'baseflow' (Dunne and Leopold 1978).

Both the pattern of flow and the chemistry of a stream will depend to a large extent on the spatial and temporal distribution of different hydraulic conductivities and soil porosities. Water derived from the surface horizons will be different to water which has percolated into deeper soil horizons. Bache (1984) intimates that water transferred rapidly through the soil by a system of macropores or pipes may not reach chemical equilibrium. Whilst Hornung (1984) reports for a catchment in mid-Wales that waters draining from macropores and ephemeral pipes are consistently more acidic than fine-pore waters. Trudgill et al (1984) and Gallie and Slaymaker (1984) also indicate that a short residence time will lead to limited solution and that soil structure and rainfall intensity may combine to encourage the dominance of rapid flow. If rapid flow is dominant the loss of rapidly soluble material occurs in preference to less soluble materials in the soil.

Classically, solute sources are divided according to residence time which has given rise to many two-component mixing models (eg. Pilgrim et al 1979, Collins 1979, Christophersen et al 1982). Pilgrim et al (1979) give the general form of a mixing model to describe streamwater solute concentrations as:

$$Q_t C_t = Q_1 C_1 + Q_2 C_2$$

In which Q is the discharge, C is the concentration of dissolved solids and 1, 2 and t are the separate flow components and total flow.

Reid et al (1981) provide indirect verification of this type of model in describing changes in water chemistry in Glendye, N.E Scotland. The authors report that flow concentrations are highest during baseflow when flow is dominated by water from the mineral soil. During storm runoff solutes reach a minimum shortly after peak dicharge which the authors interpret as flow dominated by water draining the upper organic and organo-mineral horizon. Harriman and Morrison (1980, 1982) also report from work in central Scotland that stream acidity is especially high after prolonged rainfall when the proportion of surface runoff is high. Similarly Skartveit (1981) working in western Norway indicates that during floods surface runoff is predominantly through the organic rich top-soil which yields acid runoff following ion exchange with the soil. During low runoff, on the other hand, interflow and groundwater seepage prevail. More recently Newson (1984) argues that this two-component mixing model (i.e. shallow water has a rapid transit through the soil and deep water has a slow passage) is too simplistic for the description of upland areas. He suggests that the hydrology of slopes is dominated by soil pipes and flushes. Lewin et al (1974) from work in mid Wales also observe that pipe flow is capable of both rapid response to rainfall inputs and of maintaining flow during prolonged dry spells. The significance of pipe flow is further considered by Bache (1984) who indicates very little chemical interaction will occur with water during pipe flow.

However, pipeflow is only one type of throughflow. Williams et al (1984) consider 4 distinct types of interflow components which are distinguishable on the basis of chemistry and frequency of occurrence. The deepest of these interflow pathways have the highest solute concentration because of the infrequent flows and long residence time of water through this system. In contrast the pathway nearest the surface has the lowest chemical concentration because of the greater frequency of occurrence and the increased volume of flow.

Burt (1979) indicates that throughflow has a near constant concentration of solutes in which there is no dilution during storms. This, the author attributes to infiltrating rainwater acquiring a dissolved load to supply rapid throughflow. In contrast delayed throughflow is supplied by water from a sub-surface saturated wedge often creating a small rise in solute concentration in the stream. Walling (1974) and Walling and Foster (1975) similarly note stream solute loadings increase with the onset of storms and attribute this to the flushing of soluble residues which have accumulated in the soil during preceding dry periods. Where storms follow one another in rapid succession the authors show the magnitude of the flushing effect to be severely diminished. Overrein et al (1981) report that such a process is common in Scandinavia during the first Autumnal rains and may give rise to acidic flushes in streams.

A further potential hydrological pathway that must be considered in upland areas is that associated with snowpack hydrology. Johannessen et al (1980) propose 3 stages of snowmelt which affect water chemistry. The first effluent from a melting snowpack is highly enriched due to the pressing out of older water stored in the catchment (analogous to the flushing effect). The second stage of snowmelt has a high acidity and a high concentration of solutes because of the preferential melting of snow enriched with chemical impurities. The third and final stage of snowmelt is dilution associated with a peak in discharge as the mass melting of ionically 'pure' snow progresses. The authors further suggest that following a snowmelt equivalent to 10% of the water present; 50% of the H^+ and SO^{2-}_4 are leached out. Dahl et al (1980) using radioactive tracers to calculate routing within a snowpack estimate that up to 90% of the total SO^{2-}_4 found in the meltwater arrives in the first 30% of snowmelt water. This differential melting of the snowpack gives rise to acidic flushes in streams and rivers fed by the snowpacks. In Scandinavia this phenomenon has been used to explain massive fish-kills during the

Spring acidic flushes (eg. Overrein et al 1981). However Rosvenqvist (1981) doubts this mechanism of ionic separation, suggesting instead that these acidic flushes are a result of the total mobile anion content of the snow, (further discussed in section 2:3).

In Britain the erratic pattern of snowfall eliminates extensive snowpack accumulation in all but the highest altitudes. The only documentation on acidic snowmelt flushes is from the Cairngorms reported by Morris and Thomas (1985). These authors identify 2 paths in flow routing from the snowpack. The first is a 'slow' path in which travel time is lengthy and there is little ionic variation in the water. The second pathway is described as 'fast' and along which snow impurities are washed out. Consequently this pathway shows a significant variation in ionic concentration.

Variations in hydrochemistry are also reported as a function of land-use in upland-areas. Harriman and Morrison (1982) indicate that the retention time of drainage water is dramatically reduced by modern ploughing techniques prior to the planting of conifers. Furthermore as the rooting system of the trees matures water will be channeled along preferential routeways reducing the amount of mixing within the soil matrix. Newson (1984) reports that flow routing through a forest peat will not neutralise incoming acidity but rather the reverse.

The above section has illustrated the potential variation in hydrological pathways within a catchment. It must, however, be appreciated that for any given catchment only a relatively small number of hydrological routes and sources will be important (Christophersen et al (1982), Skartveit (1981) and Bache (1984)).

2:3 A REGIONAL ASSESSMENT OF ACIDIFICATION IN UPLAND BRITAIN.

The intention of this section is to review work on acidification undertaken in Britain. A broader coverage of continental scale acidification is given by Oden (1976), Wright and Gjessing (1976), Beamish (1976) and Overrein et al (1981).

The earlier sections of this review have shown the importance of considering atmospheric deposition in addition to vegetational, geological and hydrological factors in determining an areas ability to buffer changes in surface water chemistry and particularly acidity. The relative importance of each of these is, however, a subject of considerable debate. Thus both Krug and Frink (1983) and Rosvenqvist (1985) argue that the role of acid deposition is negligible in the regional acidification of surface waters. These authors stress the importance of soil acidity in acidifying runoff particularly as related to changing land-use. Rosenqvist (1984) proposes that the large scale regeneration of forests and the reversion of land to acid heath produces large areas of increasingly acid soils, which in turn are acidifying the runoff. Krug and Frink (1983) similarly argue that aggrading vegetation results in net cation uptake and contributes to soil acidity. Bache (1984) notes that whilst natural forest growth leads to the production of acidity due to excess uptake of base cations, this is balanced by the neutralising processes resulting from the mineralisation of the organic litter layer. However, where clearfelling is practised this will disrupt the cycle giving rise to soil acidification.

In contrast to these ideas in results from Moor House (Cumbria) Gorham (1956) suggests that dilute upland waters exhibit similar ionic concentrations to those in rainfall. From this he goes on to imply that these waters derive their ions almost entirely from atmospheric deposition. This dependence on atmospheric deposition has given rise to the concern over water quality in areas characterised by a geologic environment that is resistant to chemical weathering. Areas particularly sensitive to atmospheric inputs have been identified by Likens et al (1979) as areas underlain by highly siliceous types of bedrock. Henricksen (1980) suggests the factors common to these areas will be a granitic or siliceous bedrock, thin and patchy soils with soft and poorly buffered surface waters. Henricksen goes on to suggest that the acidification of these areas is the result of a large scale acid-base titration; bases that have been set free by the weathering of primary rock are titrated with acids that are deposited from the atmosphere. Similarly he proposes an acidity transition of lake watersheds above which, in lakes dominated by bicarbonate the geology of the watershed controls the water chemistry regardless of the precipitation acidity. Below the transition in sulphate dominated acid lakes precipitation quality will dominate the water chemistry. Fig 2:5 summarises the areas in Europe that have been identified as sensitive to atmospheric inputs of acidity. The largest areas are those of highly

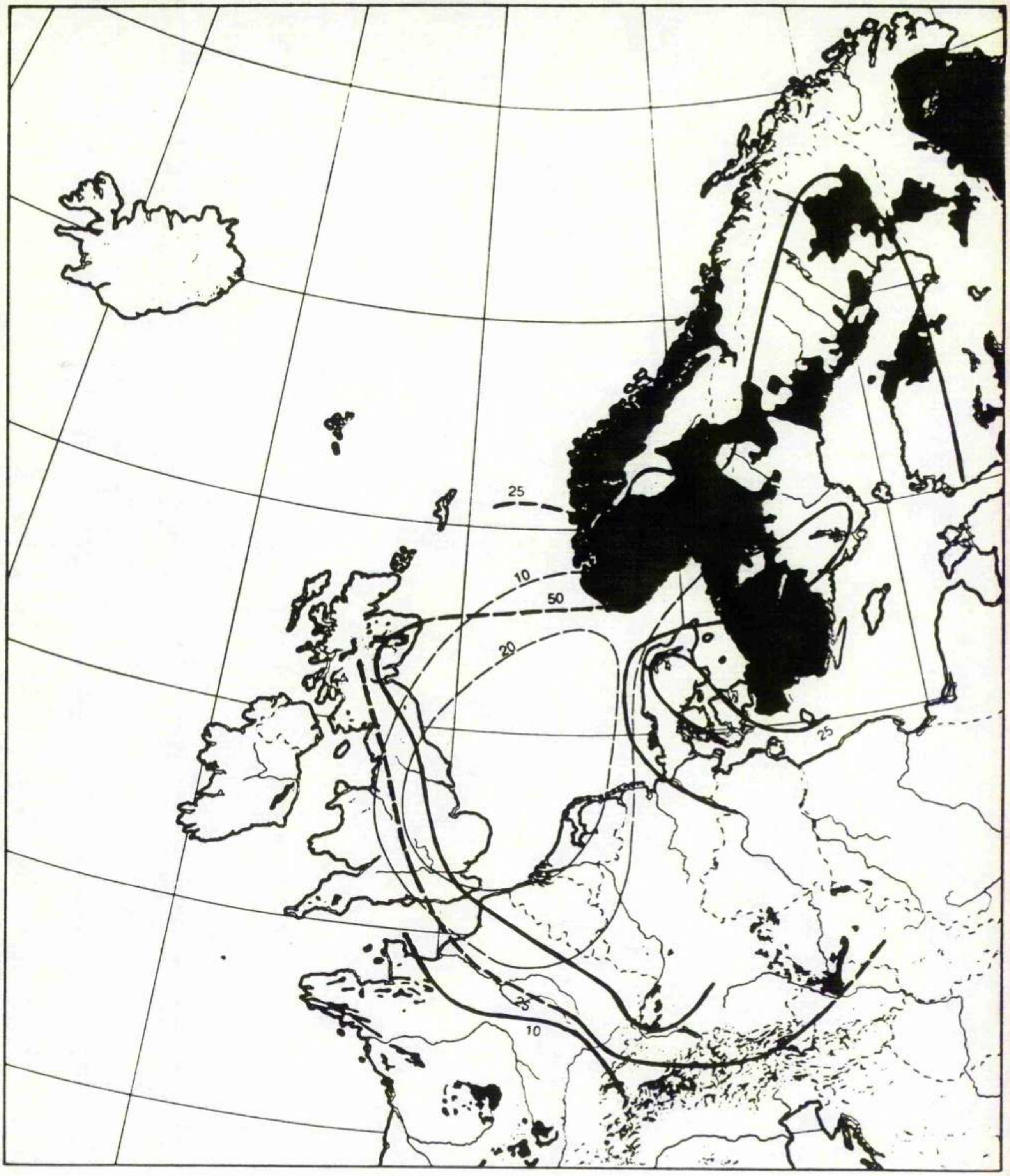


Fig. 2:5 Acid Precipitation in North-Western Europe, Comparing 1956 (thin isolines) and 1974 (thick isolines) Data

Acidity is shown by the numbers on the curving isolines. The two sets of isoline nos. are based on volume weighted, average concentrations of H^+ ions (μeq l^{-1}) of precipitation. The coloured areas of the map indicate areas that are most susceptible to acid rain because of the geology of their bedrock. In general, they are areas with highly siliceous types of bedrock.

(Source : Likens et al., 1979)

siliceous bedrock of the Precambrian shield areas.

Fundamental to assessing trends in surface water acidification is the availability of long-term records of suitable quality. However in Britain these records are at best piecemeal. Nevertheless, the following summary can be assembled from an increasing number of localised studies.

Work in mid Wales by both the Institute of Hydrology and the Welsh Water Authority have identified short-term acidification of upland streams. Newson (1984) reports the short-term acidification of streams at Plynlimon to be dramatic following rainy-periods. Newson also notes that such acidification is more marked in forested catchments. Gee and Stoner (1984) identify the area of slow weathering rocks of the Cambrian, Ordovician and Silurian series in the area surrounding Cardigan Bay as particularly vulnerable to acidification. These authors propose that water quality in this area is largely governed by land-use and the ability to buffer acidity. Using water hardness as a measure of the ability of streams to neutralise acidity the authors identify 3 groups of stream in mid-Wales:

(i) Hardness >10 $Mg.l^{-1}$
(ii) Hardness 8-10 $Mg.l^{-1}$
(iii) Hardness <8 $Mg.l^{-1}$

Such a classification allows the preliminary identification of those streams most vulnerable to acidification. Within each group, Stoner and Gee report poorer water to be exaggerated by coniferous afforestation. Both Newson (1984) and Gee and Stoner

(1984) suggest that streams in mid-Wales exhibit improved water quality conditions during the summer in association with low flows.

Acidification in upland catchments of the English Lake District is discussed by Pennington (1984). Pennington argues that natural processes have acidified much of the upland area of southern Cumbria before any possible impact of the burning of fossil fuels. Progressive acidification in this region is dated as commencing 5000 years ago. The processes involved are proposed as:

(i) The removal of basic ions from the soil by the rainfall, the rate of which increased after the removal of primary (deciduous) forest by man.

(ii) Acidification of soils and water by decomposition of Calluna and related plants which replaced the trees.

(iii) Further acidification by the natural accumulation of peat with associated impeded drainage and the proliferation of acid generating Sphagnum swamps.

These 3 processes are cited by Pennington as the cause of acidification in upland areas where the former habitat of deciduous forest has been subject to 5 millennia of land-use change by man.

The chemical composition of surface waters in the Lake District is reported by Sutcliffe et al (1982) who compare samples taken during the period 1953-56 and 1974-76. Using these data sets plus additional spot samples the authors arrive at the conclusion there has been no increase in acidity or lowering of alkalinity in the major surface waters of the Lake District over the last 50 years. However the work is centred on large catchments (eg. Windermere, Buttermere) which have a large range of lithologies and are subject to various land-uses and interferences from man (eg. liming of agricultural land) Batterbee (1984) also indicates that the study by Sutcliffe et al (1982) is based on a relatively short time base in which chemical records are unlikely to show a significant change, (compared with the long history and slow rate of acidifiction in Scotland).

A regional survey of 72 lochs in the Galloway region of Scotland by Wright et al (1980) indicates that the acidified lakes of the area have SO^{2-}_4 as the major anion, typically low calcium concentrations and are mostly located on granitic bedrock. The occurrence of these lakes is both above and below areas affected by afforestation. The authors conclude that whilst afforestation may affect the ionic composition of freshwaters, on a regional basis these variations are masked by precipitation chemistry, catchment geology and soils.

The comparative study of streams draining forested and moorland areas in the Loch Ard area of Scotland by Harriman and Morrison (1982) concludes that all streams are acidified by acid precipitation; However under low flow conditions the moorland streams achieved a non-acidified status (according to Henriksens' indicator diagram), whereas forest streams are permanently acidified. This difference is attributable to crown leaching, nutrient uptake, diminished retention time of drainage waters and greater atmospheric filtering in the forested catchments.

Fishery records are also used to provide an indication of the deterioration of surface water quality. Harriman and Wells (1984) suggest that the decline and loss of fishstocks are associated with water of pH <5.0 ($H^+ > 10$ µeq l^{-1})in areas with a high loading of acid pollutants. Using these criteria the authors document four lochs (Enoch, Arron, Narroch and Fleet) in the Galloway region which when netted during 1979-1980 failed to yield any fish. Prior to 1940 and 1970 respectively Loch Enoch and Loch Fleet are known to have had indigenous trout populations.

The singular most unambigous evidence for the acidification of lakes in Britain is the work by Flower and Batterbee (1983) and Batterbee (1984) on diatom assemblages. Changing acidity of the lakes is indirectly inferred from changes in the diatom assemblages from older sediments rich in alkaliphilous and alkalibiontic to more recent sediments rich in acidophilous and acidobiontic diatoms. The sediments are dated using isotopic ^{210}Pb methods. This work has been centred on the Lochs of Galloway, S.W. Scotland where, using these diatom techniques, the authors show a marked acidification trend in recent sediments . These results are reproduced in table 2:1. A decrease in lake pH of between 1.2 and 0.5 pH units is identified although this is subject to a standard error in the region of $^+-$ 0.25-0.5 pH units. Batterbee (1984) concludes from this work that natural acidification cannot be regarded as the major cause of observed recent acidification in Britain although the author recognises the difficulties in identifying the possible effects of land-use change. In Scotland the major land-use change has been increased afforestation in upland areas. The diatom data presented by

	Altitude m	Percentage afforestation	Date of planting	Date of acidification
Loch Enoch	493	0	--	1840
Round Loch of Glenhead	299	0	--	1850
Loch Grannoch	210	69.5	1962, 1976	1925
Loch Dee	225	20.8	1976	1890
	Pre-acidification pH	Modern pH (predicted)	Modern pH (ob) (observed)	pH decline
Loch Enoch	5.2	4.3	4.4 - 4.7	0.9
Round Loch of Glenhead	5.7	4.7	4.5 - 5.0	1.0
Loch Grannoch	5.6	4.4	4.4 - 4.9	1.2
Loch Dee	6.1	5.6	4.9 - 5.9	0.5

TABLE 2:1 Acidification Data for Galloway Based on pH Reconstruction and ^{210}Pb Dating.

(Source Batterbee, 1984)

Batterbee (1984) (table 2:1) show that lakes with non-forested catchments have been acidified. In the light of this Flower and Batterbee (1983) suggest that as forested lakes were acidified prior to afforestation, afforestation cannot be regarded as a primary or sole cause of surface water acidification. Batterbee (1984 p.) finally concludes that "......the temporal and spatial patterns of acidification within N.W Europe are consistent with the hypothesis that acid precipitation is the major cause of recent acidification of lakes so far studied."

CHAPTER 3 : LOCH DEE: A MULTIPLE CATCHMENT STUDY.

3:1 INTRODUCTION.

In formulating one's aims and objectives for a particular study it is pertinent to consider the appropriate scale of enquiry needed to meet the aims and objectives of that study. Failure to consider such a matter may lead to a totally inappropriate scale and/or experimental design to one's research.

In hydrological and hydrochemical research investigation ranges from small lysimeter and experimental plots to large scale watershed studies, small watersheds forming part of this continuum. Ward (1971 p.7) defines small experimental watersheds as ".... a small carefully selected stream basin which has been instrumented for a specific hydrological or other investigation and in which calculated environmental changes may or may not be introduced during the period of study". The justification for the use of such experimental catchments or watersheds is also discussed in detail by Ward (1971); the use of which in understanding chemical, hydrological and whole ecosystems is well established in the literature. The classic watershed study at Hubbard Brook, New England described by Likens et al (1977) provides an excellent example of how watersheds may be utilised to yield information about the relationships and internal functions of an ecosystem. Further work at Hubbard Brook described by

Bormann and Likens (1979) intimates the use of the watershed approach to assess biogeochemical budgets in which equations " relating dissolved substance and particulate matter concentrations to streamwater flux rates " (p.37) are used to predict nutrient output from stream discharge alone. In Britain the Institute of Hydrology's long term study at Plynlimon, mid-Wales has examined the hydrological characteristics of established forestry and rough pasture. One of the principal objectives of the study has been to compare the water balance of the pasture (in the Wye catchment) with that under forestry (the Severn catchment), Calder and Newson (1979). Results from 10 years of operation of the Plynlimon catchments reported by Calder and Newson (1979) indicate a mean difference in water loss from the catchments of 444mm, equivalent to 20% of the rainfall over the forested area; whilst runoff from the Wye is 83% of gross precipitation and that of the Severn 62%.

In 1979 a committee consisting of representatives from the SRPB, the Forestry Commission and the Department of Agriculture and Fisheries (Scotland) was established to initiate a combined research effort dealing with the possible effects of acid precipitation and afforestation on surface water ecology. The committee having decided the experimental watershed as the most appropriate scale of enquiry in isolating these factors, investigated several potential sites. Their selection was guided by the same basic criteria suggested by Ward (1971) p.12:

i. The area must be suitable for runoff measurement.

ii. The area must be clearly definable both topographically and in terms of subsurface flow in order to determine accurately the area of input precipitation and groundwater flow.

iii. There will have to be a range of aspects so that all types of exposure, insolation, precipitation and drainage conditions exist.

iv. The possibility of isolating tributary catchments within the experimental catchment must be present in order to quantify and compare a range of conditions (in this case land-use).

Also several 'non-scientific' criteria were considered:

i. Reasonable site accessibility to allow site maintainance and sample collection.

ii. The willingness of the land-owner (Forestry Commission) to cooperate with the research organisations.

iii. A catchment size which would be easily managed and controlled.

After careful consideration of these criteria and the options available, the committee chose Loch Dee as the most suitable.

3:2:1 The Loch Dee Project.

In late 1979 the representatives forming the afore-mentioned committee (section 3:1) initiated the Loch Dee Project. The interested parties agreed upon 2 major objectives:

i. To assess the combined and individual effects of acid precipitation and coniferous afforestation on surface water ecology; and

ii. to improve the potential of Loch Dee as a trout fishery and develop a realistic management programme for future years.

In order to meet these objectives the three major catchments of the Loch Dee basin have been monitored to detect any differences between the catchments which are differentiated by their land-use and land management.

The following sub-sections describe both the general setting of Loch Dee and the details of each of the three major catchments.

3:2:2 Loch Dee, The General Setting.

Loch Dee is situated in the remote area of the Galloway Hills, S.W Scotland (N.G.R 470790). The study area consists of three major catchments flowing into the loch, the Dargall Lane to the west, the White Laggan with its tributary the Black Laggan to the south and the Green Burn to the south-east; these are shown in fig 3:1. The catchment area measures 15.6 km.^{2} of which the loch surface occupies 1.0 km.^{2} (Burns et al 1984). Catchment altitude across the study area ranges from 225m. at the loch shore to 716m. at the head of the Dargall Lane catchment. Nearly two thirds of the catchment is above 305m. The study area is typical of much of upland Scotland comprising part of a glaciated valley which has steep and rugged sides with a broad valley floor with accumulations of peat and glacial deposits.

The climate at Loch Dee is best described as cool and wet. Annual rainfall is 2200 mm. The rainfall is dominantly cyclonic associated with the predominant westerly winds with the passage of North Atlantic depressions over the Galloway Hills. Based on a daily mean temperature threshold of 6^{o}C. Burns et al (1984) propose that the growing season varies between 220 days at the

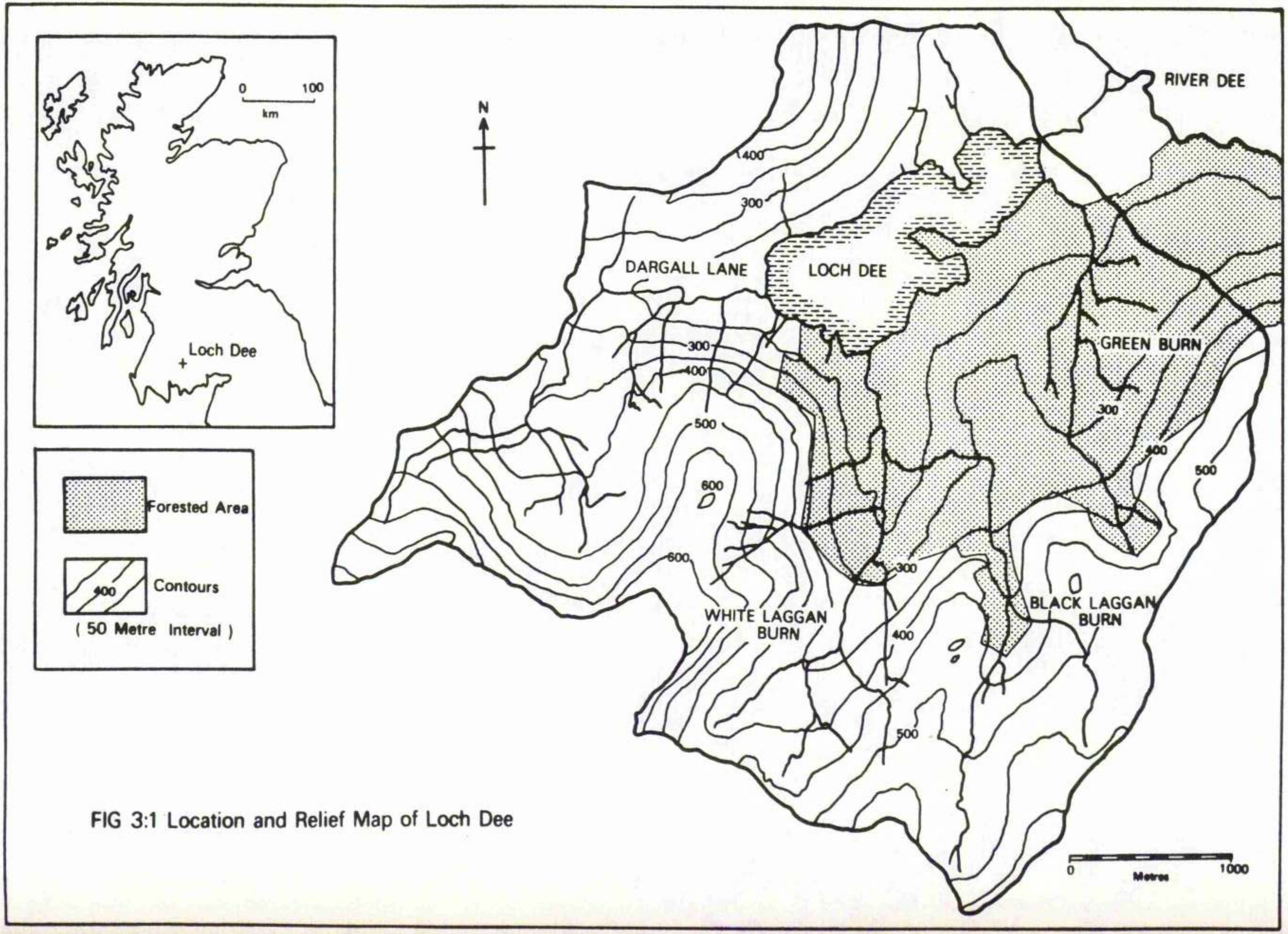


FIG 3:1 Location and Relief Map of Loch Dee

loch side to 150 days on the high ground.

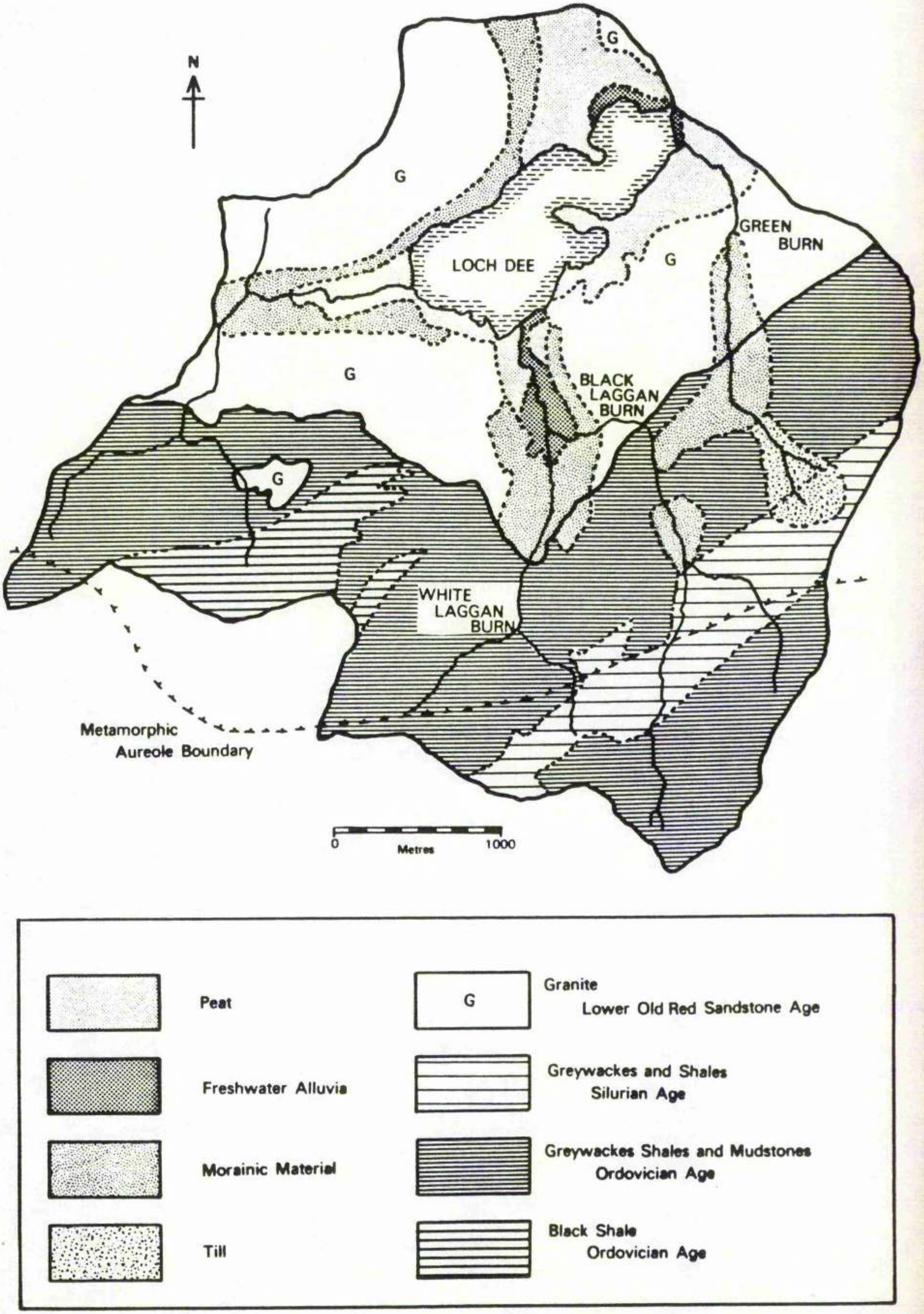
Work in the Loch Dee catchment for the period 1980-1982 reported by Burns et al (1984) suggest that if the sea-salt component of the bulk precipitation is removed from the ion chemistry sulphate is the largest remaining component. The authors also indicate that Loch Dee is transforming to a sulphate dominated system from a bicarbonate one. This conversion is typical of acidified surface waters in Scotland and other countries (Wright et al 1980).

The work reported in this particular study is confined to investigations undertaken in the three catchments, consideration of the loch is omitted. The three catchments lie in juxtaposition and are assumed to have the same meteorological input, the underlying geology is common to all three catchments in varying proportions and each catchment is readily definable

3:2:3 Solid Geology.

The area of Loch Dee is dominated by two rock-types sedimentary greywackes and shales of Ordovician and Silurian age which outcrop to the south of the area, and intrusive igneous rocks of late Silurian age outcropping predominantly in the lower areas to the north of the catchment. The distribution of these two rock types is show in fig 3:2. These igneous rocks are derived from the southern end of the Loch Doon igneous complex. Whilst in the geological survey the rocks are simply described as granite Brown et al (1979 p.746) describe the igneous rocks shown in fig 3:2 as "rapidly changing from a monzonite and monzodiorite

FIG 3:2 The Solid and Drift Geology of the Loch Dee Catchments



Source : Geological Survey of Great Britain Sheet 8E (1977)
Geological Survey of Scotland: Sheet 8 (1982)

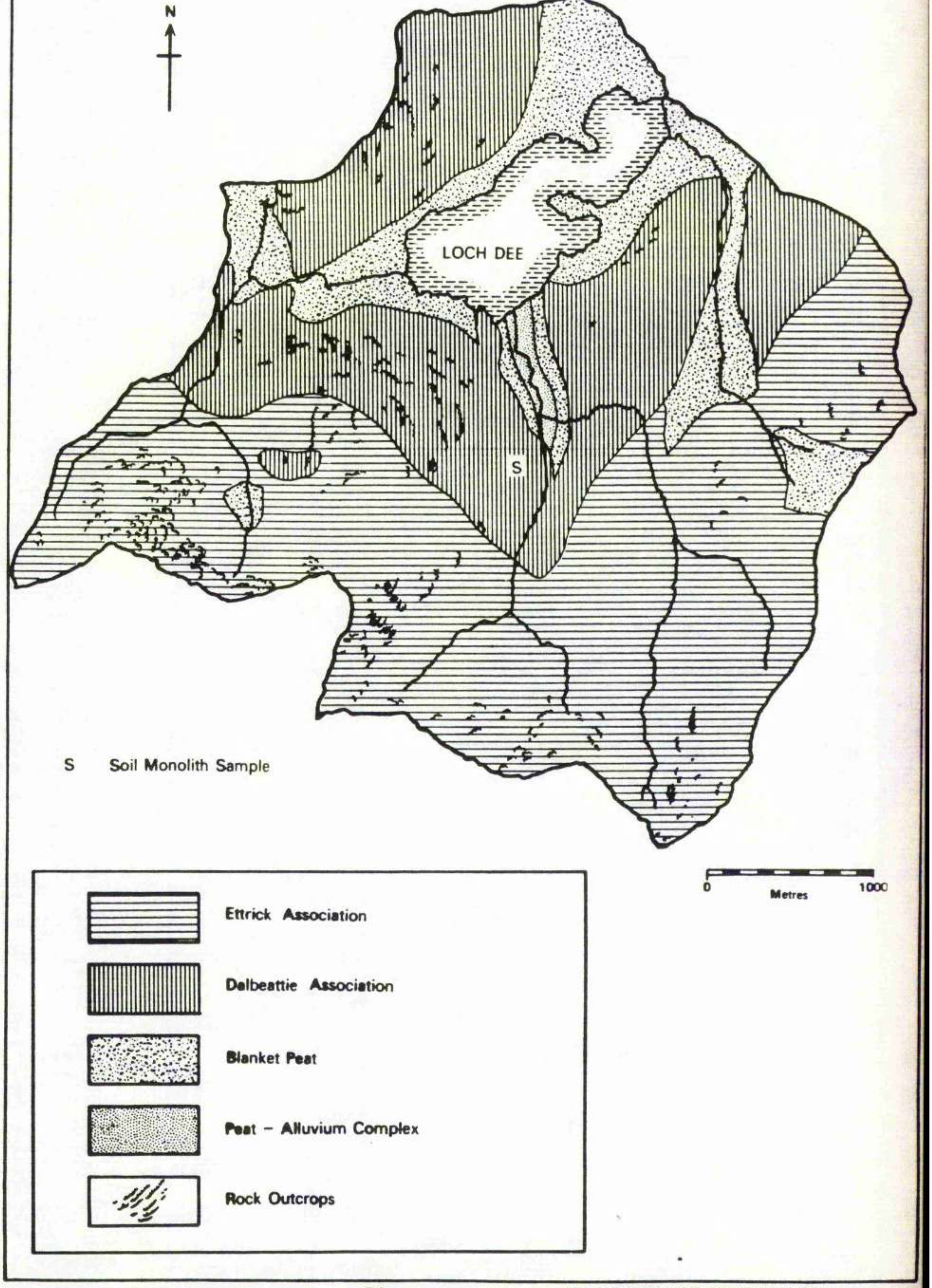
to hypersthene diorite over some 200m." This granitic type geology gives the catchments an impermeable substrate which in conjunction with the thin soils and steep upland slopes gives rise to a flashy runoff response.

3:2:4 Drift Geology and Soils.

The bedrock of the catchment area around Loch Dee is mantled by a drift cover of alluvium and peat around the loch margins. Surrounding the lower areas in each of the three catchments are substantial deposits of morainic material and till, the distribution of which is shown in fig 3:2. The soils of the catchment are dominated by climatic and basin peats which are particularly thick (>1m) in gently sloping areas. The soils on the lower slopes have some podzolic development although these soils are dominated by a peaty horizon.

Mapping of the Loch dee soils reported by Bown (1973) shows the soils to belong to two main associations, the Dalbeattie and Ettrick, shown in fig 3:3. It is the greywackes and shales of Ordovician and Silurian age which give rise to the parent material of the Ettrick association. Bown (1973) suggest these soils reflect a parent material of variable chemical composition from an acid igneous rock (granite) to that of an intermediate composition like andesite. The Ettrick soils also have a high content of glacial till and moraine which gives rise to some impeded drainage. The parent material of the Dalbeattie Association is derived from the granitic intrusions in the area (Loch Doon complex). Both parent materials have slow rates of chemical weathering and consequently the rate of chemical breakdown of

FIG 3:3 The Soils of Loch Dee



Source : Soil Survey of Scotland Sheet 8 (1968) fresh rock is slow. Fig. 3:3 shows the soil associations to be well developed across the study area, however, site evidence suggests that blanket peat is much more extensive in the higher parts of the catchments than is implied on the soil map. The soils described by Bown (1973) are those which developed pre-afforestation; with afforestation these soils have been greatly disturbed within the area of planting by the use of improved drainage techniques (section 3:3:4). Futhermore the simplicity of the soil pattern shown in fig. 3:3 is disrupted in some localities by soil complexes formed in the vicinity of rugged topography.

3:3:1 Vegetation, Land-use and Land Management.

Prior to afforestation in the Loch Dee basin the area formed part of an extensive hill farm supporting a limited sheep and cattle population. Tivy (1954) suggests that the moorland vegetation of the Southern Uplands was for the most part a sub-climax community, a biotic climax imposed by man and his grazing animals. Tivy (1954) also recognises sub-divisions of such a community due to differences in landform (particularly slope and drainage), altitude and climate. The habitats and associations described by Tivy (1954) and applicable to Loch Dee range from dry grass and heather moorland on the steeper well-drained slopes to bracken and molinia on the lower slopes. The till infill in the valley floors is dominated by peat and 'molinia flows'. Field observation suggests this is frequently the case. Bown (1973) describes the land capability classification of the area (prior to afforestation) as land classes 6 and 7 with very severe limitations restricting use to rough grazing and forestry. Local, more severe restrictions, exist with the steep slopes in the highest parts of the catchment and also the high peat content of the soils.

Between 1973 and 1975 the Forestry Commission initiated a planting programme of Sitka spruce (*Picea Sitchensis Carr*) and also small numbers of Lodgepole pine (*Pinus Contorta Loud*). However this change in land-use has been carried out on a systematic basis allowing a comparative study between the 3 major catchments at Loch Dee. The following sections describes each of the catchments, the land-use and land management each has been subject to since afforestation. A brief summary of each of the catchments is given in table 3:1.

3:3:2 Dargall lane.

The area of the Dargall Lane catchment to the gauging station is 2.1 km.^{2}. Much of this area was originally tributary to the Glenhead burn which runs into Loch Trool. However the stream has been diverted into the Dargall Lane probably in the 1930s' to boost the flow for the Galloway power scheme. The upper part of the catchment has a steep cliff-like surrounding, typical of corries. These steep surrounding slopes with a semi-enclosed floor give the catchment an armchair like shape. The corrie floor has a thick accumulation of peat which retains pools of standing water, some of which can be seen in plate I.

Catchment	Description	Area km^2	Gradient*	Afforestation	Major Vegetation Species	Treatment
Dargall Lane	Upper part of catchment forming steep sided corrie forming armchair hollow with thick accumulation of peat. Standing surface water in boggy hollows. Channel is incised into peat. Channel bed is armoured by rocks and boulders.	2.1	11.6°	0%	Sphagnum Calluna vulgaris Gramineae	Mar 1980 5 tonnes scallop shells at road bridge
White Laggan	Broad upper valley rock outcrops are common. Uppermost part of catchment - moor/rough pasture, lower area - forested, although incomplete canopy. Planted 1975. Channel cut in peat and alluvium in lower reaches. "Buffer zone" flanks major water course	5.7	10.4°	30%	In addition to above: Picea sitchensis Pinus contorta Buffer zone: Sorbus Salix Betula Alnus	Mar 1980 5T scallop shells at road bridge Oct 1980 5T " " " Mar 1981 58.2T limestone powder Oct 1981 20.4T limestone chips Jan 1982 19.6T Feb 1982 20.7T Apr 1983 56.5T limestone powder
Green Burn	Gently sloping catchment forested in all but highest altitudes. Planted 1973-75, canopy still incomplete. Catchment drainage dominated by forest drains. Some parts of channel in bedrock, otherwise in peat and alluvium.	2.5	7.2°	70%	Picea sitchensis Pinus contorta	Aug 1982 2,4D ester over 0.3 km^2 (Green Burn and Black Laggan) Sep 1982 PK fertiliser over 3.99 km^2 (Green Burn and Black Laggan See Fig. 3:3)

* Average gradient : Source Little (1985, p. 37)

T = metric tonnes

TABLE 3:1 Summary Detail of the Three Catchments

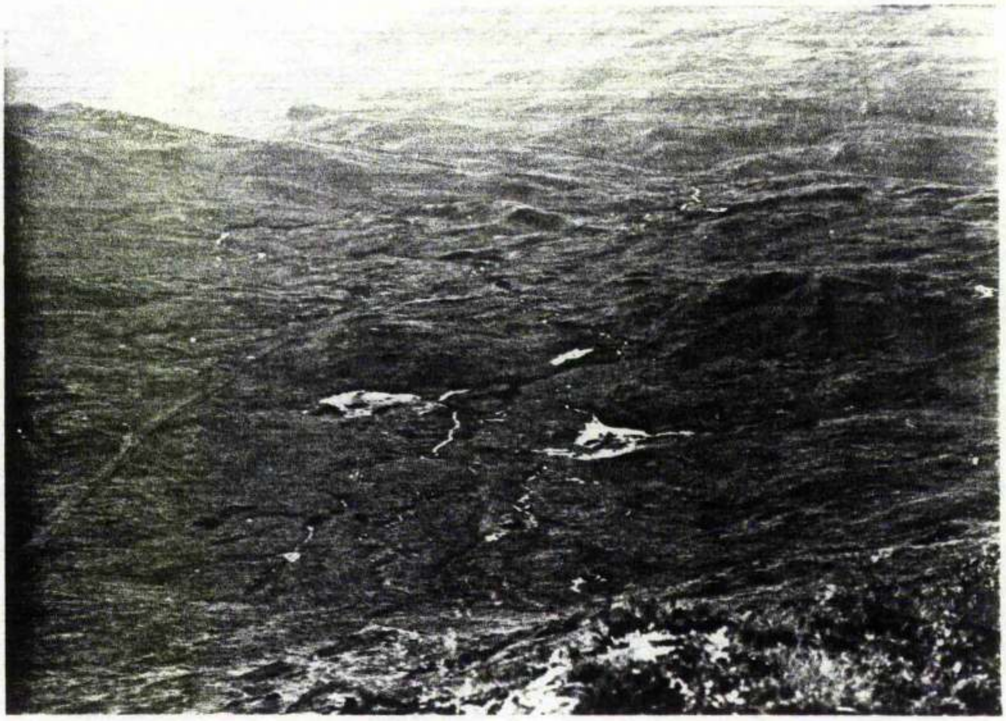


PLATE I View down the Dargall Lane Catchment from Lamachan

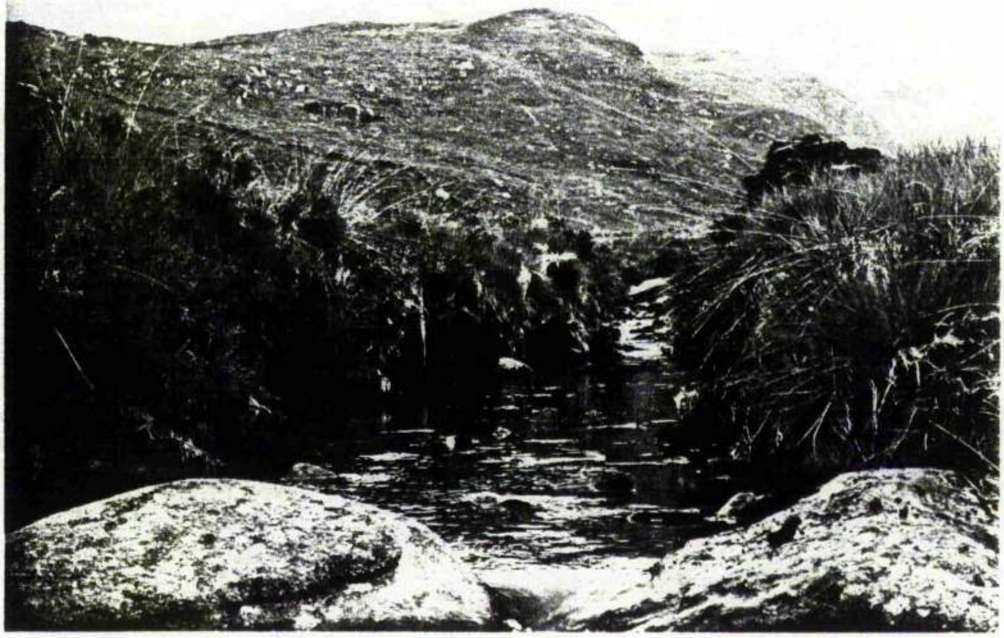


PLATE II View up the Dargall Lane from the gauging station

The Dargall Lane catchment acts as the control catchment in this study, since the Forestry Commission have agreed to leave the catchment uncultivated until at least 1990. The catchment pictured in plates I and II is dominated by Sphagnum, Molinia and grass (*) ,vegetation typical of upland moorland areas; only in the lower area of the catchment does the vegetation become more varied to include some heather and bracken.

The stream channel is incised into the peat for much of its length, the bed of which is lined with stones and boulders. Stream width varies between 1-2 m. Little (1985) has calculated the average gradient for the catchment to be 11.6°. However the gradient of the catchment is broken by a steep middle section where water issuing from the corrie falls over a rock step into the lower area of the catchment.

3:3:3 The White Laggan Catchment.

The total area of the White Laggan catchment to the gauging station is 5.68 $km.^2$, this figure includes the area drained by the Black Laggan a tributary of the White Laggan (see fig 3:1). The catchment occupies the head of a broad glacial valley. Average slope of the catchment calculated by Little (1985) is 10.4°. The stream channel is incised into the peat and soils of the upper catchment whilst in the lower catchment the stream channel runs through the alluvial deposits. In several sections of both the Black Laggan and the White Laggan the channel runs through bedrock. The stream bed reaches widths of up to 4 metres in the White Laggan and 3 metres in the Black Laggan. Along the stream

* (Nardus stricta)

bed gravel, stones and some large boulders are commonplace.

The upper part of the catchment consists of vegetation dominated by Molinia and Sphagnum. In the lower part of the catchment, including the Black Laggan, the area is forested (plates III and IV) although heather and bracken are prolific on the steeper slopes and uncultivated areas. The area of afforestation in the catchment amounts to 30% of the total area. Prior to planting the catchment drainage was improved in a manner similar to that described in section 3:3:4 for Green Burn.

The catchment was planted in 1975 with Sitka Spruce (*Picea Sitchensis*), although in 1979 conifers were cut back approximately 100m from the stream for 1km. upstream of the loch. This area has been planted periodically with clumps of Alder (*Alnus* spp.) Birch (*Betula* spp.) Willow (*Salix* spp.) and Rowan (*Sorbus aucuparia*) totalling approximately 2000 saplings per year (Burns et al 1984). Such a practice is in keeping with the recommendation of Mills (1980) to create a 'buffer zone' in order to preserve the physical, chemical and biological characteristics of upland streams following afforestation. Mills (1980) further suggests that forest drains should be terminated short of water courses to prevent the silting up of streams and allow precipitation infiltration. In the White Laggan catchment where drains connect with the water course the drains have been backfilled to prevent ditch drainage waters from entering the streams directly.

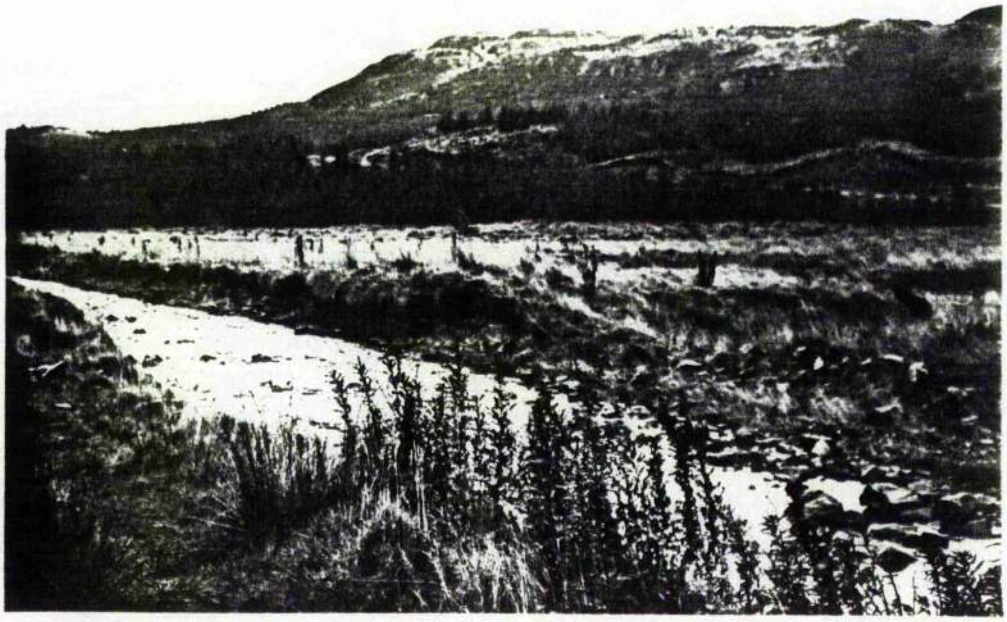


PLATE III View across the 'Buffer Zone' at White Laggan, taken from the roadbridge

PLATE IV View across the Black Laggan Sub-catchment towards White Laggan

A further ameliorating technique used to try and improve water quality in the White Laggan catchment (and consequently Loch Dee) has been the addition of calcium in various forms. Details of the location, amount and type of application are given in table 3:1 and shown in fig. 3:4. Such applications have been deemed necessary to fulfil the Loch Dee Project's second objective, the improvement of the loch potential as a trout fishery and " to counteract the effects of sulphur and acid depositions on the catchment" (Burns et al 1984 p.165). However for the two year period ending in 1982 the authors report that the quantities of limestone so far added (table 3:1) have not produced any detectable change in pH, alkalinity and calcium content in the loch outflow.

3:3:4 The Green Burn.

The area of the Green Burn catchment is 2.5 km.^{2}. Much of the area is gently sloping, with an average catchment gradient of 7.2 (Little 1985). The main stream channel is similar to that of Dargall Lane in that it is incised into peat and lined with stones and boulders, although the channel is narrower than Dargall Lane. Between 1973 and 1975 70% of the catchment was planted predominantly with Sitka Spruce (Picea Sitchensis) but also with small numbers of Lodgepole Pine (Pinus Contorta). The trees have been planted up to a maximum altitude of 460m at a planting density of 7000 trees per acre (Kite 1984).

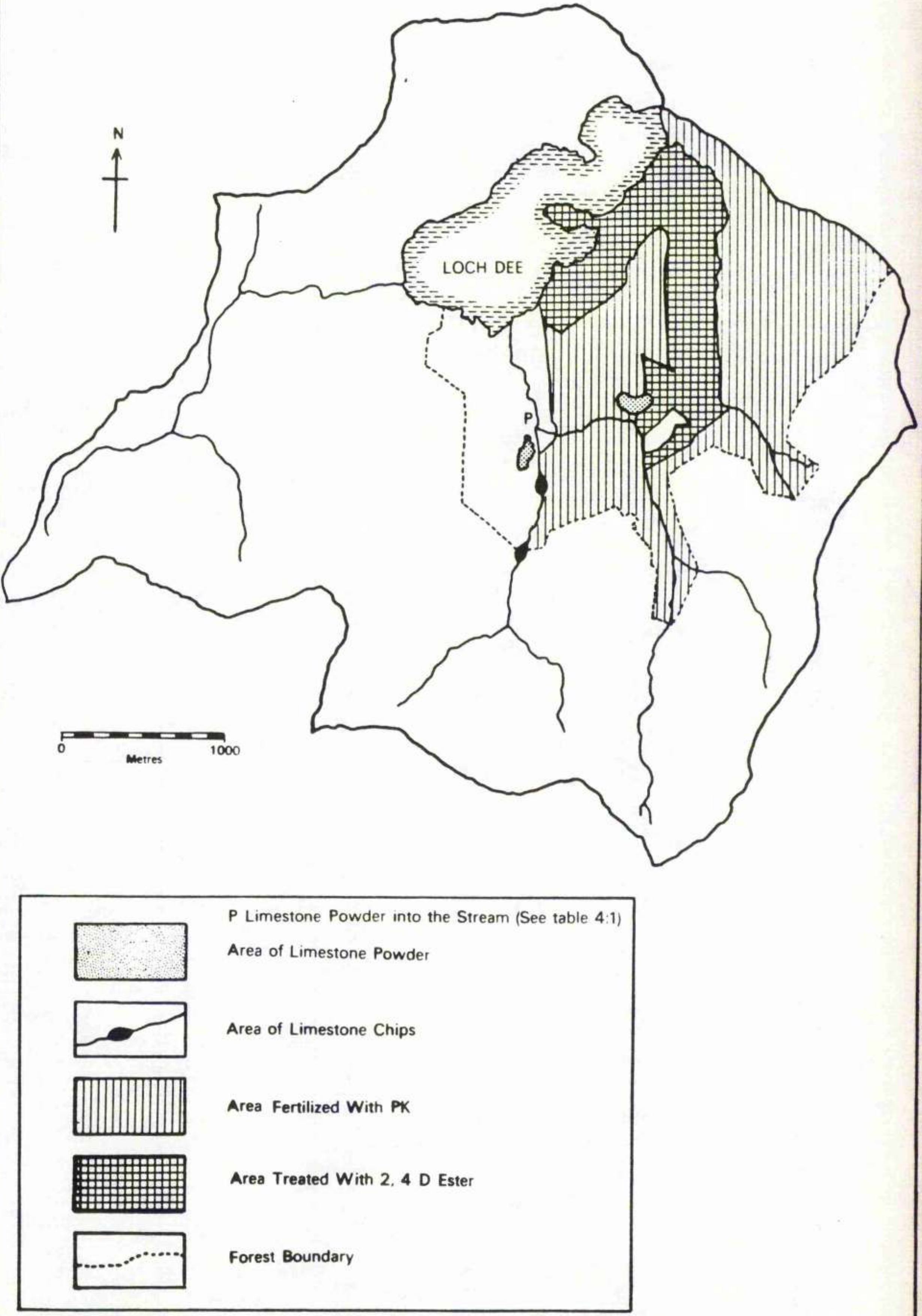
PLATE V View across the Green Burn Catchment looking east

PLATE VI View up the Green Burn taken from the roadbridge

Before planting, drainage in the catchment was improved by the cutting of plough furrows. The standard practice of double throw ploughing on the lower slopes and the more dominant practise of downhill tine ploughing (Binns 1979) on the steeper slopes have been employed at Loch Dee. Binns (1979) has commented that this type of ditching may consist of up to 20% of the land surface in an afforested area and have the effect of contributing a high percentage of rapid runoff during storm events. The single furrows run perpendicular to the land contours with a secondary system of cross drains running close to the contours to intercept water flowing from the furrows. Together they form the largest part of the permanent drainage system for Green Burn. Some of the major ditches connect directly with the Green Burn channel. Ten years after planting the trees are still quite small (between 1 and 3m high) and do not as yet form a complete canopy (plates V and VI).

As part of normal forestry management the Green Burn catchment to the east of White Laggan catchment (thereby including Black Laggan) was treated with PK fertilizer by the Forestry Commission during September 1982. The fertilizer which was applied from the air at a rate of 375 Kg Ha^{-1} which contained 20 tonnes of elemental P and 40 tonnes of elemental K^{+}. The area of application is shown in fig 3:4. Similarly fig 3:4 shows the application in 1982 of 2,4-D ester used to kill heather and restore normal height growth (Binns 1979) in the afforested areas.

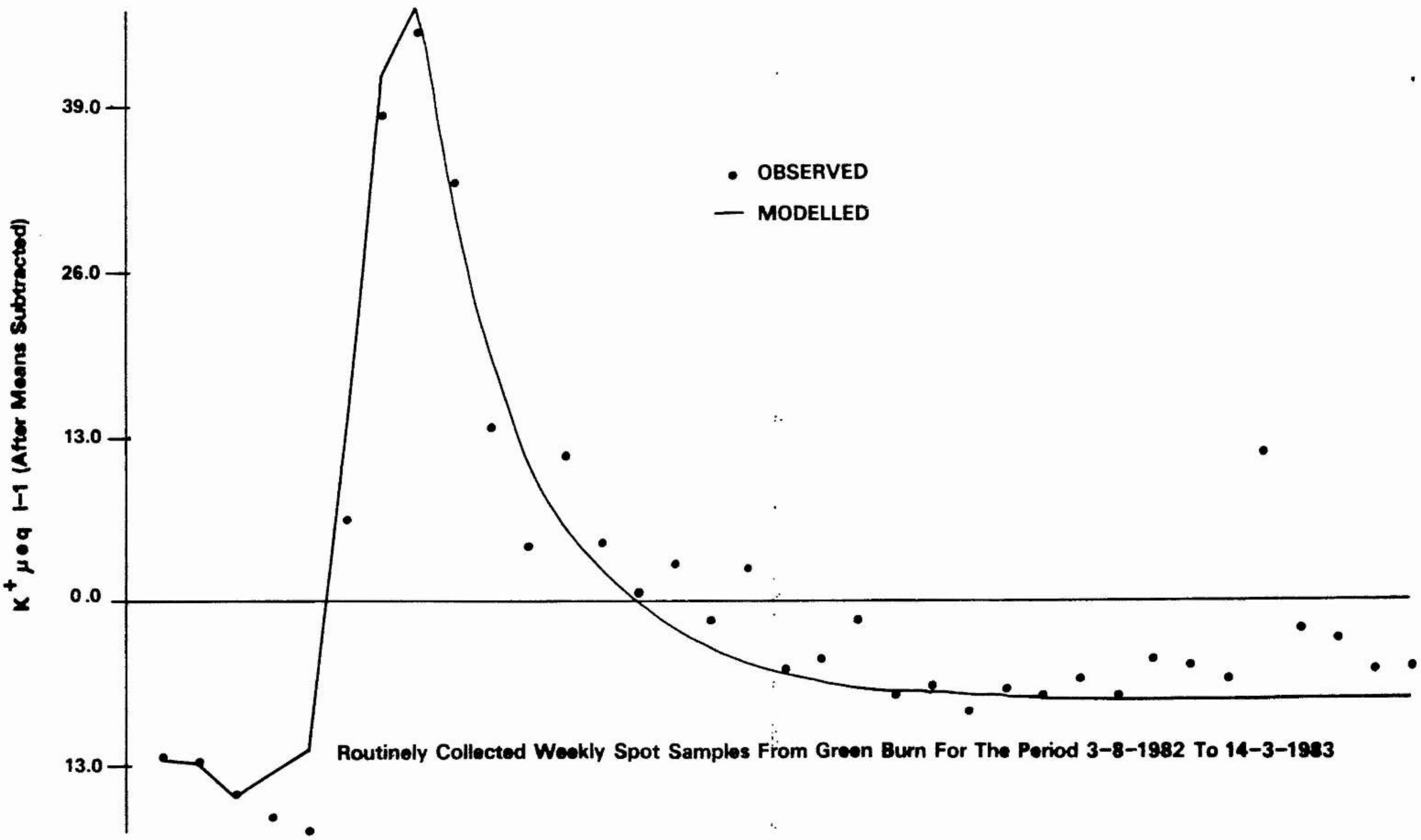
FIG 3:4 Details of Treatments Applied to the Catchments



Source : Forestry Commission

The routinely collected weekly spot samples (section 4:2) for the Green Burn during the period 3rd August 1982 to 14th March 1983 have been analysed in terms of K^+ concentrations using a time-series computer package (CAPTAIN, the details of which are given in chapter 7). The potassium concentrations in the stream showed a significant increase in early September following the application of the PK fertilizer on the 7th September 1982. The potassium rises to a peak of 64.0 μeq l^{-1} and falls steadily to 13.0 μeq l^{-1}. Assuming an impulse input of potassium (ie. the fertilizer application) the model between input and output was estimated as:

$$K_t = 0.72\ K_{t-1} + 0.83\ I_t + 1.36\ I_{t-1} + 0.73\ I_{t-2}$$



Routinely Collected Weekly Spot Samples From Green Burn For The Period 3-8-1982 To 14-3-1983

FIG 3:5 Modelled and Observed Potassium Concentrations In Green Burn

Where

K_t is the concentration of Potassium at time t

K_{t-1} " " " time t_{-1}

I_t " impulse fraction at time t

I_{t-1} " " " t-1

I_{t-2} " " " t-2

The model provides a very satisfactory result as can be seen in fig 3:5, which compares the observed and simulated stream concentrations. From the model it is possible to calculate mean residence time for the potassium in the catchment, which was shown to be 4 weeks. This suggests that a significant proportion of potassium in the fertilizer application is lost via the runoff and not utilised by the vegetation. However the phosphorous levels in the stream remain low over the same period indicating there is net retention or uptake in the catchment.

3:4 Catchment Hydrology.

For the period 1980-1982 at Loch Dee rainfall totals were 119%, 115% and 136% (respectively) of the 1941-1970 standard period average of 2232mm (Burns et al 1984). Welsh and Burns (1985) further report that monthly rainfalls of <25mm are rare with monthly averages ranging from 121mm in June to 265mm in December. Furthermore these authors indicate during most months there is a general 6% increase in rainfall per 100m increase in altitude, based on the raingauges in the catchments. Nevertheless some months show a reduced catch at higher altitudes which the authors attribute to snow and high winds. Annual snowfall in the

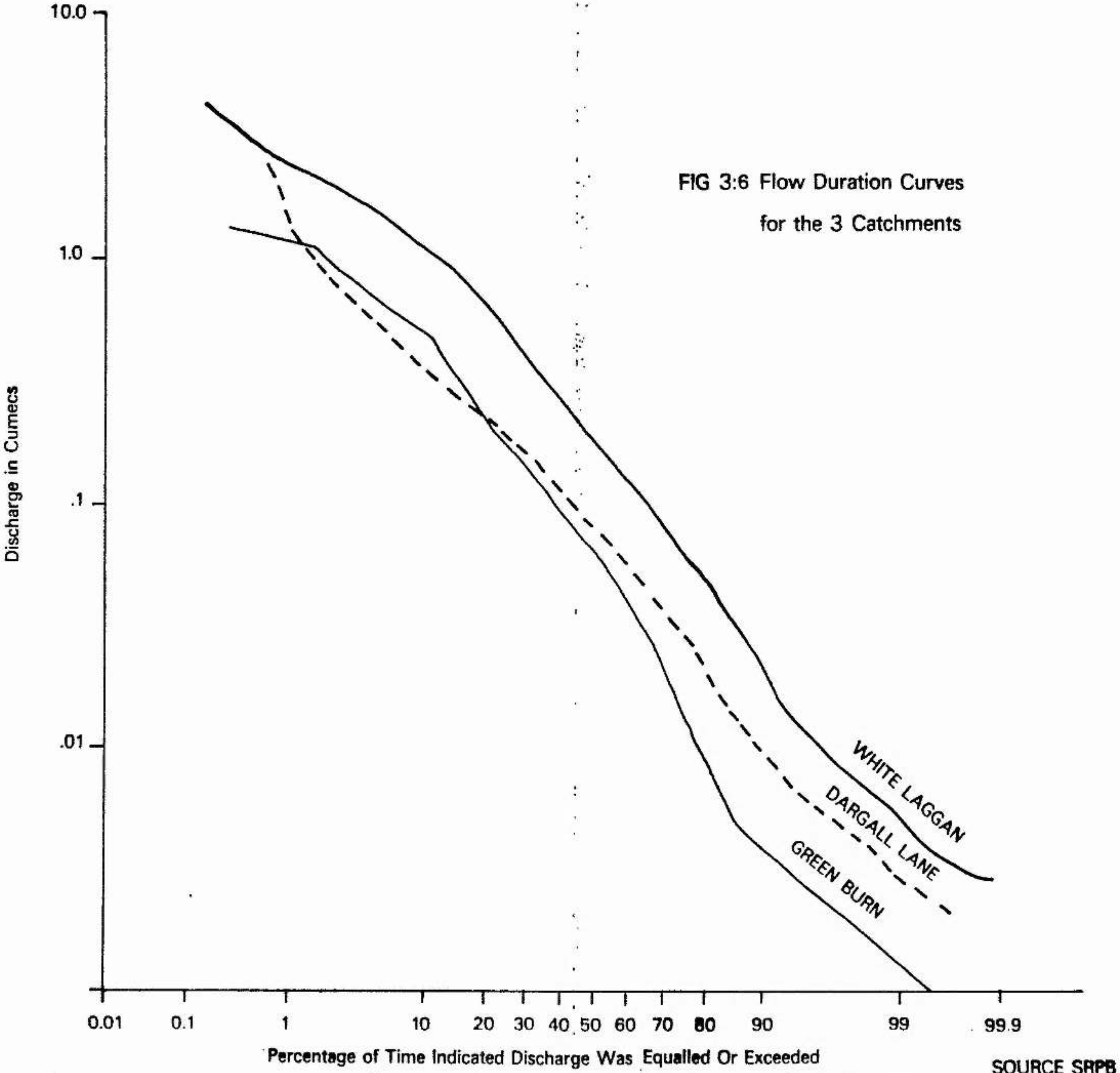


FIG 3:6 Flow Duration Curves
for the 3 Catchments

SOURCE SRPB

area is erratic with snowpatches lying for up to two months during the colder winter periods and at the highest catchment altitudes.

Welsh and Burns (1985) have also calculated the water loss for the White Laggan catchment for the period 1980-1984. The water loss calculation is based on the simplifying assumption that there has been no change in the soil moisture and secondly water storage has remained constant over the period of calculation. The results are shown in table 3:2 and indicate the annual loss in the catchment to be in the order of 430mm. This figure compares with 404.9mm obtained by using a correction factor of 0.773 (suggested by the Meteorological Office in a pers. comm to Little 1985) to the Prestwick Airport mean annual potential evaporation of 1980-1983.

Fig 3:6 shows the flow duration curves calculated by the SRPB for each of the catchments using mean daily flows. The three curves are broadly similar in outline, the most noticeable difference being the upward inflexion in the Dargall Lane curve at high flows. Welsh and Burns (1985) attribute this to three days snowmelt at the end of January 1984 producing very high flows per unit area. Care must be taken using these data as flows >2.5 $m^s s^{-1}$ are extrapolated beyond the rating (see section 4:3:3). Under low flow conditions it is interesting to note the higher (nearly double) flows of Dargall Lane compared to Green Burn, given the similar drainage areas of the catchments. This difference is probably attributable to the peat dominated hydrology of Dargall Lane which retains a higher proportion of water during storms which is then released over low flow periods. The forest ditches in the Green Burn (and White Laggan) prevent

Year	Rainfall	Runoff	Loss
1981	2783	2315	468
1982	2962	2515	447
1983	2361	1971	390
1984	2313	1898	415
Mean	2605	2175	430 mm

TABLE 3:2 Losses (in mm) from White Laggan catchment

(Source : Welsh and Burns, 1985)

	% runoff after first :				
	5 hours	7 hours	10 hours	20 hours	24 hours
Dargall Lane	33	50	63	89	94
White Laggan	49	65	79	94	97
Green Burn	44	66	81	94	97

TABLE 3:3 Percentage Runoff evacuated from the 3 catchments after different periods of time

(Source : Harper, 1984, p. 56)

Data derived from catchment average unit hydrographs such water retention.

A comparative unit hydrograph study by Harper (1984) illustrates a difference in the storm response of each of the three catchments. Table 3:3 shows the percentage runoff from the catchments after different time periods. The data illustrates the proportionally greater rapid evacuation of storm runoff in the Green Burn and White Laggan than in the Dargall Lane catchment. This rapid evacuation is a function of the faster routing of storm runoff along the forest ditches and drains than in the unditched Dargall Lane catchment. In the Dargall Lane where there has been no ploughing the drainage density is less and runoff evacuation will be slower, taking longer to evacuate the catchment. Table 3:3 shows the evacuation of storm runoff from the three catchments to converge after 20 hours when the greatest proportion of storm runoff has been evacuated.

3:5 Catchment Water Chemistry.

Whilst this dissertation is aimed at providing the baseline study for the Loch Dee catchments in terms of water quality three other smaller scale studies have been conducted. The work by Kite (1984) investigating 3 storm events in the Green Burn catchment reports an increase in ionic concentrations and acidity with its passage through the vegetational canopy. Kite also suggests that the streamwater acidity may be ameliorated downstream with the addition of well buffered waters following long residence times and percolation through the catchment soils. Little (1985) investigating the spatial variation in the electrical conductivity of the surface waters in the Loch Dee catchments reports that residence time (long residence time gives rise to high conductivity, short residence time leads to a low conductivity) and soil type (classified as either peat (high conductivity) or glaciogenic (low conductivity) are the most important factors causing spatial variations in measured conductivity. Burns et al (1984) have suggested the three feeder streams and the outflow are chemically similar, having low base cation and nutrient status. However the authors indicate that the addition of both limestone powder and limestone chips within the White Laggan catchment should provide a more amenable environment for the successful hatching and survival of trout eggs and fry , in line with the Loch Dee Project objectives as outlined in section 3:2:1.

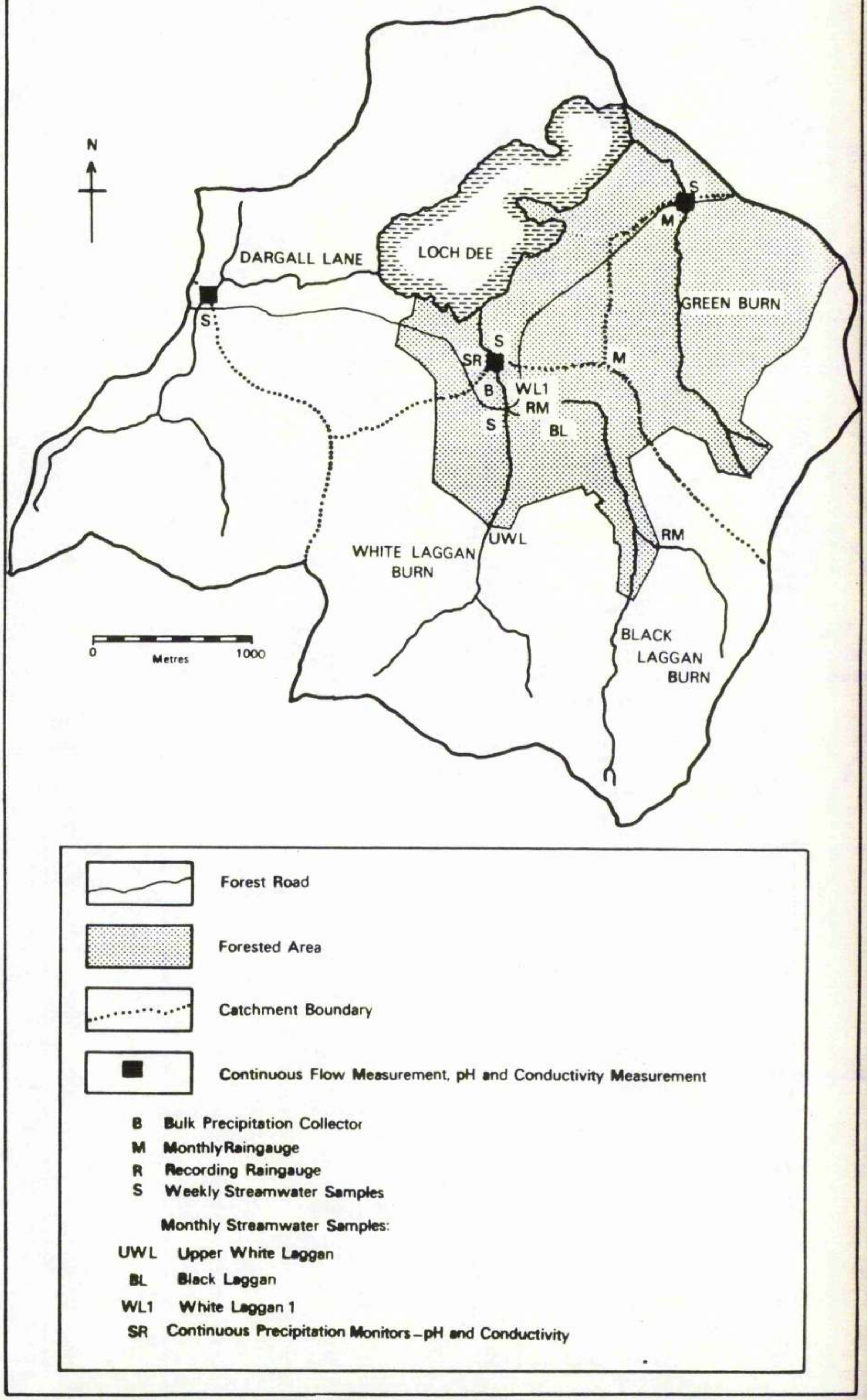
CHAPTER 4: DATA COLLECTION AND QUALITY CONTROL.

4:1 INTRODUCTION.

To provide the necessary data for the comparative and temporally based study outlined in chapters 1 and 3, a comprehensive monitoring network to measure both the variation in precipitation inputs and streamwater has been established at Loch Dee. In order to investigate the fluctuations in both precipitation and streamwater chemistry and how these are related to the catchment characteristics of the 3 catchments, has given rise to a 2 tier sampling strategy. This structure is in agreement with the implication of Walling's (1975) work in which the author indicates that the frequency of hydrochemical sampling will be determined by the expected pattern of fluctuations in the parameters measured.

Fig 4:1 shows all the sampling and monitoring stations at Loch Dee, whilst table 4:1 gives the detail of installation dates, location, frequency and nature of sampling. In order to structure this chapter details of the 2 different levels of sampling and analysis will be described in turn; firstly the weekly chemical sampling and secondly the continuous monitoring of both precipitation and stream runoff in terms of quantity and quality.

FIG 4:1 The Monitoring and Sampling Network



Station and Location		NGR	Sampling Frequency	Date Commenced
A: Weekly Chemistry				
Bulk Precipitation	White Laggan	NX 468 779	1980-fortnightly 1981-weekly	Feb. 1980
Dargall Lane	Roadbridge	NX 451 787	"	"
Green Burn	Roadbridge	NX 481 790	"	"
White Laggan 1	Upstream end of roadbridge	NX 468 778	"	"
White Laggan 2	Gauging station	NX 468 781	"	June 1981
White Laggan 3	Above confluence of Black Laggan	NX 468 777	Monthly	Feb. 1982
White Laggan Upper	Above waterfall + limestone chips	NX 466 769	"	"
Black Laggan	Above confluence of White Laggan	NX 469 777	"	"
B: Continuous Monitoring				
Precipitation Quantity	Black Laggan Lower	NX 469 776	Continuous 0.2 mm	Apr. 1981
Precipitation Quantity	Black Laggan Upper	NX 476 769	Continuous 0.5 mm	June 1983
Precipitation Quality	White Laggan	NX 468 781	Continuous 0.2 mm	Apr. 1981
Streamwater Quantity and Quality	Dargall Lane			
	Quantity	NX 452 787	Continuous	July 1983
	Quality	NX 451 787	"	June 1983
	White Laggan			
	Quantity	NX 468 781	"	Mar. 1980
	Quality	NX 468 782	"	Apr. 1981
	Green Burn			
	Quantity	NX 481 792	"	Oct. 1983
	Quality	NX 481 790	"	July 1983

TABLE 4:1 Details of Sampling Points and Monitoring Stations at Loch Dee

4:2:1 Weekly Data Collection.

Since February 1980 a low level bulk precipitation collector (Whitehead and Feth 1964) has been established in the White Laggan catchment (see fig 4:1 and table 4:1). In 1980 samples were collected fortnightly and from January 1981 on a weekly basis. The bulk precipitation collector consists of a polypropylene funnel 220mm in diameter which drains into a 5 litre polypropylene container housed in a wooden box, shown in plate VII. Both the funnel and container bottle are changed weekly. If less than 1 litre of precipitation is collected, pH and conductivity are determined on 10ml of sample and the remainder is diluted to 1 litre with deionised water poured through the funnel to collect any residual dry deposition. In weeks of high rainfall no residual dry deposition is anticipated (cf.Burns et al 1984).

From the initiation of the Loch Dee Project a programme of weekly spot samples has been established on each of the three streams. This is supplemented by additional monthly samples of the White and Black Laggan sub-catchments to monitor the effects of the liming programme (section 3:3:3). Samples are collected by Mr.I.Murray (Forestry Commission) who is asked to collect the samples at 9.00 hrs on Monday mornings, however this is not always possible due to work load, adverse weather conditions and illness. Stream samples are collected in 1 litre polypropylene bottles which are rinsed out once or twice with stream water before filling with the sample. All the sampling points are on stretches of easily accessible water which is rapidly flowing as recommended by Johnson (1971).

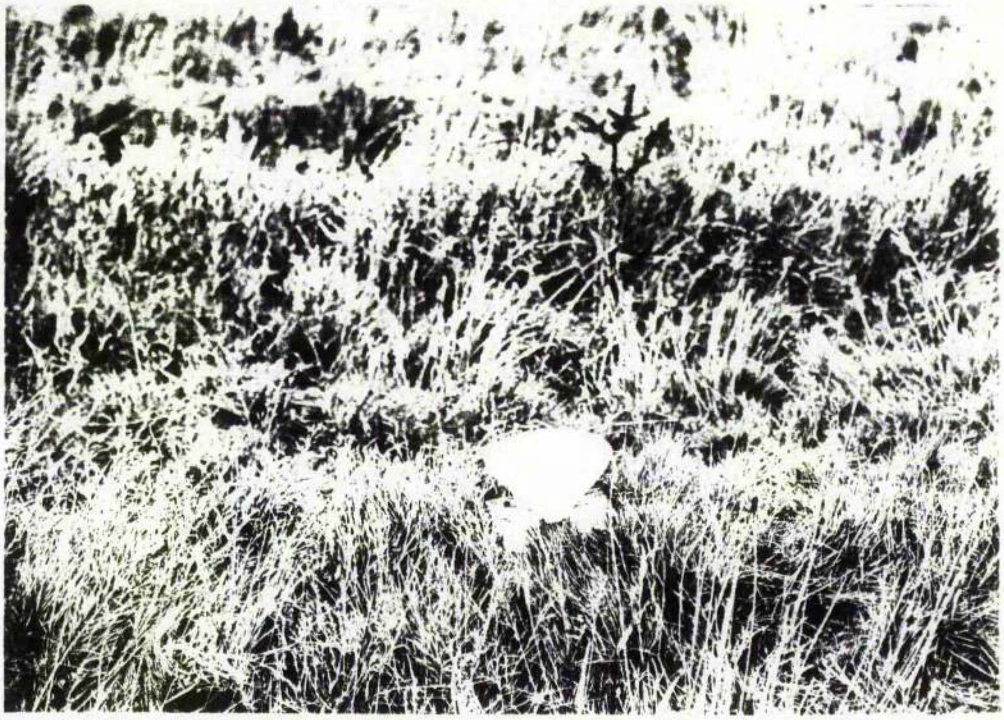
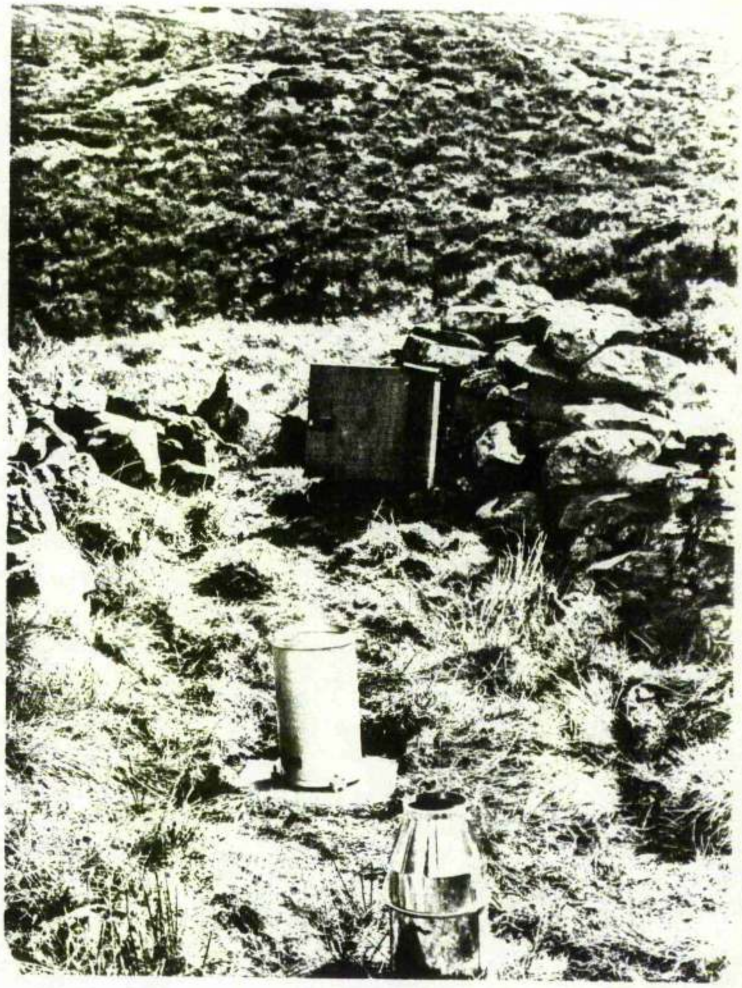


PLATE VII Weekly bulk precipitation collector in the White Laggan Catchment

PLATE VIII

The Upper Black Laggan raingauge showing the standard monthly check in the foreground with the tipping bucket guage and logger housing in the background



The weekly bulk precipitation and streamwater samples are transported to the SRPB chemical laboratories in Dumfries, where they are stored in a refrigerator at 4^{oC} until the analysis is complete (approximate average 1 week, Tervet pers. comm.)

4:2:2 Chemical Analysis of the Weekly Data.

The bulk precipitation samples and the weekly spot samples of the streams undergo the same range of analyses. Whilst the complete range of determinands for Loch Dee samples consists of pH, conductivity, Na^+, K^+, Ca^{2+}, Mg^{2+}, SiO_2, NH_3, Total Oxidised Nitrogen, O-PO_4, Cl^-,Total Alkalinity, $SO^{2-}4$, Zn, Mn, Al and Fe; only the major determinands of pH, conductivity, Na^+, K^+, Ca^{2+}, Mg^{2+},$SO^{2-}4$,NO^-3, Cl^-, and Bicarbonate Alkalinity are considered in this work. The methods of analysis used are standard River Board methods used in the analysis of all routinely collected river samples by the SRPB.

PH is analysed by using a Walden Precision Apparatus (WPA) CD 390 pH meter and Russell pH CE7L gel filled electrode; conductivity, using a Chandos Intercontinental A21/D meter which is automatically compensated to a reference temperature of 25^{oC}. Sodium and Potassium are analysed using flame emission spectrophometry after lithium addition (Suess 1982). Using this method sample concentrations are calculated from a calibration curve constructed from the measurement of flame emission intensities from standard solutions. Both the sample and solutions are introduced as a fine spray into a flame. Calcium and magnesium are analysed for by atomic absorption spectrophometry after strontium addition (Golterman et al 1978). In this method the amount of light absorbed at a specific wavelength is measured via a cathode lamp source directed through the flame (into which the sample and standard solutions are injected) onto a monochromator adjusted to the appropriate wavelength for the ion being analysed. Sample concentration is again calculated from a calibration curve constructed from known standard solutions. Both flame emission spectrophometry and atomic absorption methods described for these metals are determined on Varian model 1100 atomic absorption spectrophotometer.

Nitrate and nitrite are analysed for by means of Technicon AutoAnalyser II methods. This involves reducing the nitrates in the sample to nitrites. The nitrites are then reacted with a sulpanilamide reagent to form a diazo compound which is then coupled with N-(1-naphthyl) ethylenediamine dihydrochloride to form a reddish purplish azodye (Environment of Canada, Analytical Methods Manual 1979). The azodye intensity, which is proportional to the nitrate concentration, is then measured colourimetrically. In practise 5 ml aliquots of sample are run through the AutoAnalyser which conducts the above reactions and computes the nitrate concentrations by means of a calibration curve constructed from known concentrations in standard solutions.

Chloride is determined by titration with mercuric nitrate, a method which is more sensitive at low chloride concentration to the more established titration with silver nitrate (H.M.S.O 1972). The principle of the titration is that the mercuric ions react with the chloride ions to form a highly stable, soluble complex. Chloride in a sample may therefore be titrated with a standard solution of a soluble mercuric salt. The end point can be detected by using a diphenylcarbazone indicator which forms a blue-violet complex with an excess of mercuric nitrate. The procedure recommended and described in detail by H.M.S.O (1972) is to use 50 ml of sample in a conical flask, add 5-10 drops of the indicator; if a blue-violet or red colour develops add N/20 nitric acid until the colour changes to yellow and then exactly 1 ml in excess. Titrate the solution with standard mercuric nitrate. The end point is in the violet-blue colour range. To determine the blank correction titrate 50 ml of distilled water by the same procedure. The chloride concentration of the sample is the difference between the 2 titrations. The method for Alkalinity determination is a titration against sulphuric acid using a BDH 4.5 indicator to detect the end point. This data is then converted to bicarbonate using the method of Henrikson (1982). From 1980 to 25th January 1983 alkalinity was determined titrating with 0.02 N sulphuric acid to give alkalinity to the nearest mg l^{-1}. Post January 1983 the strength of the acid was changed (to 0.002 N) and it has become possible to give alkalinity to 1 decimal place.

During the period 1980-1981 and 1983-1984 sulphate has been determined using ion-exchange methods (Mackereth, Heron and Talling 1978) in which the sample is allowed to percolate through a column of ion-exchange material in the hydrogen form. All the cations initially present in the sample are exchanged for the H^+ so that the effluent from the column consists of a solution of free acids corresponding to the salts originally present and in equivalent concentration. This effluent is titrated with standard alkali to pH 4.5 then the amount of alkali used will provide a measure of the strong acids and therefore strong acid salts initially present in the sample.

Due to the labour intensiveness of this technique, during 1982 a trial method of sulphate determination was employed. This technique (H.M.S.O 1979) involves the precipitation of sulphate with 2-aminoperimidine followed by colourimetric determination of the excess reagent. The method failed to give consistent results and was finally abandoned under the instructions of the SRPB chief chemist (Dr. D.Tervet) in December 1982. Consequently the data from this period needs treating with caution.

Since April 1984 sulphate, chloride and nitrate have been determined using a Dionex QIC ion chromatograph. Using this technique the ionic species present in the sample move through the exchange column at a rate determined by their affinity for the resin exchange material. The differential rate of migration separates the ions into discrete bands the detection of which is achieved by conductivity. Comparison of both retention times and peak height against standard solutions allows computation of the sample concentration.

Results of analyses are given in mg l^{-1}, for comparability between ions in this study these figures have been converted to µeq. l^{-1} using the methods given in Environment of Canada Analytical Methods Manual (1979). In the case of pH, this has been converted to micro-equivalents of H+ l^{-1} with the result that this data has a stepped appearence caused by the conversion from discrete log values to linear arithmetic values (see chapter 7 inparticular).

Whilst it is not the purpose of this thesis to evaluate or assess the different methods of chemical analysis; it is appropriate that a comment should be included on the difficulties associated with some of the methods described.

The relatively recent interest in both aquatic environments which have low ionic concentrations and the increased interest in a more diverse range of ions has resulted in some analytical deficiencies becoming apparent in certain standard methods. The recently expanded field in environmental chemistry has lead to some analytical methods being pushed to their limits and no longer totally appropriate. However, until improved procedures become available the standard methods provide the best solution currently available. Of those methods listed above the least satisfactory analyses have been: alkalinity pre 1983, sulphate and pH measurement. The problems analysing for sulphate and alkalinity have already been outlined. The problem with pH is two fold; firstly the change in sample pH with time, in which as a sample ages biological activity within the sample or by CO_2 exchange with the air in the sample bottle may occur. To minimise this problem sample vessels are: (a) filled to the top to exclude as much air as possible, (b) stored in a refrigerator and (c) pH measurement undertaken as soon as possible after collection. Secondly, a more serious problem and the subject of intense research at the present, is the whole question of the measurement of pH in which doubt has been expressed as to the replicability of results, the accuracy of pH meters/electrodes in low conductivity waters and the conditions under which pH measurements are made. A discussion of these problems is given by Mason (1984) and Thomas and Neal (1984). Whilst analytical problems associated with the analysis of low conductivity waters such as those dealt with in this project is appreciated, until a reliable set of alternatives is offered by analytical chemists the methods described above provide the best available given the present level of technology and resources available. In order to avoid the worst of these errors (and others) a standard ion-balance method has been employed to screen the weekly data.

4:2:3 Data Screening of the Weekly Data.

Errors in environmental chemical data may occur from several sources, the most common being:

i. Contamination.
ii. Equipment failure/error in analyis.
iii. Human error.
iv. Deterioration of sample before analysis.

In order to reduce the possibility of using poor or incorrect chemical data for mathematical analysis an ion balance procedure was used. The procedure has been taken from the Environment of Canada, Inland Waters Directorate (1979).

$$\% \text{ error} = \frac{\text{cations (epm)} - \text{anions (epm)}}{\text{cations (epm)} + \text{anions (epm)}}$$ [1]

This equation was employed to calculate the % error each of the data lines by an SPSSX[2] programme.

---

[1] epm equivalent parts per million

[2] SPSSX - Statistical Package for the Social Sciences

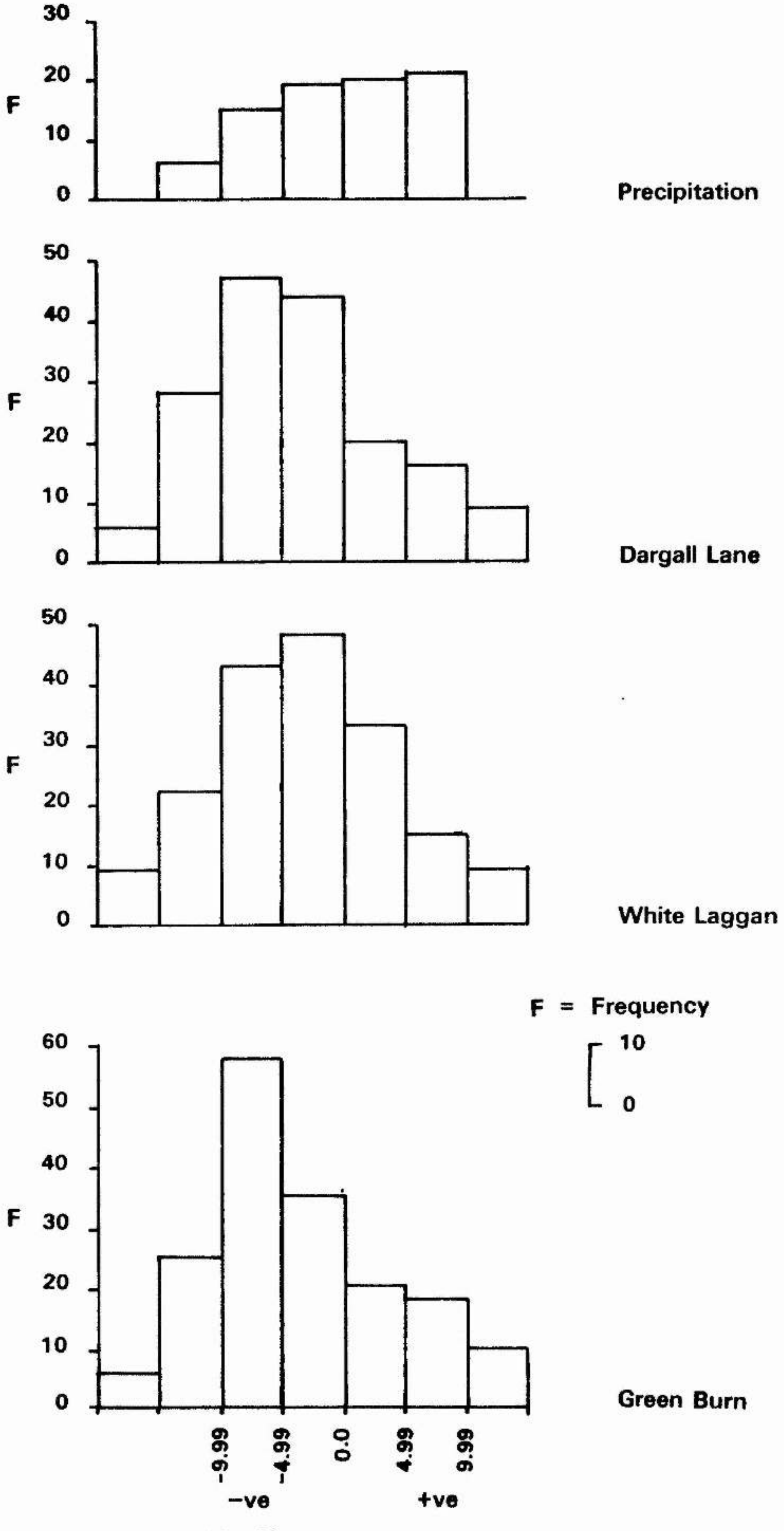


FIG 4:2 Ion Balance Distribution

Having run the programme a frequency distribution of the errors using 5% class intervals was drawn up, these are shown in fig. 4:1. Whilst the bulk precipitation shows no particular distribution all 3 streams show positively skewed ion balances. The modal class being -5% to 0%. The most plausible explanation for this 'bias' in the ion balance is the presence of organic acids which are not analysed in the Loch Dee samples (section 4:2:2). In the absence in the published literature of figures introduced by organics in such environments the author took a figure of ± 5% (ie. an ion balance within the range 0 to -10%) to account for the presence of organics. (C Neal, Institute of Hydrology in a personal communication has indicated that organics may contribute to ion balances of such environments as Loch Dee)

As the bulk precipitation samples will be free from the organic acids found in the streams (as indicated by the non-skewed ion balance distribution in fig 4:2) it is not justifiable, nor does it make sense to accept samples unless they lie within ± 5% of the 0% ion balance error.

This strict screening of the data considerably reduced the number of samples used in the statistical analysis, as given in table 4:2.

Sampling station	Tot. No. of samples	Samples within ion bal.
Bulk precipitation	(1) 169	38
Dargall Lane	194	103
White Laggan	194	97
Green Burn	194	107

TABLE 4: 2 Valid samples.

(1) the smaller No. of total samples is because of fortnightly sampling during the first 3 months of 1980. The exclusion of a considerable No. of samples for which analysis was incomplete through lack of sample volume considerably reduces the No. of valid samples.

However the loss of freedom with the reduced number of samples is compensated by the greater personal confidence in the data.

4:3:1 Continuous Data Collection.

In an area where storms and the associated change in streamflow may occur within a period of 12 hours or less there is little possibility of detecting the change in water quality through the passage of a storm from the routinely collected weekly samples. In order to asses the fluctuations in precipitation and streamwater quantity and quality over the full range of hydrometeorological events a more intensive sampling frequency is required. Walling (1975) suggests the availability of continuous monitoring would overcome the problem of sampling frequency. If this is not available the author indicates a sampling interval as short as once every 10 minutes may be necessary during storm events on small streams.

Consideration of the problems in monitoring storms in the remote Loch Dee Basin prompted the SRPB (with grant aid from the Scottish Development Department) to install a continuous monitoring network. This network was designed to measure water quantity (both precipitation and runoff) and water quality in terms of pH and conductivity. The initial network concentrated on the White Laggan catchment and monitored precipitation input in terms of both quantity and quality. With the author's research initiative, additional funds were made available by both the University of St. Andrews and the Scottish Development Department and in 1983 this monitoring network was extensively extended to include a further raingauge and the establishment of both water quantity and quality stations on the Dargall Lane and Green Burn. The instrumentation at each station is the same although the water quality equipment installed in 1983 (table 4:1) is an updated version of that installed in 1981.

4:3:2 Precipitation.

Precipitation quantity is continuously measured at two sites in the Black Laggan sub-catchment (shown in fig 4:1) using a deep throat Munro tipping bucket raingauges. The lower raingauge (plates IX and X) at 229m OD consists of a 0.2mm gold-plated tipping bucket which is linked to a DRS (Data Retrieval Services) PDL 5 event driven logger. A similar system (plate VIII) is employed at a higher altitude (405m OD) using a 0.5mm tipping bucket and a PDL 7 event driven logger. Both gauges operate on a 9 volt battery power supply. At both sites monthly totals are manually checked against a standard 280mm Octapent Meteorological Office raingauge. These two sites provide a continuous record of the timing and quantity of precipitation inputs.

Precipitation quality is monitored in the White Laggan catchment continuously in terms of pH and conductivity. Incident precipitation is collected in 400mm diameter polypropylene funnels (plate XI) and passed through a 'U' tube arrangement holding permanently immersed electrodes housed in insulated boxes. The system (designed by the SRPB) requires approximately 0.2mm of precipitation to give a complete change of water within the 'U' tube. The pH and conductivity of the

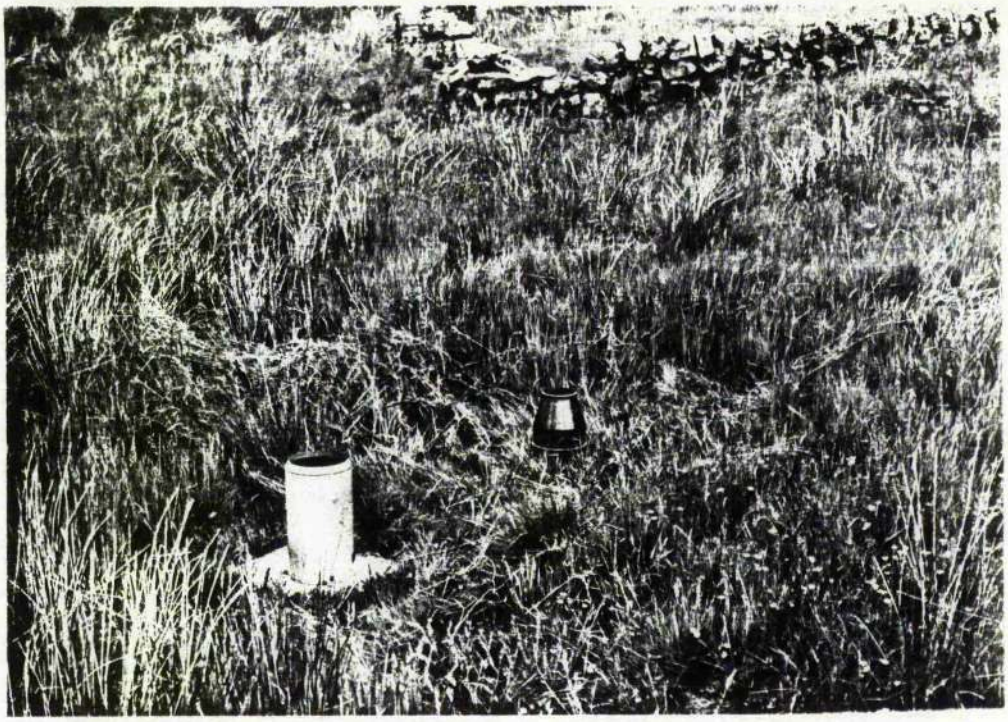


PLATE IX Black Laggan Lower raingauge site showing the automatic gauge (foreground) and monthly crosscheck gauge in the background

PLATE X

Closeup of Black Laggan Lower (0.2 mm) tipping bucket raingauge

PLATE XI

The continuous precipitation quality monitoring station, showing the collecting funnels for conductivity and pH with instrument housing in the background

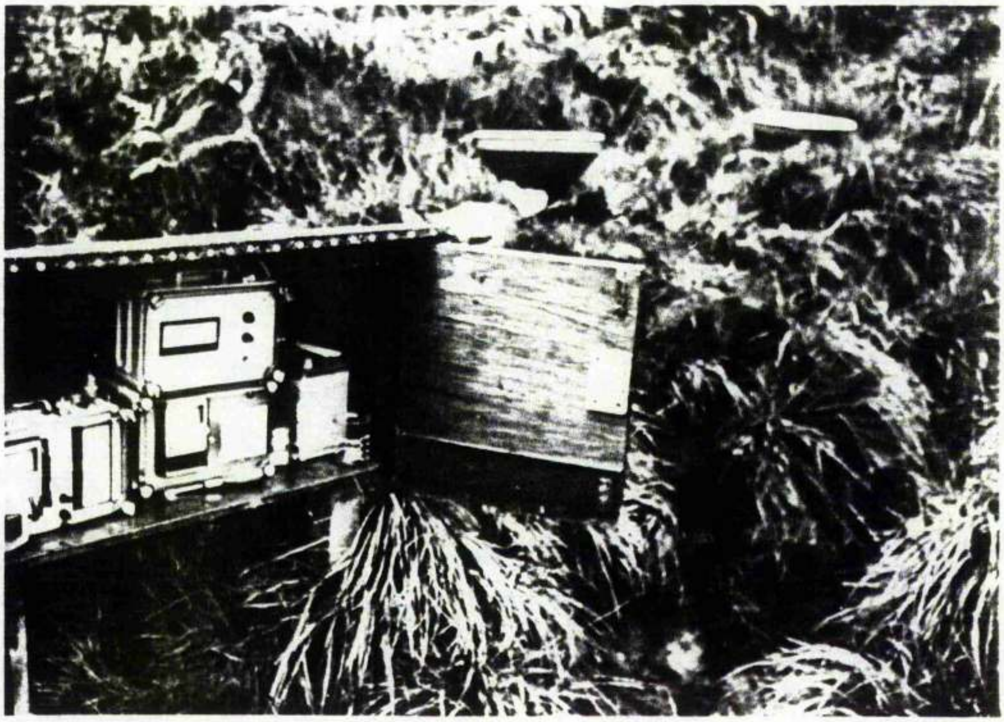


PLATE XII View of continuous precipitation quality monitoring showing instrumentation incident precipitation are recorded via a PHOX (series 47) pH and conductivity meter (series 52) onto Rustrak type strip chart recorders. These continuous records along with the weekly bulked sample provide the data from which atmospheric inputs to the catchment are evaluated.

4:3:3 Runoff.

The water levels in each of the three streams are monitored continuously using Ott R20 float operated chart recorders (plates XIX and XX). These recorders use a stilling well producing a flat water surface, the level of which is transferred from the float and counterweight system via a single reduction pulley (5 to 1) to a fibre tipped pen producing a continuous record on a 32 day clockwork driven chart (at a chart speed of 5mm hr^{-1}). Each water level recorder is sited at the downstream limit of the catchment to monitor the total flux of water from each catchment.

The relationship between water level (stage) and discharge is established by velocity-area methods (Wilson 1975). This method involves a series of current meter readings taken at different flows. Such gaugings at Loch Dee adopt the SRPB standard gauging practice, ie; the depth and velocity of the stream (at 0.6 of the stream depth) is measured at 0.1 metre intervals across the gauging section. Velocity is measured using a Braystoke current meter with a 52mm diameter propellor over a timing period of 100 seconds (pre November 1983 the timing period was 60 seconds). For each gauging the stage, time, date and weather conditions are also recorded. Plate XIII shows the author using a current meter to gauge the Green Burn during very low flow conditions in summer 1983.

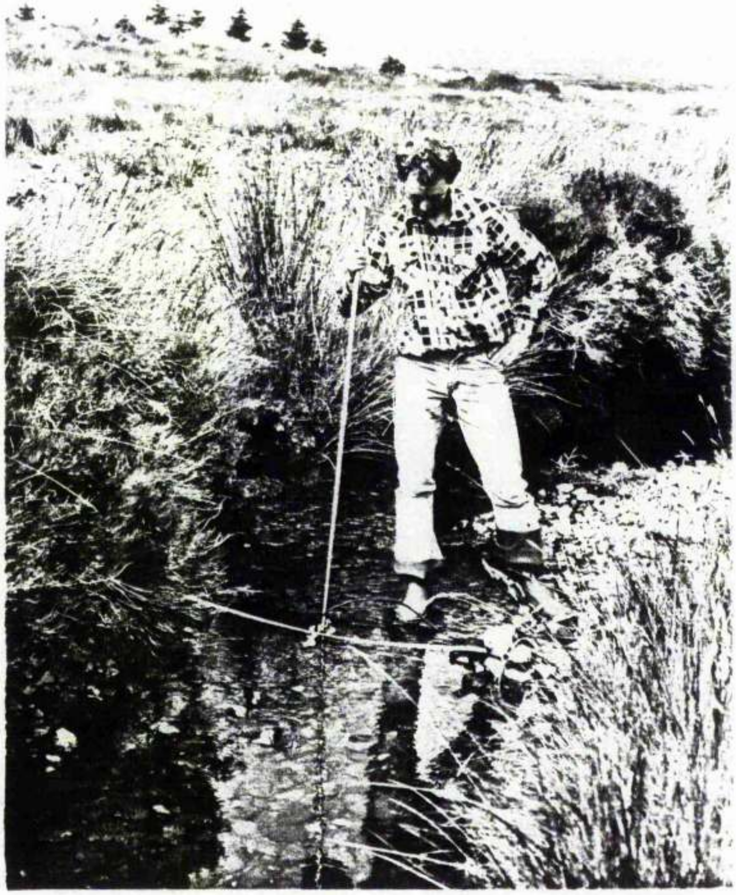


PLATE XIII The author carrying out a current meter gauging on the Green Burn during very low flow conditions

Stream discharge from the catchments is then calculated from the continuously recorded water level and the rating relationship constructed from the gaugings undertaken on each stream. The rating relationship is an empirical relationship using the correlation between stage and discharge. The rating relationship for each of the three streams for the period August 1983 to April 1984 is shown in figs 4:2 to 4:4 together with the actual gauged values.

The water level recorder on White Laggan shown in plate XXI was installed early in 1980 by the SRPB. Later in the year an artificial control was constructed in order to help stabilise the stream bed and water level. The operation of the White Laggan station over 5 years has been most satisfactory, as borne out by the stable rating relationship of fig 4:3. Following readjustment and the settling of the station, the only problem has been the occasional bank slump following undercutting by high flows which has lead to some of the less stable banks above the station falling into the channel.

With the development of the author's project and additional funding made available by the Scottish Development Department further water level recorders were purchased for installation on the Green Burn and Dargall Lane and to record the loch level. The installation of these recorders was undertaken during early summer 1983. The criteria used to site the gauging stations can be summarised as follows:

i. Stable channel section.

ii. High percentage of time the flow is contained within the defined channel.

iii. No marked increase or decrease in velocity either upstream or downstream in proximity of the proposed site.

iv. Flow not excessively turbulent so as to cause eddies or other disturbances to velocity measurement.

v. The provision of a control for the water level involving either a natural or man-made structure.

vi. Accessibility.

vii. Ease of installation.

The site for the Dargall Lane recorder was chosen in preference to other potential sites due to the presence of a natural control. The control (shown in plates II and XVI) consists of two large boulders in the stream bed forming a natural 'V' in the centre of the stream which controlled the water level on its upstream side during low flows. Plates XVI to XIX show various stages of the installation of the gauging station 5 metres upstream of this control which the SRPB hydrologists and the author completed in two days. The first records from this station were most satisfactory however after a few weeks the trace left by the pen on the chart showed excessive fluctuation. The apparent cause of this pen fluctuation was caused by the steepness of the channel creating a 'wave' like water surface which was transmitted through the stilling well and float to the pen. To dampen this effect Mr. J Howatson (SRPB) suggested the installation of a plywood board across the gauging station facing the stream. This system was adopted and has proved most successful. A further more serious problem occurred during the winter of 1983-1984 in which bank undercutting changed the control with the consequence of some loss of rating. The control was repaired by SRPB hydrologists and a new rating is being established. However the sparsity of gauged points on the old rating relationship, shown in fig 4:3, leave a certain degree of uncertaintity with regards to the accuracy of the

FIG 4:3 Rating Relationship for Dargall Lane

$H < .230\text{m}\ Q = 488.483\ (H - 0.075)^{5.152}$

$H > .230\text{m}\ Q = 3.3692\ (H - 0.134)^{2.0383}$

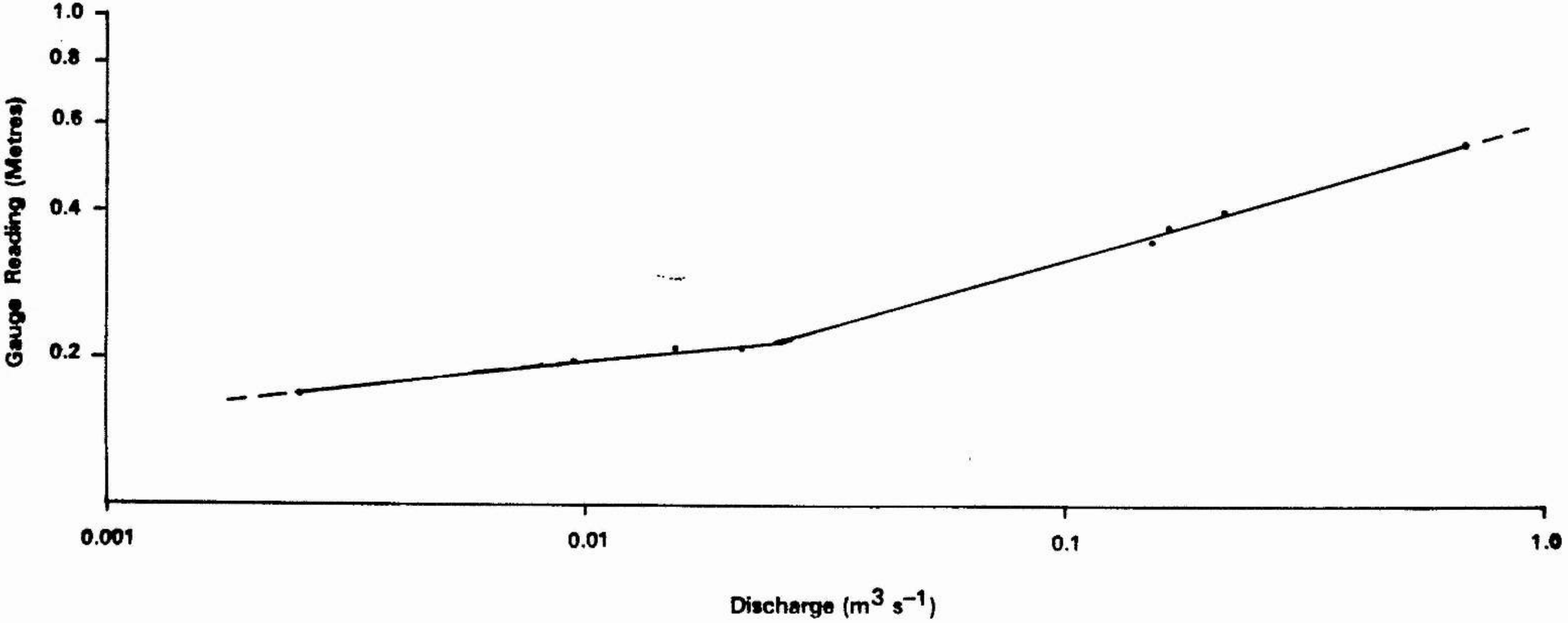
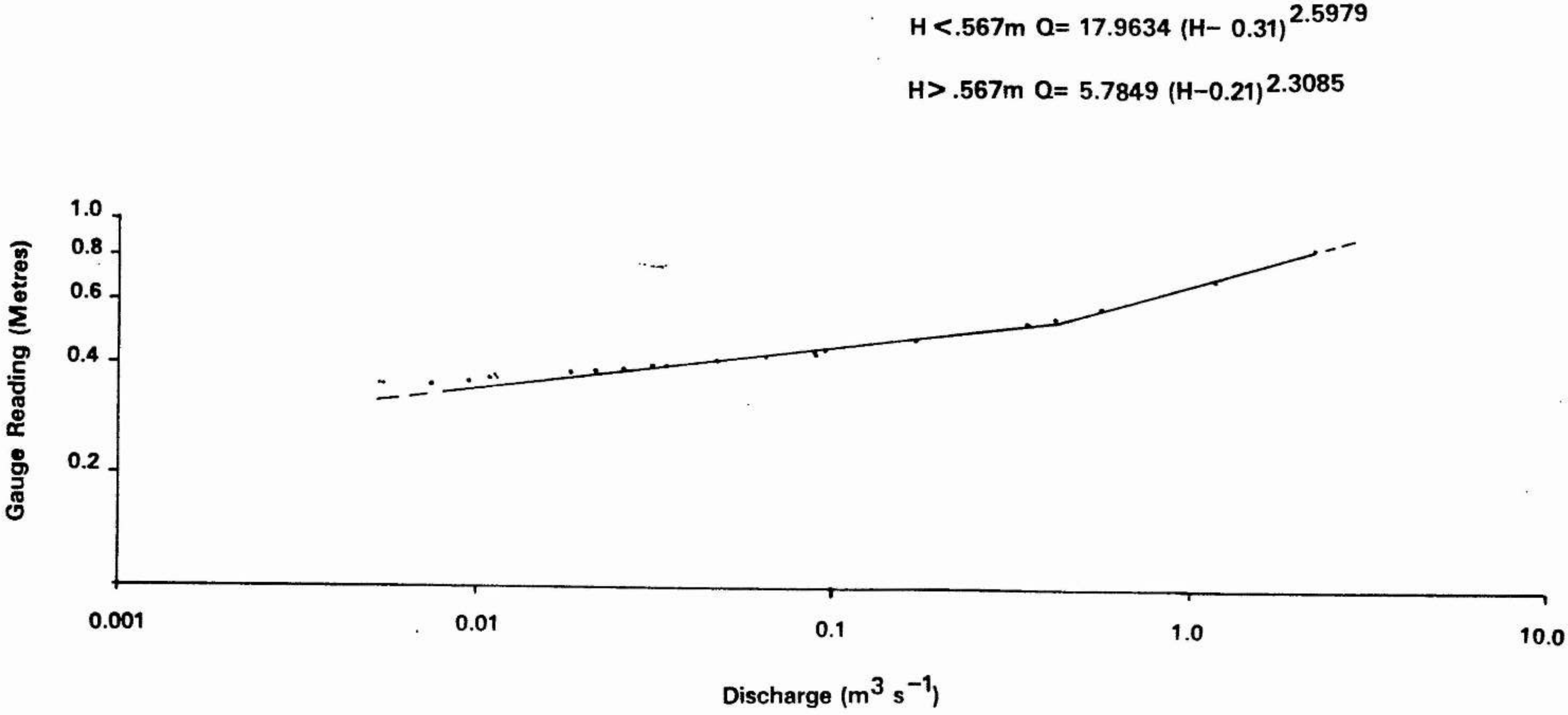


FIG 4:4 Rating Relationship for White Laggan



$H < .567\text{m} \quad Q = 17.9634\,(H - 0.31)^{2.5979}$

$H > .567\text{m} \quad Q = 5.7849\,(H - 0.21)^{2.3085}$

FIG 4:5 Rating Relationship for Green Burn

$H \leqslant .234\text{m} \quad Q = 114.216\,(H-0.163)^{3.6017}$

$H > .234\text{m} \leqslant .385\text{m} \quad Q = 3.9239\,(H-0.203)^{1.7713}$

$H > .385\text{m} \quad Q = 2.3461\,(H-0.115)^{1.9145}$

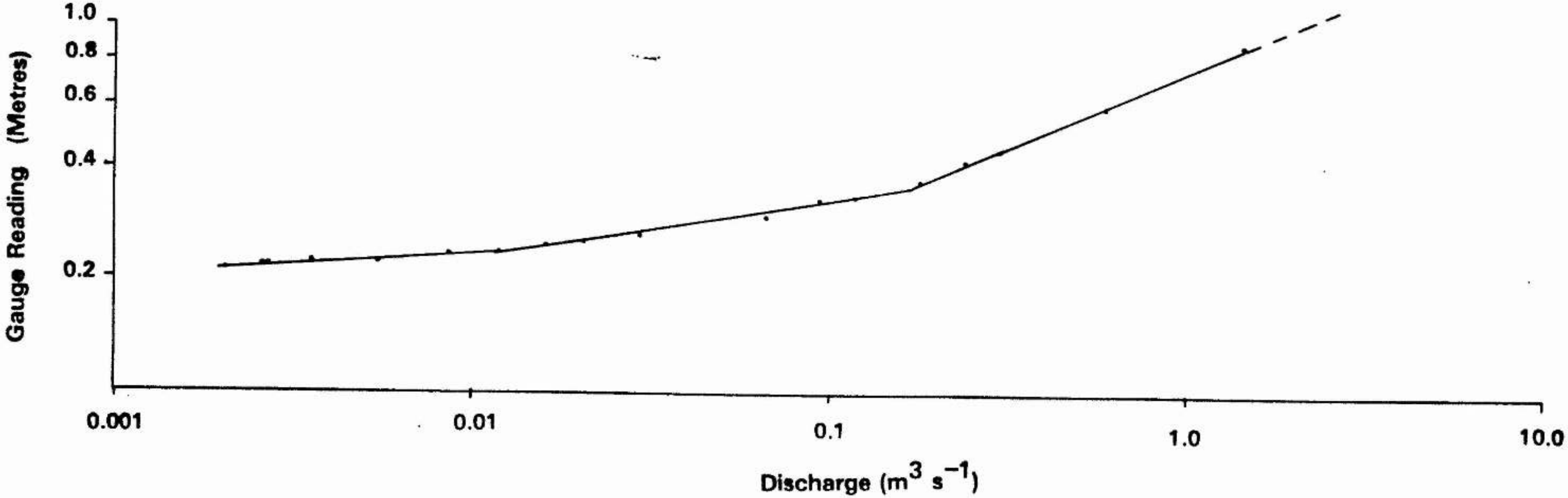


PLATE XIV

Dilution gauging using a 'gulp' injection of sodium iodide in the Green Burn (upstream of roadbridge)

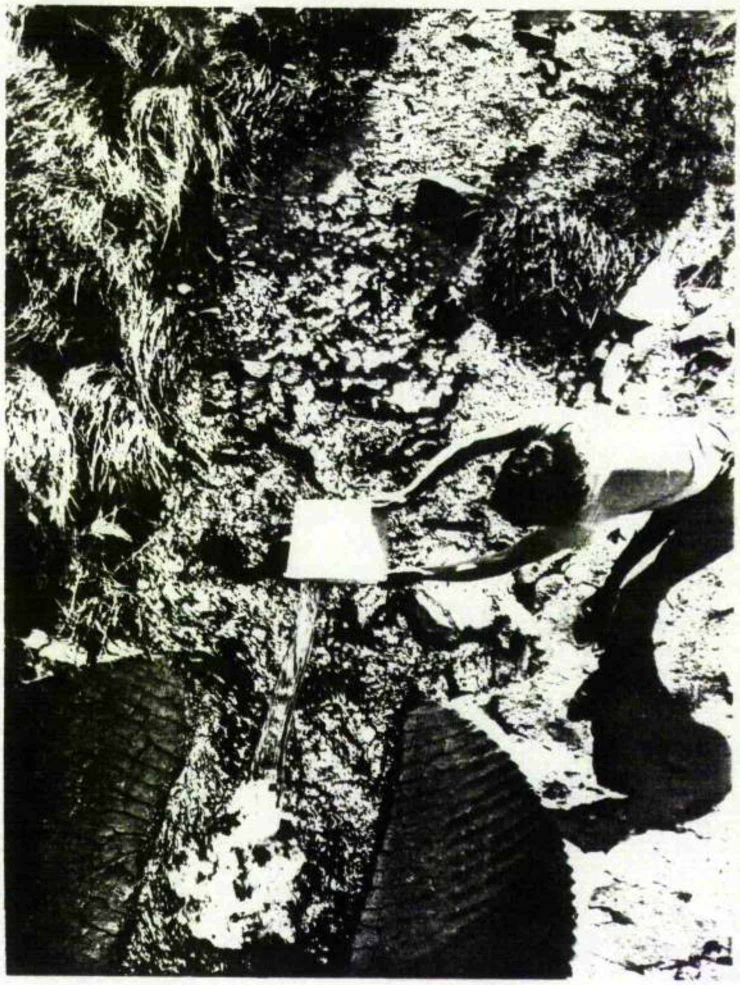
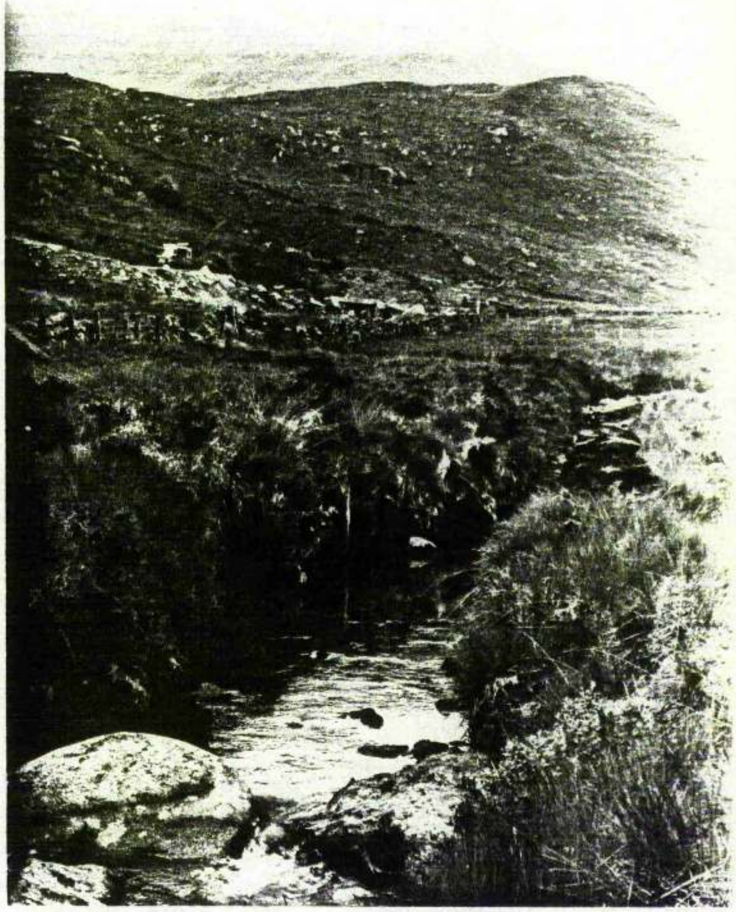


PLATE XV

The ion selective electrode mounted in floating 'boat' coupled to a chart recorder enabling the regulation of sampling frequency

PLATE XVI

Site on the Dargall Lane selected for the installation of the continuous water level recorder. The Plate also shows the natural control on water level in the foreground.



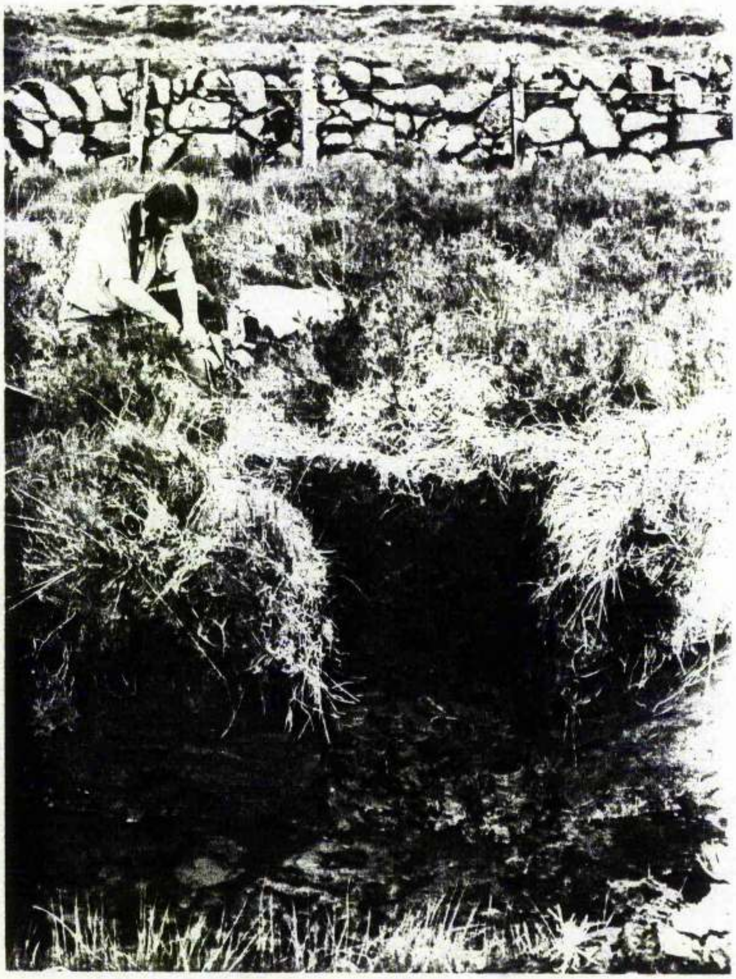


PLATE XVII

Removal of the stream bank to install the stilling well for the water level recorder

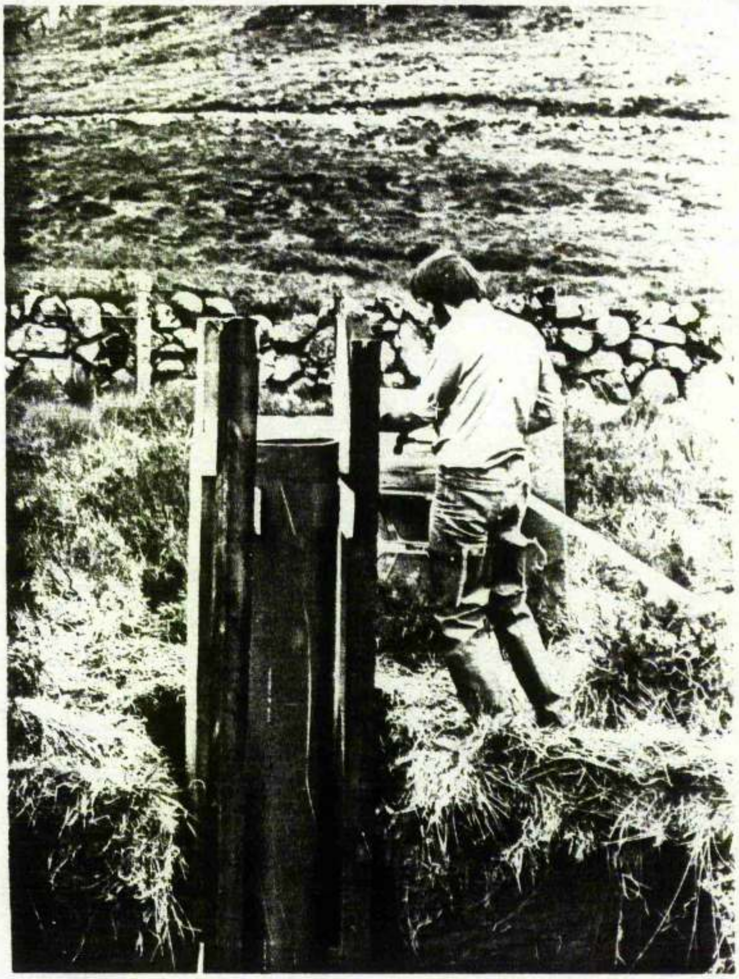


PLATE XVIII

Installation of the stilling well on Dargall Lane

(Pictured:
J.C. Burns, SRPB)

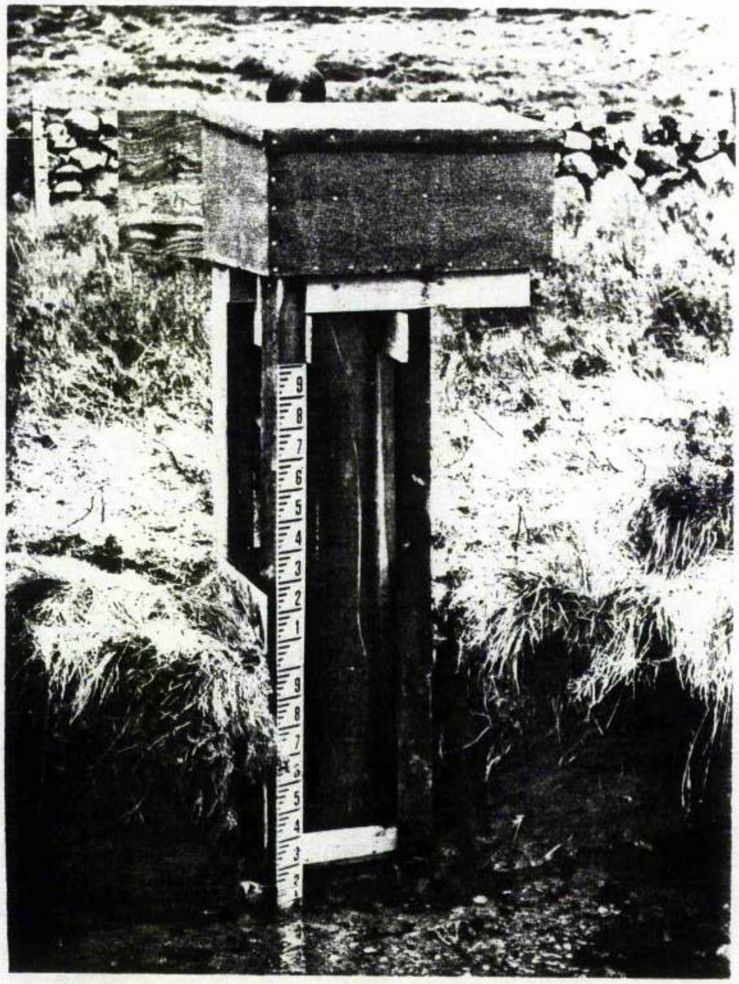


PLATE XIX

The finished water level recorder on Dargall Lane discharge data from this catchment at that time.

The problem of monitoring water level on the Green Burn was more difficult due to the nature of the channel. An ideal situation for the Green Burn recorder would have been to site it on the upstream side of the Forestry Commission roadbridge below the lowest tributary, where the channel is still steep sided and would retain most flows within the channel. However in this area the channel is incised into bedrock and thus impossible to install a suitable structure on. Below the roadbridge the channel shallows and develops a wide floodplain. Having rejected the upstream site on grounds that it was unworkable, a site 150m downstream of the bridge was chosen. In order to ensure stability in both the channel and water level a shallow 'V' shaped control of wooden construction was installed in the stream bed 5 metres downstream of the gauging station. After an initial problem with the clockwork motor on the chart recorder the station has proved most satisfactory.

In May 1984 an opportunity arose to cross-check the accuracy of current meter gaugings during low flow conditions at Loch Dee. Using equipment and laboratory facilities provided by the Institute of Hydrology a method of dilution gauging was tried. A method which Wilson (1975 p.97) has described as "..... particularly suited to small turbulent streams where depths and flows are inappropriate for current metering." An apt description of the conditions under which dilution gauging was employed at Loch Dee.

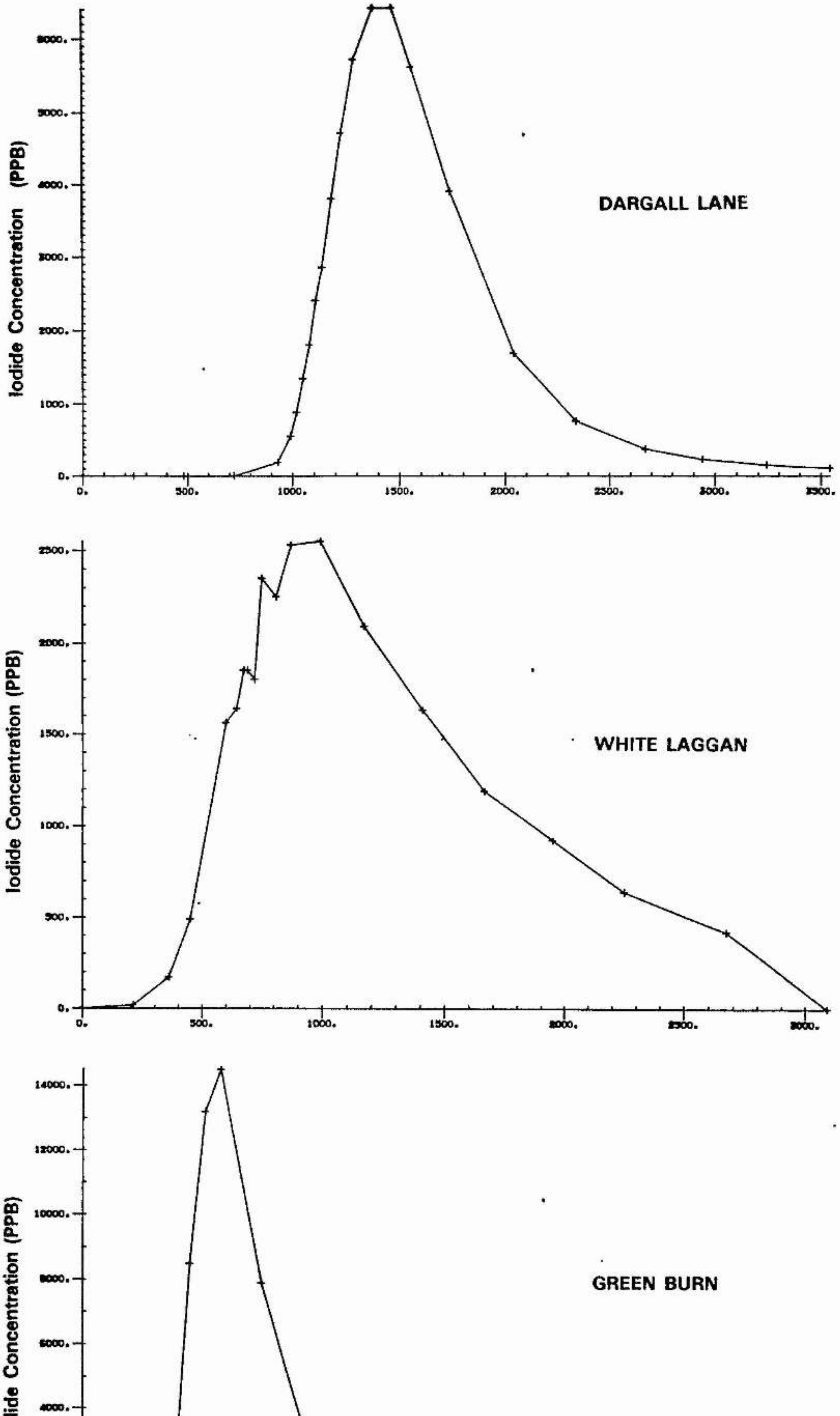


FIG 4:6 Results Of The Dilution Gaugings

Dilution gauging involves the injection either at a constant rate or as a "gulp" (ie. a single instantaneous input) of a chemical in the stream which after a long enough distance downstream to allow thorough mixing, is sampled and the concentration of the chemical determined. The concentration of the chemical in the samples is used to calculate the dilution and hence discharge. The method of dilution gauging employed at Loch Dee is that used by the Institute of Hydrology, Systems Group. This method involves injecting a known volume of sodium iodide tracer into the stream as a gulp injection (shown in plate XIV) and taking samples at a distance between 50-160 metres downstream. This iodide method has an advantage over other dilution techniques in the incorporation of an ion selective electrode. The electrode is floated in the stream at the sampling point (coupled to a meter and chart recorder on the bank), this detects the passage of the iodide past the sampling point. Plate XV shows the use of this method on the Green Burn. From the chart record from the ion selective electrode one can judge the sampling frequency necessary in order to characterise the range and distribution of concentrations whilst conserving the number of samples taken.

Fig. 4:6 shows the concentrations of iodide through each of the gaugings on the three streams. In order to calculate stream discharge the data are manipulated in the following equation:

$$Q = \frac{Z C_1}{\int_0^{\infty} (C_2 - C_0)\,dt}$$

(Gilman, 1977)

Where Z is the volume of the injected solution.

C1 is the concentration of the injected solution.

C2 is the observed concentration of tracer at the sampling station and

Co is the background concentration in the stream (assumed to be constant).

The results of the dilution gauging undertaken in the three streams are given in table 4:3. The results show that dilution gauging consistently gives a higher discharge than that obtained from the rating relationship from current metering.

Station	Rated Current Meter Gauging (m^3s^{-1})	Dilution Gauging (m^3s^{-1})
Dargall Lane	0.016	0.017
White Laggan	0.022	0.027
Green Burn	0.016	0.021

Table 4:3 Comparison of Rated Current Meter Gauging and Dilution Gauging.

The differences between the two sets of results are attributable to two reasons. Firstly, given the very low flows being dealt with, current metering is at its most inaccurate where velocities of stream flow are low and variable across the stream width. The proportionally greater boundary effects of the stream bed and banks also act to create variable turbulence which can generate errors in the measurement process. Dilution gauging avoids such errors and will work efficiently given a long enough channel length to ensure complete mixing of the iodide tracer. However dilution gauging may introduce errors through infrequent sampling and analytical error or more likely through the presence of slack water between the injection and sampling points preventing a thorough mixing of the tracer.

A second source of discrepancy between the methods used occurs as a result of the rating relationships developed at Loch Dee. The number of gaugings at the extremes of flow on all three streams is rather limited giving rise to a less well-defined rating relationship under these flows and discrepancies between methods of measurement may be expected at these flows. Given these difficulties the two sets of gauging data given in table 4:3 compare remarkably well.

It is likely that neither method of flow measurement described here is ideal under the full range of flows at Loch Dee, however with the present resources and technology at Loch Dee these techniques provide the best estimate of stream discharge available.

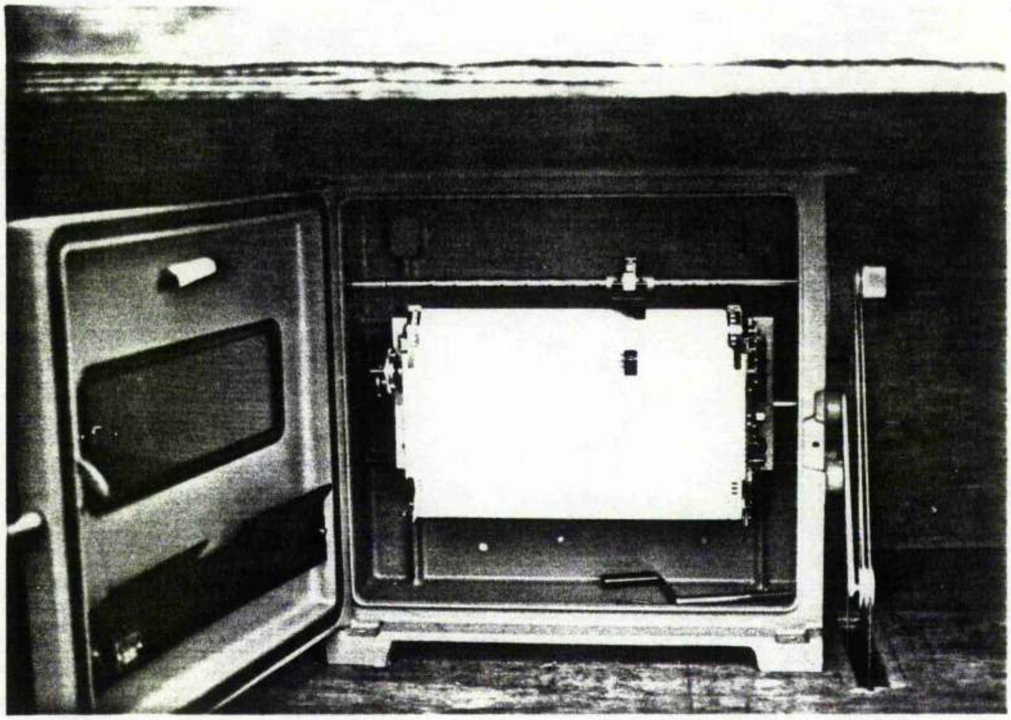


PLATE XX The float-operated chart recorders for the continuous measurement of water level in the Loch Dee Catchment

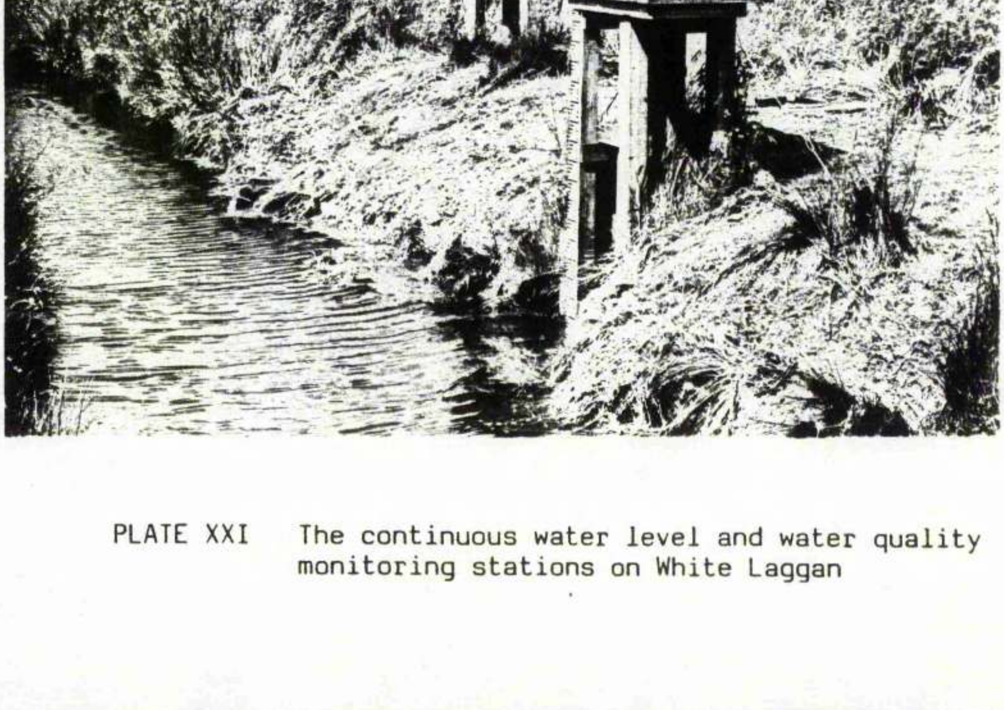


PLATE XXI The continuous water level and water quality monitoring stations on White Laggan

PLATE XXII The continuous water level and water quality monitoring station on Dargall Lane

PLATE XXIII

The continuous water level recorder on Green Burn

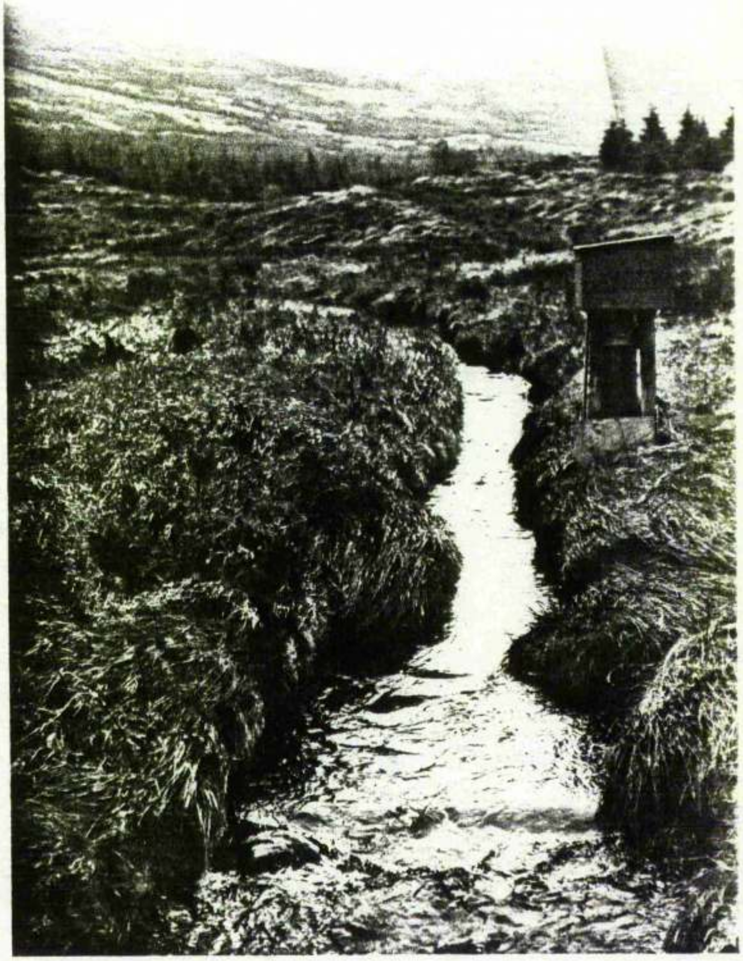
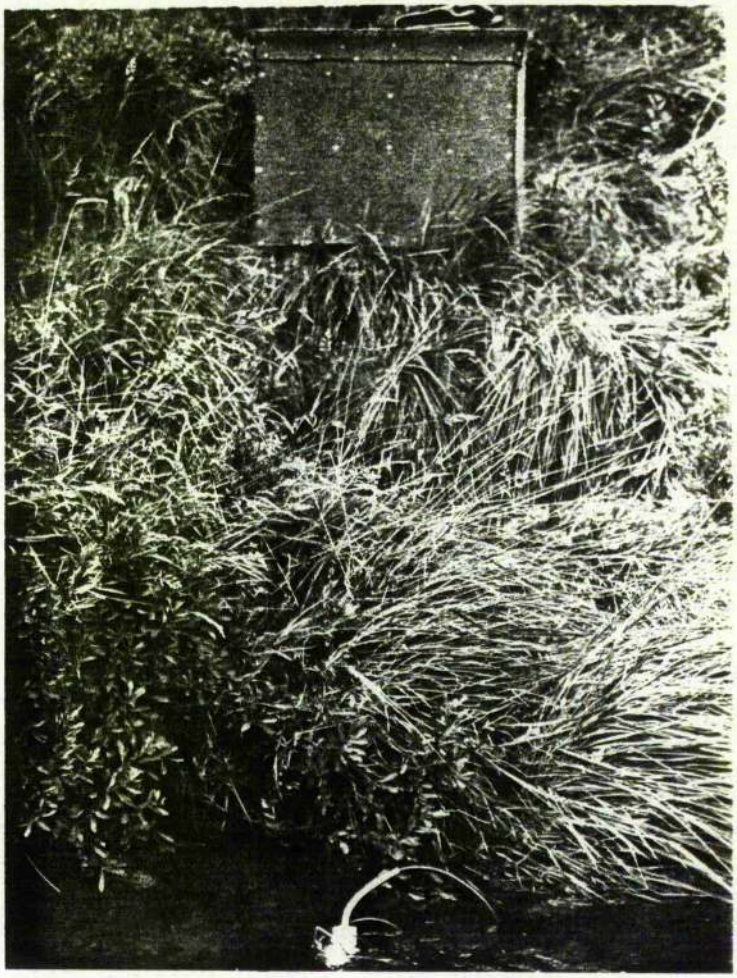


PLATE XXIV

The continuous water quality station on the Green Burn showing the permanently immersed pH electrode



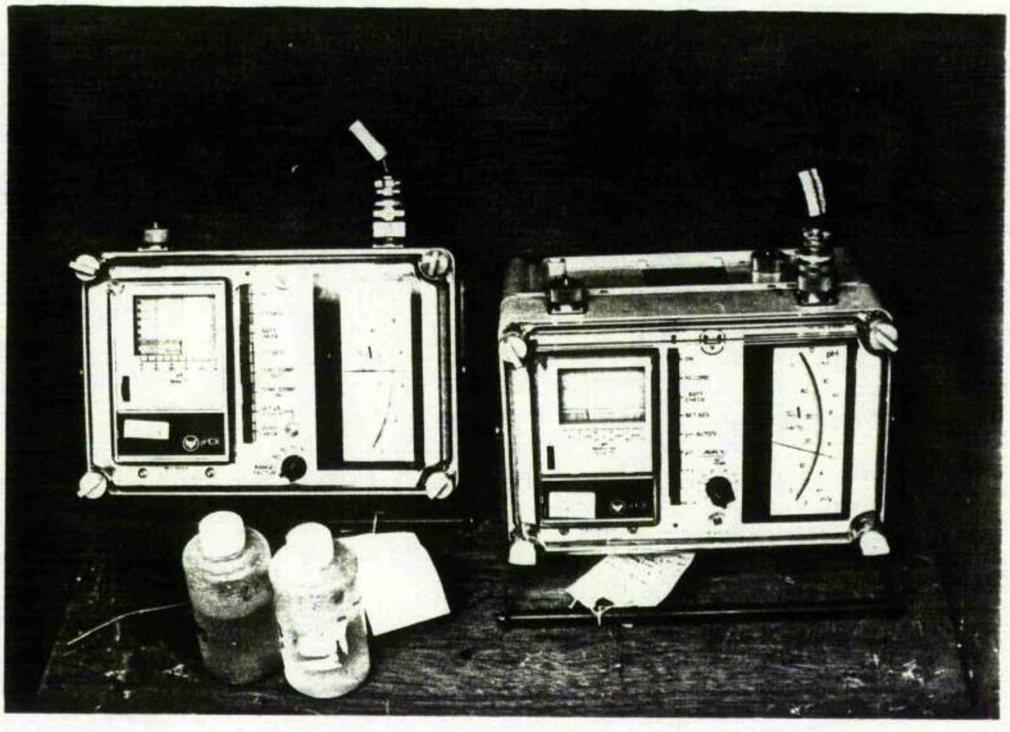


PLATE XXV The continuous water quality instrumentation common to all monitoring stations at Loch Dee

Water quality (pH and conductivity) in the streams has been measured in White Laggan since early 1981 by the SRPB. With the involvement of the author in the project in 1983 similar systems were bought and installed in the Green Burn and Dargall Lane catchments. The system at each site consists of a PHOX series 57 mk.II conductivity meter and a PHOX series 47 mk.II pH meter, shown in plate XXV. These systems are powered by 6v rechargable batteries and record onto 'Rustrak' paper strip chart recorders operating at a speed of 6-7 mm hr^{-1} with the charts lasting for 3 months. Both pH and conductivity are automatically temperature compensated to the standard reference temperature of 25^{oC}. The systems are housed in 'weather-proof' boxes on the stream banks with the probes permanently immersed in the streams attached to a wooden stake driven into the stream bed. The pH probe consists of a Russell pH CE7L/NH gel filled combination electrode (compatible to the laboratory model) and is protected by a plastic guard. In the White Laggan Burn and the Dargall Lane the water quality instruments are alongside the gauging station (plates XXI and XXII). However in the Green Burn the water quality monitors are 150m. upstream of the gauging station (plates XXIII and XXIV).

The nature of the water quality measurements dictates the greater need for maintenance than is needed for the water level recorders. Pre 1984 the instruments were checked weekly (during the summer by the author) by SRPB personnel. Since 1984 and the appointment of a scientific officer (Dr. P.Hutchinson) to the Loch Dee Project the instruments have been checked on a more frequent basis. A routine check of the instruments involves checking the battery voltage and when low changing the batteries; time checking the strip chart recorders; cleaning the conductivity probe and cleaning and buffering (pH 4 and 7) the pH probe using standard BDH buffer solutions supplied by the SRPB laboratories. A record of all adjustments, problems and battery voltage is also taken. The most common problems with these type of monitors appear to be the variable speed of the chart recorders, making accurate time correction important in the regular check of the monitors.

More serious problems occur when the site is inaccessible during cold winter periods during which time the batteries drain very quickly thus resulting in the loss of records. In the summer there can be substantial build up of algae on both the pH and conductivity probes which may distort the readings. A further problem with the pH electrodes is the perishing of the water-tight housing for the electrode and also the limited life of the electrodes themselves, both resulting in the loss of records.

4:3:4 Quality Control and Data Reduction of the Continuous Data.

The use of continuous monitors produces large amounts of data which in their most basic format may be both bulky and too detailed for general use. In order to reduce the continuous data into a more usable and useful format much of the data has been reduced into a more manageable form via a computer.

The strip charts are removed monthly from the water level recorders and 3 monthly from the water quality instruments. The charts are checked manually (water level by SRPB and water quality, over the study period by the author) for recorder malfunctions and equipment failure. For the water quality charts cross reference is also made to the maintenance records taken at the site to determine any additional faults or notes which may affect the quality of the records. It is at this stage that data are rejected on one or more of the following criteria:

i. Equipment failure or malfunction-this is usually readily evident from the charts.

ii. Excessive or variable 'time-slippage'-where the chart recorders have failed to maintain a relatively constant speed the data are rejected because of problems in identifying the timing of events between the time marks. This factor occurs during extreme weather conditions or low battery voltage.

iii. Where excessive algal growth on the water quality electrodes is reported in the maintenance notes to have adversely affected the readings. This is evident from a significant change in the readings before and after cleaning the probes.

iv. An additional control placed on the pH data is that for the data to be usable the pH electrode must buffer at the beginning and end of each time checked period to within ± 0.1 of a pH unit at both pH 4 and 7. This problem most commonly arises with excessive algal growth (surpresing the pH range) or as the electrode ages.

Whilst these factors reduce the amount of available data the author felt these stringent checks necessary to maintain a high level of quality and therefore confidence in the data.

The stream water data for both quantity and quality are transferred from chart to computer by means of a digitising tablet, where the trace on the strip chart is replaced by a series of digital readings characterising the shape of the line. This data is held on the SRPB Data General Micronova computer. This digitised data is then run through a programme which converts the digitised line into hourly values of pH and conductivity. For the production of hourly discharge, digitised water levels are run through a programme which converts water level into discharge (m^3s^{-1}) using the rating relationship for each stream. All the data are stored in files of one calender month duration (hourly values) with separate files for pH, conductivity and discharge. With the help of Mr.T.Poodle and Mr.J.Rooney of the Clyde River Purification Board the data have been transferred from Data General computer disk to DEC compatible magnetic tape for use on St. Andrews university VAX network.

4:4 The Data Base.

The data used in this thesis amounts to over 20,000 pieces of data and has therefore been omitted as an appendix. However the data used in this thesis is available on magnetic computer tape. Access to the data base is achieved in the first instance by contact with either the University of St. Andrews, Dept. of Geography or the Solway River Purification Board, Dumfries. Appendix A gives the details of the stations and dates for which records are available.

CHAPTER 5 : ATMOSPHERIC AND STREAMWATER CHEMISTRY VARIATION IN THE THREE CATCHMENTS OF LOCH DEE.

5:1 INTRODUCTION.

The objective of this chapter is to characterise the three catchments of Loch Dee in terms of their overall streamwater chemistry; to investigate the temporal variation in atmospheric input to the catchment and the influence this may have on the streamwater chemistry and to identify hydrochemical controls on streamwater chemistry. The routinely collected weekly data from the period 8th January 1980 to 28th May 1984 for weekly bulked precipitation, Dargall Lane, White Laggan(1) and Green Burn provide the data on which this chapter is based. Before using these data it was necessary to 'screen' the raw data to eliminate data of a poor quality. The method of screening has been described in section 4:2.

Due to the poor representation (38 samples) of the bulk precipitation inputs no attempt has been made to investigate input-output budgets. The time-based data presented in figs. 5:2 to 5:12 are the full (unscreened) data sets for the period January 1980 to May 1984 and are only used to give a visual and descriptive impression of the time based variation in ionic concentrations.

5:2 RESULTS.

To give an impression of the general setting for atmospheric inputs and streamwater outputs and any interrelation of the various ionic species at Loch Dee the screened weekly data were subject to a series of summary statistical techniques. In view of the considerable problem in normalising the data for some of the parameters considered the data are described in terms of mean, median, and a non-parametric (Spearman Rho) correlation technique. The results are given in tables 5:1 to 5:7. These statistical techniques are standard statistical methods and are described elsewhere (eg. Norcliffe 1982.) Given the uncertainty in the exact time of the weekly sample collection during the initial years of the project when the time of sampling was not recorded the mean daily flow (MDF) was used in calculating flow-ionic concentrations. This has two implications for subsequent analysis. The flashy runoff response of White Laggan implies that using MDF values will reduce the strength of the flow- concentration correlation over that which might have been obtained using instantaneous flow. Secondly, averaging flows into an MDF has the effect of skewing the data towards smaller flows. A skewed data set infringes the assumptions of regression analysis and care must be taken in interpreting this type of analysis. Values of MDF for the date of the weekly chemical sample have been plotted to construct a flow overlay for use with figs. 5:2 to 5:12 (insert inside back cover). The length of continuous flow records permits this type of analysis for White Laggan only.

Ion	Station	Mean	Median	S. Dev.	Max.	Min.	Range
H^+	Bulk	22.5	17.7	19.3	78.8	0.0	78.8
	DL	8.5	6.3	10.1	78.8	0.0	78.8
	WL	2.1	0.0	3.7	24.9	0.0	24.9
	GB	5.9	2.0	10.9	78.8	0.0	78.8
Na^+	Bulk	108.7	67.4	89.2	435.0	1.7	433.3
	DL	160.3	156.6	42.6	266.2	NA	266.2
	WL	173.4	176.2	44.5	267.1	NA	267.1
	GB	174.0	173.6	39.5	253.6	93.5	160.1
K^+	Bulk	8.6	6.0	13.4	87.0	2.0	84.9
	DL	8.9	9.5	3.8	16.4	0.0	16.4
	WL	8.6	8.7	3.2	21.0	0.0	21.0
	GB	11.8	10.7	8.4	58.1	3.3	54.7
Ca^{2+}	Bulk	21.3	19.0	20.9	119.8	4.5	115.3
	DL	50.8	51.4	12.6	84.3	24.9	59.4
	WL	79.9	76.8	20.6	137.7	40.9	96.8
	GB	68.5	67.8	19.0	124.2	NA	124.2
Mg^{2+}	Bulk	25.8	18.1	19.2	83.9	1.6	82.2
	DL	54.3	54.3	11.8	92.1	32.1	60.0
	WL	73.4	74.0	15.4	106.1	38.6	67.4
	GB	78.5	77.3	21.2	139.0	0.0	139.0
SO_4^{2-}	Bulk	56.1	53.1	41.7	145.7	NA	145.7
	DL	85.3	83.3	34.2	177.0	NA	177.0
	WL	99.9	93.7	42.1	239.4	NA	239.4
	GB	86.9	89.5	41.0	229.0	NA	229.0
NO_3^-	Bulk	18.5	13.2	17.0	57.1	0.7	56.4
	DL	11.5	7.9	11.8	51.4	0.0	51.4
	WL	10.5	6.4	10.7	50.7	0.0	50.7
	GB	8.1	3.6	9.9	49.3	0.0	49.3
Cl^-	Bulk	132.9	95.9	104.3	490.7	14.1	476.6
	DL	201.0	203.0	71.4	394.8	84.6	310.2
	WL	226.3	225.6	73.7	406.1	84.6	321.5
	GB	238.6	242.5	80.9	496.3	84.6	411.7
HCO_3^-	Bulk	17.8	13.4	31.2	188.2	0.0	188.2
	DL	22.1	20.2	10.2	51.1	0.0	51.1
	WL	38.4	34.3	22.0	116.9	2.7	114.3
	GB	39.1	28.2	31.8	162.7	0.0	162.7

Key

Bulk = Bulk precipitation
WL = White Laggan
DL = Dargall Lane
GB = Green Burn

All figures in $\mu eq.l^{-1}$

NA = Not available

TABLE 5:1 Summary Statistics for Weekly Samples

Station / Ion	Bulk Precipitation	Dargall Lane	White Laggan	Green Burn
Sodium	58.2	56.6	51.4	51.5
Potassium	4.6	3.2	2.5	3.4
Calcium	11.4	17.9	23.7	20.2
Magnesium	13.8	19.3	21.8	23.1
Hydrogen	12.0	3.0	0.6	1.8
Sulphate	24.9	26.6	26.6	23.3
Nitrate	8.2	3.6	2.8	2.2
Chloride	59.0	62.9	60.4	64.0
Bicarbonate Alkalinity	7.9	6.9	10.2	10.5

TABLE 5:3 Percentage Contribution of Individual Cations and Anions

	H^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	SO_4^{2-}	NO_3^-	Cl^-	HCO_3^-
Flow	.525	--	.260 (.006)	-.674	-.604	-.420	--	--	-.556

All significant at .001 unless otherwise stated

TABLE 5:4 Spearman Rho Correlations for White Laggan Mean Daily Flow

Bulk Precipitation

	H^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	NO_3^-	Cl^-	HCO_3^-
Hydrogen ion		-	-	-	-	.4648 .002	.6551	-	-.8801
Sodium	-		-	-	.8397	-	-	.9443	-
Potassium	.3558	.2660 .003		.6158	-	-	-	-	-
Calcium	-	.4515	-		.6167	-	-	-	-
Magnesium	-	.7754	.4097	.7498		-	-	.8846	-
Sulphate	-	-	-	.2774 .002	-		.8105	-	-
Nitrate	.3687	.4333	.6341	-	.4956	-		-	-.5502
Chloride	-	.8906	.3537	.4423	.7768	-	.5014		-
Bicarbonate Alkalinity	-.4837	-	-	-	-	-	-.2709 .003	-	

Dargall Lane

White Laggan

	H^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	NO_3^-	Cl^-	HCO_3^-
Hydrogen ion		-	.3196 .001	-.4182	-.2980 .002	-.3092 .001	.3525	-	-.5562
Sodium	-		.3390	.4224	.6360	-	.4802	.8331	-
Potassium	.3489	.3477		-	-	-	.5776	.4178	-.2958 .002
Calcium	-.4894	.4660	-		.8676	.5159	-	.3120 .001	.3894
Magnesium	-.4581	.5263	-	.8657		.5159	.2908 .002	.4836	-
Sulphate	-	-	-	-	-		-	-	-
Nitrate	.4097	.3432	.4255	-	-	-		.4739	-.4362
Chloride	-	.8297	.5266	.2880 .001	.3354	-	.3649		-
Bicarbonate Alkalinity	-.7778	-	-.3207	.4751	.5047	-	-.4104	-.2873 .001	

Green Burn

Note : All significant at .001 unless otherwise stated

TABLE 5:5 Spearman Rho Correlations for the weekly samples

5:2:1 Hydrogen ion.

The weekly bulked precipitation median concentration of 17.7 µeq $H^{+}l^{-1}$ (table 5:1) compares with a volume weighted (mean) of 20.0 µeq $H^{+}l^{-1}$ given by Welsh and Burns (1985) for Loch Dee over the same period. Both of these values are substantially less than the mean weighted annual average of 30-40 µeq $H^{+}l^{-1}$ suggested by Barrett et al (1983) for the period 1978-1980. On closer inspection of the work by Barrett et al it is apparent that the regional average given by the authors for the area is based on 3 annual weighted means (1978, 1979 and 1980) from Glentrool (38,22 and 29 µeq $H^{+}l^{-1}$) and 1 annual weighted mean from Cairnsmore of Fleet (1979, 38 µeq $H^{+}l^{-1}$). This single high value for Cairnsmore of Fleet elevates the regional acidity value given by the authors. In the light of this it is likely the results presented here and by Welsh and Burns (1985) covering a longer time span are a more appropriate indication of the acidic inputs to Loch Dee and the surrounding area. (See section 5:3)

Comparison of the three streams in terms of their acidity (table 5:1) shows Dargall Lane to be the most acidic with a median concentration of 6.3 µeq $H^{+}l^{-1}$. Green Burn is not quite so acidic in general terms with a median concentration of 2.0 µeq $H^{+}l^{-1}$. However comparison of the two streams range and standard deviation (Green Burn s.dev 10.9, range 78.8, Dargall Lane s.dev 10.1, range 78.8 µeq. $H^{+}l^{-1}$) suggest there is a large amount of variation away from these median values. The median values for White Laggan indicate that more than 50% of the weekly samples had a negligible acidity (ie. a pH> 6.0). White Laggan also has a much lower maximum acidity value. The lower standard deviation (3.7) and range (24.9) indicate that the fluxes in acidity and the magnitude of acidic episodes are much less in White Laggan than in the other two streams.

Figure 5:1 provides a comparison of all the stream sampling points and their associated frequency of acidities. In constructing the cumulative frequency curves only data passing the ion balance technique were included with the consequence that the curve tails are represented by a few samples which may exaggerate these sections of the curve. The figure shows an interesting transition from Dargall Lane through Green Burn to the least acidic samples taken over the White Laggan catchment. Comparison of the curves for the various sampling points within the White Laggan catchment are interesting in their implications. White Laggan (1) reflects the joint acidities derived from the two tributary sub-catchments represented by the samples from upper White Laggan and Black Laggan. Futhermore the acidity of White Laggan (2) is consistently lower than any of the sampling stations higher in the catchment, and the H^+ duration curve is the flatest. A further indication of the ability of the White Laggan catchment to buffer acidity is provided by comparing the percentage of weekly samples with an acidity > 10 µeq H^+l^{-1} (pH 5.0) which is given in table 5:2.

Dargall Lane	24%
White Laggan	2%
Green Burn	17%

Table 5:2 % weekly samples with acidities > 10 µeq H^+l^{-1}

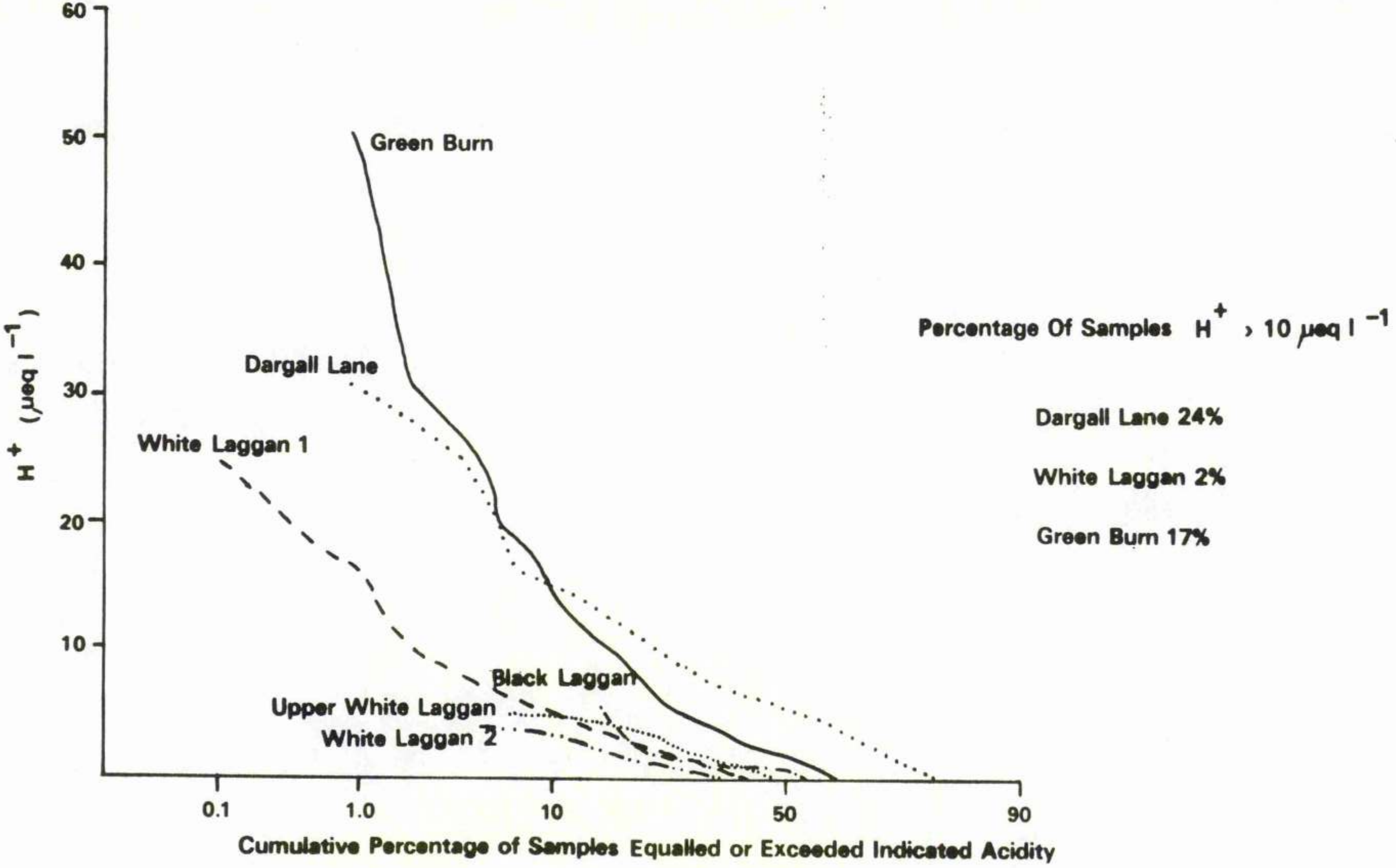
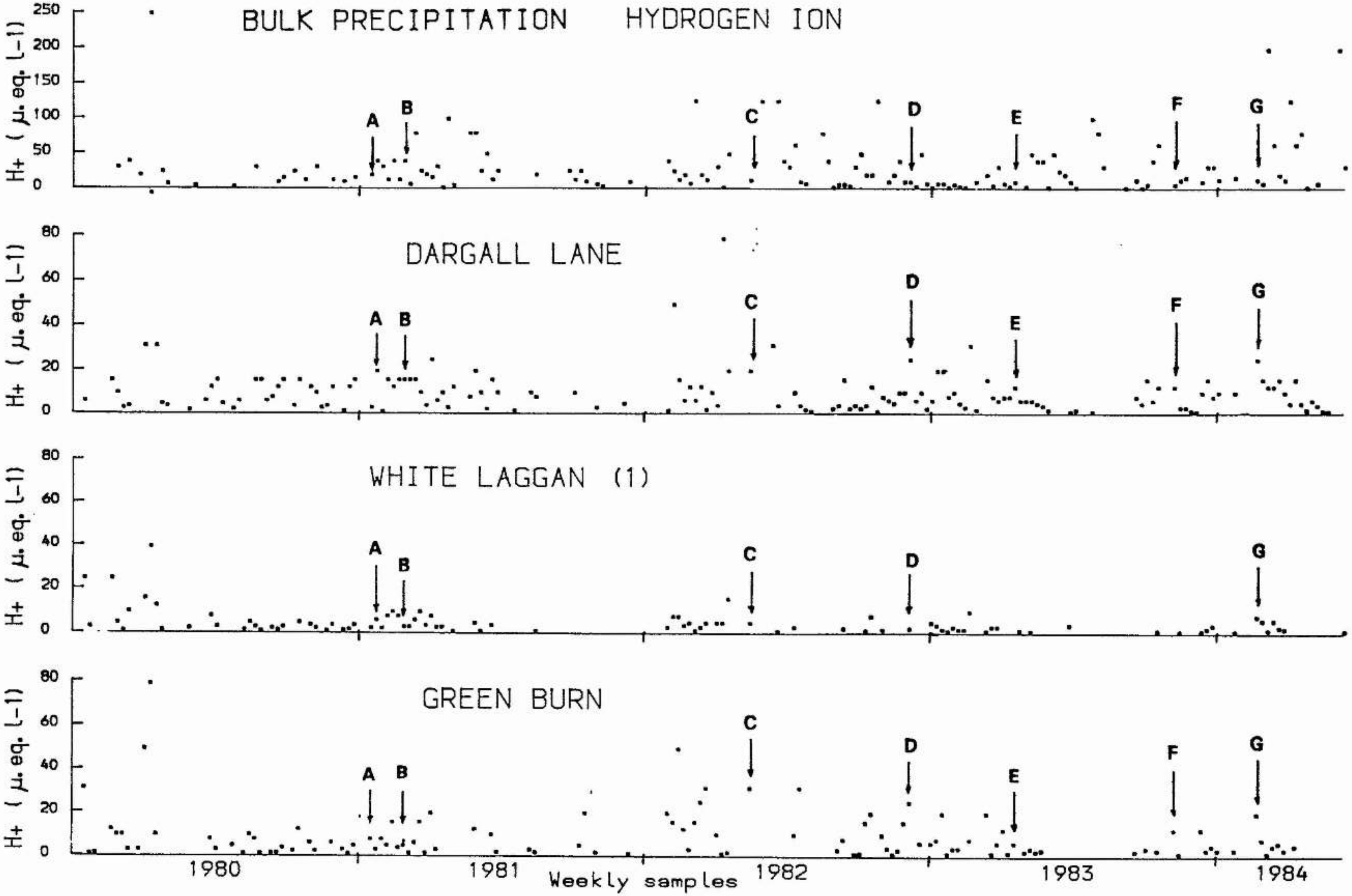


FIG 5:1 Hydrogen Ion Frequency Curve



For an explanation of annotated points see Fig 5:7

FIG 5:2 Weekly Variation In Hydrogen Ion

Using the data from tables 5:1 and 5:2 substantial differences are indicated between the stream acidities in terms of magnitude and duration.

Reference to fig 5:2 illustrates that whilst some of the most acidic rainfall events are also seen in the streams, not all the acidic stream events are readily explained by acid deposition. A further source of stream acidity (the annotated points on fig. 5:2) involves an exchange mechanism within the soil, a point discussed in section 5:3 and in greater detail in chapter 6.

Using the White Laggan concentrations and corresponding MDF values a Spearman Rho correlation indicates, as expected, a positive relationship (Rs 0.5252) between flow and acidity. This positive relation explains the strongly seasonal trends displayed in the weekly H^+ concentration in fig. 5:2, in which high flows in the winter are associated with high acidity levels.

Table 5:5 shows incoming precipitation acidity to be correlated with the presence of nitrate and sulphate. The stronger correlation of precipitation acidity with nitrate intimates the single dominant source of atmospheric nitrate whereas sulphate is derived from both anthropogenic pollution and maritime inputs (section 5:2:8). As maritime sulphate is not associated with acidity the strength of the sulphate- acidity correlation is weakened.

In the streams acidity is not positively correlated particularly strongly with any other major ions although there is some association with nitrate and potassium. Similarly it is interesting to note the inverse correlation of sulphate with acidity in White Laggan. These correlations are likely to be the function of a common process which governs the concentrations of these ions in the streamwater, a factor which is discussed in greater detail in section 5:3. Both precipitation and streamwater acidity are inversely correlated with alkalinity. In Green Burn and White Laggan acidity is also inversely correlated with calcium and magnesium.

5:2:2 Calcium.

Reference to the mean and median ionic concentrations (table 5:1) indicates an increase in 'average' calcium levels in the order precipitation (lowest), Dargall Lane, Green Burn and White Laggan. Values for the Green Burn and White Laggan are broadly similar, whereas Dargall Lane is intermediate between these two and the low precipitation input.

Comparison of the calcium results for the three streams given in table 5:1 shows White Laggan to have the highest median concentration. In contrast Dargall Lane has the lowest calcium concentration of the streams with a markedly lower range of values. The contrast in calcium ranges between Dargall Lane and the other two streams is further supported by fig 5:3. Using the MDF overlay there is evidence for an inverse flow-calcium relationship. For White Laggan this can be shown statistically using a Spearman Rho correlation. At a significance level of P=.0001 Rs= -.6736 i.e. 45%

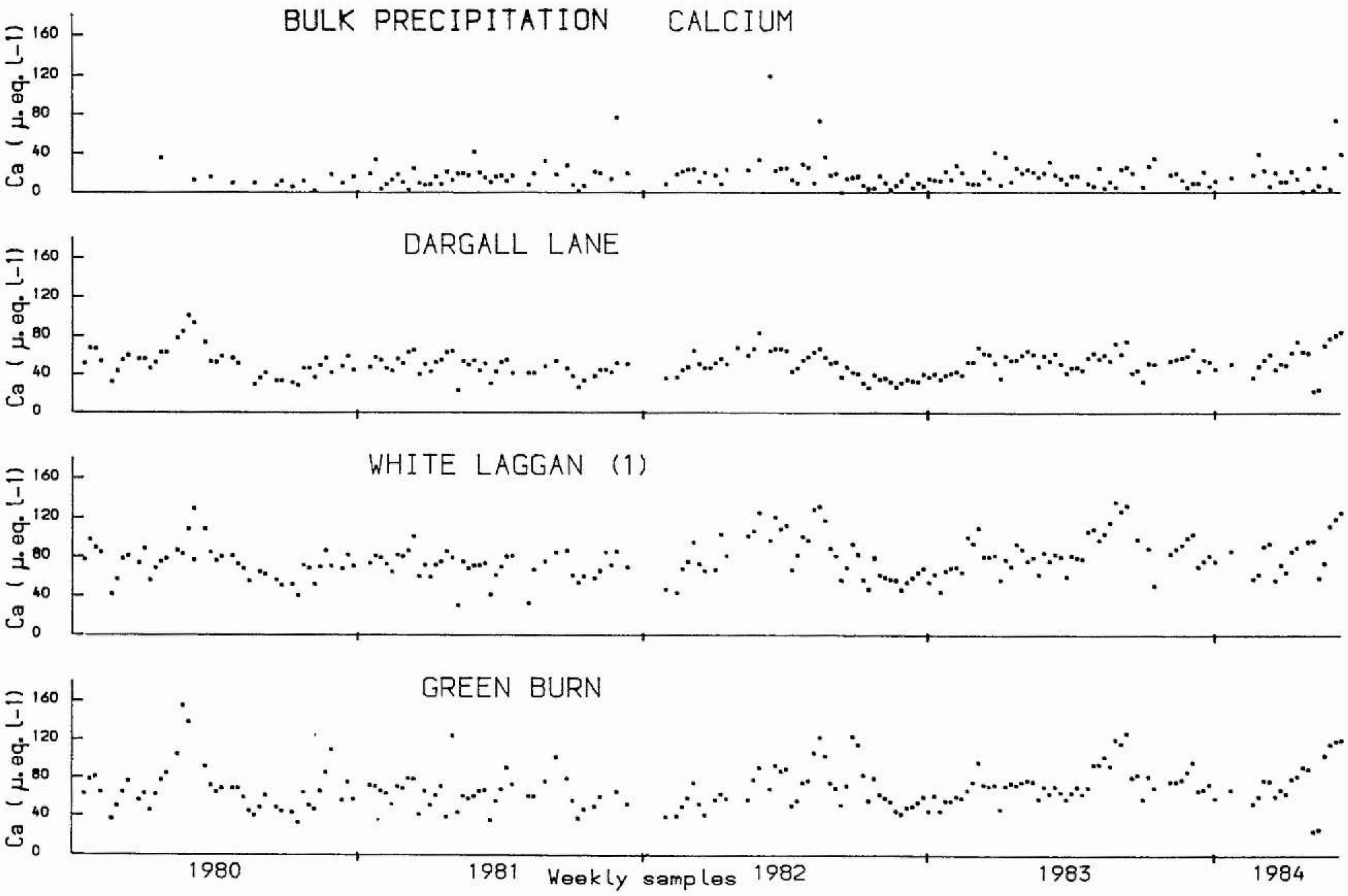


FIG 5:3 Weekly Variation In Calcium

of the variation in calcium concentration can be accounted for by variation in the flow. This figure would be much higher were instantaneous flow records available. As with hydrogen ion values this flow relation accounts for the apparent seasonality of the data, with low summer flows associated with high calcium concentrations.

The generally lower concentrations (table 5:1) of Dargall Lane give an indication of the poorer water quality draining from this catchment. This point is discussed in greater depth in section 5:3.

The atmospheric inputs of calcium to the catchment are associated with inputs of magnesium and potassium (table 5:5) the sources of which are likely to be maritime in origin. The strongest correlation with calcium in all three catchments is magnesium. This correlation is a function of the predominant process determining the stream concentrations of both these elements. i.e. flow conditions. A similar explanation, that flow (in part) determines the concentrations of sulphate, alkalinity and acidity accounts for these correlations with calcium.

5:2:3 Magnesium.

The general behaviour of magnesium as an ionic constituent of streamwater and precipitation is similar to that of calcium. A comparison of figs. 5:3 and 5:4 demonstrates the affinity in the behaviour of these two ions in each of the three streams. Thus Dargall Lane has a smaller range of concentration than the other streams and in all three streams concentrations appear to be higher in the summer months. Table 5:5 similarly indicates a high degree of covariance between these two ions. Using a Spearman Rho correlation

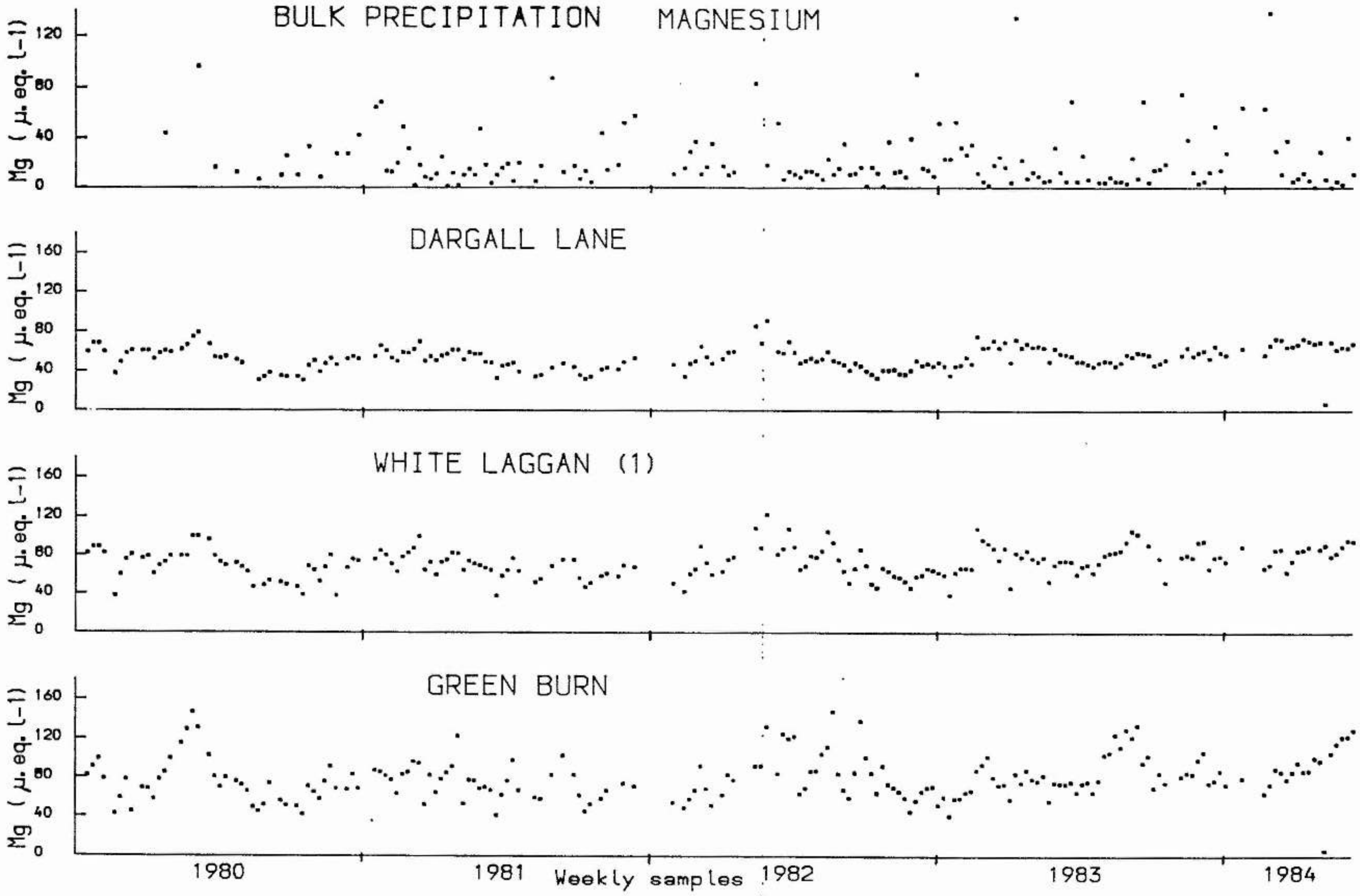


FIG 5:4 Weekly Variation In Magnesium

for magnesium-flow an inverse relation exists (i.e. dilution) in which 37% of the variation in magnesium can be explained by flow conditions in the White Laggan. As with calcium this suggests that flow is one of of the dominant controls on streamwater magnesium concentration.

Taking calcium and magnesium together they provide 25% of the cation input (table 5:3) from the atmosphere whilst they represent 37%, 45% and 43% of the cations in Dargall Lane, White Laggan and Green Burn respectively. Table 5:5 indicates a strong covariance between these two ions in each of the streams. This relationship was explored in terms of a linear regression the results of which are shown in fig. 5:5. It is evident that White Laggan is markedly different from the other two catchments. Fig. 5:5 shows calcium and magnesium values to occur over a limited range of concentrations in the Dargall Lane, however of interest is the dispersion of points away from the best fit line. At low concentrations there is little dispersion whilst at high concentrations there is a wider dispersion of values with values in between grading from one extreme to the other. This dispersion of values accounts for the lower r value (0.74) than those observed in the other two streams. Green Burn (fig. 5:5) shows the dispersion of values to be much lower (r=0.92). Comparison of these two regressional equations shows a close similarity in the catchment relationships for Green Burn and Dargall Lane. Further comparison of these two with that of White Laggan intimates the difference of the White Laggan catchment. The significant aspect of this relationship is the much higher slope value (1.57) suggesting the greater availability of calcium in White Laggan. This has interesting implications in terms of the water quality of the catchment. The strength of the relationship between

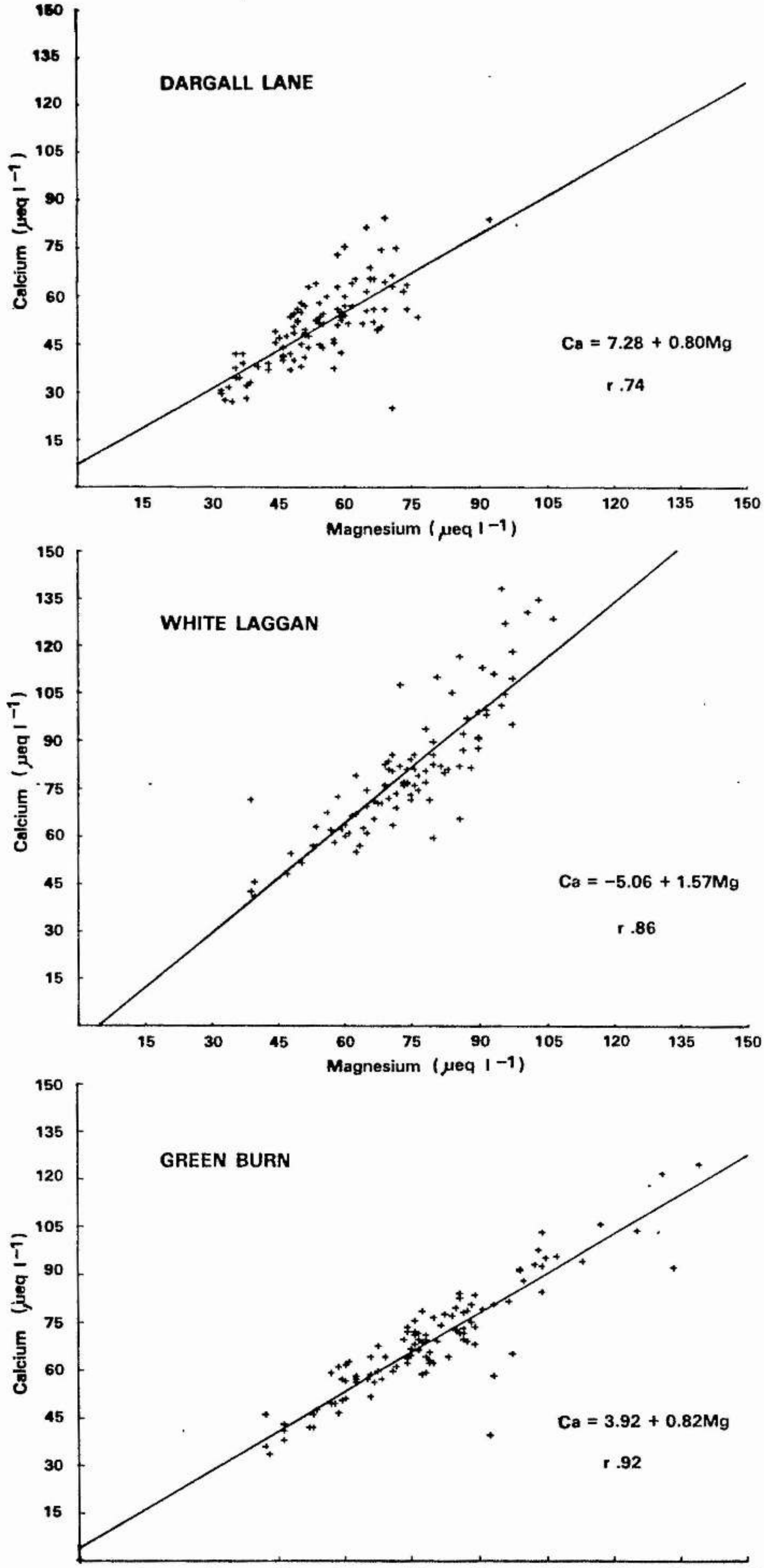


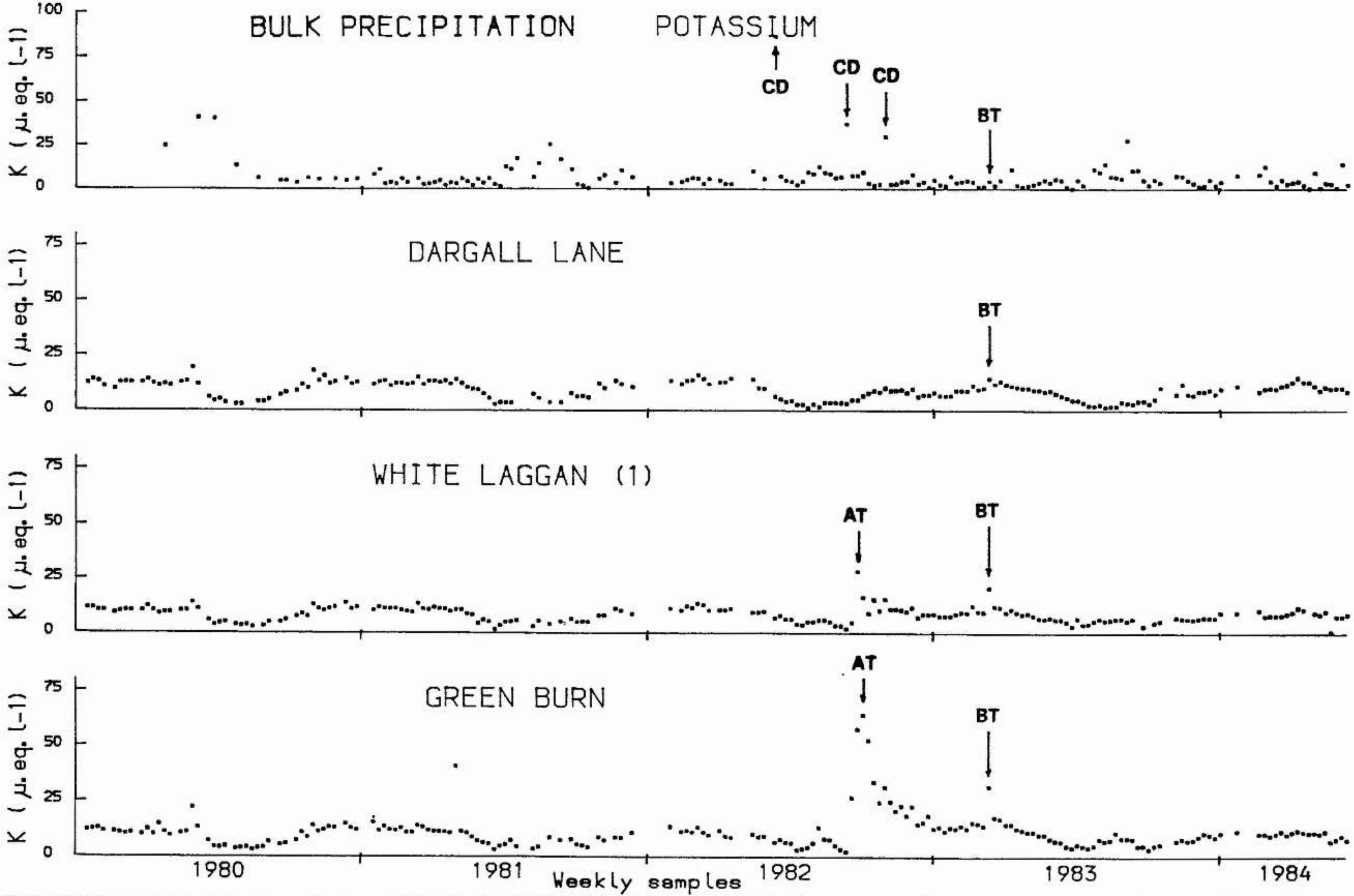
FIG 5:5 The Relationship Between Calcium and Magnesium

flow and both calcium and magnesium in the White Laggan infers that this process predominantly accounts for the relationships and differences seen in figs 5:1 to 5:4 (see section 5:3:5).

Magnesium levels in the precipitation are correlated strongly with chloride and sodium indicative of the maritime inputs of these ions, although the correlation with calcium indicates that there may be some terrestrial input. In the Dargall Lane magnesium concentrations vary with these maritime atmospheric inputs of sodium and chloride and also with nitrate and potassium. In both Green Burn and White Laggan magnesium is inversely related to streamwater acidity, in addition to the weaker correlations with sodium and chloride. The Green Burn also indicates a correlation of magnesium with alkaliity whilst White Lagganshows a correlation with with sulphate.

5:2:4 Potassium.

The streamwater data of fig 5:6 indicates a clear seasonal pattern in potassium levels with concentrations low during the summer and high over the winter months. Such a clear pattern suggests a biological control. Figure 5:6 also shows a peak in potassium concentrations in Green Burn during summer 1982 (point A). This peak is the result of the application of the P-K fertilizer described in chapter 3. A further interesting point from fig 5:6 is the occurrence of three spuriously high concentrations of potassium recorded in the precipitation collectors (points CD) this highlights the susceptibility of continuously open bulk precipitation collectors to contamination. As a consequence of this fertilizer application to the Green Burn catchment this stream shows a higher mean, median and

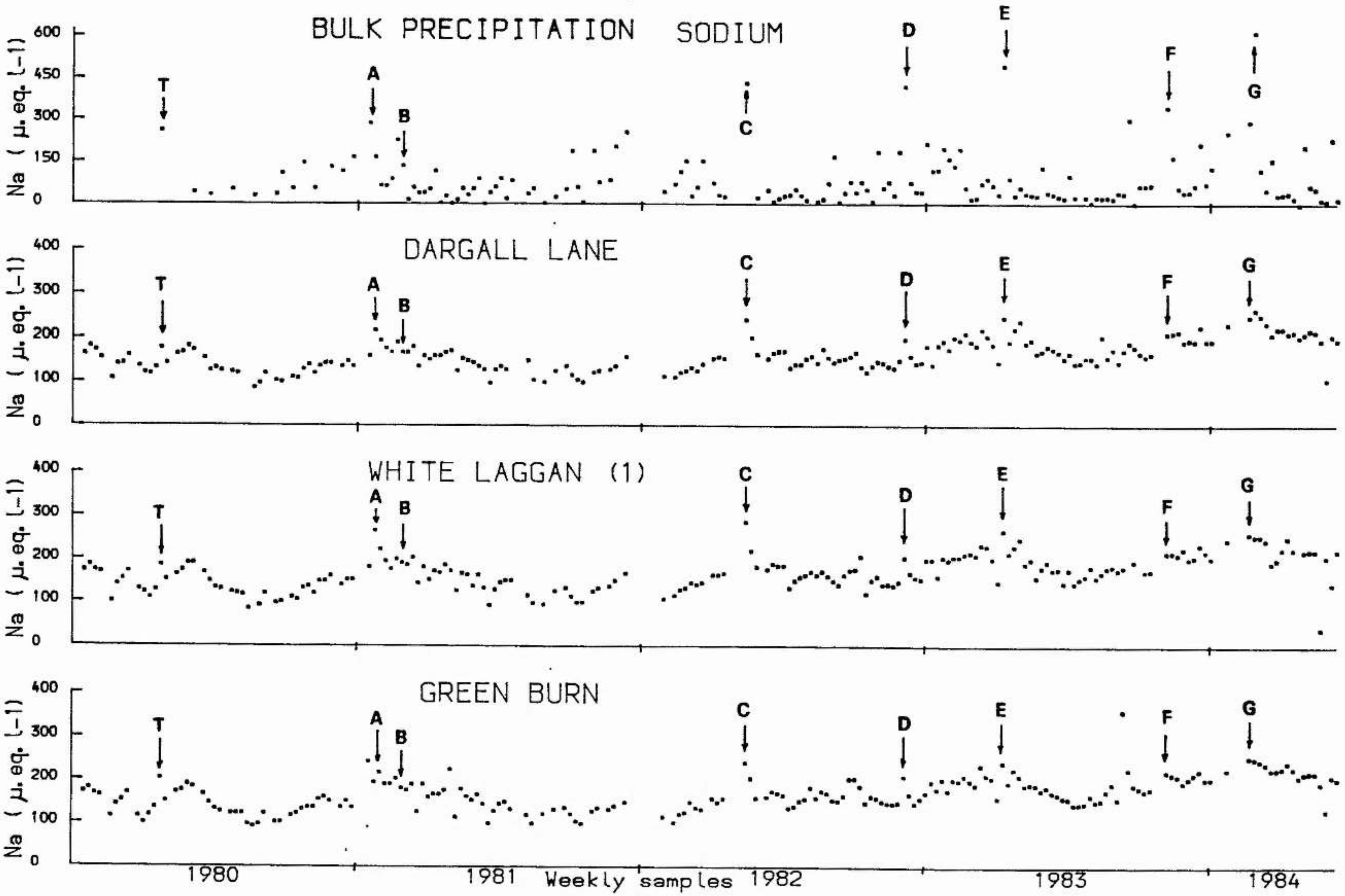


AT: PK Fertilizer Applied To Green Burn BT : Washing Off Of Dry Deposits CD : Contamination Of Bulk Precipitation Collector By Fertilizer

FIG 5:6 Weekly Variation In Potassium Ion range of potassium concentrations. The positive (weak) correlation between flow and potassium (table 5:4) is in common with other British works (Edwards 1973 and Walling and Webb 1981). Table 5:5 suggests that variations in potassium levels in the streams are correlated (positively) with changes in stream acidity, and for Green Burn and White Laggan potassium has an inverse relation with stream alkalinity. These correlations illustrate the common process of stream discharge in determining the ionic concentrations of these elements.

5:2:5 Sodium.

Sodium dominates both the atmospheric input (58% of cations) and the water chemistry of the three streams. Inputs of sodium are highly correlated (table 5:5) with the principal sea-salt components of magnesium and chloride, illustrating the predominant role of maritime sources in supplying atmospheric inputs at Loch Dee. Fig 5:7 shows the large variation in these sea-salt inputs. The episodic nature of these inputs is further evident from the large range and standard deviation figures of table 5:1. Highlighted on fig 5:7 are the exceptionally high concentrations of sodium in the precipitation (points A to G) which have lead to direct consequences in streamwater chemistry. A further point to note from the diagram is the increased number of these 'sea-salt' episodes since 1982. This increased input of sea-salts has lead to an increase (over the sampled period) of sodium concentrations in the streams. Furthermore cross-reference between fig 5:1 and 5:7 indicates there is an apparent link between high sodium concentrations in the precipitation samples and elevated stream acidity (points A to G on figs 5:1 and 5:7). This hypothesis is examined in greater detail in section 5:3 and chapter 6.



A–G Sea –Salt Inputs : **A** 6.1.1981 **B** 17.2.1981 **C** 4.5.1982 **D** 23.11.1982 **E** 27.3.1983 **F** 24.10.1983 **G** 13.2.1984

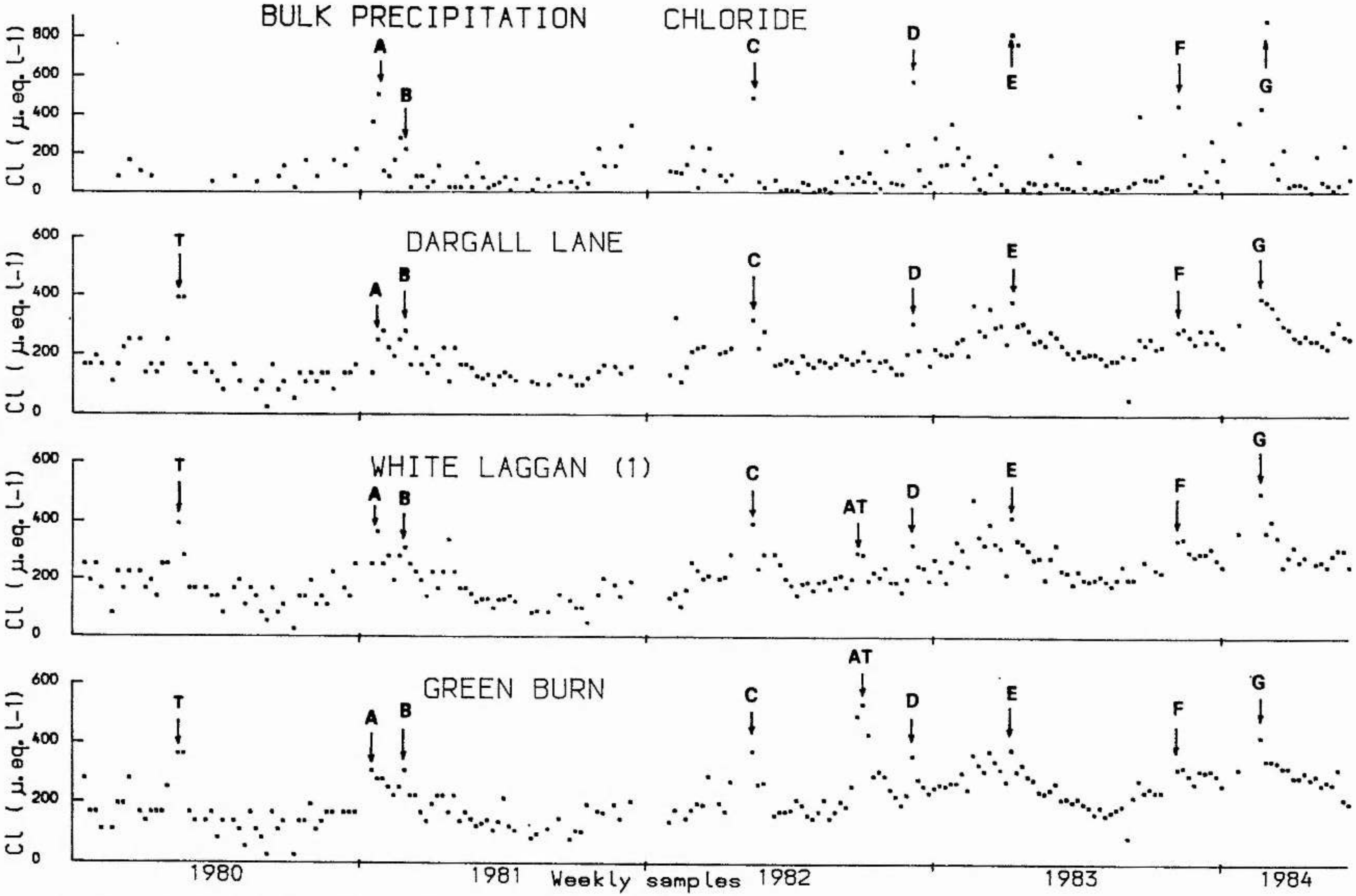
FIG 5:7 Weekly Variation In Sodium Ion

The correlation of sodium in the streams is strongest with chloride implying the dominant source of sodium in the streams is derived from atmospheric inputs of a maritime origin, although this correlation does vary in strength between the three streams.

5:2:6 Chloride.

Chloride is the dominant anionic constituent at Loch Dee contributing between 59% to 64% of the anions in the precipitation and streamwater. Table 5:5 shows that the atmospheric deposited chloride accounts for much of the variation in both sodium and magnesium in the bulk precipitation samples illustrating the predominant maritime source of these ions. Calculating a mean Na:Cl ratio for these precipitation samples gives a ratio of 0.83 (fig 5:9). This compares to a seawater Na:Cl ratio of 0.86 (Sutcliffe et al 1983). This indicates there is an atmospheric excess of chloride above that of a maritime origin. Whilst the excess chloride represents only a small proportion of the total input, the complications involved in assigning relative proportions to maritime and non-maritime input ruled out further analysis in determining the amount of natural and anthropogenic sulphate.

Fig 5:8 has been annotated to highlight the incidents of sea-salt episodes, where the input of sea-salt laden precipitation has been sufficiently large (under conducive hydrometeorological conditions) to have an immediate impact on streamwater quality. Fig 5:8 also shows a seasonality to these chloride inputs with incidents of high concentrations occurring over the winter months. As a consequence of this seasonal variation in the inputs of chloride the



T : High Sea – Salt Input Suggested By High Sodium Concentration In Weekly Bulk Precipitation Sample (Fig 5:7a)

AT : PK Fertilizer Application To Green Burn Catchment

FIG 5:8 Weekly Variation In Chloride Ion

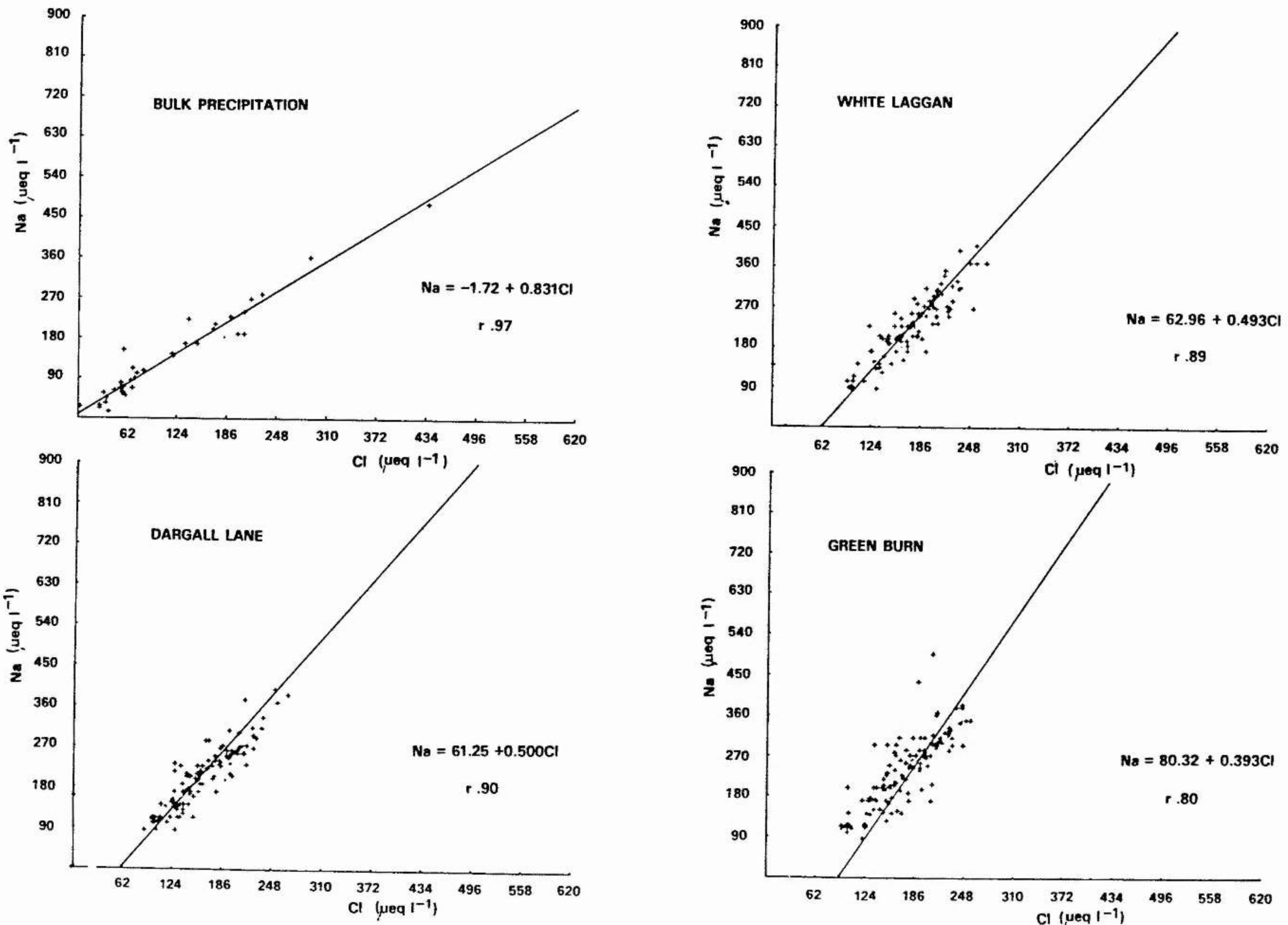


FIG 5:9 The Relationship Between Sodium And Chloride

streams show an approximate seasonal pattern, with concentrations high during the winter months and low during the summer months. Such findings have been reported for western Norway by Skartveit (1981).

Point AT on fig 5:8 is of unusual interest, this peak corresponds to the flushing out of potassium from the P-K fertilizer (described in chapter 3) and indicates that potassium is flushed and leached out of the soils with chloride whilst the phosphate input is retained.

Plotting the scatter of chloride againest sodium reveals a linear relationship for both precipitation and the streams. Fig 5:9 illustrates the relationship for each of the sampling stations. The Na:Cl relationship for Dargall Lane and White Laggan accounts for approximatley 80% of the variance of these ions. For Green Burn the scatter of points is much greater and the relationship only accounts for 65% of the variance. This is explained in part by the input of chloride with the fertilizer (ie. KCl) following the application of the P-K fertilizer to the catchment.

Fig 5:9 shows the Na:Cl ratio for the streams to have a systematic progression away from the precipitation ratio in the order Dargall Lane, White Laggan, Green Burn. A similar progression can be seen in table 5:5 for the correlation of chloride with sodium, magnesium and calcium. A point further discussed in section 5:3.

5:2:7 Nitrate.

Fig 5:10 shows clearly the biological control of nitrate concentrations in the streams. Minimum nitrate levels occur during the summer months rising during late autumn to reach a peak in early spring. A similar seasonal pattern for the forested and grass pastures of the Severn and Wye catchments (Wales) have been reported by Roberts et al (1983). The general pattern of nitrate levels is the same for all three streams at Loch Dee, however the magnitude differs between them. Biological uptake in the catchments is further suggested in table 5:1 in which precipitation concentrations are higher than the stream concentrations. Table 5:1 also suggests a progressive difference between the three streams in terms of range and concentration of nitrate. Dargall Lane has the largest range and concentration whilst Green Burn the smallest.

Table 5:5 shows precipitation to be correlated with the acidifying compounds of sulphate and hydrogen ion illustrating the role of nitrate in precipitation acidity (section 5:2:8). The correlation of nitrate in the 3 streams with potassium underlies the common role played by vegetation in controlling the streamwater concentrations of these two elements.

5:2:8 Sulphate.

Chapter 4:2:3 has indicated the possible sources of error in the collection of environmental chemical data. Fig 5:11 illustrates an example of a type II error, where for the major part of 1982 the method of sulphate analysis was found to be unreliable (chapter

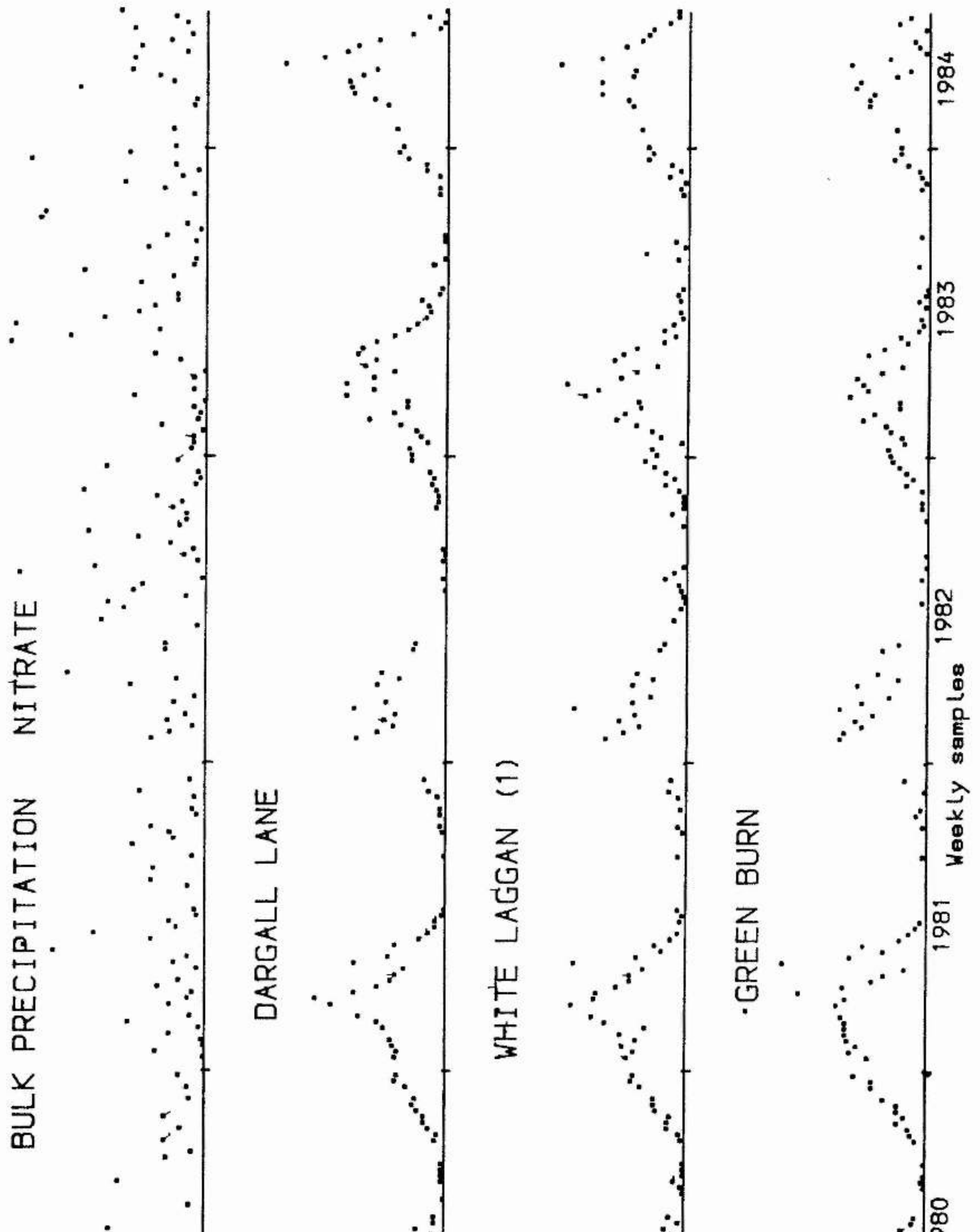


FIG 5:10 Weekly Variation In Nitrate

4:2:2). Such unforeseen problems in chemical analysis justify the use of an ion-balance technique to screen the data.

A further point illustrated by fig 5:11 is the large range and scatter of sulphate concentrations in both the precipitation and the streams. From the figure there appear to be occasions where high concentrations of sulphate in the precipitation have resulted in elevated sulphate concentrations in the three streams. Using the White Laggan MDF and sulphate, the data intimate a weak inverse correlation accounting for 17% of the variation in sulphate concentrations (table 5:4). In terms of contribution to the chemistry at Loch Dee sulphate is the second largest anionic input and output from the catchments contributing between 23% and 27% of the anionic constituents.

In the light of the uncertaintities surrounding the source of atmospheric chloride (section 5:2:6) i.e. the contribution from natural and unknown sources, it was not possible to assign the proportion of precipitation acidity to the sulphate and nitrate ions. Nevertheless reference to table 5:5 does suggest that a proportion of incident sulphate is of anthropogenic origin in its correlation with nitrate and hydrogen ions. In the Green Burn sulphate shows no correlation with other streamwater ions which is somewhat surprising. In Dargall Lane sulphate is correlated with calcium and magnesium whilst inversely correlated with hydrogen ion concentrations. These correlations illustrate the role of discharge in determining streamwater concentrations.

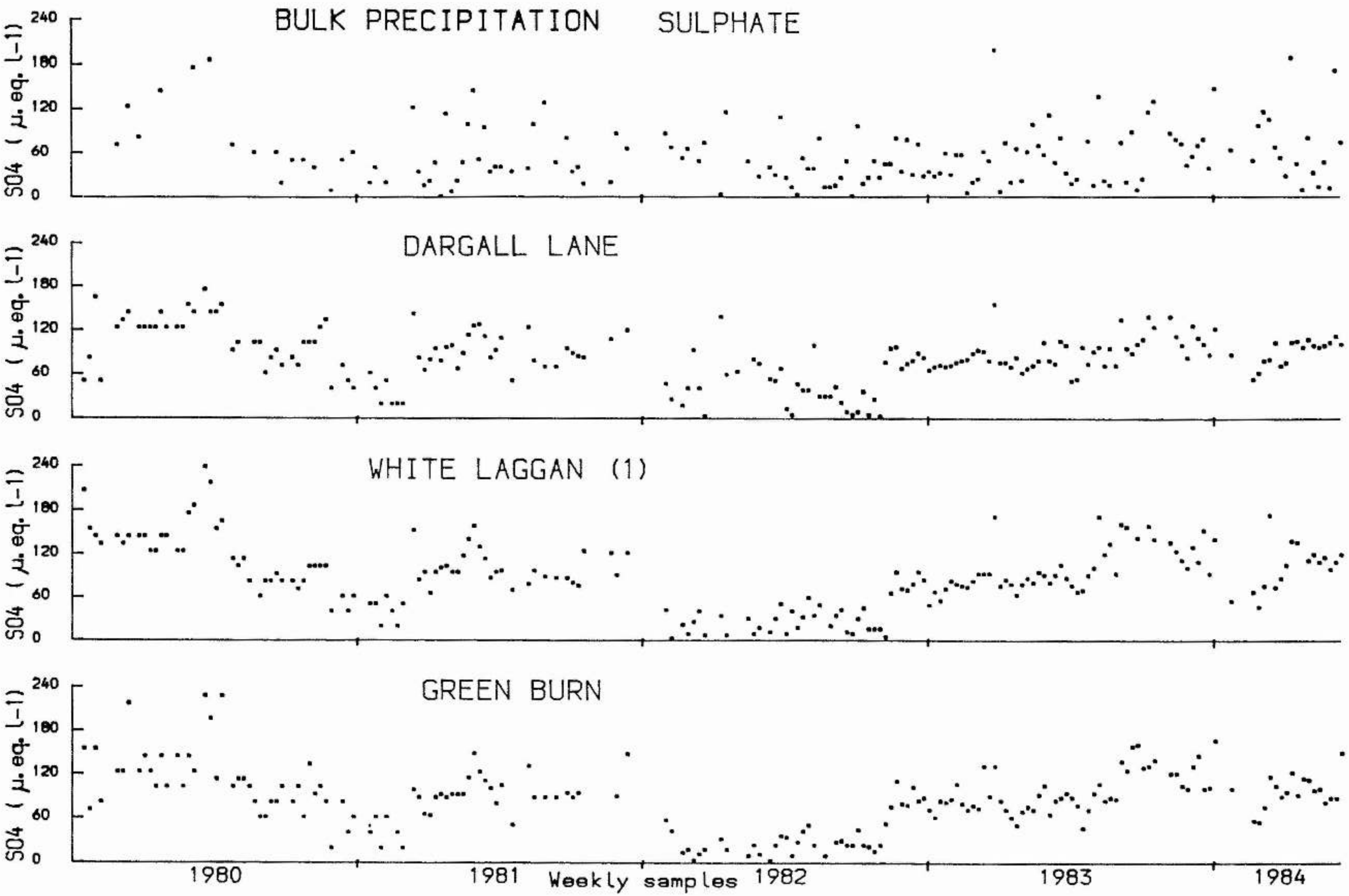


FIG 5:11 Weekly Variation In Sulphate

5:2:9 Bicarbonate Alkalinity.

The value of 'average' alkalinity data from before December 1983 is limited by the method of determination (chapter 4:2:2) quoting alkalinity to the nearest mg l^{-1}, from December 1983 however, alkalinity has been determined to 1 decimal place. This difference is evident from fig 5:12

Fig 5:12 and table 5:1 provide an interesting contrast between the alkalinity variation in the 3 streams. Dargall Lane has very low levels of alkalinity and only a small range of concentrations. This is in contrast to the large range of concentrations in Green Burn and the generally higher levels of alkalinity in White Laggan. Similarly this difference is seen in table 5:3 in which alkalinity contributes 6.9% of the anions in Dargall Lane, in comparison to the 10.2% and 10.5% for White Laggan and Green Burn respectively. A further contrast between the three catchments' alkalinity is provided by the cumulative frequency curves shown in fig 5:13. The curves show a significant difference for the Dargall Lane which has a lower maximum level of alkalinity as well as showing a lower concentration of alkalinity for a higher percentage of the samples. In contrast Green Burn and White Laggan have higher levels of alkalinity in a greater number of samples. As with the H^+ curves of fig 5:1 White Laggan (1) is the product of the contribution of alkalinities in the two tributary catchments of Black Laggan and upper White Laggan. Also fig 5:13 shows a significant increase in alkalinity downstream between White Laggan (1) and White Laggan (2).

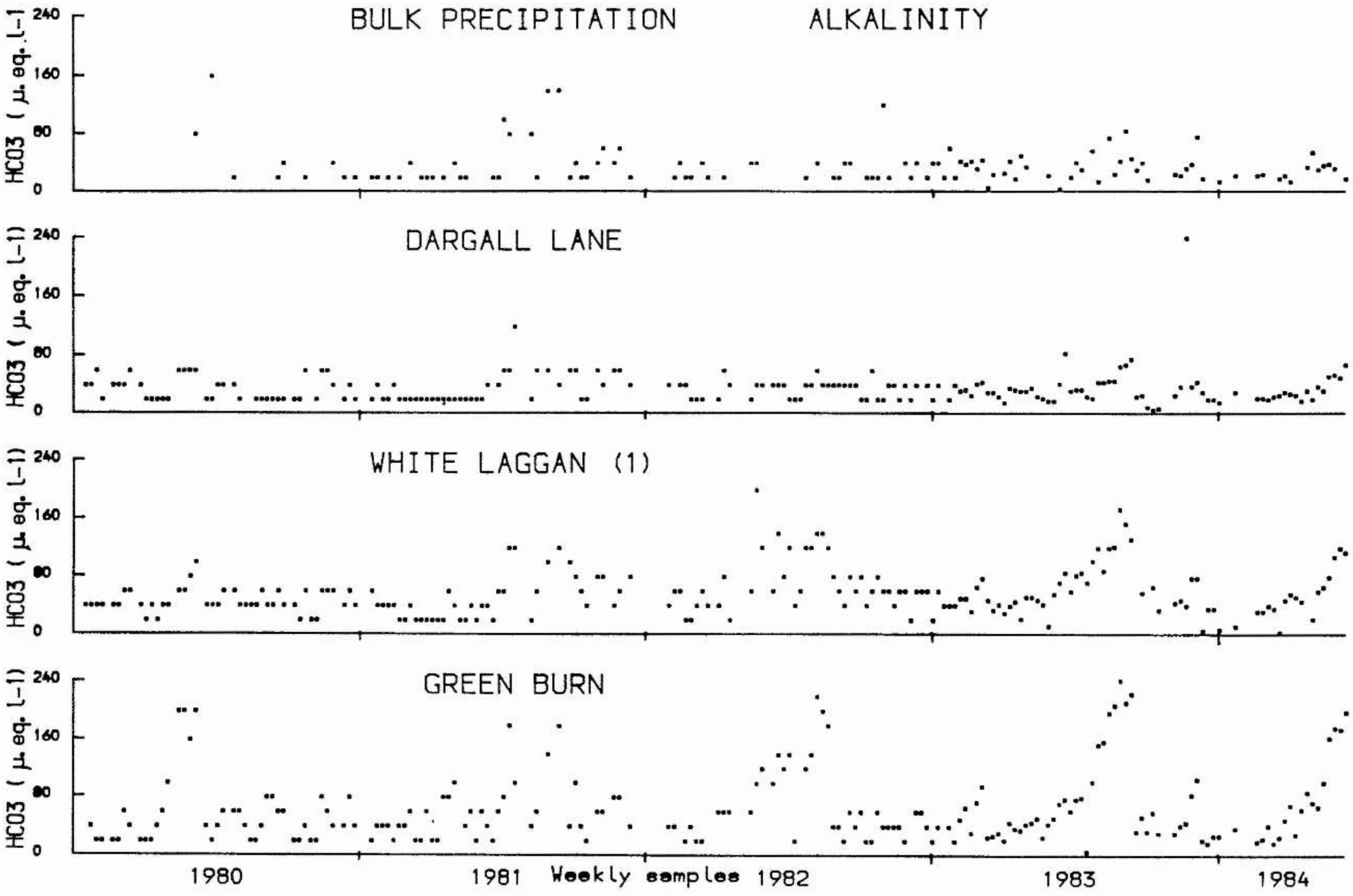


FIG 5:12 Weekly Variation In Bicarbonate Alkalinity

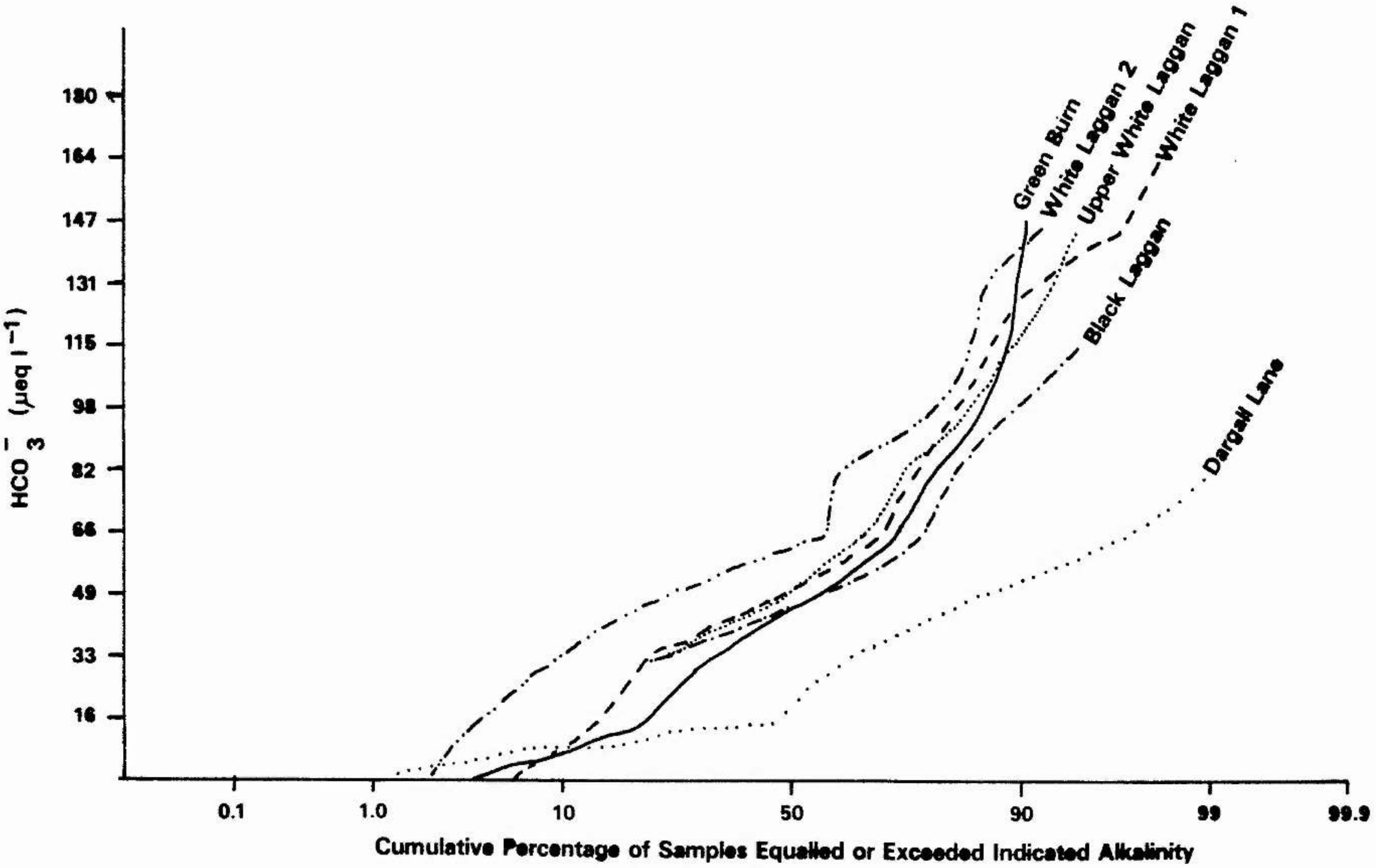


FIG 5:13 Alkalinity Frequency Curve

In the bulk precipitation samples alkalinity is inversely correlated with the acidifying ions of hydrogen and nitrate. In the streams the increase of acidity with increased discharge has already been noted (5:2:1) it is therefore not surprising to find the inverse relation between alkalinity and acidity as well as flow (table 5:4 and 5:5). The further correlations of alkalinity in the streams demonstrate the association with flow, the exception being nitrate which whilst seemingly flow independent has a close association with acidity.

5:3 DISCUSSION.

Section 5:2 has described the variation of the different ionic species through time and across the three catchments at Loch Dee. The results indicate that the variation in streamwater chemistry can be explained in terms of five systems. These five systems and the ions they regulate are given in table 5:6.

Control.	Ion.
I. ATMOSPHERIC	Cl^-, SO^{2-}, Na^+, Mg^{2+}, H^+
II. WEATHERING	Ca^{2+}, Mg^{2+}, Na^+, HCO^-_3
III. ION EXCHANGE	Na^+, H^+
IV. BIOLOGICAL	NO^-_3, K^+
V. FLOW	H^+, Ca^{2+}, Mg^{2+}, K^+, SO^{2-}, HCO^-_3

Table 5:6. The systems regulating the composition of streamwater chemistry at Loch Dee.

The systems proposed in table 5:6 combine in varying proportions within the different catchments to regulate streamwater chemistry. These systems are best looked at in turn before giving an overview of streamwater variation at Loch Dee.

5:3:1 Atmospheric.

Atmospheric inputs to Loch Dee provide an important source of the major ions to the streams. Those streamwater ions which are predominantly controlled by atmospheric inputs are those of a maritime origin. The predominance of these ions reflects the proximity of Loch

Dee to the Solway Firth to the south, the Irish Sea and Atlantic Ocean to the west.

Of particular importance to streamwater chemistry is the atmospheric input of chloride. Section 5:2:6 has intimated that there is an excess of chloride beyond that derived from maritime sources. This excess chloride at Loch Dee has also been postulated by Welsh and Burns (1985). Assuming all the sodium in the precipitation to be of a maritime origin it is suggested that 5% of the total chloride is from this indeterminate source. Stevenson (1968) similarly describes an excess of chloride for central England apparently attributable to anthropogenic pollution. More recently Sutcliffe and Carrick (1983) found precipitation in the Windermere catchment (Cumbria) to have chloride of a 'non-marine' origin which accounted for between 2.4% and 5.7% of total chloride. Sutcliffe and Carrick suggest this excess chloride input to be of anthropogenic origin. Also of importance is the atmospheric input of sodium. Section 5:2:5 has already indicated that much of the fluctuation in sodium concentrations in the streams is the result of fluctuations in the atmospheric input of this ion. Maritime air masses at Loch Dee also provide significant inputs of magnesium and sulphate.

In addition to the 'natural' inputs of ions a significant contribution to the precipitation chemistry is apparently derived from anthropogenic pollution. The correlation of bulk precipitation acidity with both nitrate and sulphate is consistent with the hypothesis that the acids in precipitation are attributable to a combination of sulphuric and nitric acids. The restrictions on the source of atmospheric chloride however prevents the calculation of their relative importance. In section 5:2:1 it was suggested that the difference of precipitation acidity between that reported for Loch Dee and that reported for S.W. Scotland by Barrett et al (1983) may be a function of a singularly high acidity reported for Cairnsmore of Fleet. However one must also speculate that part of the difference is due to a downward trend in SO_2 emissions since the mid 1970's (see Barrett et al 1983, p.49) or at least a fluctuation in precipitation acidity between the sampled years.

The role of atmospheric inputs to Loch Dee is most evident when sea-salt inputs undergo cation exchange in the soils or when the atmospheric concentrations are high and deposited under hydrometeorological conditions conducive to having an immediate effect on streamwater chemistry. Most of these points have been highlighted on figs 5:2, 5:7 and 5:8.

The atmospheric input of ions will be supplemented and modified by chemical weathering, vegetational requirements, ion exchange and flow routing through the catchment before reaching the streams.

5:3:2 Ion Exchange.

The principal ions involved in ion exchange within the catchment soils at Loch Dee are Na^+, H^+ and Cl^-. Chapter 2 has cited evidence from the literature (Skartveit 1981) where precipitation heavily laden with sea-salts has caused a rise in stream acidity. The mechanism is apparently one where sodium in the precipitation is exchanged on soil and peat colloids for H^+ whilst Cl^- passes through the soil unchanged and thereby acidifying the runoff whilst the sodium is retained in the catchment. This process accounts for several of the very acidic streamwater episodes over the period of study (see chapter 6).

5:3:3 Weathering.

In addition to atmospheric inputs the weathering of bedrock and subsurface materials provides a primary source of major ions which may be leached or exchanged by water percolating through the catchments. The study by Little (1985) on chemical denudation rates at Loch Dee indicated the order of denudation between the catchments to be: Dargall Lane (least), White Laggan, Green Burn (greatest). Assuming chloride to be a conservative ion, derived from the atmosphere consider table 5:7.

correlation (Spearman Rho)

	Na:Cl	Mg:Cl	Ca:Cl
Dargall Lane	.89	.77	.44
White Laggan	.88	.48	.31
Green Burn	.83	.33	.29

Table 5:7 Spearman Rho correlations for chloride in the weekly spot streamwater samples.

Table 5:7 suggests that there is progressively higher concentrations of non-conservative ions (ie. sodium, magnesium and calcium) in the same order proposed by Little for chemical denudation rates. This implies that the chemical weathering of sodium, magnesium and calcium supplies cations at different rates according to the catchment. Similarly the Na:Cl regression lines of fig. 5:9 show a progression away and a reduction in the strength of the Na:Cl association found in the bulk precipitation. The implication of these results is that there is an increasing amount of sodium weathered and released from the catchments. Little (1985) reasonably argues that these differences are attributable to the forest ditches over 70% of Green Burn and 27% of White Laggan. The forest ditches have the effect of exposing a greater surface area of soils and underlying bedrock to weathering which will cause an increase in the denudation rates.

Figure 5:5 indicates that the calcium and magnesium ratios are of the same order (0.8 x Mg) for Dargall Lane and Green Burn although the relationship for Green Burn is much stronger. White Laggan shows a higher proportion of calcium (1.57 x Mg) than either of the other 2 streams, particularly at higher concentrations. This suggests some inherent source of calcium within the White Laggan catchment but absent in the other catchments.

This difference in weathering rates is also manifest in the catchments' varying abilities to buffer streamwater acidity. The higher weathering rates of Green Burn and White Laggan will consume more acids in weathering reactions such as acid hydrolysis. Furthermore the faster release of base cations will also alleviate streamwater acidity.

Using a cation triangle and depicting the streams in terms of the percentages of sodium, potassium, calcium and magnesium, as in fig. 5:14 a broad similarity between the three streams is shown. From work undertaken in the S.W of England Walling and Webb (1981) found this cation composition, and a predominance of sodium to be typical of small and unpolluted streams draining granite areas. The authors

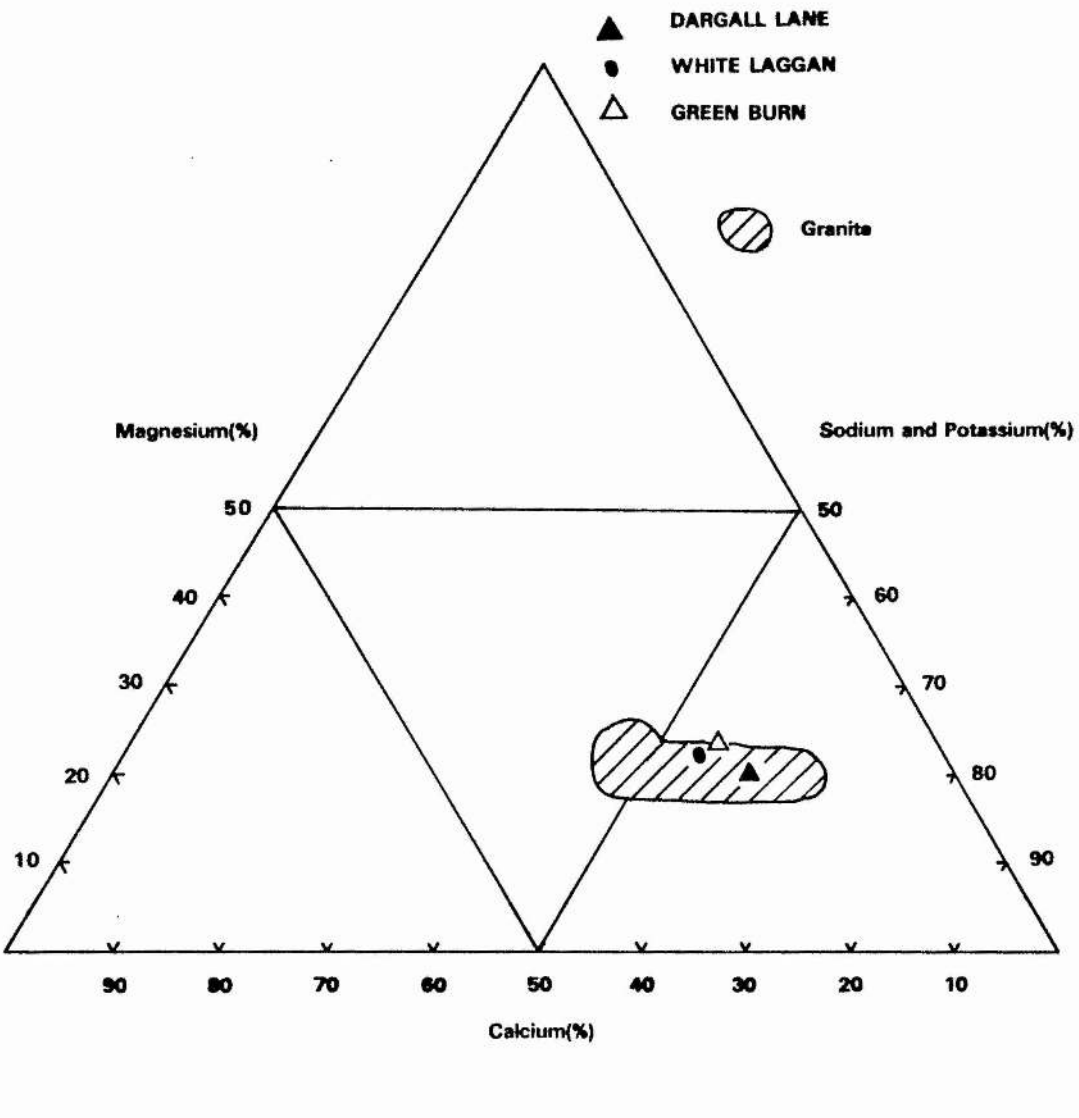


FIG 5:14 Cation Triangle Depicting Water Composition

(After Walling and Webb 1981)

suggest that (in the S.W penninsula) this composition of drainage waters differs from that originating from younger sedimentary rocks which are rich in calcium or from the metamorphic rocks dominated by magnesium.

The amount of streamwater modification achieved by differences in the weathering rates will also depend on the flow routing and hydrological modification in the catchments.

5:3:4 Biological.

The biological control of ionic concentrations is of two types. The processes affecting potassium which are vegetational and the processes affecting nitrate which are vegetational and micro-bacterial.

During the winter months when plant tissue growth is minimal there are higher concentrations of potassium in the streams, whilst during the summer growing season there is plant growth and the uptake of potassium, consequently potassium levels in the streams are depressed in the summer. Likens et al (1967) have also observed a similar pattern and control in the Hubbard brook catchments. From the median potassium concentrations it would seem that the potassium demand of the conifer trees in Green Burn (and to a lesser extent White Laggan) is greater than that of the moorland heath vegetation of Dargall Lane. Comparison of the minimum concentrations suggests that the fertilizer application elevated the otherwise 'natural' minimum concentration of potassium and without the application of this fertilizer to the forests potassium would be a limiting supply to further growth.

The pattern of nitrate levels in the streams is governed by bacterial activity in the soils and plant requirement. Nitrate is produced in the catchment soils by nitrogen fixing bacteria. During the winter months (outside the growing season) this nitrate is surplus to vegetational requirements. This nitrate is flushed out of the soils during storm events and may contribute to streamwater acidity. The rate of bacterial activity is positively related to soil and air temperatures with the consequence that as the year progresses soil nitrate levels increase. However with the onset of the growing season this increased concentration of nitrate in the soils is utilised by the vegetation with the affect that stream concentrations rapidly decrease to a zero concentration. At the end of the growing season there is plant die-back of bracken, heather and grasses reducing the vegetational demand for nitrate. With continued bacterial production of nitrate and the flushing of soils by winter storms stream concentrations once again rise. A similar control on stream nitrate levels has been reported by Scott and Scott-Swank (1984) for catchments in the Coweeta watersheds, U.S.A.

From the raw data used to construct fig 5:10 it is possible tentatively to speculate that the growing seasons for the four years under study to have been:

May to October 1980
early June to November 1981
May to November 1982
May to November 1983

Furthermore the progression of mean and median values for nitrate between the three streams intimates the change in nitrate demand between the three catchments, Green Burn with a high percentage of forest having the largest demand. Differences in the standard deviation between the streams implies this larger vegetational demand of Green Burn buffers the stream against changes in concentration more effectively than White Laggan and Dargall Lane in which the vegetational demand of the plant communities is less.

The significance of a deficiency in soil nitrate concentration during the growing season has substantial implications for future years in the Green Burn. Miller (1984) reports from a site in central Scotland that where conifer trees are deficient in nitrogen throughfall will be acidified. In the light of these findings it is possible to suggest that with further tree growth in the Green Burn catchment and the increasing importance of throughfall as an input mechanism that these inputs will be acidified.

5:3:5 Flow.

In the absence of instantaneous flow records for all three catchments over a sufficiently long period and the use of mean daily flows for the White Laggan data, some of the detail in the relationship between discharge and ionic concentration will be lost. However section 5:2 illustrated several ionic species to be flow related. Comparing the results for these ions is useful in outlining the hydrological differences between the catchments.

The peat dominated hydrology of the Dargall Lane catchment gives rise to a significant difference from the other two catchments. The affect of the peat bogs is to delay rapid storm runoff ensuring mixing of the various component sources of water. This is expressed in the streamwater chemistry by a surpressed range of flow dependant ions, particularly evident in figs 5:3 and 5:4. Contrasted to the peat bogs of Dargall Lane are the fast evacuation routes of the forest drains in both the Green Burn and White Laggan catchments. These forest drains promote storm runoff the rapid evacuation of which in turn is amplified by the difference of streamwater chemistry between dilute (rapid runoff dominated) storm flow and the more concentrated baseflow.

One of the strongest flow-concentration relationships was found for the calcium and magnesium ions which illustrate the dilution of the calcium and magnesium rich groundwater component by the more dilute storm runoff. This dilution effect can be imagined using fig 5:5. At low flows the concentrations of calcium and magnesium will be high, with increasing discharge the concentrations of the ions will decrease according to the relationship described in fig 5:5. The dispersion of points away from this relationship particularly at high concentrations in the Dargall Lane suggests the baseflow component is not chemically as homogenous as in the other catchments. This scatter of points reflects differences in the water quality draining the different peat bogs of the Dargall Lane catchment. The White Laggan and Green Burn streams are fed by a single homogenous groundwater component. Further scatter of the points will be caused by the antecedent conditions. After long dry spells there may be a significant accumulation of dry deposits which may also deviate from the regression relationship.

Acidity in the streams is also flow dependant with higher acidities associated with higher flows. One interprets this as the dilution of base rich groundwater by the more acidic storm-runoff which is derived from the acid rich upper soil horizons and has not had time to percolate into the deeper soil horizons to allow some acid neutralisation. Such a flow-acidity relationship has been reported for sites in mid-Wales by Newson (1984) and Stoner and Gee (1984). It is interesting to speculate that part of the differences in acidity between the catchments is in response to different hydrological routing. The peat bogs of Dargall Lane with slow evacuation of storm runoff maintains higher acidity levels in the stream over longer periods than allowed by the fast evacuation routes of Green Burn and White Laggan.

The positive relationship of Potassium with flow indicates the high mobility of this ion through the catchment soils. Similar relationships for this ion have been reported by Walling (1981) Edwards (1973) and Foster and Walling (1975).

5:4 SUMMARY AND CONCLUSION.

The five systems described above interact to regulate the streamwater chemistry and determine the variation both through time and between the three streams at Loch Dee. The variation between streams is dependant upon the relative importance of each system which in turn is dependant upon the constituent 'make-up' of each catchment.

The slow chemical weathering and release of base cations in the Dargall Lane promote a stronger dependence of water quality on atmospheric inputs than in either of the other catchments. Furthermore the interaction of the peat hydrology and slow release of cations give rise to the deficiency of Dargall Lane to buffer streamwater acidity which is both greater in (mean) magnitude and occurrence than for either of the other two catchments. In contrast to the Dargall Lanes' hydrology are the fast evacuation routes of the forest drains in both Green Burn and White Laggan. These forest drains are probably responsible for the higher chemical denudation rates and provide a greater measure of buffering than in the Dargall Lane. In addition the White Laggan catchment is inherently well buffered against acidity from an unidentifiable source. Without the availability of baseline data for the White Laggan catchment before the initiation of the liming programme it is impossible to verify precisely the role of the various lime applications in alleviating streamwater acidity. However, given the overall similarity of all three catchments described in chapter 3 it is likely that the liming has given rise, at least in part, to the improved water quality in the White Laggan.

The greater vegetational demand for nitrate and potassium in the Green Burn catchment provides a greater buffer to the variation of stream concentrations of these ions, although nitrate is probably providing an important contribution to streamwater acidity during the winter months. Ion exchange as a mechanism for streamwater acidification is important in all three catchments particularly with the predominance of atmospheric inputs of sea-salt. The three streams are similar in terms of cations to those described by Walling and Webb

(1981) draining from granitic areas in S.W England.

Whilst the discussion of the average and variable behaviour of streamwater chemistry at the weekly scale is useful in outlining the general setting at Loch Dee; the ranges and standard deviations for individual ions suggests that this scale of investigation masks the episodic nature of important hydrochemical events. Subsequent chapters of this report investigate changes in hydrology and the influence this has on streamwater chemistry over shorter time periods.

CHAPTER 6 : EPISODIC ACIDITY IN THE STREAMS AT LOCH DEE.

6:1 INTRODUCTION.

In studying the role of precipitation chemistry in the acidification of water bodies, one of the major problems is whether short lived acidic episodes or longer term increased levels of acidity are more detrimental to aquatic ecosystems. Recently both of these phenomena have been attributed to increased precipitation acidity (Wright and Gjessing 1976, Overrein et al 1981, Wright et al 1980 and Likens et al 1976).

Short lived episodic acidity in streams and lakes is frequently associated with particular storm events; such 'acidity-waves' often being cited as the cause of extensive fish-kills. In Scandinavia these fish-kills are especially well documented (Overrein et al 1981) and often result from the first spring snow-melt which is rich in acidic pollutants preferentially melted out of the snowpack. Episodic acidity on this scale is not common in S.W Scotland because of the erratic pattern of snowfall. Nevertheless, fish-kills have been reported in the area (R.Newland, J.Gordon pers. comm.).

This chapter investigates three specific episodes of short-term acidity, which have not been generated by acid deposition in the Loch Dee catchments. In order to structure the chapter section 6:2 describes the three storms under specific investigation and for the duration of the third storm calculates a H^+ budget for the atmospheric input and output from each of the three catchments. Section 6:3 analyses a series of laboratory experiments undertaken on catchment soils in order to try and simulate the field conditions; and finally sections 6:4 and 6:5 discuss both the field and laboratory data and their implications.

6:2 The Storms.

The first short-lived acidity 'pulse' occured during the passage of a frontal system across the Loch Dee basin over the period 15-17 November 1982. Preceeding these dates precipitation acidity and conductivity showed variation representative of the Loch Dee catchment (0-70 μeq $H^+ l^{-1}$ and conductivity 5-120 μs cm^{-1}). With the onset of precipitation on the 15th (<1.0 mm hr^{-1}) the associated conductivity and acidity were 5-20 μs cm^{-1} and 6 μeq $H^+ l^{-1}$ respectively (fig 6:1) this continued through the succeeding period of higher intensity precipitation (3.0-5.0 mm hr^{-1} from 18.00 hrs on the 15th to 03.00 hrs on the 16th). As the precipitation rates slackened, acidity occasionally increased to > 10 μeq $H^+ l^{-1}$ and conductivity dramatically increased to >200 μs cm^{-1} exceeding the upper limit of the recorder. With the passage of the second front at 20.00hrs precipitation intensities again increased (from 3.0 to 5.0 mm hr^{-1}) and a decrease in conductivity

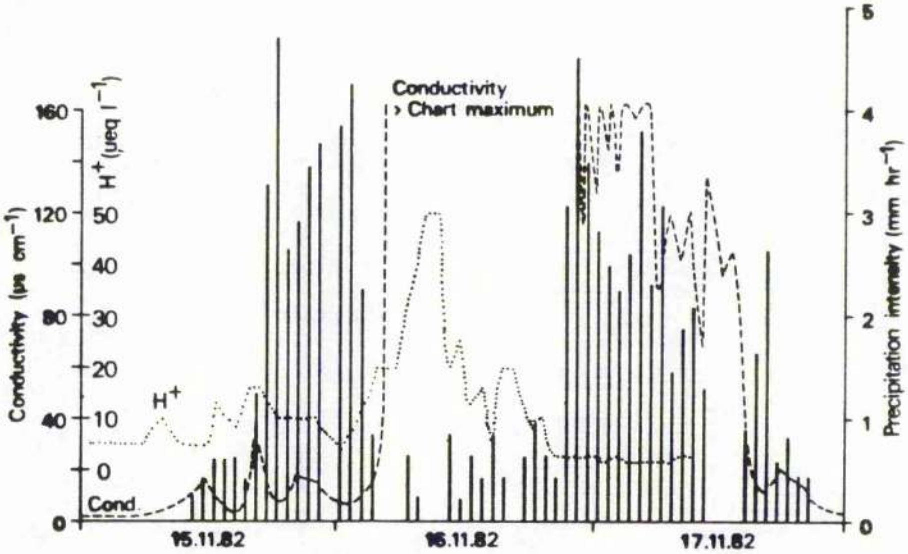


FIG 6:1 Hourly Values Of H$^+$, Conductivity And Precipitation Intensity; 15—17 November 1982

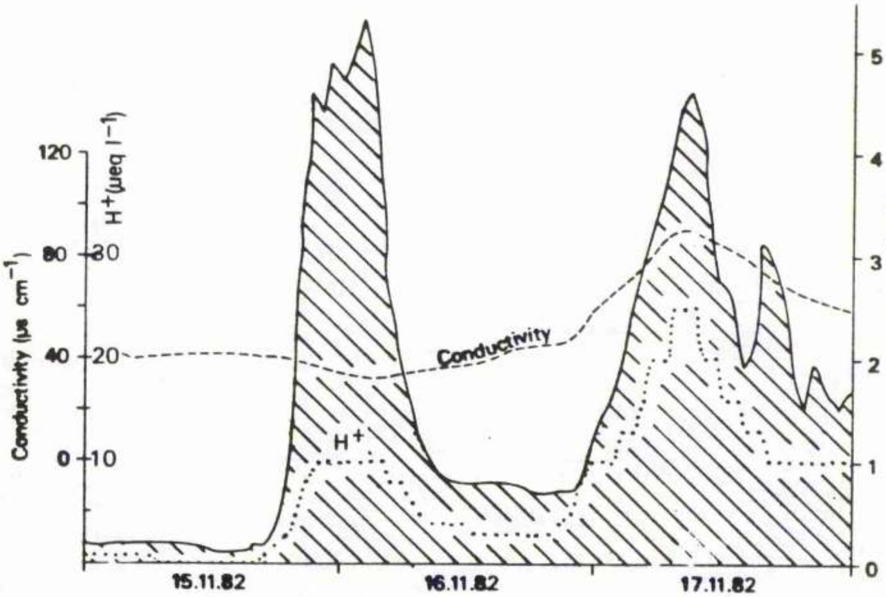


FIG 6:2 Hourly Values Of H$^+$, Conductivity And Discharge ; 15—17 November 1982

was recorded. Later chemical analysis of the weekly bulk precipitation sample showed a weekly precipitation acidity of 10 μeq H^+ l^{-1} a sodium concentration of 424 μeq Na^+ l^{-1} and a chloride concentration of 575 μeq Cl^- l^{-1} suggesting that the exceptional conductivity in the precipitation was due to high concentrations of sodium chloride presumably of marine origin. Independent confirmation of a high sea-salt concentration in the precipitation was provided by the daily analysis at Eskdalemuir 80 km to the east (Irwin pers. comm)

The runoff and water quality records for the White Laggan Burn during the same period showed an almost instantaneous response to precipitation inputs (fig 6:2). The first hydrograph at 01.00 hrs on the 16th is associated with a marked increase in stream acidity and a more modest reduction in conductivity. Acidity in the stream increased from a pre-storm level of 2 μeq H^+ l^{-1} to 10 μeq H^+ l^{-1} over a period of 5 hours. The second storm hydrograph on the 17th whilst similar in magnitude, has a quite different profile in terms of water quality. As storm discharge increased to a peak of 4.6 m^3 s^{-1} conductivity also increased to 90 μs cm^{-1}, a level greater than twice the mean background. Simultaneously acidity increased from 3 μeq H^+ l^{-1} to 25 μeq H^+ l^{-1} and remained at that level for 20 hours only showing a slight recovery on the falling limb of the hydrograph.

The second acidity pulse occurred over the period 21-23 March 1983. On this occasion the precipitation acidity record is missing due to instrument malfunction. On March 21st from midday onwards, precipitation conductivity exceeded 200 μs cm^{-1}. During this period the quantity of precipitation was negligible (the fact that

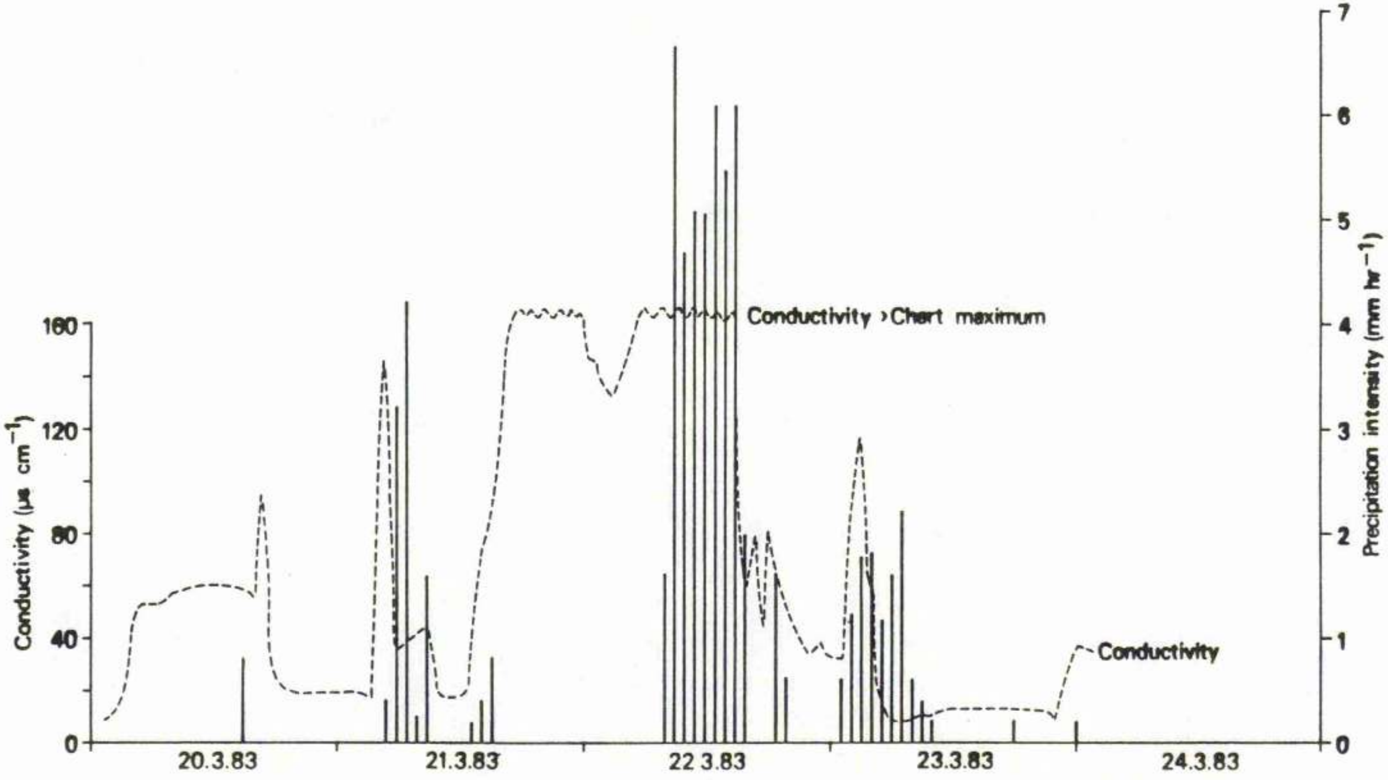


FIG 6:3 Hourly Values Of Conductivity And Precipitation Intensity; 20—24 March 1983

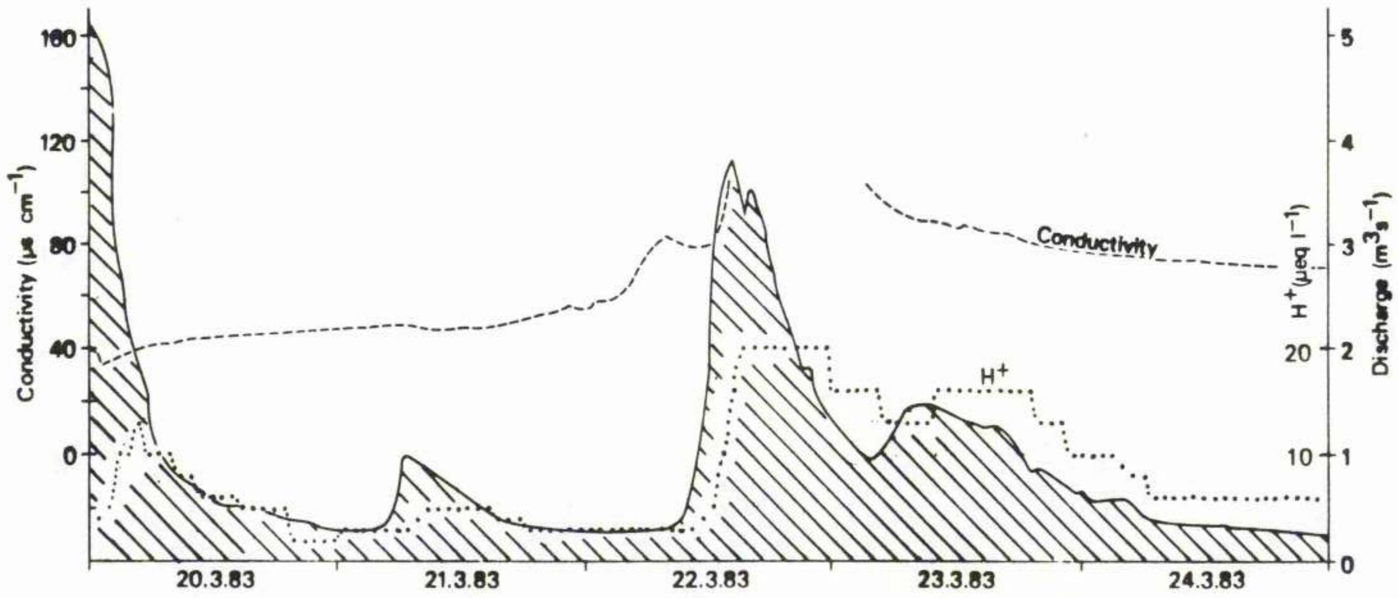


FIG 6:4 Hourly Values Of H$^+$, Conductivity And Discharge ; 20—24 March 1983

there is no recorded precipitation is explained by an occult type deposition (cf. Rutter 1975, Dolland et al 1983). This conductivity level continued even with the onset of heavy precipitation of intensities 5.0-7.0 mm hr^{-1} (fig 6:3) until the end of the storm. In response to this precipitation input the discharge on White Laggan rose to a peak of 3.6 m^3 s^{-1}. Conductivity in the burn rose to a level >100 μs cm^{-1} (the chart maximum) where it remains for 9 hours before decreasing during the recessional flow (fig 6:4). During the same period stream acidity in the burn increased from a pre-storm level of 3 μeq H^+ l^{-1} to 20 μeq H^+ l^{-1} and remained at an acidity of >10 μeq H^+ l^{-1} for 24 hours. Again the weekly bulk precipitation sample showed a high conductivity (89 $\mu s.cm^{-1}$) an acidity of 4 μeq H^+ l^{-1} and a sodium concentration of 496 $\mu eq.$ l^{-1} compared to the weekly bulk precipitation mean of 109 $\mu eq.$ Na^+ l^{-1} (table 5:1).

The third and final storm investigated here occurred during 27-29 November 1984. With the onset of precipitation at 01.00 hours (fig 6:5) conductivity was initially high (up to 200 μs cm^{-1}) although this decreased with the slackening precipitation rate (at 02.00 hours.). As precipitation rates again increased with the passage of the storm conductivity similarly rose again to a level in excess of 200 μs cm^{-1} which only significantly fell towards the end of the storm and a decreasing precipitation rate. Precipitation acidity steadily increased during the initial part of the storm after which it fell to a level <5 μeq H^+ l^{-1}.

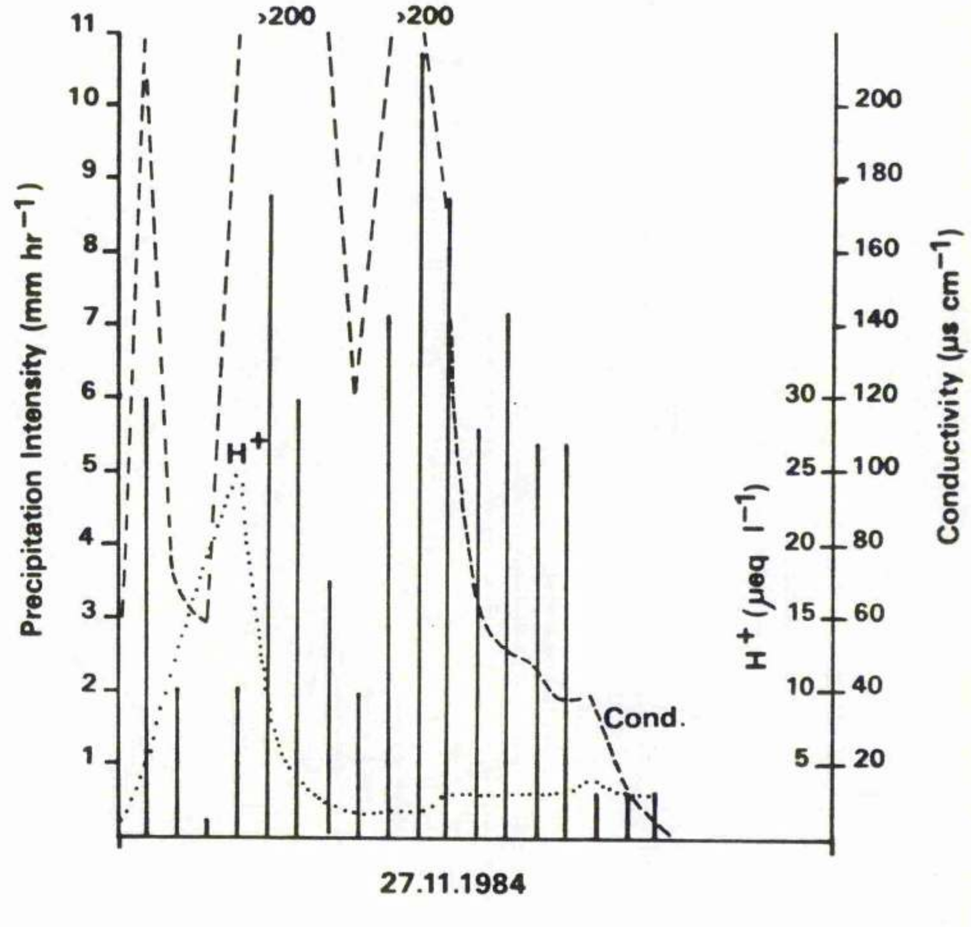


FIG 6:5 Hourly Values Of H$^+$, Conductivity

And Precipitation Intensity; 27 November 1984

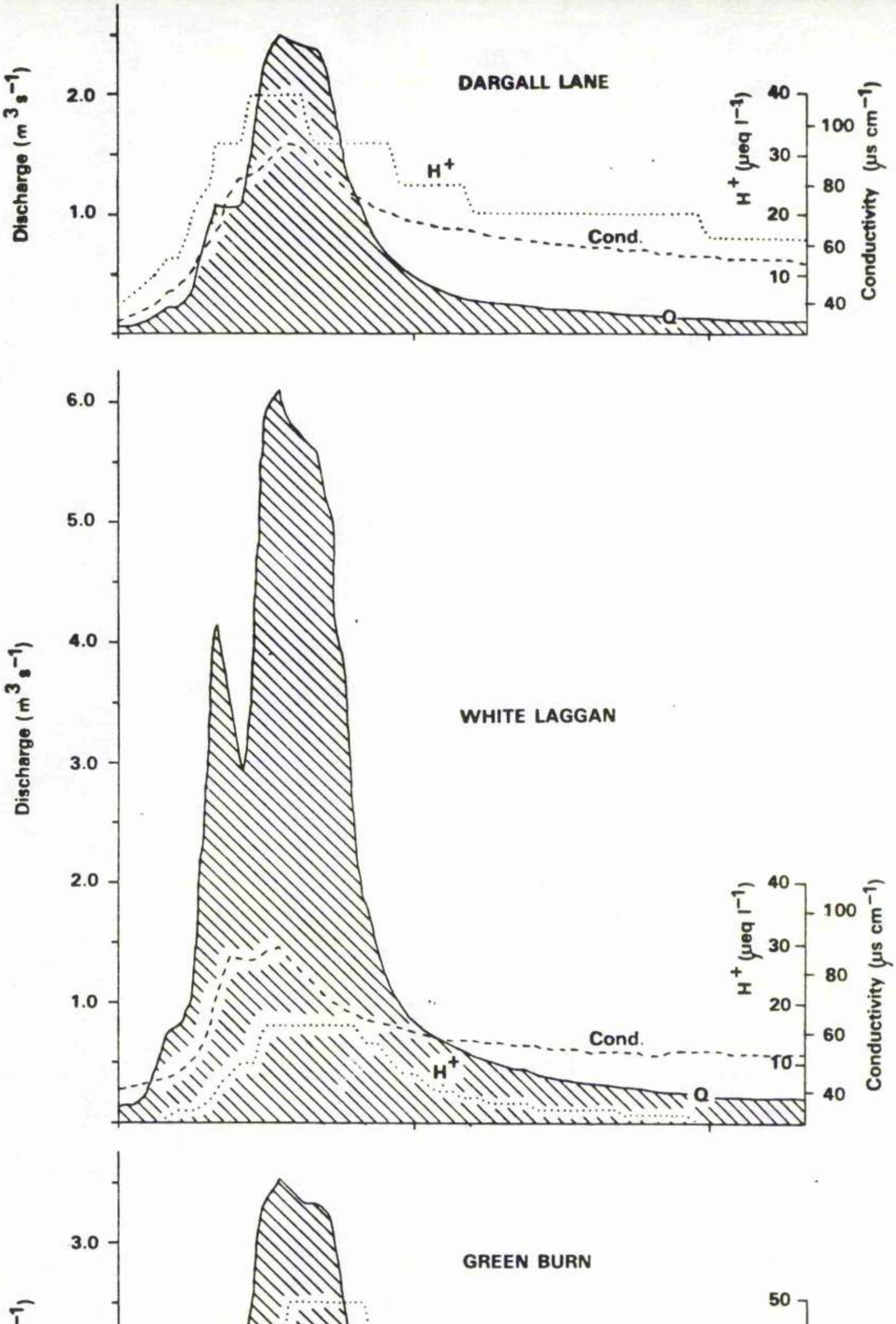


FIG 6:6 Hourly Values Of H$^+$, Conductivity And Discharge 27–29 November 1984

With water quality monitors installed and operative on all three streams, fig 6:6 show the almost immediate response and consequences on the streamwater of this particular storm. Comparison of the three streams' response to the storm is of some interest. In terms of discharge the streams had relatively similar hydrographs', although White Laggan showed a more clearly defined double peak in comparison to the other two streams. In all three streams discharge rose to a peak within 12 hours of the onset of the storm and a recession limb extended over some 36 hours. In terms of water quality the streams showed a different responses in the form of the acidity and conductivity traces.

In the Dargall Lane, discharge rose to a peak of 2.5 m^3s^{-1} whilst over the same period conductivity peaked at 94 $\mu s\ cm^{-1}$ and acidity at 40 $\mu eq\ H^+\ l^{-1}$. With the onset of the recessional flow, acidity decreased, although at a slow rate maintaining streamwater acidity at a level of 15-20 $\mu eq\ H^+\ l^{-1}$ for a period in excess of 36 hours. In contrast to this is the Green Burn in which the discharge reached a peak of 3.54 m^3s^{-1} together with a peak in conductivity of 95 $\mu s\ cm^{-1}$. Lagged behind this by 1 hour was the peak in acidity (50 $\mu eq\ H^+\ l^{-1}$). Whilst this level of acidity was greater than the acidity in the Dargall Lane, it declined more rapidly than was seen in the Dargall Lane, although the stream still took a considerable time to return to pre-storm concentrations.

In the White Laggan conductivity peaked at 88 us cm^{-1} along with peak discharge (6.11 m^3s^{-1}). Both the magnitude (16 µeq H^+ l^{-1} maximum) and duration of streamwater acidity was much smaller and shorter than for either of the other streams. However the general pattern in terms of acidity and conductivity was broadly similar.

In order to gain an indication of the flux in H^+ between the precipitation input and streamwater output in the three catchments an approximate mass balance was applied to the data for the November 1984 storm. In calculating a mass-balance budget from the data several simplifying assumptions have been made:

i. The precipitation input (as measured in the White Laggan catchment) is both quantitatively and qualitatively similar over the whole of the Loch Dee basin.

ii. The catchment area defines both the area of input and of output.

iii. For storm input the whole precipitation event represents the total input. Whilst in calculating the storm output a hydrograph separation technique (after Boorman and Reed 1981) has been used. This method utilises stream data from the level of initial discharge to the time of peak runoff plus 4x the lag; where the lag is the time from peak precipitation to the time of peak discharge.

iv. There is no evapotranspiration during the event.

Using these assumptions and the continuous data from the catchments the following calculations were undertaken for 27-29 November 1984.

Total H^+ = (H^+ x 10^3 ((P x 10^{-3})x(A x 10^6)x 10^3)) ..(6:1)
Input per hour
(μeq l^{-1})

Total H^+ output from each = (H^+ x 10^3 (Q x 3600)) ..(6:2)
catchment per hour (μeq l^{-1})

Where H^+ = Hydrogen Ion Concentration (μeq H^+ l^{-1})
P = Precipitation Rate (mm hr^{-1})
A = Area (km^2)
Q = Discharge ($m^3 s^{-1}$)

The total storm input and ouput of H^+ was then calculated by summing the hourly values obtained from (6:1) and (6:2). The results of these mass balance budgets are given in table 6:1.

	Precipitation Input (μeq H^+)	Total Stream Output (μeq H^+)	Unit Area Output (*) (μeq H^+)
Dargall Lane	6.15×10^8	3.69×10^9	1.8×10^6
White Laggan	16.60×10^8	3.21×10^9	0.6×10^6
Green Burn	7.32×10^8	6.60×10^9	2.6×10^6

* Unit Area Precipitation Input = 2.9×10^5 (μeq H^+)

TABLE 6:1 Hydrogen Ion Input and Output for the three Catchments During 27-28 November 1984.

Table 6:1 illustrates that considering the storm in isolation there is a significant net output of H^+ from the catchments. In

Green Burn and Dargall Lane the differences between inputs and outputs are almost an order of magnitude. For White Laggan the loss is not as large (this is further discussed in section 6:4). However this mass balance does further support the suggestion of streamwater acidification occurring within the catchment following precipitation inputs with high concentrations of sea-salts.

The most satisfactory explanation of the processes which lead to such short-lived acidity pulses appears to be one involving the exchange of sodium ions derived from the precipitation with hydrogen ions in the catchment soils. This process has already been indicated both in the literature (chapter 2) and in chapter 5 although this section has emphasised the significance of such a process in affecting streamwater chemistry over storm periods. To attain a better understanding of the changes in streamwater chemistry following precipitation inputs similar to those described for the storms, a series of exploratory laboratory experiments have been carried out.

6:3:1 Laboratory Simulation.

The field data presented above have indicated that an ion-exchange mechanism may provide a plausable explanation for the production of short-term episodic acidity. Following the second episode of stream acidification described above a series of soil-leaching experiments were conducted. The aim of conducting these leaching experiments was to explore the variation in water chemistry following a variety of simulated precipitation inputs, and more importantly to verify the changes in water chemistry associated with precipitation inputs heavily laden with sea-salt, similar to those described in section 6:2.

The soils used in the experiments were collected from the White Laggan catchment (NGR NX 467 776, point S on fig 3:4), and are best described as peaty podzols belonging the Dalbeattie Series. The soil was collected by digging and removing a soil section with a surface area measuring 0.5 x 0.5m. The section was dug from the vegetation surface down to the weathered bedrock (C horizon), a depth of some 0.4m. The soil monolith was carefully removed, placed in a plastic sample bag in a box and transported back to the River Board Laboratories, where it was stored in the laboratory refrigerator overnight. The following morning, three individual soil monoliths were removed from the soil section and placed into three glass leaching columns (measuring 31mm x 150mm), with great effort being taken to preserve the soil in its natural state (particularly soil structure). To do this the soil monoliths were cut from the top of the soil section downwards using a sharp edge at a diameter fractionally less than that of the leaching columns. The soil monolith was then left in place lying horizontally on the bench-top and the glass leaching tube pushed up around the soil. This had to be repeated on several soil cuts before the author was satisfied that disturbance had in fact been kept at a minimum.

The leaching columns were then mounted vertically in retort stands and each assigned a letter A, B, C. With the exception of experiment 4 each column was treated in an identical manner by 'dripping' a variety of precipitation inputs on to the columns from a ponded supply above the leaching columns. As far as possible the 'drip-rate' of application was kept constant between

40-45 ml hr^{-1}. The precipitation inputs to the soils were aliquots derived from excess routine samples in the laboratory, collected by SRPB personnel, diluted to resemble actual precipitation inputs at Loch Dee. Samples of the soil water effluent were removed from beneath the leaching columns every 40 minutes when 25 ml of effluent had been collected. 10 ml of the effluent was used to determine pH, conductivity, calcium and magnesium; 10 ml of the effluent for sodium and potassium and 5 ml for chloride, sulphate and nitrate. Slightly fluctuating rates of leaching from the soils has resulted in some slightly smaller sample volumes which then have not been analysed for all 6 parameters.

The methods of analysis employed for both inputs and soil water effluents are the same as described in section 4:2:2 (with the anions being determined by ion chromatography). In order to minimise accepting 'false' data through contamination of the small sample bottles, each experiment was run in triplicate. Each experiment was run in parallel on the three columns until 7-8 samples of the effluent had been collected by which time any significant short-term change in the soil-water should have occurred. Only one experimental run was possible per day although where possible experiments were run on consecutive days to minimise the effects of soil deterioration and microbiological activity.

In the first of the four experiments described here a distilled water input was used on the columns primarily to attain a common starting reference for subsequent experiments and also to reveal any inherent differences in the soil. In the second experiment a precipitation input of dilute sea-water composition was used; experiment 3 employed an input closer to that of a more acidic input at Loch Dee. Finally experiment 4 used a variety of sea-salt concentrations across the three columns.

The results of these experiments are presented graphically in figs 6:7 to 6:10 and described in turn in the subsequent sub-sections prior to a more detailed discussion of the broader implications and mechanisms in section 6:4. In each of the figures the results for column A are represented by a full line, column B by a dashed line and column C by smaller dashed line. The concentration of each ion in the input solution is given on the figures in parentheses. All figures are in microequivalents (conductivity in microsiemens).

6:3:2 Experiment 1.

The input solution for this experiment was not analysed (apart from pH and conductivity), although by definition distilled water, can be considered to have a zero concentration of ionic constituents. The effect of the distilled water input on the soil was quickly to leach the major ions. The conductivity trace (for all 3 columns) in fig 6:7a also illustrates the rapidity with which flushing and leaching of the major ions occurred. Fig 6:7a also indicates the removal of soil acidity by flushing until the soil water effluent approximates to the acidity of the input solution. The potassium trace indicates both the ease with which it can be leached from the soils and the low concentrations of this ion in the soil. Fig 6:7b shows similar trends (ie. dilution) for calcium, magnesium, sulphate and chloride. The

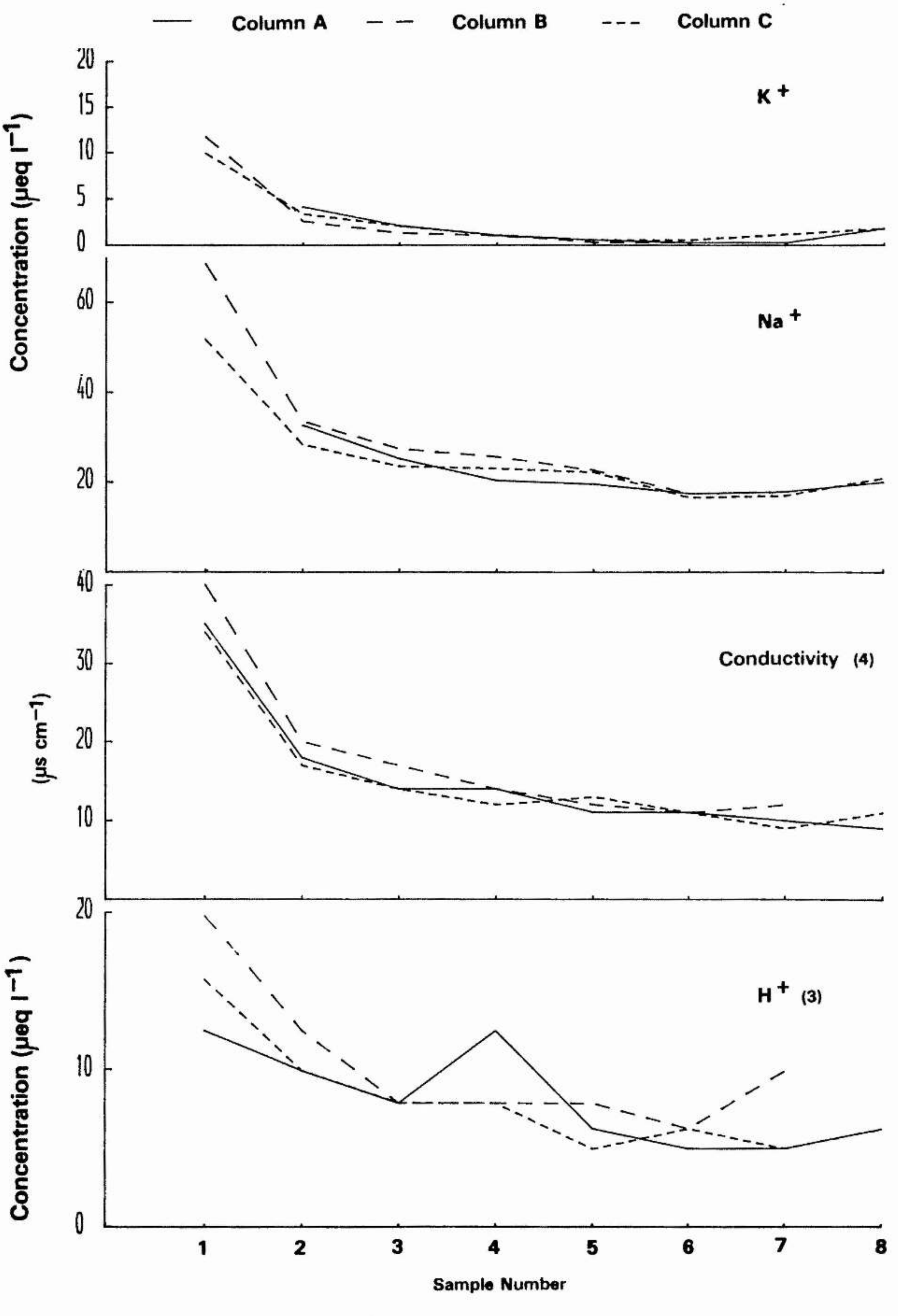


FIG 6:7a Experiment 1: Variation In Soil Water Effluent With An Input Of Distilled Water

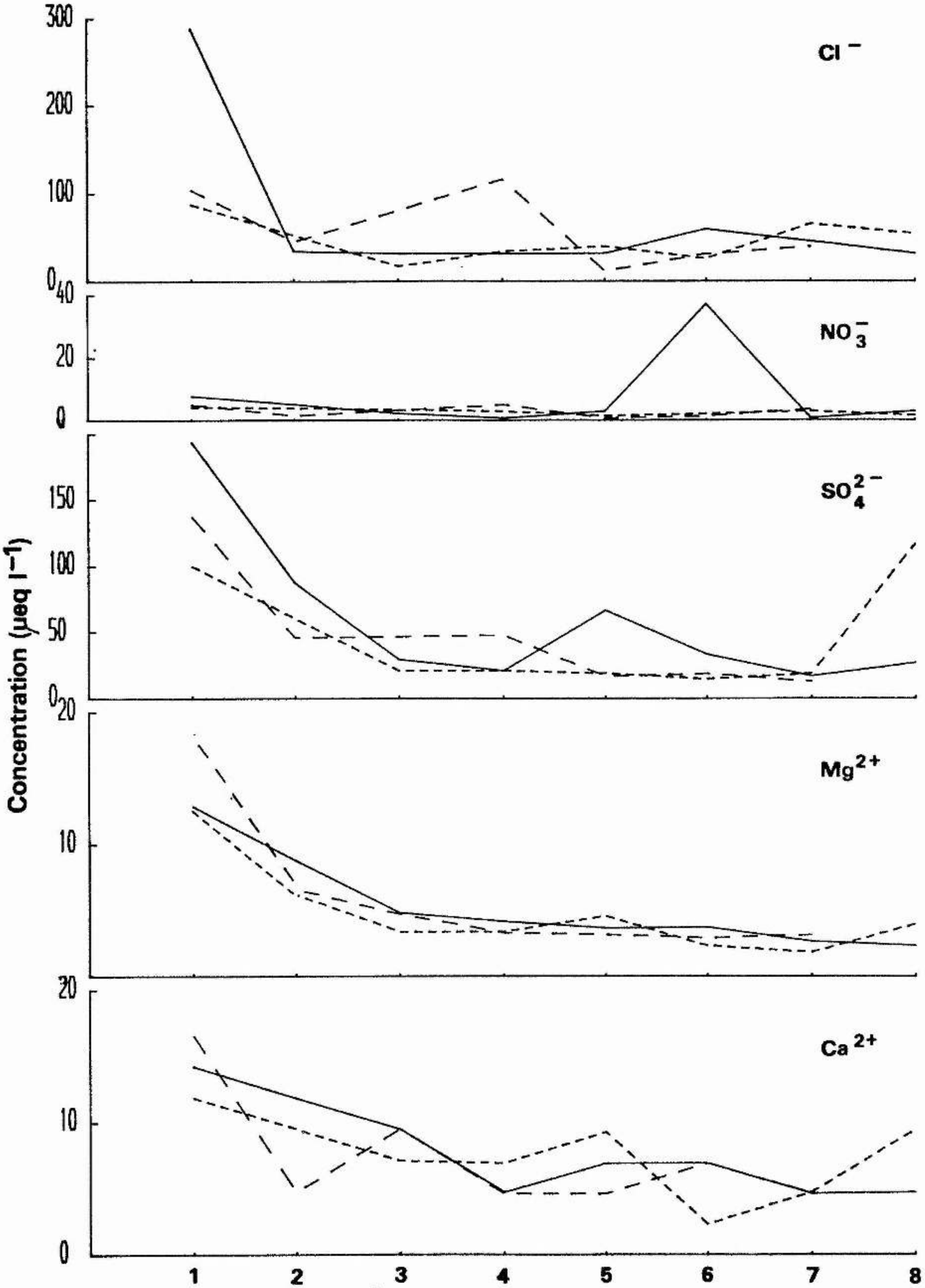


FIG 6:7b Experiment 1: Variation In Soil Water Effluents With An Input Of Distilled Water

initial low concentrations of calcium and magnesium and the flatness of the curves indicate the relative deficiency of these ions in the soils. Nitrate levels remain low throughout the experiment with the exception of sample 6A in which the high concentration is probably the result of gross contamination.

This experiment shows some similarities with some of the field data from section 6:2 and particularly the first storm during the November 1982 event, a point further discussed in section 6:4. The experiment also indicated no significant differences in the inherent properties of the 3 soil columns.

6:3:3 Experiment 2.

In the second experiment an input to the soils similar to the precipitation input experienced during the storms was desirable. This was done by taking a sample of the Solway Firth water and diluting it using distilled water until the final input solution had a conductivity of approximately 200 $\mu s\ cm^{-1}$ and an acidity of 2-4 $\mu eq\ H^{+}l^{-1}$ Fig 6:8 illustrates the effect on soil water chemistry following such an input, the results are most interesting. Potassium concentrations in the first samples are relatively constant (although elevated in comparison to experiment 1) at 8-12 $\mu eq\ K^{+}l^{-1}$ a level which is approximately half of the input solution. This suggests there is strong potassium adsorbtion onto the humus and clay colloids in the soil. As the adsorbtion sites become saturated more and more potassium passes through the soil column and the effluent concentration increases towards the input concentration of potassium. Sodium concentrations in the samples show an immediate increase although

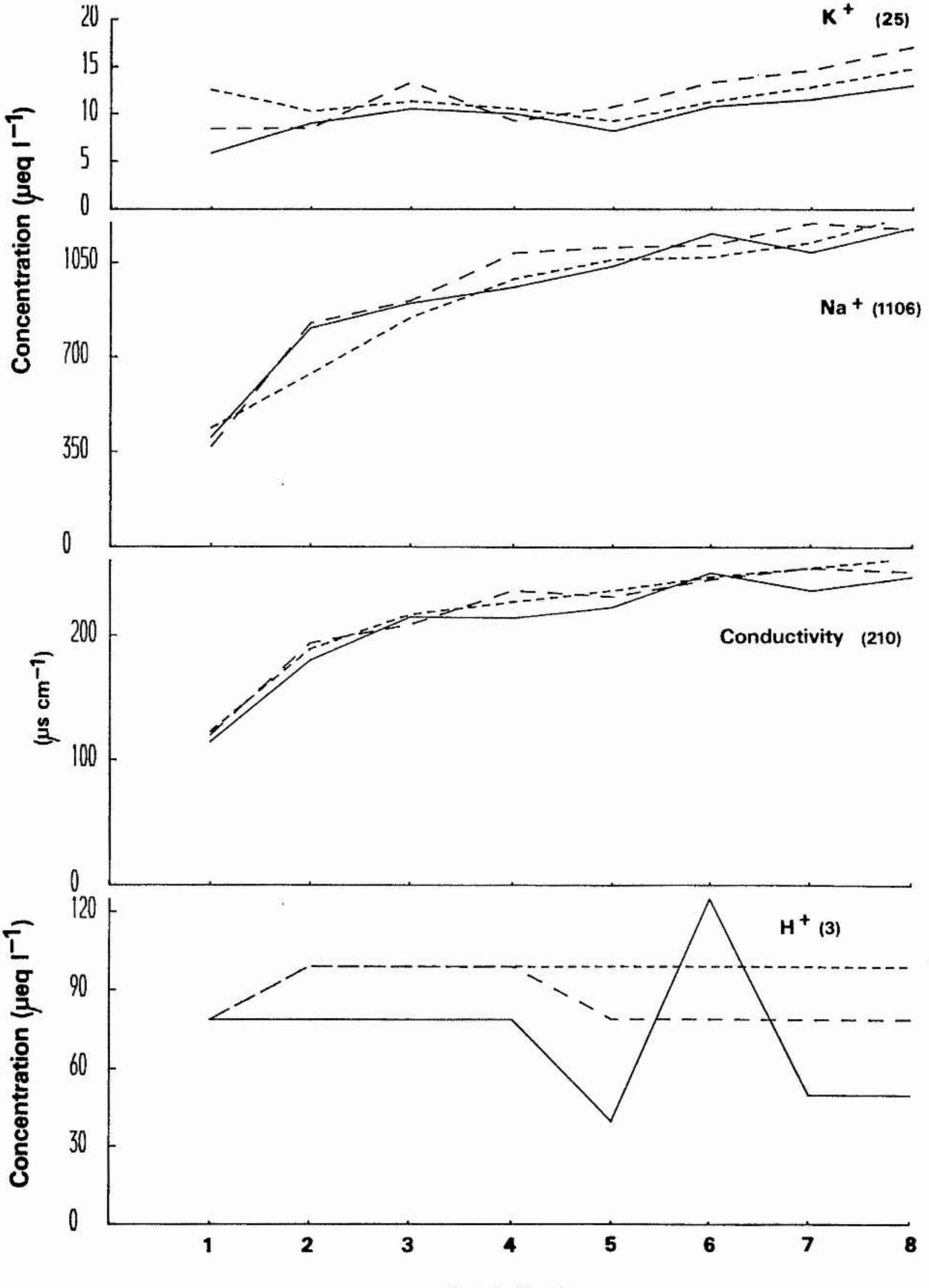


FIG 6:8a Experiment 2: Variation In Soil Water Effluent With An Input Of Dilute Sea-Water

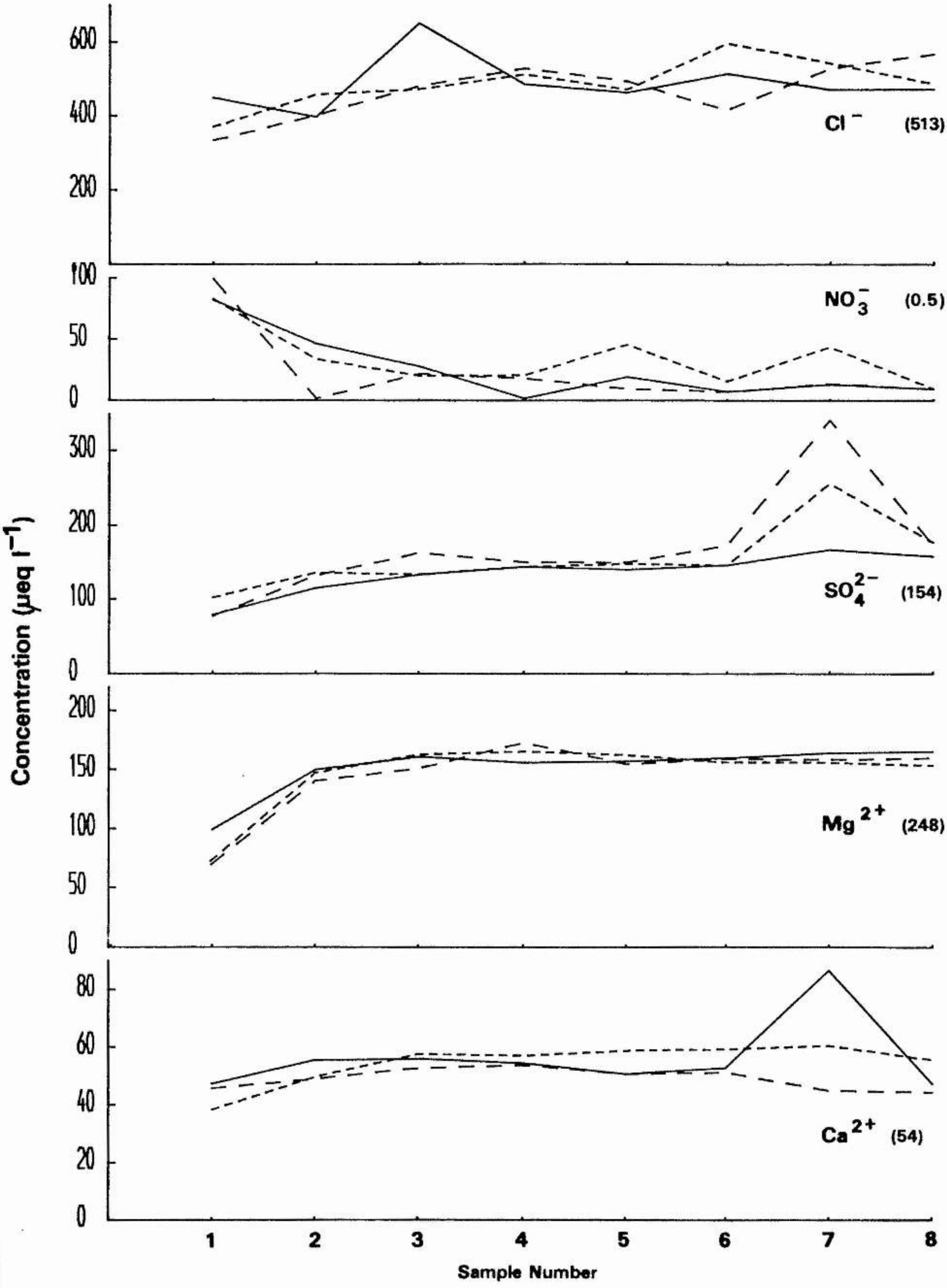


FIG 6:8b Experiment 2: Variation In Soil Water Effluents With An Input Of Dilute Sea-Water

again there is some sodium adsorbtion or retention by the soils. Over the period of the samples sodium shows a 3 fold increase in concentration. A similar progression is illustrated by the conductivity trace of the samples, most of this increase being probably accountable for by the increase in the effluents' sodium and chloride concentrations. The conductivity traces are further made interesting by the fact the maximum recorded conductivity in the effluents (260 μs cm^{-1}) is considerably higher than the input (200 μs cm^{-1}). Tied in with this and of greatest interest in terms of the experiment is the difference in acidity between the input solution (3μeq H^+l^{-1}) and that of the soil effluent (50-120 μeq H^+l^{-1}). This increase in acidity occurs very rapidly. If one compares the acidity from pre-experiment 2 (ie. sample 8, experiment 1) of 10 μeq H^+l^{-1} to an acidity in excess of 75 μeq H^+l^{-1} in experiment 2, sample 1. This rapid and massive increase is most satisfactorily explained in terms of an ion-exchange mechanism in which the sodium (and probably to a lesser degree the potassium) ions from the precipitation input are exchanged for H^+ ions held on the soil and clay colloids. This exchange also explains the soil water conductivity in excess of the input conductivity as the H^+ ion will contribute proportionally more to the solutions' conductivity than the sodium ion. Concentrations of calcium shown in fig 6:8b show some increase through the samples although the general trend is a stability of concentration in equilibrium with the input solution. Contrasting with this is the difference between magnesium concentration in the input and of the effluent. Magnesium after showing an initial increase stabilises at a concentration of approximately 150 μeq $Mg^{2+}l^{-1}$ in the samples compared to an input of 250 μeq $Mg^{2+}l^{-1}$. This suggests the soils have a high adsobtion capacity for magnesium, the retention of which represents an increase in the base saturation of the soils.

Chloride concentrations in the experiment show a limited increase over the first two samples after which they they stabilise at a concentration close to that of the input solution, indicative of the conservative nature of the chloride ion. The initially high levels of nitrate in experiment 2 result from the microbiological activity in the soils, having been left overnight between experiments 1 and 2. Nitrate concentrations in the effluent reflect the ease with which nitrate is flushed from the soils without being replaced, playing a minor role in the soil-water chemistry after this flushing. Sulphate in a similar manner to chloride, shows a slow increase in concentration with time to reach a concentration close to the input concentration, indicative of the ion's high mobility.

In broad general terms experiment 2 shows an increase in concentration of most of the major ions. The magnesium trace also shows that some soil adsorbtion has taken place; whilst sodium chloride in the input principally activates an exchange of sodium and H^+ held on soil colloids and the humus complex, the result being a significant increase in soil water acidity. The conductivity and acidity traces also show similarities to the situation analysed in the field situation described in section 6:2.

6:3:4 Experiment 3.

The object of experiment 3 was to simulate an acidic precipitation input comparable to such events at Loch Dee. However, in order to achieve a controlled acidic input a dilute sample composed of brackish water was acidified to 50 $\mu eq\ H^{+}l^{-1}$ using sulphuric acid, thus avoiding any nitric acid input. The results of the experiment are shown in fig 6:9.

The general pattern for the behaviour of all the ions is one of dilution in which the ions are leached from the soil to a level which is equal to that of the input solution. In this situation the ions retained in the soil are "stripped-off" from the 'sea-salt' input thereby acidifying the soil. There is little else one can extrapolate from this experiment, although it is interesting to suggest that this experiment may represent a situation similar to that at the beginning of the first storm on 15-16 November 1982 described in section 6:2.

6:3:5 Experiment 4.

This experiment was designed to see if one could identify the point at which the sea-salt concentration in the input at Loch Dee was sufficient to initiate streamwater acidification. To do this 3 strengths of input solution were made up and one applied to each of the columns A, B, C. Input to column A consisted of a solution 30% the strength of the solution used in experiment 2, column B 40% and column C 70% . The results shown in fig 6:10 clearly illustrate the variation in soil water effluent chemistry to be

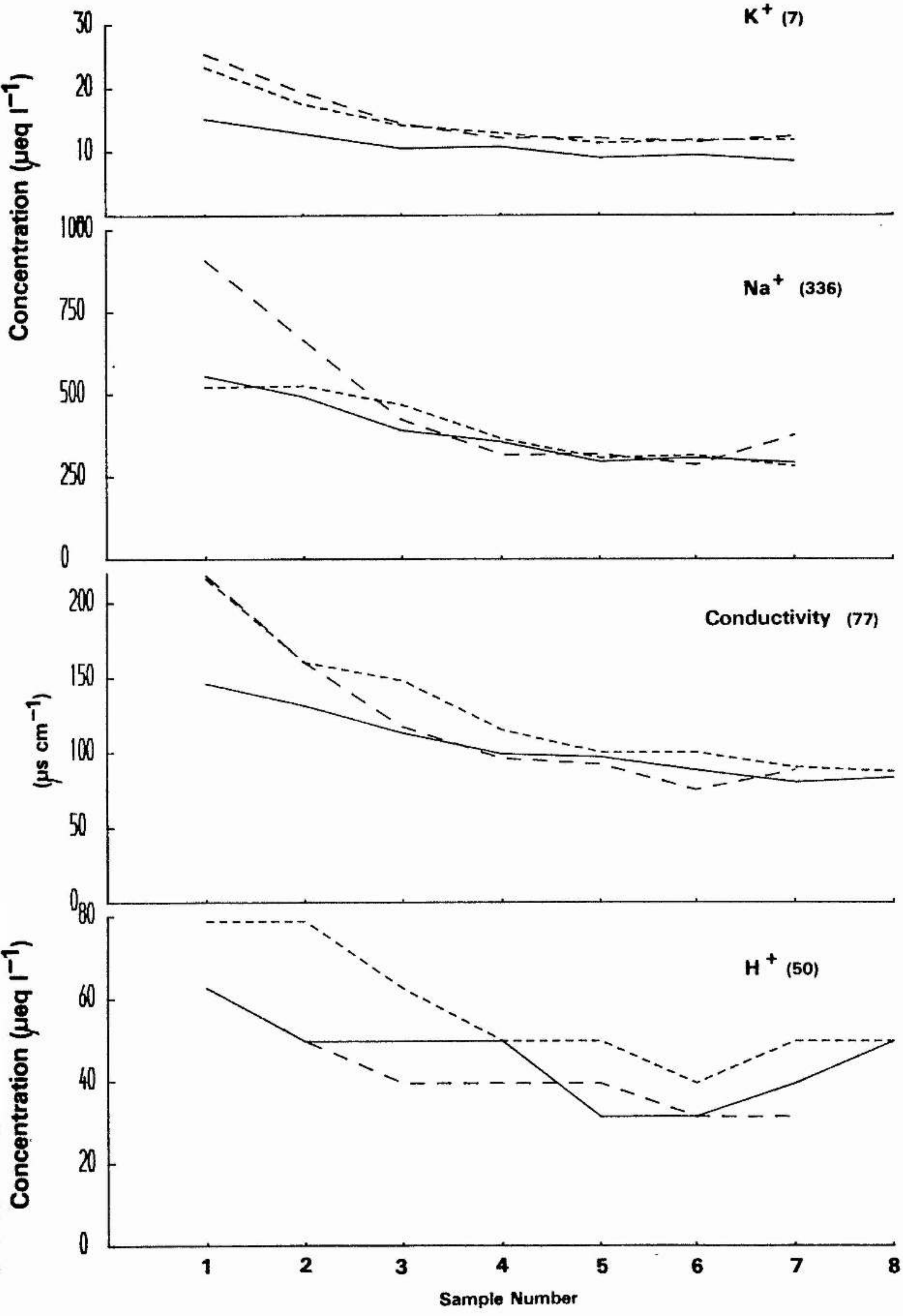


FIG 6:9a Experiment 3: Variation In Soil Water Effluent With An Input Of 'Acid Precipitation'

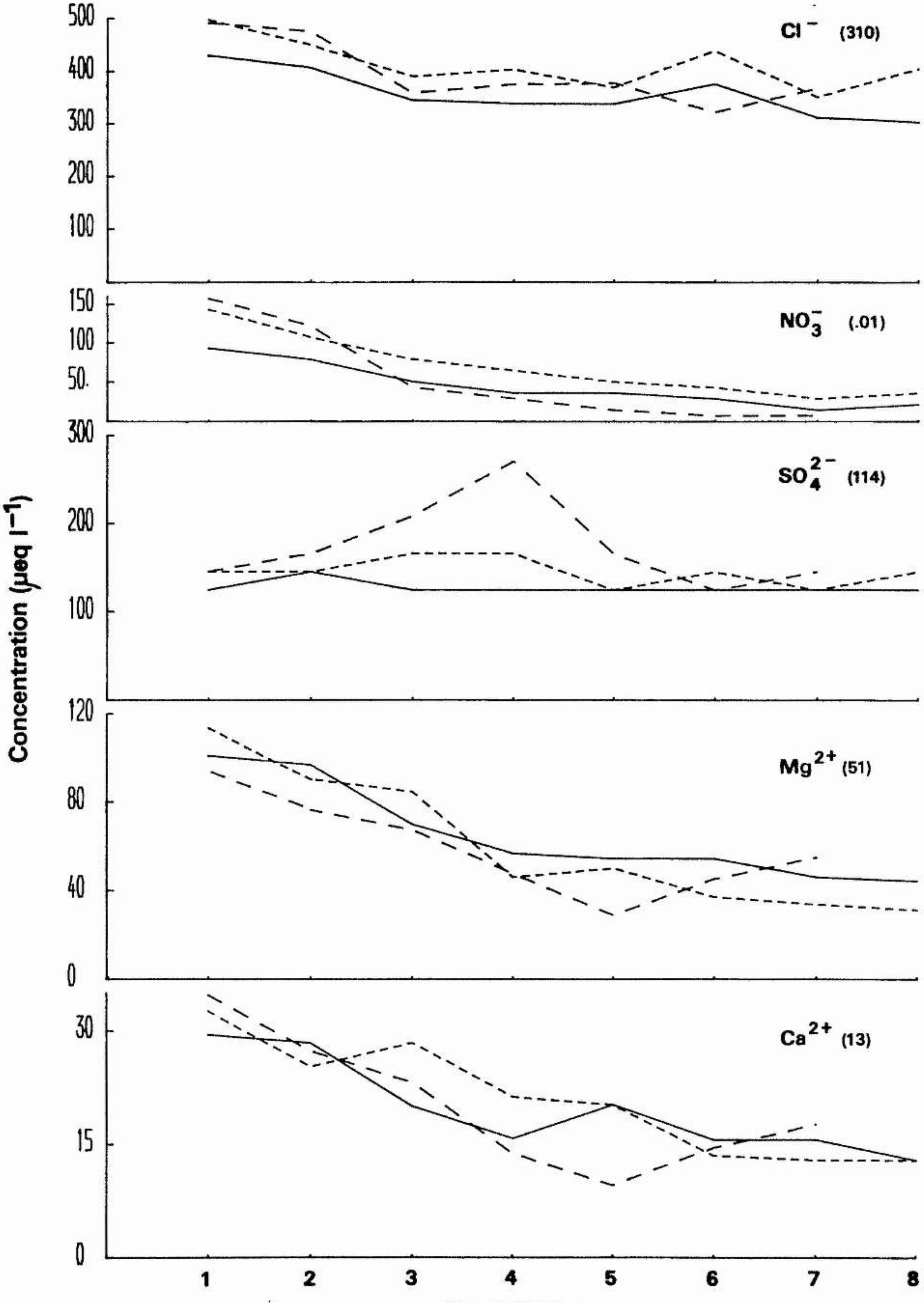


FIG 6:9b Experiment 3: Variation In Soil Water Effluents With An Input Of'Acid Precipitation'

determined by the composition of the input solution. In all 3 columns the soil water is acidified, although one may argue that samples 6 to 8 begin to show some differencing between the columns (ie. A and B show a slight reduction whilst column C maintains a high acidity). Reference to the 3 conductivity traces demonstrates that whilst C is similar to that of experiment 2, A and B show a gradual decline to levels similar to their input. This may be due to an initial high conductivity following the exchange of sodium for H^+ in the catchment soils raising the conductivity; however as time progresses the exchange ceases or reverts thereby lowering both conductivity and acidity. This conclusion along with the tentative differences in acidity shown in fig 6:10 are somewhat speculative and would require more experiments to establish such progressions.

As already stated column C maintains a high acidity, and after an initial increase a high conductivity which stabilises at a level in excess of the input. This is caused by a change in the relative proportions of ions (ie. less Na^+ and K^+ but more H^+) contributing to the conductivity of the soil water effluent.

Sodium concentrations in the effluents indicate a net adsorbtion in the soils for all 3 columns. Whilst this adsorbtion rate is constant for columns' A and b, it apparently decreases with time in column C. Comparison of the 3 columns potassium effluents in fig 6:10 are most interesting. In column A there is a net loss of potassium from the soils. In column B output approximately equals input whilst in C the columns show a net retention. One may tentatively suggest that the experiments bridge the potassium threshold for these soils. In column A the

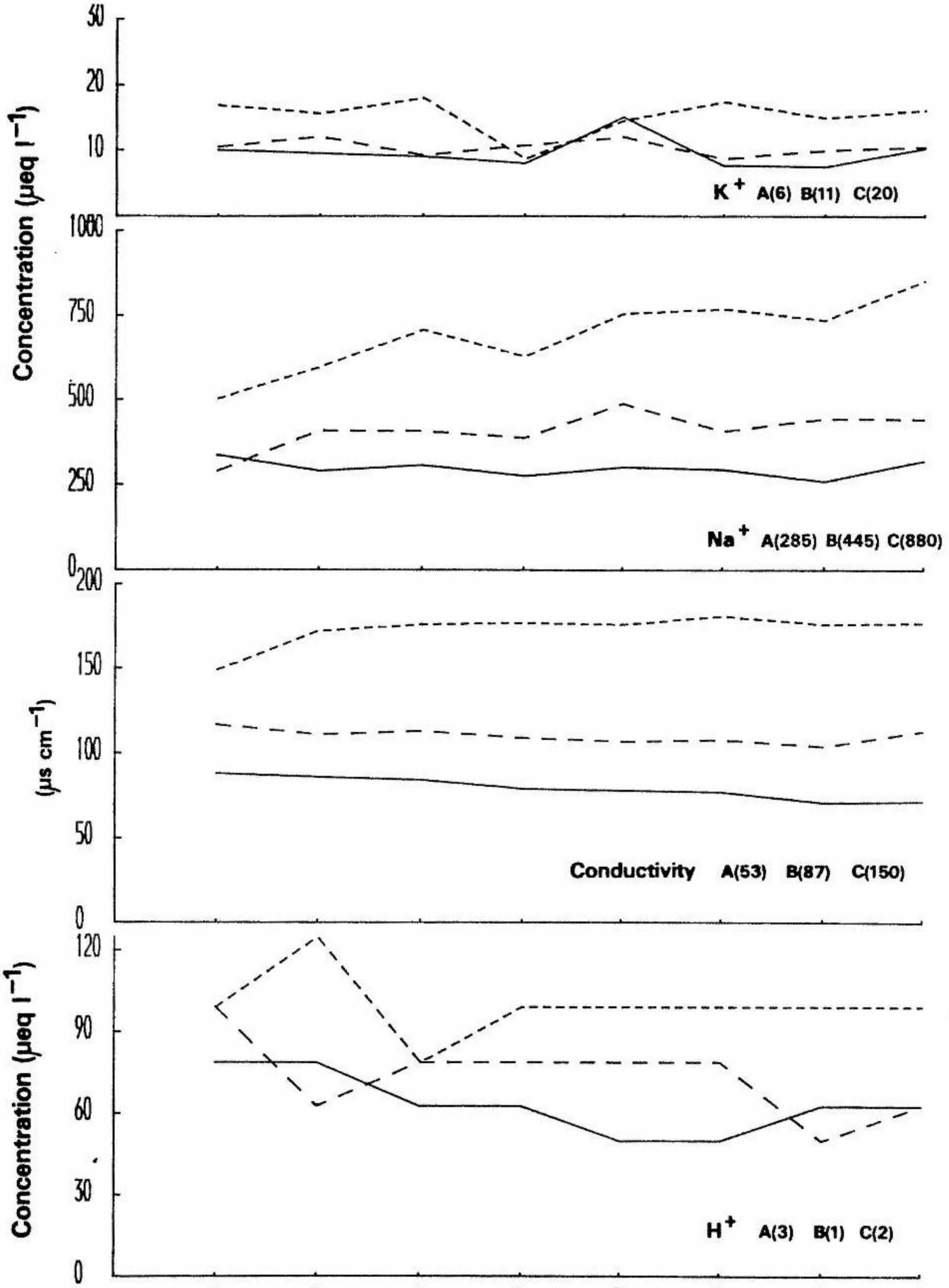


FIG 6:10a Experiment 4: Variation In Soil Water Effluent With An Input Of Various Strengths Of Sea-Water

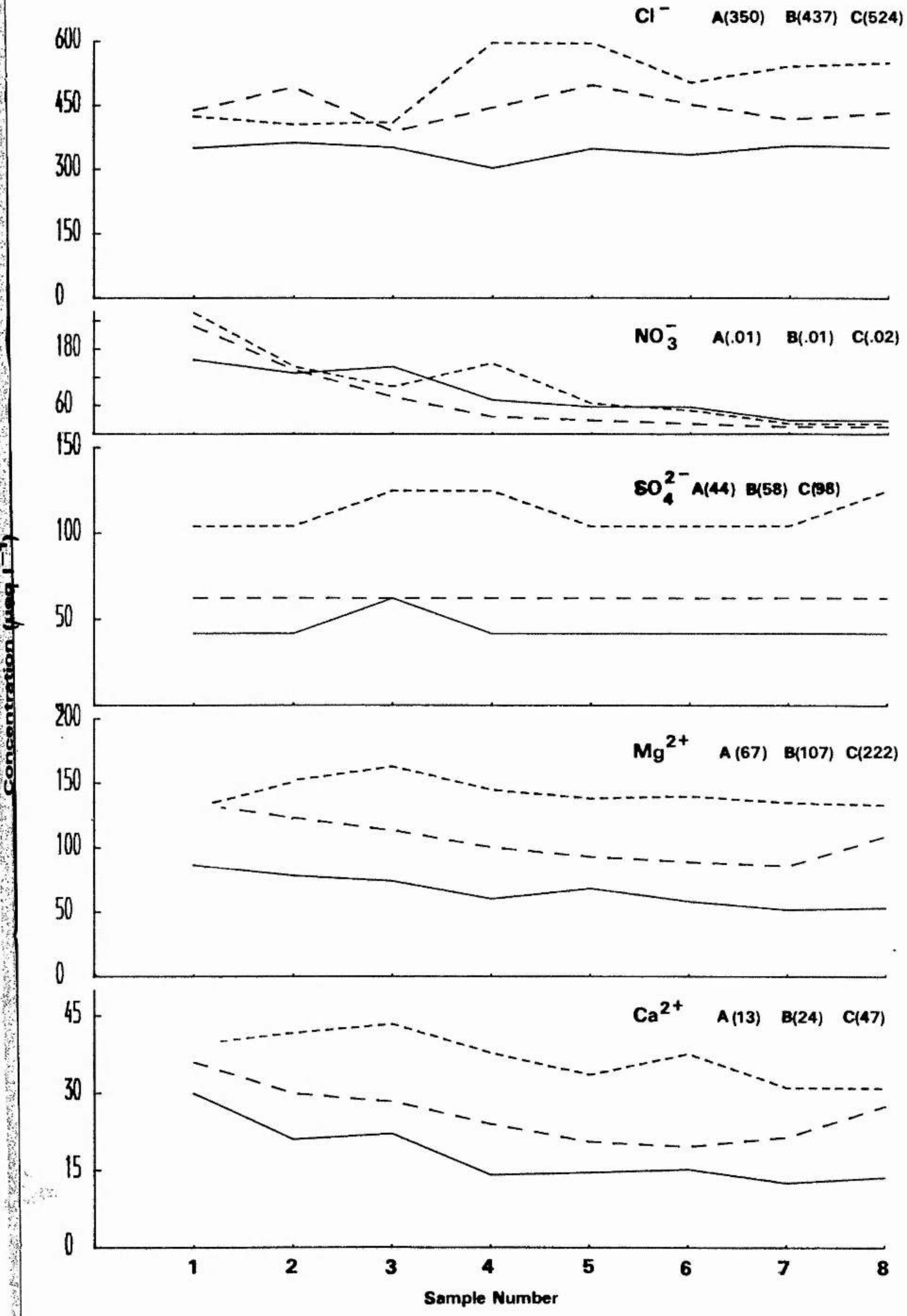


FIG 6:10b Experiment 4: Variation In Soil Water Effluent With An Input Of Various Strengths Of Sea-Water

input concentration was insufficient to replenish the potassium lost from the soil by leaching. In column B however the concentration of potassium adsorbed by the soil approximately equalled that lost through leaching by the percolating water; and in C the concentration of K^+ permitted a net adsorbtion by the soils in excess of that lost through leaching.

For column C there is a net retention of calcium whilst columns A and B show concentrations more similar to those of their inputs (fig 6:10b). Although this relationship is by no means clear there is a suggestion that the high acidity is associated with a high calcium level. The difference between the input magnesium concentrations and soil water effluent indicate there is strong adsorbtion of magnesium by the soils in column C. In columns A and B however there is an initial decrease in concentration presumably caused by flushing and exhaustion after which the concentrations stabilise at concentrations equal to their input solution. Sulphate in the samples shows little variation and effluent concentrations are of the same order as the input solution indicative of sulphates high mobility through the soils. Chloride is somewhat similar to sulphate although it does show some apparent random and spurious fluctuations. Tervet (pers. comm) has suggested these may in fact be a result of equipment error on the ion chromatograph. The 'average' concentrations of each trace however does reflect the concentration of the input solution.

These results along with the field data will now be discussed in greater detail.

6:4 DISCUSSION.

Section 6:2 and 6:3 have presented both field evidence and laboratory data which illustrate that some of the short-lived acidic episodes witnessed in the streams at Loch Dee are the result of an ion-exchange mechanism. In detail the following sequence of events is proposed.

Associated with all three storms described above was the occurence of cyclonic activity off the Atlantic Ocean coupled with strong winds (as shown on the daily weather summary charts supplied by the Meteorological Office, Edinburgh). This resulted in the atmospheric entrainment of large amounts of sodium chloride in the form of sea-spray. These hygroscopic nuclei ultimately reached the land in the form of a substantial sea-salt component in rain or snow. The peaty podsolised catchment soils have a high cation exchange capacity. Bown (1973) gives a total cation exchange value of 109 me/100g for a peat soil site in the neighbouring Loch Doon catchment and describes the peat as having "high exchangeable bases in the top 13 cm ", Bown (1973) p.296. Thus the percolation of sodium chloride enriched waters results in the exchange of Na^+ for H^+ on the humus and peat colloid surfaces.

The laboratory data suggest that the effect of this process on streamwater chemistry will be a rapid increase in streamwater acidity which will be associated with more elevated concentrations of other major ions than would be otherwise seen in a more typical storm. Particularly one observes an increase in the base cations (magnesium and calcium) which in a more typical storm one would expect to be rapidly diluted. Experiment 4 has shown that whilst streamwater acidification occurs with a range of input concentrations of sea-salt; with a sea-salt input and input conductivities of <150 μs.cm^{-1} some dilution may occur. The increase in streamwater acidity with sea-salt deposition gives rise to an increase in base saturation of the soils through the process of ion adsorbtion. This conclusion is supported by the mass balance calculation in which there is a net export of hydrogen ion acidity from the catchment.

The catchments show a significant difference in their export of H^+ over the storm period. The largest export is from Green Burn and the smallest from the White Laggan catchment. One possible cause of the difference between the Green Burn output and the Dargall Lane output is the higher atmospheric scavenging efficiency of the trees in the Green Burn compared to the moorland heath of Dargall Lane. The smaller output from White Laggan is rather difficult to explain given that the soils used in the experiments in section 6:3 were from the White Laggan catchment. However, one may speculate that the difference arises either because of a natural inherent buffering system in the catchment or as a result of the liming programme. With this respect it would be most interesting to repeat the experiments on soils from the different soil associations (see fig 3:3) from different parts of all 3 catchments.

The rapidity with which the change occurs in streamwater chemistry indicates that cation exchange is likely to occur in the upper horizons of the soil profile (humus rich) in response to saturated overland flow or return flow (Dunne and Leopold 1978). The high conductivity levels seen in the streams, twice that of background concentrations, are a function of the elevated atmospheric inputs of the major ions. However there is a change in the relative proportion of the ions contributing to conductivity with the exchange of Na^+ for H^+ causing a proportional increase in the streamwater conductivity.

Both the routinely collected weekly spot samples and the laboratory data indicate that following a sea-salt input the sodium retained in the catchment soils is leached and flushed into the streams over the subsequent time period. The laboratory experiments also show there is sodium in excess of that required by the cation exchange process provided by precipitation inputs.

In contrast to the sea-salt storms is the first storm shown in fig 6:2 in which with an increase in stream discharge there is a dilution of the major ions, (illustrated by the fall in conductivity) accompanied by an increase in streamwater acidity. The dilution of ions is represented in experiment 1. However, a better simulation of this situation is a combination of experiments 1 and 3. In the field situation it is unlikely that the acidity would be diluted as in experiment 3; as prior to any storm (regardless of the timing of a preceeding storm) there is some loss of streamwater acidity with the growing contribution of delayed flow and groundwater of negligible acidity.

Other workers (eg . Edwards 1973, Walling 1974 and Foster and Walling 1978) have reported an initial rise in the dissolved load (and therefore the conductivity of streamwater) with the onset of a storm following a dry period caused by the flushing of accumulated ions from the soil. Foster and Walling (1978) illustrate this effect to produce a 3-4 fold increase in several ions in the autumnal flush following the extreme drought conditions of 1975/1976 in S.Britain. The storms described here produce streamwater conductivities greater than twice mean background levels and may cause proportionally greater changes in ionic concentrations than those reported by the process of flushing.

In the discussion to this work it has been implicitly suggested that there are 2 types of storm profile which need to be distinguished.

Type I: in which there is an increase in streamwater acidity and a dilution of the other major ions. This situation is the classical dilution effect which is well documented in the literature. Such dilution may be preceeded by a flushing of accumulated solutes from the catchment soils. In terms of acidity, streamwater shows a rapid decrease following the cessation of the precipitation input.

Type II: an increase in both streamwater acidity and conductivity, the details of which have been investigated here. Rather than dilution there is an increase in concentration of the atmospherically derived sea-salts through the storm. The field data indicate that the acidity of the streamwater does not decrease as rapidly as in the type I situation following the cessation of precipitation but is maintained as cation exchange within the soils continues to operate. This second type of storm, whilst more rare, may occur 3-4 times a year (see fig 5:7) to differing degrees and contribute significantly to streamwater acidity.

6:5 SUMMARY AND CONCLUSION.

Other workers have investigated the role of sea-salts in different situations; notably Skartveit (1981) who identifies the same process as the cause of short term episodic acidity for a remote catchment on the western coast of Norway, and Wiklander (1975) who suggests that the input of neutral salts such as those investigated here will reduce the acidification of soils by acid precipitation. Nevertheless, the investigation undertaken here has provided the first detailed account of the role of sea-salts in affecting streamwater chemistry in Britain. Furthermore the investigation provides a full synthesis from a precipitation input to streamwater output and provides some initial quantification of the ionic concentrations and budgets (for differing land uses) involved in the process.

Such a synthesis has only been possible through the use of a continuous monitoring network measuring both precipitation and streamwater quantity and quality. As Walling (1975) points out such continuous monitoring overcomes the problem of intensive sampling in which a less frequent sampling strategy may omit to detect the type of variation described here.

CHAPTER 7: MODELLING STREAMWATER ACIDITY IN THE THREE CATCHMENTS AT LOCH DEE.

7:1 INTRODUCTION.

In the study of water resources the ability to model water quality is desirable from two aspects:

a) To improve our understanding of the processes and dynamics within catchment systems.

b) To predict or forecast with the view to managing a basic resource.

Modelling may help to improve our understanding of a system by identifying relationships between different components in the system under study. In identifying such relationships there are two generations of model types.

Firstly, there are static models in which relationships 'at a point' are considered. Two examples of this static type model are provided by the study of DeWalle et al (1984) and Nicholson et al (1984). DeWalle developed a geological model which used the amount of Mauch chunk formation as a predictor variable in estimating upland stream sensitivity to acidification in the Laurel Hill region, Pennsylvania. The study of Nicholson et al proposes a series of regression models which characterise the mean weighted concentrations of selected ions in throughfall as a function of canopy cover. These regression-type models described above only account for a simultaneous response between the variables. As Walling (1974) implies such univariate water quality models are inadequate; the potential role of system dynamics via hysteresis needs exploration. These models do not consider the dynamics of the system and therefore remain useful only whilst the system is in a steady state.

In order to study system dynamics it may be necessary to move from a physically-based approach which identifies the differently contributing processes in a relationship to a more statistical approach in which relationships are established between measurable parameters. Amorocho and Hart (1964) discuss at length the utility of the system synthesis approach in hydrology. Similarly such an approach is useful in hydrochemistry where the environment is constantly changing. To model these situations there is a need for models to incorporate a system's dynamics.

Consider the processes in an upland catchment which interrelate to determine the hydrochemistry of the effluent stream during a storm. When the catchment receives an input stimulus, (eg. rain) it will respond according to the internal structure of the catchment hydrochemical processes. This internal structure which governs the input-output relationship filters the input signal into an output response.

To understand these systems and processes better, one of two approaches may be adopted. These two approaches are shown in fig 7:1. The decision as to which modelling procedure should be used will be determined by:

a) The objective of the analysis.

b) How much is known about the system and process under investigation.

c) Available data.

Where modelling is undertaken with a prior knowledge of the processes and their theoretical behaviour a partial system synthesis approach (Amorocho and Hart 1964) will provide the appropriate modelling approach. This is shown on the right hand side of fig 7:1. The use of such models is common in the hydrochemical literature (Christophersen et al 1982, Lam and Babba 1984, Galloway et al 1980). A classic example in the use of these models is provided by the North American ILWAS study (Integrated Lake-Watershed Acidification Study). This model simulates the physical and chemical transformations occurring in watersheds and lakes, as induced by acid-deposition and internal acid generation (Chen et al 1982). Such models tend to be highly complex using physical, chemical and biological theories to derive partial differential equations to describe the system under investigation. These models can be useful in explanation and prediction but lose their ability to predict accurately when system synthesis is incomplete or when some of the modelling assumptions are not met (see Christophersen et al 1982). This type of model will also be inappropriate if there is insufficient

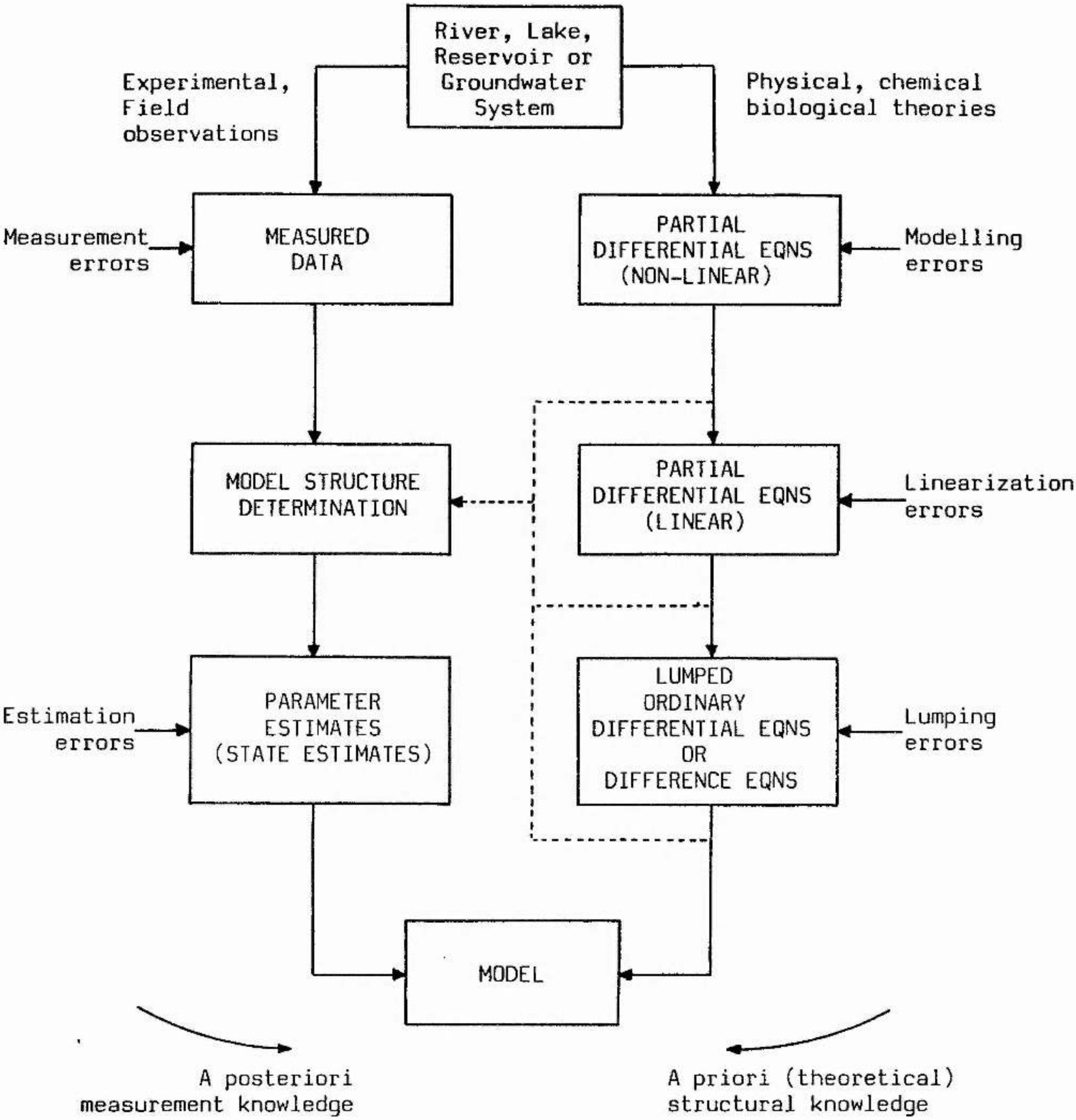


FIGURE 7:1 Two possible approaches to modelling

(Source Whitehead et al., 1984)

data to characterise the relevant processes in the model.

An alternative approach to this system synthesis is the use of system analysis (Amorocho and Hart 1964). In a system analysis approach the system processes are replaced by mathematical functions which do not attempt to represent the true working of the system. Where a system is exceedingly complex or where there is an inadequate knowledge of the processes governing the input-output relationship, this system analysis will provide a more appropriate modelling technique, (shown on the left hand side of fig 7:1). This black-box approach offers relatively simple but robust models which may provide an initial understanding of a system. They are particularly useful where input-output relationships are of primary concern. This type of model has been successfully applied to a variety of environmental studies eg. Lai (1979) and Bennett (1976). The development of such models may in turn give an insight to the processes to which a system synthesis approach may be fitted.

The object of the modelling investigation described in this chapter is to model streamwater acidity over storm periods in each of the catchments. The model relies on the flow-acidity relationship discussed in chapter 5. Subsequent sections of this chapter describe the mathematical theory of one particular black-box model, the steps involved in the building of this model and how the use of a computer package has been utilised to develop and test the models.

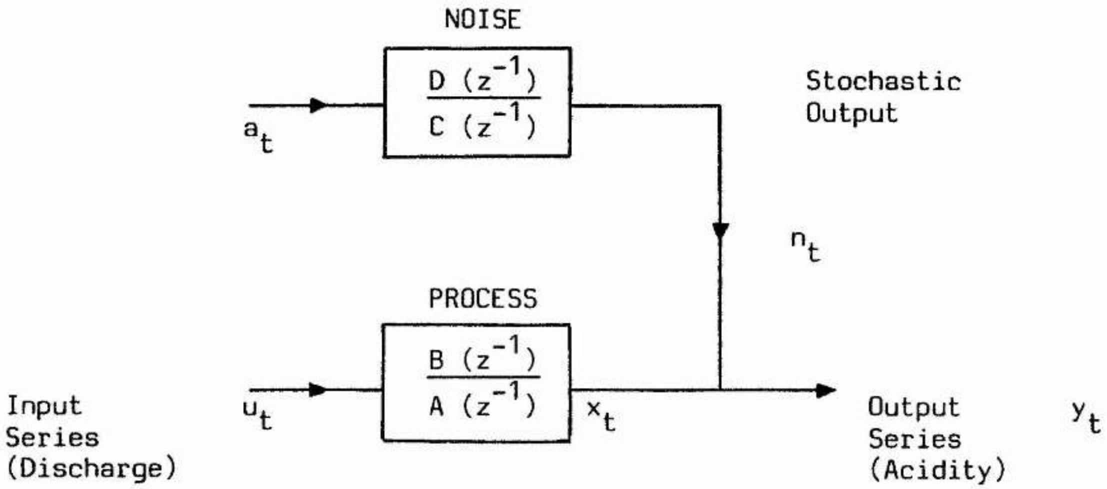
7:2 MATHEMATICAL THEORY.

In this investigation both the series input and output of the system is known, what remains is to identify and estimate the transfer function; where the system (catchment) receives an input stimulus (discharge) and responds to the input according to the internal structure (hydrochemical processes) of the system which determines the system output (acidity, expressed as hydrogen ion concentration, H^+). This flow-acidity relation, represented by a transfer function has no physical realisation, it is a mathematical approximation which will behave in the same way as the system behaves over the same time increments as that of the data.

Figure 7:2 illustrates the various components of the transfer function model. This single input single output model consists of two parts a process model and a noise model. The observed input (u_t) causes most of the output variation (y_t), however superimposed on this process model is a stochastic input (a_t) which arises from random disturbances to the system. These disturbances are accounted for by uncertaintities in the measurement (see Bennett 1979, Whitehead and Beck 1984). PH measurements as discussed in earlier chapters are particularly vulnerable to such 'unknown errors.'

From fig 7:2 it can be seen that the observed output at time t (y_t) is given by the sum of the deterministic (x_t) and stochastic (n_t) outputs. ie.

$$y_t = x_t + n_t$$



In this way, the x_t variable (acidity) is assumed to depend on past values of acidity, as well as present and past observed input data, while n_t is generated in a similar manner but from a hypothetical white noise input, a_t.

FIGURE 7:2 Representation of a general transfer function with superimposed noise model.

(Adapted after Venn & Day, 1977)

X_t is assumed to be generated by an autoregressive moving average (ARMA) discrete time model (Box and Jenkins 1970) In such models the moving average term describes the contribution of each lagged input term (u_t, $u_{t-1}, \ldots,$ u_{t-n}) to the output. The autoregressive terms represent the memory and association within the sequence of output (y_t) data. The model takes the form:

$$Az^{-1}\ x_t = Bz^{-1}\ u_t$$

Where z^{-1} is a backward shift operator $z^{-1}x_t = x_{t-1}$.

While $Az^{-1} = 1 + az_1^{-1} + a_2z^{-2} + \ldots\ldots.\ a_nz^{-n}$

and $Bz^{-1} = b_o + b_1z^{-1} + \ldots\ldots\ldots\ldots\ b_nz^{-n}$.

The noise term at time t, n_t is also generated by a similar ARMA model of the form:

$$Cz^{-1} = Dz^{-1}\ a_t$$

Where

$Cz^{-1} = 1 + c_1z^{-1} + \ldots\ldots\ldots + c_nz^{-n}$

and $Dz^{-1} = 1 + d_1z^{-1} + \ldots\ldots\ldots + d_nz^{-n}$

Where a_t is a serially uncorrelated sequence of random variables. This white noise component is unknown and has to be estimated from the data.

The full transfer function can then be written as :

$$y_t = [\ B(z^{-1})/\ A(z^{-1})]u_t + [\ D(z^{-1})/\ C(z^{-1})]a_t$$

This equation provides a basic model structure governing the input-output of the system.

7:3 MODEL BUILDING.

In time-series analysis Box and Jenkins (1970) suggest that the problem of model building can be separated into four main stages :

i. Data validation.
ii. Identification of model structure.
iii. Estimation of model parameters.
iv. Model verification.

Use of these four stages provides a convenient and practical step-by-step approach to the problem.

The initial stage of modelling is to set out the objectives one hopes to achieve with the model. Once this is achieved 'data validation' describes the process of checking the data collected to ensure it meets the necessary requirements of modelling. The data set must be of a sufficient length to characterise the main features or processes to be modelled. Futhermore the input and output data for the model must be in a continuous form, in the sense that samples are regularly spaced through time. Time-series analysis will not work with discontinuities in the data. In the case of missing data the full data set may be truncated to avoid breaks or 'appropriate' value(s) may be inserted for missing data.

The quality control checks of chapter 4:3:4 described the methods of data validation used with the continuous data used in this study. Having ensured the data is compatible with modelling, as described the next step in model-building is to identify the number of model parameters and any appropriate lags between input and output. In identifying such a model structure one should follow the assumption of parsimony using as few parameters as possible to characterise the data.

The final stage in model-building is the assigning of appropriate values to the parameters of the model. Assuming the correct model structure has been identified the parameter values will regulate the fit of the model to the data. This fit of the modelled to the observed data leads to the rejection or verification of either the model hypothesis, model structure or parameter values.

7:3:1 Computer Aided Procedure for Time-series Analysis and Identification of Noisy processes (CAPTAIN).

The suite of programmes constituting the CAPTAIN package were designed by Professor P.Young and Dr.S.Shellswell (Young, Shellswell and Neethling 1971 and Shellswell 1972, cited in Venn and Day 1977) as an analytical tool to aid in the analysis of time-series. The package is most commonly run in an interactive mode allowing the user to work progressively through the stages of model building. All data, after initial presentation by the user is handled internally by CAPTAIN package using the basic organisational unit of data series. CAPTAIN in an interactive mode facilitates graphical development of progress during data validation, model identification, parameter estimation and model verification.

The package is well established in the field of water resources and there are numerous examples of its successful application (Venn and Day 1977, Whitehead et al 1979, 1981, 1984)

The CAPTAIN package described and utilised in the proceding analysis is the version mounted on the GEC 4090A computer at the Institute of Hydrology, Wallingford. The procedures and routines therefore refer to the implementation of this version of the package. A more thorough treatment of the package is given in the Institute of Hydrology user manual (Venn and Day 1977).

7:3:2 Data Validation.

In order to meet the objectives of the modelling analysis it was necessary to have a complete data set of stream pH (converted to μeq $H^{+}l^{-1}$) and discharge ($m^{3}\ s^{-1}$), for the same period for all three catchments. Bearing in mind that this investigation focuses on storm variation the period of November 1983 to March 1984 provided data of suitable type and quality. Having set up CAPTAIN and read in the data series it was desirable to describe and display the observed input and output series graphically. Describing the series on CAPTAIN produces plots of the correlation functions (autocorrelation, partial autocorrelation and cross correlation) which are helpful in the model identification stage. In graphically displaying the series, discontinuities and spurious data points may be detected as well as identifying obvious input-output lag relationships.

7:3:3 Model Identification.

The input to any stochastic model assumes that the input itself is the result of a stochastic process which may be assumed to be generated by a series of random shocks. To meet this assumption it is necessary to prewhiten the data so it is random in nature ie. white noise.

By examination of the original data series' partial autocorrelation function, the flow input to the model could be generated by an autoregressive model with three significant terms. In order to prewhiten this input series the data was run through the inverse of this model using the prewhiten programme in CAPTAIN, similarly the output series were transformed in the same way. The data is now said to have been 'prewhitened'. The remaining significant terms in the cross-correlation function between the prewhitened input and output series indicated a maximum value after 1 hour with a rapid decline. This pattern suggests a first-order model as appropriate for the process model. This pattern was observed for all three catchment series, giving rise to a common model structure.

As Venn and Day (1977) and Bennett (1979) comment the interpretation of different patterns and shapes of the functions is an experienced-based process. In the identification of the model structure in this investigation help and guidance in the interpretation was given by Dr.P.G.Whitehead

7:3:4 Parameter Estimation.

In Box and Jenkins (1970) estimation of the parameter values are assigned after reading the whole data block. One of the principal features of CAPTAIN is the incorporation of an instrumental variable technique Young (1970). Using this technique the parameters of the identified model are updated after each variable is read. This involves an auxiliary model which is subject to the same input sequence as the process to be identified (see fig 7:3). The output from the model (x_t) approximates to a theoretical noise free output ($\hat{x}_t$). The difference between x_t and the observed process output y_t gives an estimate ($\hat{n}_t$) of n_t, the noise component. On the first iteration estimation is based on a biased least squares method. Subsequent iterations utilise a recursive parameter estimation (Whitehead 1980) to update the auxiliary model parameters and enhance the quality of the instrumental variable.

These components (i.e auxiliary model output and estimate of the noise) shown in fig 7:3 along with the input and output series provide the input to the identification algorithm. This whole sequence of parameter estimation is run under the Estimate programme of CAPTAIN.

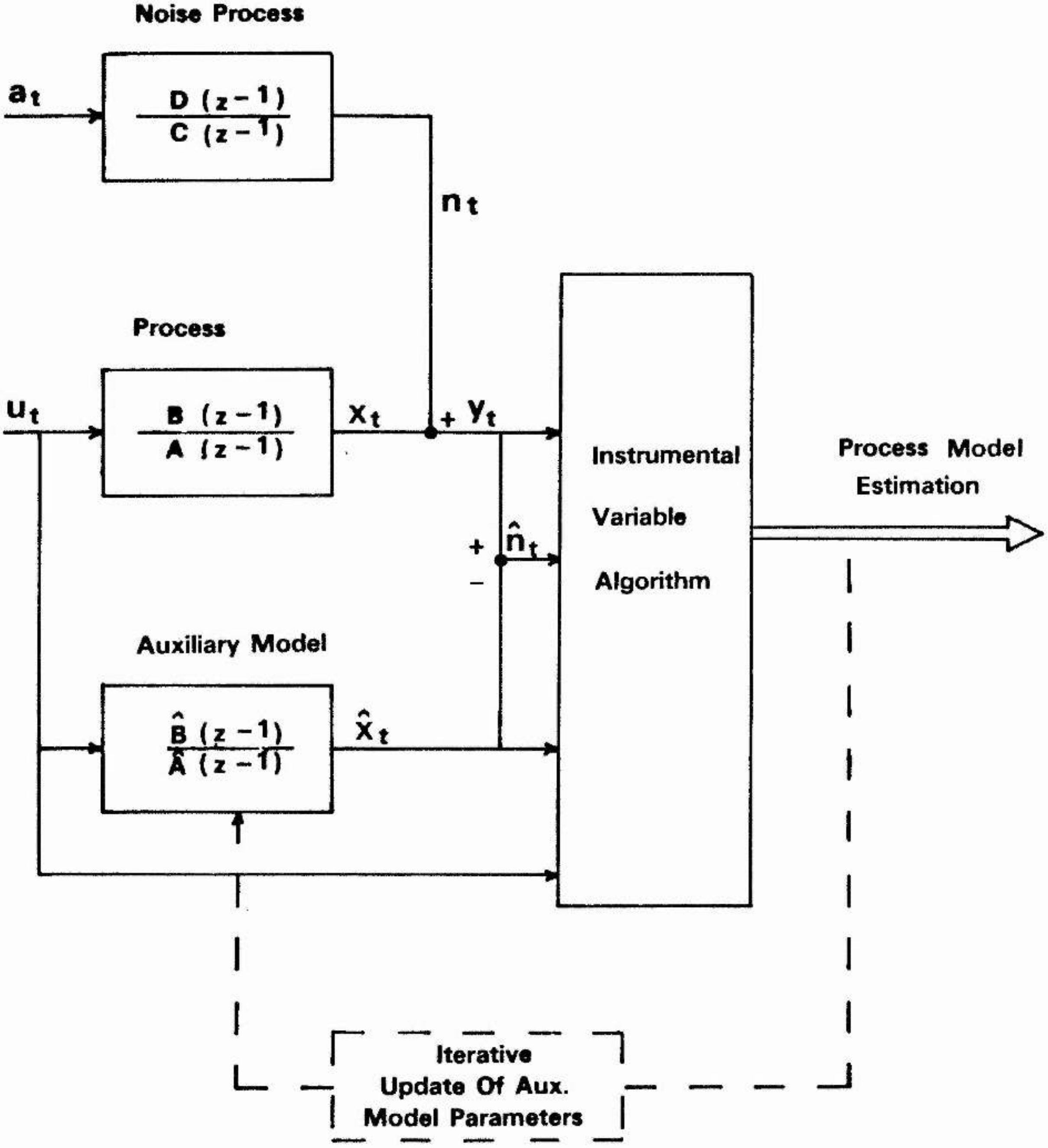


FIG 7:3 Instrumental Variable Approach To Parameter Estimation

7:3:5 Model Verification.

In order to ensure that the estimated structure and parameters of the model provided the best fit of the data, the estimate programme displays graphically the comparison between observed and predicted acidity values. However the ultimate test of the model is to apply the model in a forecasting mode to other data sets from the same catchment. The results of both the initial estimate run and the subsequent forecasting runs for each catchment are shown and discussed in sections 7:4 and 7:5.

7:4 APPLICATIONS and RESULTS.

A CAPTAIN analysis was run on data from Dargall Lane and Green Burn for the period of November 1983. For reasons discussed later a model could not be generated for November 1983 on White Laggan, it was therefore necessary to use another data set, March 1984 was chosen.

The general form of the model was the same for all 3 catchments, a first order ARMA model. ie. one autoregressive and one moving average parameter. The general form of the model may be written as:

$$y_t = a_1 y_{t-1} + b_o u_t$$

where y_t is the Hydrogen ion concentration (μeq $H^+ l^{-1}$) and u_t is the stream discharge ($m^3\ s^{-1}$) at time t.

Whilst there was no time lag for Dargall Lane it was necessary to incorporate a time lag of 1 hour for both White Laggan and Green Burn models. The specification of the three models are given in table 7:1. From the model parameters it is also possible to calculate the systems mean response time (T) and the gain of the system (G). Mean response time is defined by:

$T = 1 / \ln(-a_1)$ .... (Whitehead et al 1984)

and system gain

$G = b_o / 1 + a_1$ .... (Whitehead et al 1984)

A system gain of 2.0 would imply (for this study) that for every 1 $m^3 s^{-1}$ increase in discharge there would be an increase of 2.0 μeq $H^+ l^{-1}$.

The value of these two parameters for each model is given in table 7:1. Also included in table 7:1 are % variance values; % variance in this case refering to the amount of variance in the H^+ concentration which can be accounted for by the flow-acidity model;

$$\text{Variance Accounted for by Model} = \frac{\underline{\text{Variance accounted for by Model}}}{\text{total variance}} \times 100$$

	Parameters and their Standard Deviation				Time Delay (hours)	Model	Mean Response Time (hours)	Gain	% Variance in H^+ accounted for by Q
	a_1	S. Dev.	b_0	S. Dev.					
Dargall Lane	-0.7652	0.0496	8.7489	1.822	0	$Y_t = -0.7652Y_{t-1} + 8.7489u_t$	3.7	37.3	81
White Laggan	-0.7864	0.0767	0.8697	0.0256	1	$Y_t = -0.7864Y_{t-1} + 0.8697u_{t-1}$	5.2	4.1	94
Whitehead et al. (1984)	-0.680	0.012	0.659	0.022	0	$Y_t = -0.680Y_{t-1} + 0.659u_t$	2.6	2.1	93
Green Burn	-0.8208	0.0271	7.7390	1.0614	1	$Y_t = -0.8208Y_{t-1} + 7.7390u_{t-1}$	6.0	43.2	86

TABLE 7:1 Summary Detail of the Models

Figures 7:4 to 7:6 show graphically how the models match the observed data. In both the graphical output and in the variance figures (table 7:2) it is evident some degree of dissimilarity exists. This is due in part to the stepped nature of the input data compared to the smoothed model output data. The stepped appearance of the observed data is a function of the conversion of field measurement of discrete pH values to hydrogen ion concentration (see section 4:2:2). However, in calculating model output values the CAPTAIN package uses fractions of the input and output, this has the effect of smoothing the model output and producing a continuum of H^+ values.

	November	January			February			March		
Dargall Lane	81	92	84	70	89	73	29	96	91	78
Green Burn	86	95	89	71	95	87	61	97	93	84
prediction time (hours)		1	2	5	1	2	5	1	2	5

Table 7:2 % H^+ Variance accounted for during different model runs.

Figures 7:7 to 7:10 show how well these models were able to predict streamwater acidity over additional data sets, under differing conditions and with varied prediction (lead) times. In general the models show a very good agreement between the observed and modelled series. The main areas of deviation are at the extremes of concentration. From table 7:2 and from the figures

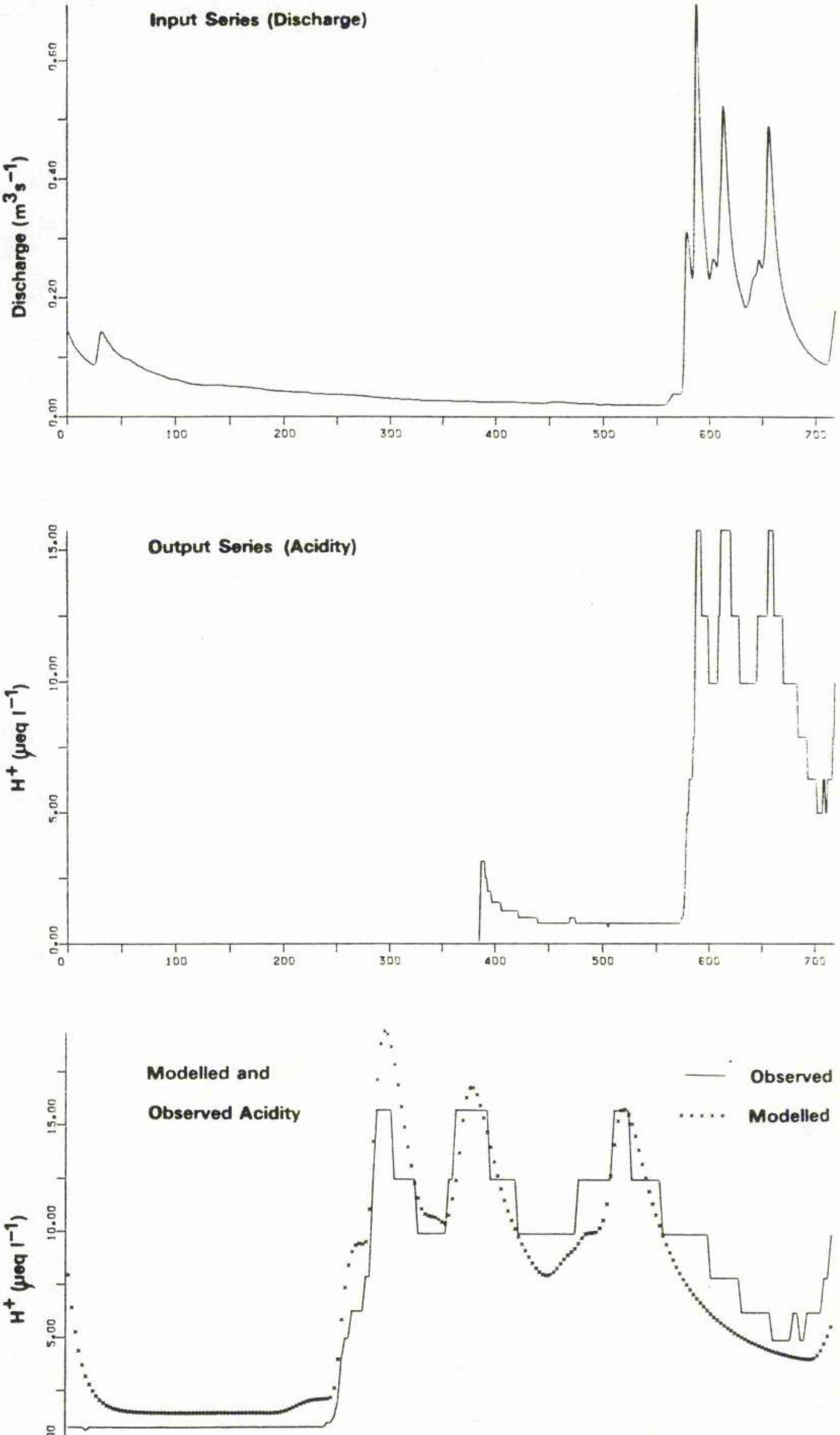


FIG 7:4 Observed Input, Output And Modelled Series For Dargall Lane November 1983

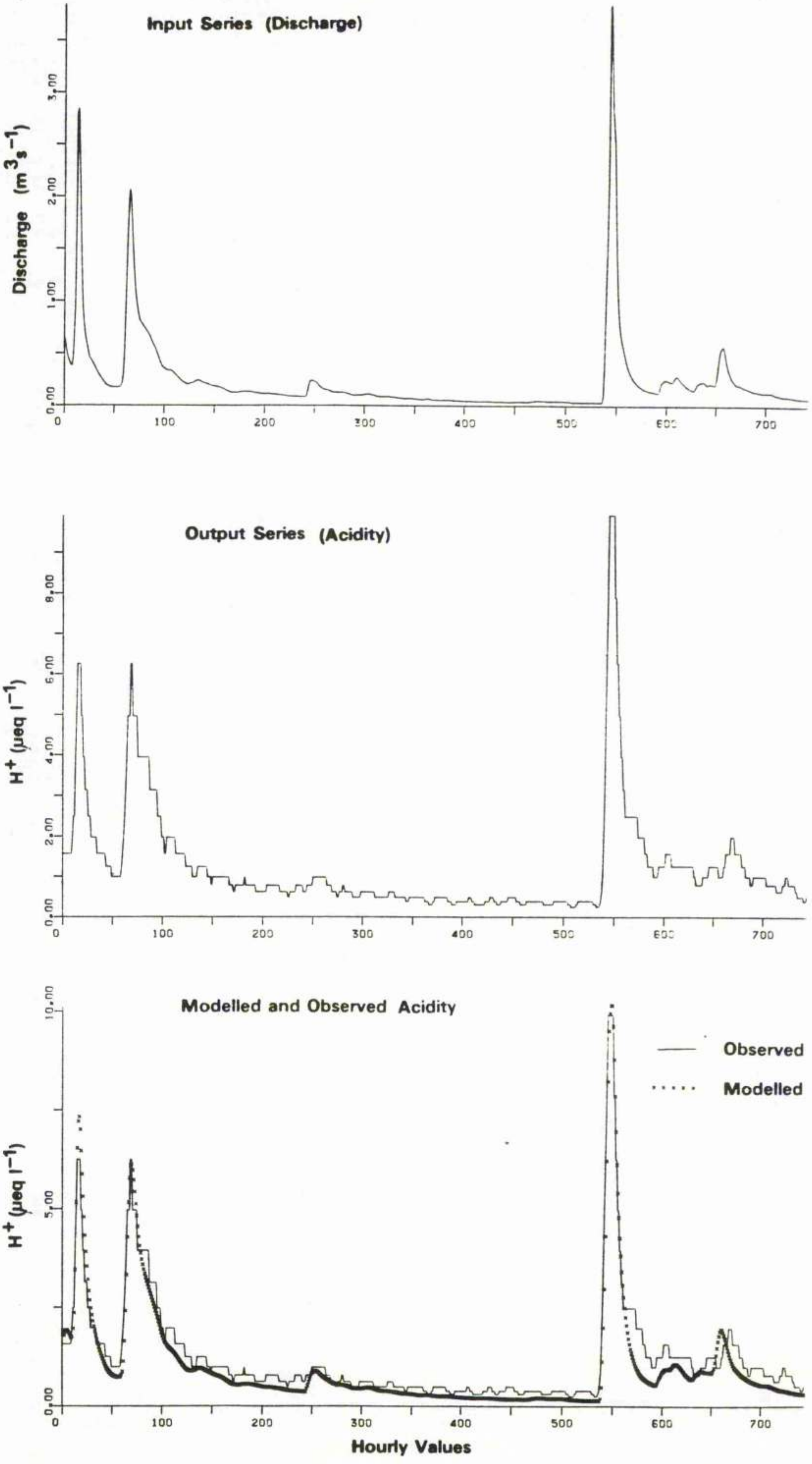


FIG 7:5 Observed Input, Output And Modelled Series For White Laggan March 1984

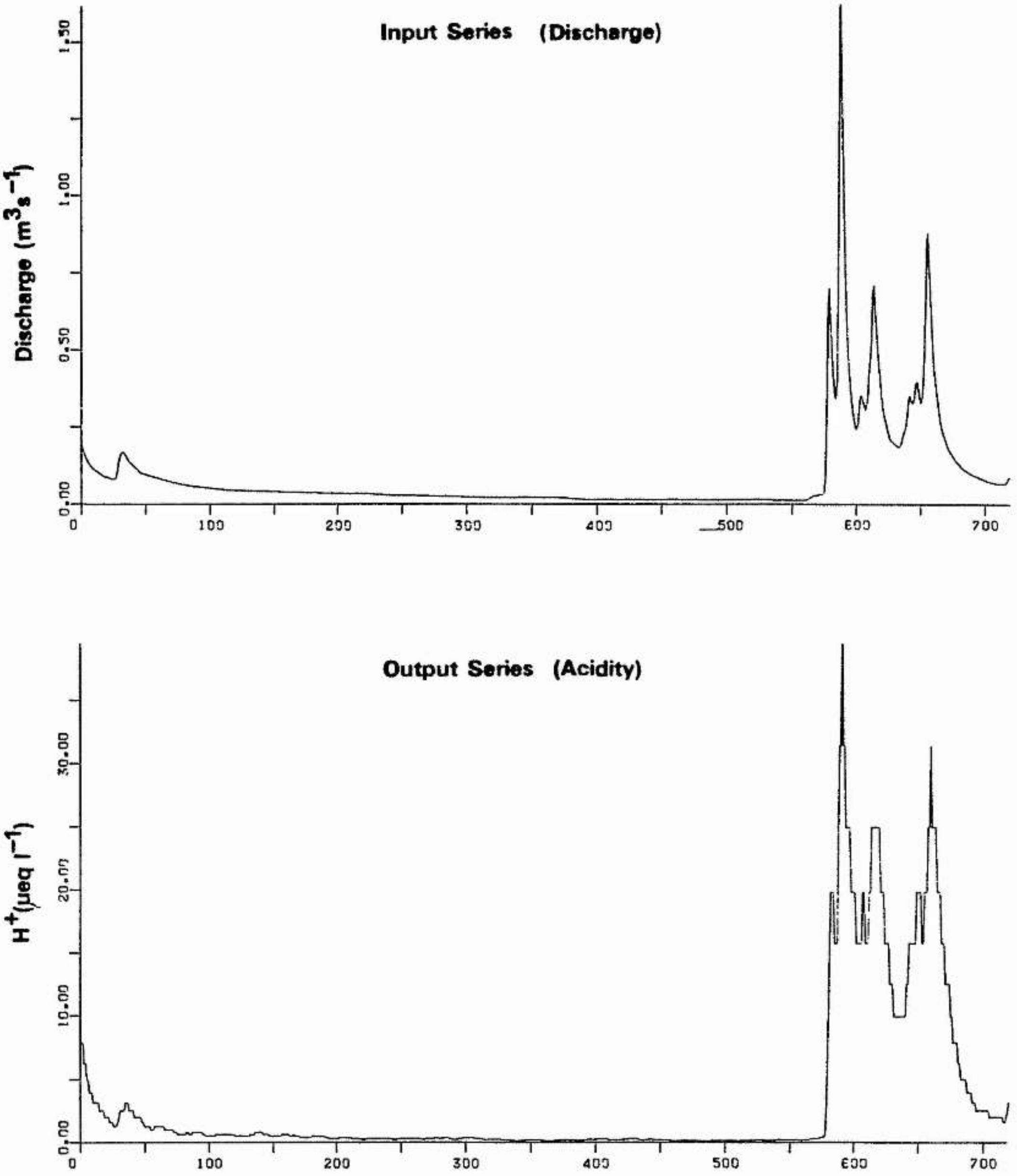


FIG 7:6 Observed Input, Output And Modelled Series For Green Burn November 1983

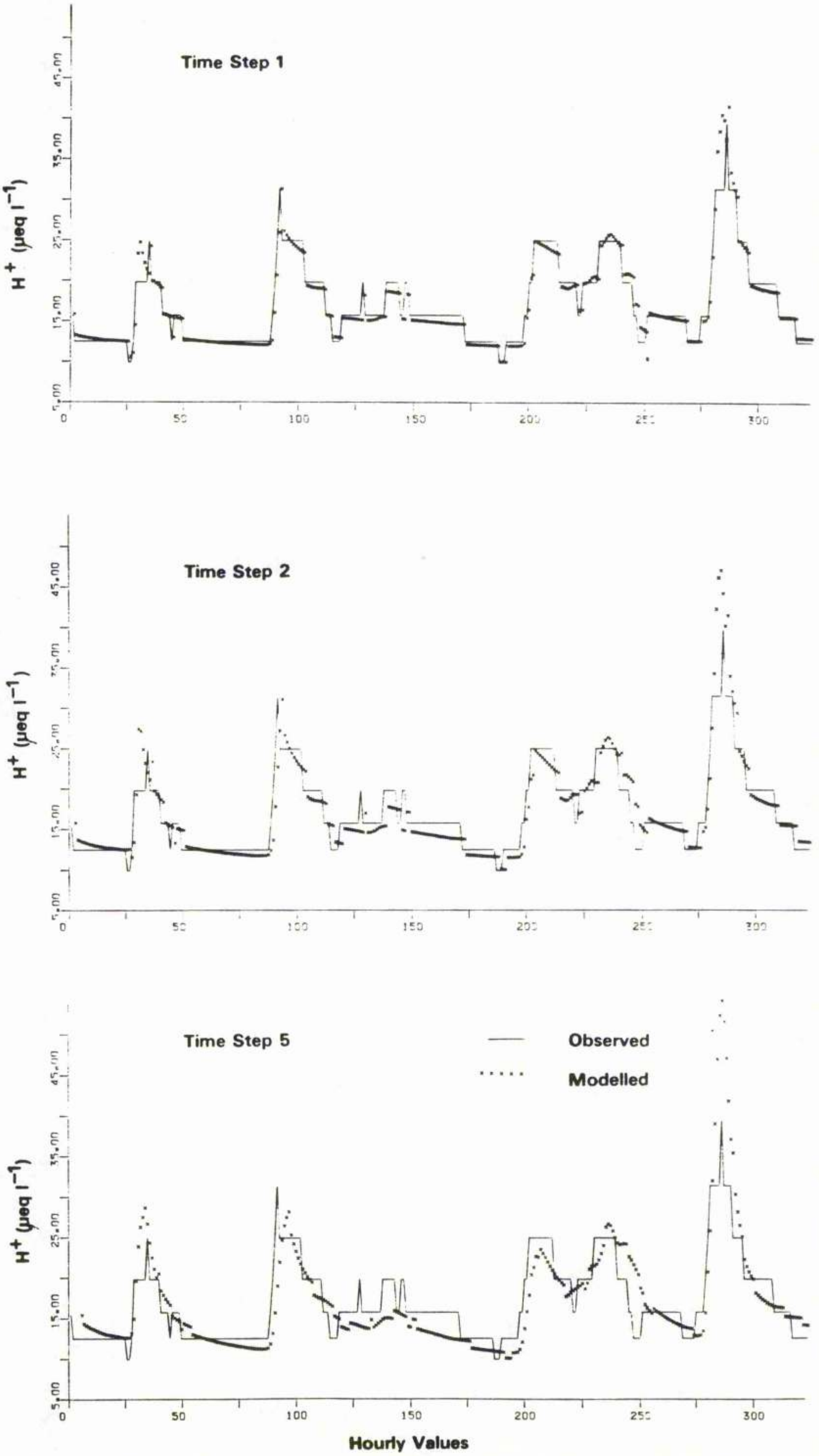


FIG 7:7 Modelled Streamwater Acidity Using Time-Steps Of 1,2,5 For Dargall Lane

January 1984

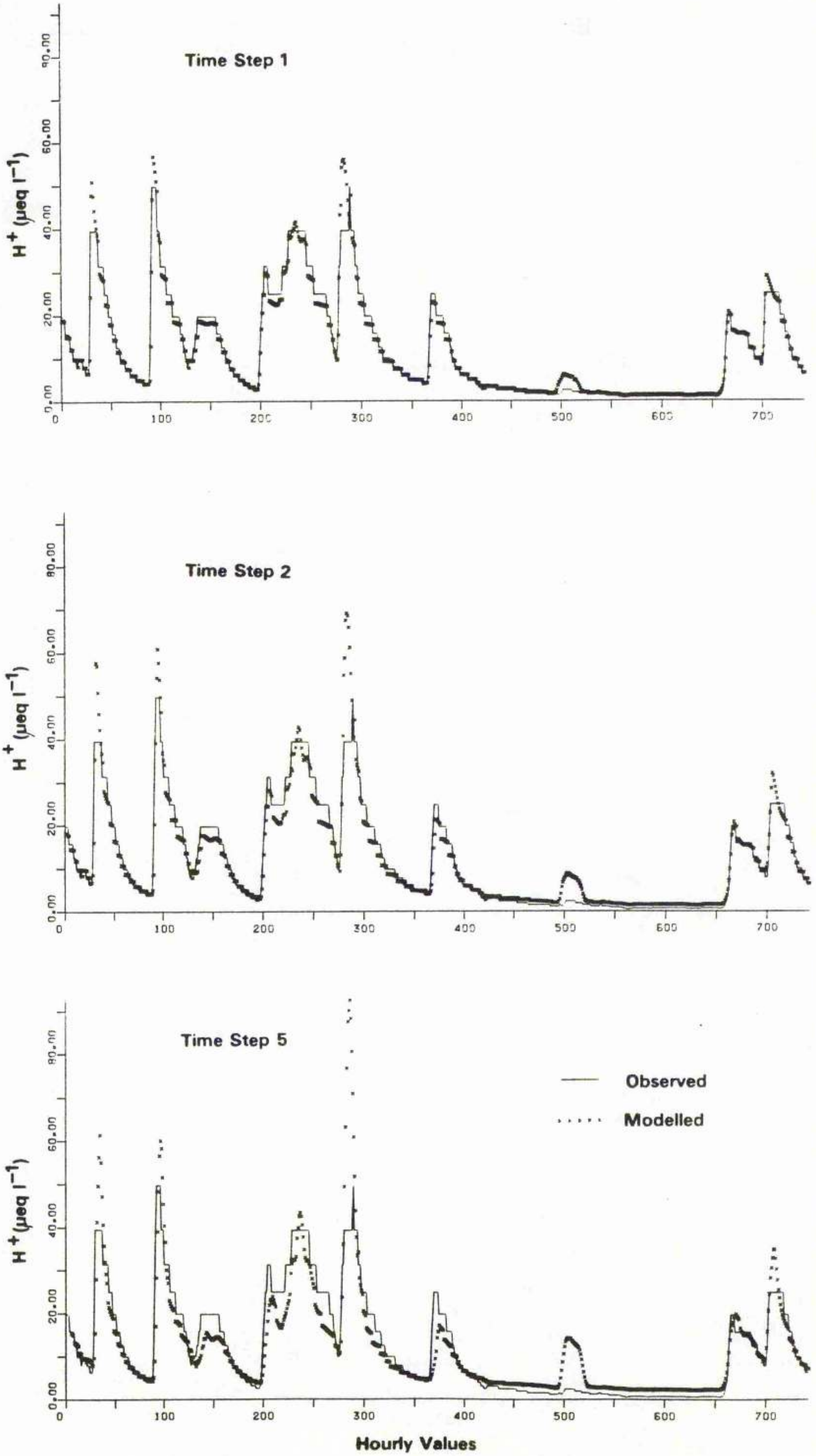


FIG 7:8 Modelled Streamwater Acidity Using Time-Steps Of 1,2,5 For Green Burn January 1984

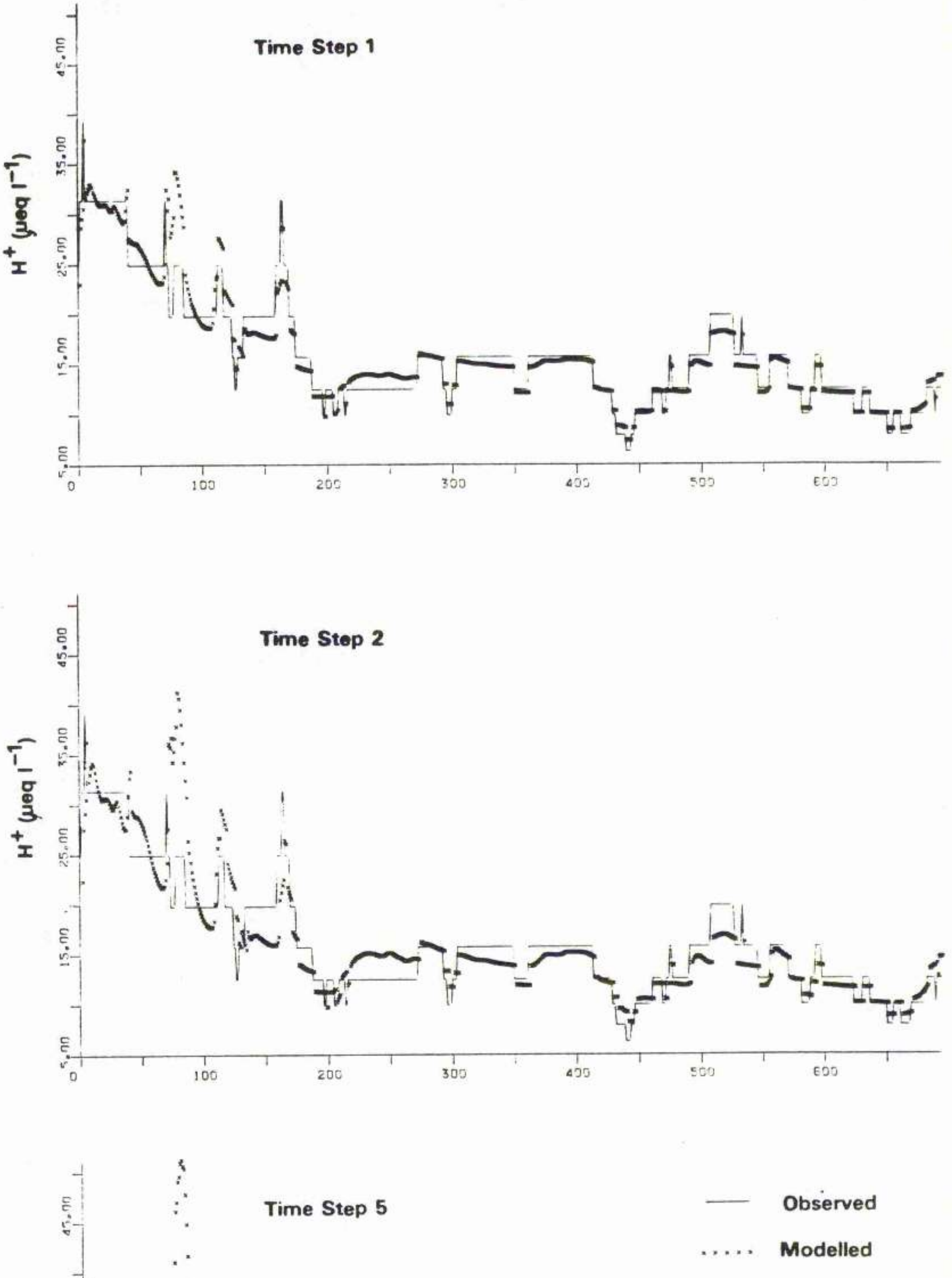


FIG 7:9 Modelled Streamwater Acidity Using Time-Steps Of 1,2,5 For Dargall Lane February 1984

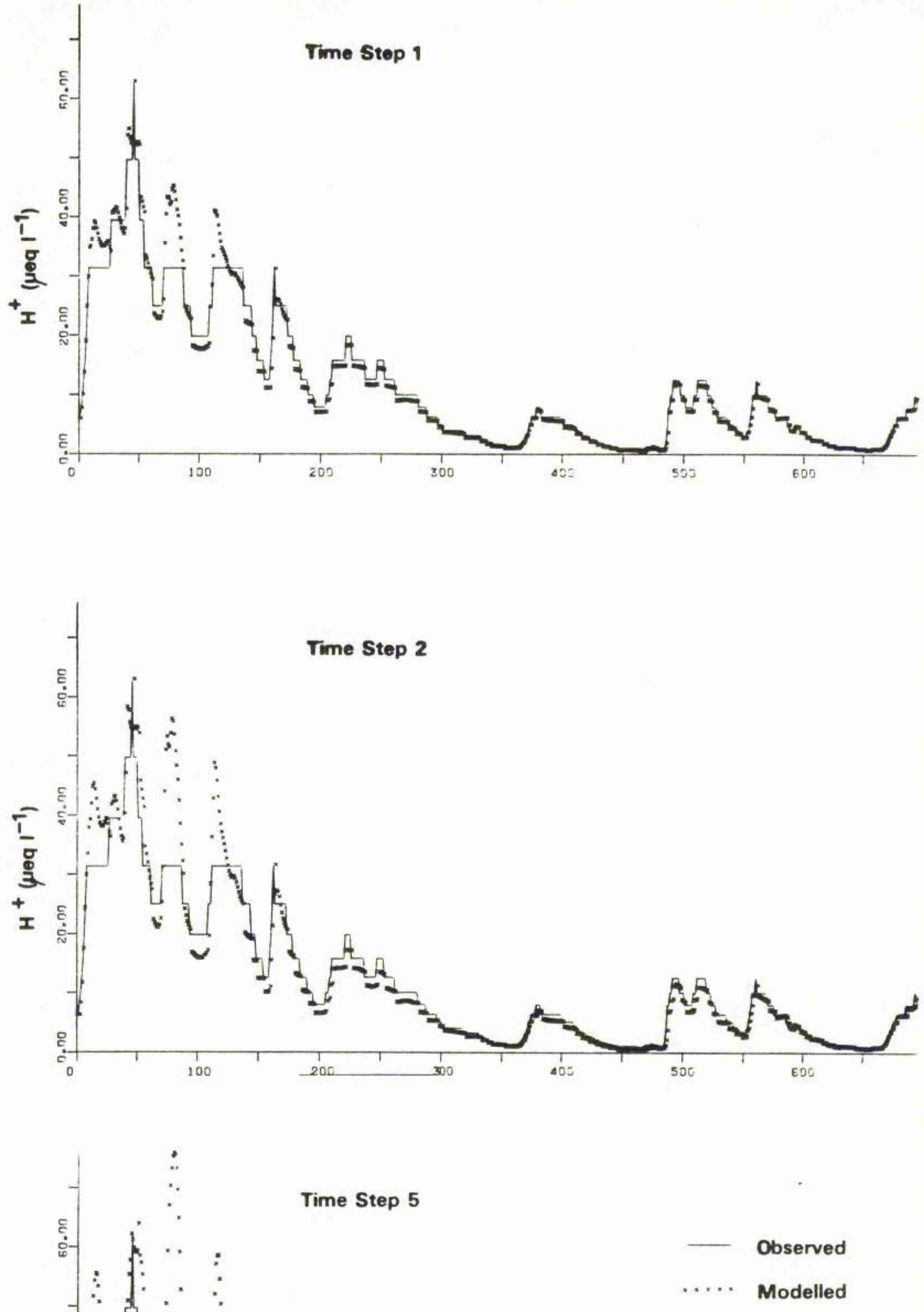


FIG 7:10 Modelled Streamwater Acidity Using Time-Steps Of 1,2,5 For Green Burn February 1984

the influence of varying the prediction time is evidently seen. Also apparent from table 7:2 is the consistently better fit of the data given by the Green Burn model in comparison to the Dargall Lane model, these differences are further discussed in section 7:5.

Examination of the Dargall Lane forecast for November 1983 (fig 7:4) shows that the model adequately explains the rising and falling levels of H^+ during storms, however is unable to replicate the first storm peak. It is also interesting to note that the subsequent storms during November all reach the same 'acidity-plateau' concentration, these observations are in direct contrast to the Green Burn forecast for November 1983 (fig 7:6). On Green Burn the same 4 storm peaks generate concentrations of acidity proportional to the amount of flow. Again the model adequately describes the general pattern of observed acidities but fails to predict the first acidity peak.

The model fit during January 1984 for both Dargall Lane and Green Burn (figs 7:7 and 7:8) are very good with the models accounting for a wide range of acidity with different flow conditions. The major differences arise from the stepped nature of the original data. Predictions for the February storms after the first storm are less reliable, the models overpredicting the observed acidity (see section 7:5). This gives an indication of the models' simplicity and suggests that a 'factor' other than that described by the model is effecting streamwater acidity during the latter part of February.

Figure 7:5 shows the White Laggan model generated on data from March 1984. March 1984 was used as a direct consequence of the 1983 liming programme (chapter 3:3:3). The liming of White Laggan during this period had the effect of eliminating a flow-acidity response in the catchment until most of the lime had been flushed from the catchment, a point which is discussed further in section 7:5.

However, by March 1984 a flow-acidity relationship (albeit small) was restored, enabling the application of the model given in table 7:1. From fig 7:5 the model can be seen to give a good fit over a range of flow conditions in the White Laggan. This limited run of CAPTAIN on data from White Laggan again showed the versatility and power of the model under differing conditions. Comparison of these results with those from 1982 (Whitehead et al 1984) reinforce the nature of the relationship in White Laggan.

7:5 DISCUSSION and CONCLUSION.

Both the graphical output and table 7:2 illustrate the efficiency with which the simple models fit the observed data. Such a good association suggests there is a close relationship between H^+ concentration and flow. As a predictive method the models are thus effective in forecasting acidity over storm periods. However, before considering in greater detail the implications of the models it is of interest to examine the model deviations and failures which arise when the model is used to make predictions.

In general terms the model results deviate from the observed acidity at either low or high concentrations of H^+. This is likely to be a function of the non-linearity of the flow-acidity relationship at these concentrations. This is particularly noticeable when the models lose some ability to predict either over periods of low flow or when small storms create a disproportionate increase in acidity beyond that predicted by the model, such as seen in the February 1984 data (figs 7:9 and 7:10). When low recessional flow conditions prevail in the catchments the streams are fed by groundwater and subsurface flows which have a different regime in terms of flow-acidity. This can be readily seen in figs 7:4 and 7:5 for the November 1984 data in which during the earlier part of the month there were no appreciable sized storms and streamwater acidity was negligible. Storms following dry periods may flush accumulated H^+ from the catchment (see chapter 2:2:4) thereby creating an anomalous increase in acidity in comparison with that produced under more 'normal' conditions. To incorporate these additional variables one would have to use a more complex second order model, which in the present study was considered unecessary.

In all runs of the models for Green Burn and Dargall Lane (see figs 7:7 to 7:10) increasing the prediction time reduces the models reliability to predict over long time spans. Should the modelling objective be changed from modelling storm storm to longer term variations, a more complex model is likely to be required.

In predicting stream acidity over storm periods the success of the model depends not only on the lead time but also on the character of the month. The differences in % variance explained (table 7:2) from month to month reflect the differences in the degree to which unaccounted variables (processes) may influence streamwater acidity. It is evident from figs 7:4 to 7:10 that contrasting sizes and timing of storms have differing effects on H^+ concentration which may need a second or third variable to account for processes such as groundwater and antecedent conditions.

During both November and over the predicted data series the percentage explained variance of the H^+-flow relationship is consistently higher for Green Burn than Dargall Lane. This probably reflects a real difference in the hydrochemical processes of the catchments. The forest drains of Green Burn promote a rapid flushing and evacuation of water from all parts of the catchment. Dargall Lane however with its armchair like shape and pools of surface water will take longer to flush the acidity from all parts of the catchment. If this were to lead to substantial discrepancies in the model a more complex structured model may have been appropriate.

For the Green Burn November forecast the model failed to predict the first Autumnal flush following a long dry spell (fig 7:6). Whitehead et al (1984) using the same modelling strategy for data from Birkenes, Norway noticed a similar failure of the model in these circumstances. For the total period of prediction of high flows for Green Burn the model overpredicts the acidity.

This is in direct contrast to the Dargall Lane system where the growing contribution of delayed flow maintains a higher level of acidity than that predicted by the model. Such a delayed flow process has also been implied by the results of a unit hydrograph study (Harper 1984, section 3:4). Table 3:3 provides a comparison of the percentage runoff after different periods of time and shows the delayed flow element of the Dargall Lane catchment.

As outlined in section 7:4 the Dargall Lane and Green Burn models reasonably predict the first acidity storm of February before failing. From the continuous data it is not readily apparent why this is so. Reference to the the weekly chemical data suggest that a sea-salt episode occured at this time over Loch Dee. During this week a high amount of H^+ was exchanged and leached out of the catchment (described in chapter 6). There is some evidence for this assertation in the elevated levels of sodium chloride in the weekly bulked sample (Na 625 µeq l-1, Cl^- 886 µeq l-1) and also the relatively high levels of Cl^- in the streams:

Dargall Lane 384 µeq l-1.
Green Burn 350 µeq l-1.

With the present simple model structure there is no attempt made to incorporate the role of sea-salt as this will have a markedly different flow-acidity regime.

Comparison of the catchments' mean response times and delay factors (table 7:1) shows Dargall Lane to respond the fastest. This implies that for an increase in flow Dargall Lane will respond the fastest in terms of an increase in acidity. This reflects the poor ability of the catchment to buffer any acidity. The longer response times for Green Burn and White Laggan indicate that these catchments are able to buffer some acidity. In the case of Green Burn this buffering capacity is eventually exhausted giving rise to a high gain, whilst White Laggan is able to maintain an effective buffer against acidity.

The results from the White Laggan model are interesting in the contrast they provide to the other two models. The White Laggan model suggests the catchment to be much better buffered than the other two catchments. The similarity between the two sets of results (for White Laggan) confims the magnitude of the gain for the catchment which is markedly smaller than for either of the other catchments. The difference in mean response times between the two studies is an indication of the different antecedent conditions during the calibration of the models.

A further contrast is provided by using the model to calculate the discharge needed to produce a concentration of 10 µeq H^+l^{-1} (pH <5.0). Table 7:3 shows the results and the percentage of time the flows are greater than this value. This provides an indication of the time each stream has an acidity > 10 µeq H^+l^{-1} (flow derived from MDF duration curves.)

station	threshold discharge $H^+>10$ µeq l^{-1}.	% time exceeded
Dargall Lane	0.24 m^3s^{-1}	18
White Laggan	3.50 m^3s^{-1}	0.5
Green Burn	0.30 m^3s^{-1}	15

Table 7:3 flow-acidity duration figures.

These flow-acidity duration figures compare surprisingly well both in magnitude and order with those suggested by the H^+ frequency figures given for the weekly samples in fig 5:1.

The implications of these results are interesting and primarily reflect differences in the hydrology and geology of the catchments. The Dargall Lane catchment as already discussed has longer retention times, the water being transmitted through nutrient deficient peats which maintain streamwater acidity rather than neutralise any incoming acidity. During very high flows the presence of a scum on the water suggests the acidity is of an organic form (fluvic acid).

The discharge value to attain an acidity value of 10 µeq H^+l^{-1} is approximately the same for Green Burn as Dargall Lane. In Green Burn the percentage time of lower flows is greater than that for Dargall Lane this being a result of the generally steeper catchment and preferential movement of water down the forest drains. This explains the lower percentage of time in which higher acidities prevail.

The large discrepancy between White Laggan and the other two streams may be partly explained by different flow regimes. However, there is little evidence to support this from the flow duration curves (fig 3:6). More plausible explanations are differences in geology or land management. Chapter 5 intimated that the White Laggan has a greater ability to buffer stream acidity as given by the lower weekly mean and median H^+

concentrations. However, the differences outlined in chapter 5 are not sufficient to account for the differences described here. The data used in chapter 5 suggested that acidity related ions were controlled to a large extent by the flow conditions. Futhermore data for chapter 5 were from White Laggan (1), (above most of the lime) and the data presented here are from White Laggan (2), (below all of the liming applications). The most significant difference is thus likely to be explained by the liming programme. Section 7:4 has already described the difficulties in establishing a flow-acidity relationship for earlier periods due to the applications of limestone powder. It is likely that the diminished effect of the limestone lasted over a substantial period providing an effective buffer againest streamwater acidity.

Whilst the model used here is not a particularly powerful model in terms of predictability, the model has been useful in identifying differences between the three catchments in terms of hydrochemistry and land-management. The White Laggan findings and the modifying influence of limestone applications are particularly pertinent to the short term solution of streamwater acidity, a subject which deserves a greater depth of study and modelling than has been presented here.

CHAPTER 8 : CONCLUSIONS.

To conclude this dissertation several aspects of the preceding work need to be drawn together and reviewed. This conclusion addresses three specific topics:

i. A review of the findings of this piece of research.

ii. An evaluation of the methods used in the investigation

iii. Suggestions of future lines of enquiry which may help to gain a better understanding of the factors governing water quality in upland areas.

This piece of research work has investigated a relatively new area of interest in the natural environment in which two problems are thought to have been compounded to affect water quality in upland Britain. This dissertation as a pilot study of these problems has tried to isolate and evaluate the major factors and processes affecting water quality. The achievments are best viewed in terms of the aims laid out in chapter 1 and listed below:

What are the processes and factors governing water quality in upland catchments in S.W Scotland? The work in the preceding chapters has outlined the five principal factors governing water quality in the streams at Loch Dee. The five factors (rate of weathering, biological production and consumption, atmospheric deposition, stream discharge and ion-exchange) have been shown to operate differentially according to the ionic species involved. Further more detailed work in later chapters has also identified how the process of ion exchange operates to induce short-term streamwater acidification and how the varying processes of runoff production within the catchments may affect streamwater acidity.

Do the factors and processes governing water quality vary through time and space according to atmospheric inputs and land-use?

Chapter 5 has illustrated the seasonal variation of those ions predominantly determined by meteorological inputs and their variation over an annual cycle. The seasonal distribution of nitrate is the result of differences in production and consumption of nitrate according to microbacterial activity in the soils and consumption during the vegetative growing season; whereas those ions principally determined by flow show a seasonal distribution associated with high winter flows and low summer flows. Those ions involved in ion-exchange depend upon the input of high concentrations of sea-salts which occur during the winter period with gales and deep depressions sweeping in off the Atlantic Ocean. Comparing and contrasting the results from the three catchments has also revealed that those ions which are principally determined by biological factors show significant differences between the catchments as a result of contrasting land-use. It has also been suggested that with the growth of the forest these inter-catchment differences will become more pronounced. The storm budget work described in chapter 6 has also indicated a difference between the catchments as a result of the different land-use, ie. the trees of the Green Burn catchment capture more of the atmospherically entrained sea-salt allowing the ion-exchange acidification of the stream to proceed further than in the other catchments (over the storm period). Chapter 7 has also shown that there is a significant difference between the catchments' water quality as a result of the differences in their hydrology, part of which is due to the improved drainage associated with afforestation.

<u>Having identified the major controls on water quality in such environments can they be mathematically modelled and thus provide a basis for predicting water quality responses to storm inputs</u>? Once the factors and processes governing water quality have been understood it is possible to try and predict future water quality fluctuations. Chapter 7 (of this work) describes a modelling exercise undertaken at Loch Dee in which mathematical parameters are used to replace the unknown catchment processes to predict the variation in water quality over storm events. Using the model to compare and contrast the three catchments illustrates there are large differences between the water quality of the three catchments. The model developed here is also useful in the prediction of streamwater acidity up to 5 hours in advance.

The results of this dissertation have shown that there is a large variation in water quality draining catchments under different land-use despite the same atmospheric input. The results are in contrast with those of Harriman and Morrison (1982) in which the authors report that catchments draining forested areas have a higher acidity than those draining moorland areas. In the research conducted here the moorland control catchment (Dargall Lane) has the highest acidity this is attributable to the poor drainage of the catchment through extensive peat and bog conditions, slow rates of geological weathering and a dependence on atmospheric inputs of the major ions. In contrast to the

Dargall Lane is the better water quality (ie. lower acidity) of the White Laggan. Part of this buffering ability of White Laggan is likely to be a direct result of the ameliorating techniques used to improve water quality in the catchment. The water quality of the forested Green Burn lies intermediate between that of the Dargall Lane and the White Laggan. The results presented here indicate that at the present time the forest drains are as important (if not more so) than the forest itself in affecting water quality. It is expected, however, that the water quality in the catchment will deteriorate with the ageing of the forest.

In concluding this work it is also necessary to expand on the shortcomings of the research and where or how these failings may be avoided in future work. Considering the initial aims of the work there are three identifiable areas of weakness.

The first area of weakness is the lack of control on the White Laggan data. It is unfortunate that there was only a minimal amount of sampling conducted before commencing the liming programme. It is thus difficult to be completely certain as to the benefits of the liming programme on the White Laggan catchment. It is possible that the catchment was inherently better able to buffer poor water quality without the addition of the limestone. One solution to this problem would be to conduct an in depth survey in which all the contributing areas of the catchment are sampled under differing flow conditions.

A second area of weakness is the reduced amount of weekly chemical data which arose following the quality control checks. This loss of data ruled out the possibility of work on budgets and loadings for individual ions. It is only fair to say that this loss of data arose from a combination of problems which since 1984 have been drastically reduced. This, however occurred too late to be of benefit to the authors own project reported here. The increased quality of the data has arisen as a result of three improvements within the project. The employment of Dr. P Hutchinson as a scientific officer has ensured a higher level of site maintenance and quality control of the continuous monitors and also the prompt return to the SRPB chemical laboratories of the weekly routine samples. This decrease in transit time of the samples should serve to reduce sample deterioration to a minimum. The second improvement to the project has been the marking of sample bottles with their date, time and water level at time of sampling. A third improvement to the weekly chemical data is a technological improvement with the introduction of nitrate, chloride and sulphate determinations by ion chromatography.

The final area of weakness in this piece of work has been the lack of full chemical analyses for samples taken through storms both in terms of precipitation inputs and runoff outputs. This lack of storm data is the result of two exceptionally dry field seasons in S.W Scotland. From July to October 1983 there were <10 storms of any appropriate size recorded at Loch Dee of which the author successfully sampled one. During the period April 1984 to October 1984 6 storms were recorded two of which were sampled (although the data set is incomplete for one storm because of equipment failure). Given the opportunity the author hopes to re-undertake this work in the near future. Detailed analysis of the water chemistry of storms is likely to be an important aspect of further work on upland acidification.

This research has successfully utilised the multiple catchment approach to study water quality in an upland environment. However, the multiple catchment method is not without its' flaws as a research tool. It is evident from this piece of research that despite a general similarity in size, geology and soil type there are still likely to be inherent differences between the three catchments other than those isolated for study. These in turn can cause less readily controlled variations in water quality.

This problem highlights the difficulties which arise by taking a black-box approach to catchment modelling, ie. by concentrating entirely on the inputs and ouputs the subtle contrasts within the catchments are ignored in favour of aggregated processes and factors. Nevertheless, the method is a valid one since by comparing and contrasting the results from the three catchments the researcher is required to interpret differences in terms of the effectiveness of the factors operative within each "black-box". In this study this aggregated approach has been shown to be successful since the major factors have been identified along with their spatial and temporal variation. In turn this has lead to further studies in which two factors affecting water quality have been separated and evaluated.

Much of the originality in this work is the result of using continuous monitors to measure the key parameters of discharge, pH and electrical conductivity. Whilst these monitors are labour intensive to maintain and not totally robust in their operation they have provided an invaluable source of data and show variations in water quality which otherwise would have been missed.

There are two levels of further work suggested here. The first relates to site-specific investigations aimed at a better understanding of the temporal and spatial variation in water quality at Loch Dee. The second area of future work is concerned with applying the findings of this work on a more regional and national scale.

At Loch Dee there is an obvious need to maintain the present sampling network in order to monitor changes in the streamwater chemistry. Particularly important is the effect of the continuing lime programme on the White Laggan and also the deterioration of water quality in the Green Burn associated with canopy closure and the limited supply of nutrients in the catchment discussed in chapter five.

Two lines of further investigation arise from the results of chapter six in which it is possible to visualise spatial variations in water quality occuring as a function of the different soil associations at Loch Dee. If, using more detailed and sensitive soil experiments one could predict, which soil associations (and therefore proportions of the catchment) were likely to give rise to high acidity waters; it may be possible to implement a more effective system of water quality management using lime applications. In conjunction with this experimental soil work there is a need to conduct a more detailed investigation of sub-environments within the catchments to determine further the sources and sinks of streamwater acidity. If these results indicate the lime applications to White Laggan are ameliorating the acidity in the catchment it should be possible to undertake a cost-benefit analysis in terms of improved aquatic environments of the White Laggan againest the other two catchments.

On a more regional/national scale there is still much research needed to try and isolate the influence of land-use from atmospheric deposition in determining water quality. The work reported here concentrates solely on one location in the Scottish Southern Uplands. Whilst the processes and factors influencing streamwater chemistry are likely to be common to other areas of Britain they will not necessarily interact in the same manner. For instance it is unlikely that catchments in the east of Britain will receive the same maritime dominated atmospheric inputs which induced the streamwater acidification described in chapter 6. Further differences may exist because of the drier climate where dry deposition will play an increased role over that seen at Loch Dee. This may cause more serious acidic flushes in streams following dry spells, particularly in afforested catchments where the trees may act as efficient scavengers of atmospheric pollutants. Further reseach is also needed on the interaction of forestry and atmospheric deposition across a greater range of lithologies.

There is a need to test the hypothesis that the five factors regulating streamwater chemistry at Loch Dee apply to much larger catchments than the small catchments investigated at Loch Dee. It is interesting in this respect that since the author drafted an initial report on sea-salt episodes at Loch Dee the SRPB have sampled the river Cree catchment. The Cree with a drainage area of 368 km^2 represents one of the larger and important rivers under the care of the SRPB. during February 1984 the average acidity across the catchment was found to be 32 ueq H^+l^{-1} (pH 4.5) and was apparently high in heavily forested areas of the catchment. This episode of high acidity was attributed by the Board to a sea-salt incursion (Welsh pers. comm) and is supported by the proposition in chapter 7 that the model failed during early February because of such an incursion; thus demonstrating that such events can have a regional significance.

Whilst this work has not answered the problem of the origin of long term acidification processes, this dissertation represents the first comprehensive report on the controls of water quality and acidification over short and medium time scales in upland Scotland. In the absence of reliable historic data such work is fundamental to understand the factors and processes affecting water quality in such environments. Without such knowledge it will be impossible to develop reliable and robust models which will reproduce field observations of the processes to predict not only what may occur in the short term but also the more sensitive question of long term surface water acidification.

BIBLIOGRAPHY.

ALLEN S.E, CARLISLE A, WHITE E.J, EVANS C.C.1968 The Plant Nutrient Content of Rainwater. Journal of Ecology. Vol.56 p.497-504.

AMOROCHO J. and HART W.E. 1964 A Critique of Current Methods in Hydrological Systems Investigation. Transactions of American Geophysical Union. Vol.45 p.307-321.

BACHE B.W. 1984 Soil-Water Interaction. Philosophical Transactions of the Royal Society London. Series B Vol.305 p.393-407.

BARRETT C.F, ATKINS D.H.F, CAPE J.N, FOWLER D, IRWIN J.G, KALLEND A.S, MARTIN A, PITMAN J.I, SCRIVEN R.A and TRUCK A.F 1983 Acid Deposition in the United Kingdom. Warren Spring Laboratory, Stevenage. U.K Review Group on Acid Rain.

BARRETT C.F and IRWIN J.I 1984 Acid Deposition Over Great Britain. Presented to Institute of Water Pollution Control and Institute of Water Engineers and Scientists Joint Meeting on Acid Rain at Post House, Birmingham.

BATTERBEE R.W 1984 Diatom Analysis and the Acidification of Lakes. Philosophical Transactions of the Royal Society London. Series B Vol.305 p.451-477.

BEAMISH R.J 1976 Acidification of Lakes in Canada by Acid Precipitation and the Resulting Effects on Fish.

In Dochinger L.S and Seliga T.A (Eds.) Proceedings of 1st. International Symposium on Acid Precipitation and the Forest Ecosystem. Columbus, Ohio. USDA Forest Service General Technical Report NE-23. p.479-498.

BENNET R.J 1979 Spatial Time Series. Pion Ltd. London.

BINNS W.O 1968 Some Effects of Tree Growth on Peat. In Proceedings of 3rd. International Peat Congress. p.358-365.

BINNS W.O 1979 The Hydrological Impact of Afforestation in Great Britain. In Mans Impact on the Hydrological Cycle in the United Kingdom. Ed. G.E Hollis. Geo-Abstracts Ltd, Norwich. p.55-69.

BOORMAN D.B and REED D.W 1981 Derivation of a Catchment Average Unit Hydrograph. Institute of Hydrology Report No. 71.

BORMANN F.H and LIKENS G.E 1979 Pattern and Process in a Forested Ecosystem. Springer-Verlag, New York.

BOX G.E.P and JENKINS A.M 1970 Time Series Analysis, Forecasting and Control. Holden-Day, San-Francisco.

BOWN J.C 1973 The Soils of Carrick and the Country around Girvan. Memoirs of the Soil Survey of Great Britain. HMSO.

BROWN G.C CASSIDY J, TINDLE A.G and HUGHES D.J 1979 The Loch Doon Granite: An Example of Granite Petrogenesis in the British Caledonides. Journal of the Geology Society, London. Vol.136 p.745-753.

BURNS J.C, COY J.S, TERVET D.J HARRIMAN R, MORRISON B.R.S and QUINE C.P 1984 The Loch Dee Project: A study of the Ecological Effects of Acid Precipitation and Forest Management on on an Upland Catchment in S.W Scotland. Fisheries Management. Vol.15 p.145-167.

BURT T.P 1979 Relationship Between Throughflow Generation and the Solute Concentration of Soil and Streamwater. Earth Surface, Processes and Landforms. Vol.4 p.257-266.

BURT T.P and WALLING D.E (Eds.) 1984 Catchment Experiments in Fluvial Geomorphology. Geo-Books Norwich.

CALDER I.R and NEWSON M.D 1979 Land-Use and Upland Water Resources in Britain-A Strategic Look. Water Resources Bulletin. Vol. 15 p.1628-1639.

CARLISLE A, BROWN A.H.F and WHITE E.J 1966 The Organic Matter and Nutrient Elements in the Precipitation Beneath a Sessile Oak (Quercus Petraea) Canopy. Journal of Ecology. Vol.54 p.87-98.

CHARLESON R.J and RODHE H. 1982 Factors Controlling the Acidity of Natural Rainwater. Nature. Vol. 295 p.683-685

CHEN C.W, DEAN D.J, GHERINI S.A and GOLDSTEIN R.A 1982 Acid Rain Model: Hydrologic Module. Journal of Environmental Engineers. Vol.108 No.EE3 p.455-472.

CHORLEY R.J and KENNEDY B.A 1971 Physical Georaphy: A Systems Approach. Prentice Hall Inc.

CHRISTOPHERSEN N, SEIP H.M and WRIGHT R.F 1982 A Model for Streamwater Chemistry. Water Resources Research. Vol.18 p.977-996.
vol.18 p.977-996.

CLESCERI N.L and VEUSDEVAN C 1980 Acid Precipitation, Throughfall Chemistry and Canopy Processes. In Drablos D and Tollan A (Eds.) Ecological Impact of Acid Precipitation. Proceedings of International Conference Sandefjord, Norway. P.258-259.

CLYMO R.S 1984 Sphagnum Dominated Peat Bogs: A Naturally Acid Ecosystem. Philosophical Transactions of the Royal Society Society, series B. Vol.305 p.487-499.

COLLINS D.N 1979 Quantitive Determination of the Subglacial Hydrology of two Alpine Glaciers. Journal of Glaciology. Vol. 23 p.347-362.

CRISP D.T 1966 Input and Output of Minerals for an Area of Pennine Moorland: The Importance of Precipitation, Drainage, Peat Erosion and Animals. Journal of Applied Ecology. Vol. 3 p.327-348.

CRONAN C.S and SCHOFIELD C.L 1979 Aluminium Leaching Response to Acid Precipitation: Effects on High Elevation

Watersheds in the Northwest. Science. Vol.204 p.304.

CRYER R. 1976 The Significance and Variation of Atmospheric Nutrient Inputs to a Small Catchment System. Journal of Hydrology. Vol.29 p.117-137.

DAHL J.V, QVENILD C, TOLLAN O, CHRISTOPHERSEN N and SEIP H.M 1980 Use of Radioactive Tracers to Study Runoff and Soil Interactions in Natural Mini-Catchments. In Drablos D and Tollan A (Eds.) Ecological Impact of Acid Precipitation. Proceedings of International Conference Sandefjord, Norway. p.160-161.

DAVIES T.D, ABRAHAMS P.W, TRANTER M, BLACKWOOD I, BRIMBLECOMBE and VINCENT C.E 1984 Black Acidic Snow in the Remote Scottish Highlands. Nature. Vol.312 p.58-61.

DEWALLE D.R, DINICOLA R.S and SHARPE W.E 1985 Geologic Models for Predicting Baseflow Alkalinity in Headwater Streams on Laurel Hill in Pennsylvania. In Johansson E (Editor) Hydrological and Hydrogeochemical Mechanisms and Model Approaches to the Acidification of Ecological Systems. Nordic Hydrological Programme Report No. 10. p.107-118.

DOCHINGER L.S and SELIGA T.A (Eds.) 1976 Proceedings of the First International Symposium on Acid Precipitation and Forest Ecosystem Columbus, Ohio. USDA Forest Service General Technical Report Ne 23. Published by NE Forest Experimental Station.

DOLLAND G.J, UNSWORTH M.A and HARVE M.J 1983 Pollutant transfer in Upland Regions By Occult Precipitation. Nature. Vol.302 p.241-243.

DRABLOS D and TOLLAN A (Eds.) 1980 Ecological Impact of Acid Precipitation. Proceedings of an International Conference SNSF Project, NISK 1432 AS-nlh, Norway.

DUNNE T and LEOPOLD L.B 1978 Water in Environmental Planning. Published by W.H Freeman and Co.

EATON J.S, LIKENS G.E and BORMANN F.H 1973 Throughfall and Stemflow Chemistry. Journal of Ecology. Vol.61 p.495-508.

EDWARDS A 1973 The Variation of Dissolved Constituents with Discharge in Some Norfolk Rivers. Journal of Hydrology. p.219-242.

ENVIRONMENT OF CANADA INLAND WATERS DIRECTORATE 1979 Analytical Methods Manual. Inland Waters Directorate Water Quality Branch, Ottawa, Canada.

ERIKSSON E 1960 The Yearly Ciculation of Chloride and Sulphur in Nature; Meteorological, Geochemical and Pedological Implications. Part 2. Tellus. Vol.12 p.63-109.

FLOWER R.J.L and BATTARBEE R.W 1983 Diatom Evidence for Recent Acidification of Two Scottish Lochs. Nature Vol. 305 p.130-133.

FOSTER I.D.C and WALLING D.E 1978 The Effects of the 1976 Drought and Autumn Rainfall on Stream Solute Levels. Earth Surface Processes. Vol.3 p.393-406.

FOWLER D 1980 Wet and Dry Deposition of Sulphur and Nitrogen Compounds From the Atmosphere. In Drablos D and Tollan A (Eds.) Ecological Impact of Acid Precipitation. Proceedings of International Conference Sandefjord, Norway. p.9-27

FOWLER D, CAPE J.N, LEITH I.D, PATERSON I.S, KINNAIRD J.W and NICHOLSON I.A 1982 Rainfall Acidity in Northern Britain. Nature. Vol.297 p.383-386.

FOWLER D 1984 Transfer to Terrestrial Surfaces. Philosophical Transactions Royal Society London. Series B Vol 305 p.281-297.

FOX D.G 1976 Modelling Atmospheric Effects-An Assement of the

Problems. In Dochinger L.S and Seliga T.A (Eds.) Proceedings of 1st. International Symposium on Acid Precipitation and the Forest Ecosystem. Columbus, Ohio. USDA Forest Service General Technical Report NE-23. p.57-85.

GALLIE T.M and SLAYMAKER H.O 1984 Variable Solute Sources and Hydrologic Pathways in a Coastal Subalpine Environment. In Catchment Experiments in Fluvial Geomorphology. Ed Burt T.P and Walling D.E. p.347-357

GALLOWAY J.N, LIKENS G.E and EDGERTON E.S 1980 Hydrogen Ion speciation in the Acid Precipitation of Northeastern U.S.A. In Torribara T.Y, Miller M.W, and Morrow P.E (Eds.) Polluted Rain. Plenum Press. p.383-396.

GEE A.S and STONER J.H 1984 The Effects of Seasonal and Episodic Variations in Water Quality on the Ecology of Upland Waters in Wales. Presented to Institute of Water Pollution Control and Institute of Water Engineers and Scientists Joint Meeting on Acid Rain at the Post House, Birmingham.

GILMAN K 1977 Dilution Gauging on the Recession Limb: 2 The Integration Method. Hydrological Sciences Bulletin. Vol.XXII, 4 12/1977. p.469-481.

GOLTERMAN H.L, CLYMO R.S, OHNSTAD M.A.M 1978 Methods for Physical and Chemical Analysis of Freshwaters. IBP Handbook No. 8. Blackwell Scientific Publications, Oxford.

GORE A.J.P 1968 The Supply of 6 Elements by Rain to an Upland Peat Area. Journal of Ecology. Vol.56 p.483-495.

GORHAM E 1956 On the Chemical Composition of Some Waters From the Moor House Nature Reserve. Journal of Ecology. Vol.44 p.375-382.

GORHAM E 1961 Factors Influencing the Supply of Major Ions to

Inland Waters With Special Reference To the Atmosphere. _Bulletin of the Geology Society of America_. Vol.72 p.795-840.

GORHAM E 1976 Acid Precipitation and its Influence Upon Aquatic Ecosystems: An Overview. Dochinger L.S and Seliga T.A (Eds.) _Proceedings of 1st. International Symposium on Acid Precipitation and the Forest Ecosystem_. Columbus, Ohio. USDA Forest Service General Technical Report NE-23. p.245-458.

GORHAM E and McFEE W.W 1980 Effects of Acid Deposition Upon Outputs From Terrestrial to Aquatic Ecosystems. In _Effects of Acid Precipitation on Terrestrial Ecosystems_. Ed. Hutchinson T.C and Havas M. Plenum Press. New York and London. p.465-480.

GRANAT L 1978 Sulphate in Precipitation as Observed by the European Air Chemistry Network. _Atmospheric Environment_. Vol 12. p.413-424.

HARPER S 1984 _A Comparative Unit Hydrograph Study, Loch Dee S.W Scotland_. Unpublished Undergraduate Dissertation , University of St. Andrews.

HARRIMAN R and MORRISON B.R.S 1982 Ecology of Streams Draining Forested and non-Forested Catchments in an Area of Central Scotland.

In Drablos D and Tollan A (Eds.) _Ecological Impact of Acid Precipitation_. Proceedings of International Conference Sandefjord, Norway. p. 312-313.

HARRIMAN R and MORRISON B.R.S 1982 Ecology of Streams Draining Forested and non-Forested Catchments in an Area of Central Scotland. _Hydrobiologica_.p.251-263.

HARRIMAN R and WELLS D.E 1984 Causes and Effects of Surface Water Acidification in Scotland. paper presented to _Institute of Water Pollution Control Annual Conference_

September, Glasgow.

HAVAS M and HUTCHINSON T.C 1983 The Smoking Hills: Natural Acidification of an Aquatic Ecosystem. _Nature_. Vol. 301 p.23-27.

HENRIKSEN A 1980 Acidification of Freeshwaters - A Large Scale Titration. In Drablos D and Tollan A (Eds.) _Ecological Impact of Acid Precipitation_. Proceedings of International Conference Sandefjord, Norway. p.68-74.

HENRIKSEN A 1982 Alkalinity and Acid Precipitation Research. _Vatten_. Vol. 38 p.83-85.

H.M.S.O 1972 _The Analysis of Raw, Potable and Waste Waters_. Dept. of Environment.

H.M.S.O 1979 Sulphate in Waters, Effluents and Solids. _Methods for the Examination of Waters and Associated Materials_.

HORNBECK J.W, LIKENS G.E and EATON J.S 1976 Seasonal Patterns in Acidity of Precipitation and Their Implications for Forest Stream Ecosystems. In Dochinger L.S and Seliga T.A (Eds.) _Proceedings of 1st. International Symposium on Acid Precipitation and the Forest Ecosystem_. Columbus, Ohio. USDA Forest Service General Technical Report NE-23. p.597-609.

HORNUNG M 1984 Precipitation-Canopy and Soil-Water Interactions. Presented to _Institute of Water Pollution Control and Institute of Water Engineers and Scientists Joint Meeting on Acid Rain_ at Post House, Birmingham.

HUTCHINSON T.C and HAVAS M (Eds.) _Effects of Acid Precipitation on Terrestrial Ecosystems_. Plenum Press London and New York.

JACOBSON J.S, HELLER L.I and LEUKEN P.Van 1976 Acidic Precipitation at a Site Within the Northeastern Conurbation. Dochinger L.S and Seliga T.A (Eds.)

Proceedings of 1st. International Symposium on Acid Precipitation and the Forest Ecosystem. Columbus, Ohio. USDA Forest Service General Technical Report NE-23. p.267-277.

JOHANNES A.H GALLOWAY J.N and TROUTMAN D.E 1980 Snowpack Storage and Ion Release. In Drablos D and Tollan A (Eds.) Ecological Impact of Acid Precipitation. Proceedings of International Conference Sandefjord, Norway. p.260-261.

JOHANNESSEN M SKARTVEIT A and WRIGHT R.F 1980 Streamwater Chemistry Before, During and After Snowmelt. In Drablos D and Tollan A (Eds.) Ecological Impact of Acid Precipitation. Proceedings of International Conference Sandefjord, Norway. p.224-225.

JOHNSON F.A 1971 A Note on River Water Sampling and Testing. Water and Water Engineering. February, p.59-61.

JORANGER E, SCHAUG J and SEMB A 1980 Deposition of Air Pollutants in Norway. In Drablos D and Tollan A (Eds.) Ecological Impact of Acid Precipitation. Proceedings of International Conference Sandefjord, Norway. p.120-121.

JUNGE C.E AND WERBY R.T 1958 The Concentration of Chloride Sodium, Potassium, Calcium and Sulphate. Journal of Meteorology. Vol.15 p.417-425.

JUNGE C.E and GUSTATSON P.E 1957 On the Distribution of Sea-salt over the U.S.A and its Removal by Precipitation. Tellus Vol 9. p.164-173.

KITE A.J 1984 The Modification of Atmospheric Inputs and Resulting Water Quality in the Green Burn Loch Dee, S.W Scotland. Unpublished Undergraduate Dissertation

: University of St. Andrews.

KRUG E.C and FRINK R 1983 Acid Rain on Acid Soil: A New Perspective. <u>Science</u>. Vol.221 p.520-525.

LAI W.P 1979 Transfer Function Modelling: Relationship Between Time-Series Variables. <u>CATMOG 22</u>. Published by Geo-Abstracts, Norwich.

LAM D.C.L and BOBBA A.G 1985 Modelling Watershed Runoff and Basin Acidification. In Johansson E (Editor) <u>Hydrological and Hydrogeochemical Mechanisms and Model Approaches to the Acidification of Ecological Systems</u>. Nordic Hydrological Programme Report No. 10. p.205-216.

LEWIN J, CRYER R and HARRISON D.I 1974 Sources for Sediments and Solutes in mid-Wales. Edited by Gregory K and Walling D.E. In <u>Institute of British Geographers, Special Publication No. 6</u>. p.73-85.

LIKENS G.E and BORMANN F.H 1974 Acid Rain: A Serious Environmental Problem. <u>Science</u>. Vol.184 p.1176-1179.

LIKENS G.E, BORMANN F.H, PIERCE R.S and JOHNSON N.M 1976 Hydrogen Ion Input to the Hubbard Brook Experimental Forest, New Hampshire During the Last Decade. In Dochinger L.S and Seliga T.A (Eds.) <u>Proceedings of 1st. International Symposium on Acid Precipitation and the Forest Ecosystem</u>. Columbus, Ohio. USDA Forest Service General Technical Report NE-23. p.397-407.

LIKENS G.E, BORMANN F.H PIERCE R.S, JOHNSON N.M 1977 <u>Bio-Geo- Chemistry of a Forested Ecosystem</u>. Published by Springer-Verlag, New York.

LIKENS G.E, WRIGHT R.F, GALLOWAY J.N and BUTLER T.J

1979 Acid Rain. Scientific America. Vol.241 p.39-47.

LIKENS G.E, BORMANN F.H and EATON J.S 1980 Variations in Precipitation and Streamwater Chemistry at Hubbard Brook Experimental Forest During 1964-1977. In Effects of Acid Precipitation on Terrestrial Ecosystems. Ed. Hutchinson T.C and Havas M. Plenum Press. New York and London. p.443-465.

LITTLE R 1985 A Comparative Water Quality Analysis in the Loch Dee Basin, S.W Scotland. Unpublished Undergraduate Dissertation: University of St. Andrews.

LOVETT G.M, REINERS W.A and OLSON R.K 1982 Cloud Deposition in Subalpine Balsam Fir Forests: Hydrological and Chemical Inputs. Science. Vol 218 p.1303-1305.

MACKERETH F.J.H, HERON J and TALLING J.F 1978 Water Analysis: Some Revised Methods for Limnologists. Freshwatr Biological Association. Scientific Publication No. 6.

MADGEWICK H.A.I, OVINGTON J.D 1959 The Chemical Composition of Precipitation in Adjacent and Open Plots. Forestry. Vol.32. p.14-22

MASON B.J 1984 The Current Status of Research on Acidification of Surface Waters. Royal Society Publication.

MAYER R and Ulrich B 1974 Oecologia Plantarum Vol 9 p.157.

MAYER R and ULRICH B 1980 Input to Soil, Especially the Influence of Vegetation in Intercepting and Modifying Inputs-a Review. In Effects of Acid Precipitation on Terrestrial Ecosystems. Ed. Hutchinson T.Cand Havas M. Plenum Press. New York p.173-181

MILLER H.G, COOPER J.M, MILLER J.D 1976 Effect of Nitrogen Supply on Nutrients in Litter Fall and Crown Leaching in a Steand of Corsican Pine. Journal of Applied Ecology. Vol.13.p.233-248.

MILLER H.G and MILLER J.D 1980 Collection and Retention of Atmospheric Pollutants by Vegetation. In Drablos D and Tollan A (Eds.) Ecological Impact of Acid Precipitation. Proceedings of International Conference Sandefjord, Norway. p.33-40.

MILLER H.G 1984 Deposition-Plant-Soil Interactions. Philosophical Transactions of the Royal Society of London. Series B Vol. 305 p.339-352.

MILLS D.H 1980 The Management of Forest Streams. Forestry Commission Leaflet No.78. Published by H.M.S.O.

MOHN E, JORANGER E KALVENESS S, SOLLIE B and WRIGHT R.F 1980 Regional Surveys of the Chemistry of Small Norwegian Lakes: A Statistical analysis of the Data from 1974-1978. In Drablos D and Tollan A (Eds.) Ecological Impact of Acid Precipitation. Proceedings of International Conference Sandefjord, Norway. p.234-235

MORRIS E.M, THOMAS A.G 1985 Hydrochemical Processes in a Small Sub-Artic Catchment. In Johansson E (Editor) Hydrological and Hydrogeochemical Mechanisms and Model Approaches to the Acidification of Ecological Systems. Nordic Hydrological Programme Report No. 10. p.25-28.

NEAL C and THOMAS A.G 1984 Field and Laboratory Measurement of pH in low conductivity Natural Waters. Institute of Hydrology Internal Working Paper.

NEWSON M.D 1984 Slope and Channel Runoff Processes in

Upland Catchments: Interfaces Between Precipitation and Streamflow Acidity. Presented to Institute of Water Pollution Control and Institute of Water Engineers and Scientists Joint Meeting on Acid Rain at Post House, Birmingham.

NICHOLSON I.A, CAPE J.N, FOWLER D, KINNAIRD J.W and PATERSON I.S 1980 Effects of a Scots Pine (pinus sylvestris) Canopy on the Chemical Composition and Deposition Pattern of Precipitation. In Drablos D and Tollan A (Eds.) Ecological Impact of Acid Precipitation. Proceedings of International Conference Sandefjord, Norway. p. 148-149

NORCLIFFE G.B 1982 Inferential Statistics for Geographers. Second edition. Published by Hutchinson and Co.

ODEN S 1976 The Acidity Problem-An Outline of the Concepts. Dochinger L.S and Seliga T.A (Eds.) Proceedings of 1st. International Symposium on Acid Precipitation and the Forest Ecosystem. Columbus, Ohio. USDA Forest Service General Technical Report NE-23. p.1-36.

OLLIER C 1984 Weathering. 2nd. Edition. Published by Longman.

OTTAR B 1976 Monitoring Long Range Transport of Air Pollutants: The OECD Study. Ambio. Vol.5 p.203-206.

OVERREIN L.N, SEIP H.M, TOLLAN A 1981 Acid Precipitation -Effects on Forest and Fish: Final Report of the S.N.S.F Project 1972-1980. Oslo

OXLEY N.C 1974 Suspended Sediment Delivery Rates and the Solute Concentration of Stream Discharge in Two Welsh Catchments. Edited by Gregory K and Walling D.E. In Institute of British Geographers, Special Publication No. 6 p.141-154.

PENNINGTON W 1984 Long-Term Natural Acidification of Upland sites in Cumbria: Evidence from Post-Glacial Lake Sediments. Freshwater Biological Association 52nd. Annual Report. p.28-46.

PILGRIM D.H, HUFT D.D and STEELE T.D 1979 Use of Specific Conductance and Contact time relations for Separating Flow Components in Storm Runoff. Water Resources Research. Vol.15 p.329-339.

REID J.M, MacLEOD D.A and CRESSER M.S 1981 Factors affecting the Chemistry of Precipitation and River Water in an Upland Catchment. Journal of Hydrology. Vol.50 p.129-145.

ROBERTS G, HUDSON J.A and BLACKIE J.R 1983 Nutrient Cycling in the Wye and Severn at Plynlimon. Institute of Hydrology Report No. 86.

RODDA J.C, DOWNING and LAW F.M 1976 Systematic Hydrology. Newnes-Butterworths. London Boston.

ROSENQVIST I Th 1978 Acid Soil-Acid Water. Oslo, Norway.

ROSENQVIST I Th. 1981 Importance of Acid Precipitation and Soil in Freshwater Lake Chemistry. Vann. No.4 p.402-409.

ROSENQVIST I.Th 1985 Acid Precipitation and Acid Soil in Freshwater Lake Chemistry. Land Use Policy. Vol.2 p.70-73.

RUTTER A.J 1975 Vegetation and the Atmosphere. Vol 1 Edited by Monteith J.L. Published by Academic Press, London.

SCOTT W.T and SCOTT SWANK W.T 1984 Dynamics of Water Chemistry in Hardwood and Pine Ecosystems. In Catchment Experiments in Fluvial Geomorphology.

Ed Burt T.P and Walling D.E. p. 335-346.

SEIP H.M 1980 Acidification of Freshwaters-Sources and Mechanisms. In Drablos D and Tollan A (Eds.) Ecological Impact of Acid Precipitation. Proceedings of International Conference Sandefjord, Norway. p.358--365.

SHELLSWELL S.H 1972 A Computer Aided Procedure for Time-Series Analysis and Identification of Noisy Processes (CAPTAIN). Technical Report CUED/B-Control/TR25 Dept. of Engineering University of Cambridge.

SKARTVEIT A 1981 Relationships Between Precipitation Chemistry, Hydrology and Runoff Acidity. Nordic Hydrology. p.65-80.

STENSLAND G.J 1980 Precipitation Chemistry Trends in the Northeastern U.S.A. In Torribara T.Y, Miller M.W, and Morrow P.E (Eds.) Polluted Rain. Plenum Press. p.87-108.

STEVENSON C.M 1968 An Analysis of the Chemical Composition of Rainwater and Air Over the British Isles and Eire for the Years 1959-1964. Quaterly Journal Royal Meteorological Society. Vol.94 p.56-70.

SUESS M.J 1982 (Ed.) Examination of Water for Pollution Control. A Reference Handbook. Published by Pergamon Press (Oxford) on behalf of the World Health Organisation.

SUTCLIFFE D.W, CARRICK T.R, HERON J, RIGG E, TALLING J.F WOOF C, and LUND J.W.G 1982 Long-term and Seasonal Changes in the Chemical Composition of Precipitation and Surface Waters of the Lakes and Tarns in the English Lake District. Freshwater Biology. Vol.12 p.451-506.

SUTCLIFFE D.W and CARRICK T.R 1983 Relationships Between Chloride and Major Cations in Precipitation in the

Windermere Catchment (English Lake District). _Freshwater Biology_. Vol.13 p.415-441.

TERVET D.J 1979 _Geochemical Investigations at Dun Moss_. Unpublished Ph.D Thesis Dundee University.

TIVY J 1954 Reconnaissance Vegetation Survey of Certain Hill Grazings in the Southern Uplands. _Scottish Geographical Magazine_. Vol.70 p.21-33.

TORIBARA T.Y, MILLER M.W and MORROW P.E (Eds.) 1980 _Polluted Rain_. Environmental Science Research Vol 17. Proceedings 20th. Rochester International Conference on Environmental Toxicity. Plenum Press New York, London.

TRUDGILL S.T, CRABTREE R.W, PICKLES A.M, SMETTEM K.R.J and BURT T.P 1984 Hydrology and Solute Uptake in Hillslope Soils on Magnesian Limestone. In _Catchment Experiments in Fluvial Geomorphology_. Ed Burt T.P and Walling D.E. p.183-215.

ULRICH B 1983 Soil Acidity and its Relations to Acid Deposition. In _Effects of Acculumation of Air Pollutants in Forest Ecosystems_. Edited Ulrich B and Pankrath J. Reidal, Dordrecht.

VENN M.W and DAY B 1977 Computer Aided Procedure for Time-Series Analysis and Identification of Noisy Processes. _Institute of Hydrology, Report No.39_. Wallingford.

VERMEULEN A.J 1980 The Acidic Precipitation Phenomenon: A Study of this Phenomenon and of the Relationship Between the Acid Content of Precipitation and the Emission of SO_2 and NO_x in the Netherlands.

In Torribara T.Y, Miller M.W, and Morrow P.E

(Eds.) Polluted Rain. Plenum Press. p.7-57.

VOIGT G.K 1980 Acid Precipitation and Soil Buffering Capacity. In Drablos D and Tollan A (Eds.) Ecological Impact of Acid Precipitation. Proceedings of International Conference Sandefjord, Norway. p.53-57.

WALLING D.E 1974 Suspended Sediment and Solute Yields from a Small Catchment Prior to Urbanisation. Edited by Gregory K and Walling D.E. Institute of British Geographers Special Publication No.6. p.169-192.

WALLING D.E 1975 Solute Variations in Small Catchment Streams: Some Comments. Transactions of the Institute of British Geographers No.64. p.141-147.

WALLING D.E and FOSTER I.D.C 1975 Variations in the Natural Chemical Concentration of River Water During Flood Flows, and the Lag effect: Some Further Comments. Journal of Hydrology. Vol.26 p.237-244.

WALLING D.E and WEBB B.W 1981 Water Quality. Chapter 5 in British Rivers Edited by Lewin J. p.126-169.

WARD R.C 1971 Small Watershed Experiments. An Appraisal of Concepts and Research Developments. University of Hull Occasional Papers No.18.

WEBB A.H 1980 The Effect of Chemical Weathering on Surface Waters. In Drablos D and Tollan A (Eds.) Ecological Impact of Acid Precipitation. Proceedings of International Conference Sandefjord, Norway. p.278-279.

WELSH W.T and BURNS J.C 1985 Aspects of Acid Rain in S.W Scotland. Unpublished Presentation to the Scottish Hydrological Group, Glasgow.

WHITE E, STARKEY R.S, SARUNDERS M 1971 Nutrient Flux in

Upland Catchments. Journal of Applied Ecology. Vol.8 p.743-749.

WHITEHEAD H.C and FETH J.H 1964 Chemical Composition of Rain ,Dry Fallout and Bulk Precipitation at Menlo Park, California, 1957-1959. Journal of Geophysical Research. Vol.69 pt.II p.3319-3333.

WHITEHEAD P.G, YOUNG P.C and HORNBERGER G 1979 A Systems Model of Flow and Water Quality in the Bedford Ouse River System: Part I Streamflow Modelling. Water Resources Research. Vol.13 p.1155-1169.

WHITEHEAD P.G, BECK M.B and O'CONNELL P.E 1981 A Systems Model of Flow and Water Quality in the Bedford Ouse River System: II Water Quality Modelling. Water Resources Research. Vol.15 p.1157-1171.

WHITEHEAD P.G and LANGAN S.J 1984 Some Preliminary Modelling Studies at Loch Dee Catchment. An Unpublished Report to the Solway River Purification Board, Dumfries, Scotland.

WHITEHEAD P.G and O'CONNELL (EDITORS) 1984 Proceedings of an International Workshop, Water Quality Modelling Forecasting and Control. Institute of Hydrology, Wallingford.

WHITEHEAD P.G and WILLIAMS R.J 1984 Modelling Nitrate and Algal Behaviour in the River Thames. Water Science Technology. Vol.16 p.621-633.

WHITEHEAD P.G, NEAL C,SEDEN-PERRITON S , CHRISTOPHERSEN N LANGAN S.J 1985 A Time Series Approach to Modelling Streamwater Acidity. In Johansson E (Editor) Hydrological and Hydrogeochemical Mechanisms and Model Approaches to the Acidification of Ecological Systems.

Nordic Hydrological Programme Report No. 10. p.179-204.

WIKLANDER L 1975 The Role of Neutral Salts in the Ion Exchange Between Acid-Precipitation and Soil. _Geoderma_. Vol.14 p.93-105.

WILLIAMS A.G, TERNAN J.L, KENT M 1984 Hydrochemical Characteristics of a Dartmoor Hillslope. In _Catchment Experiments in Fluvial Geomorphology_. Ed. Burt T.P and Walling D.E. p.379-415.

WILSON E.M 1975 _Engineering Hydrology_. 2nd. Edition. Macmillan Press Ltd.

WRIGHT R.F and GJESSING Y.T 1976 Changes in the Chemical Composition of Lakes. _Ambio_. Vol.5 p.219-223.

WRIGHT R.F 1980 Input-Output Budgets of Major Ions at Gauged Catchments in Norway. In Drablos D and Tollan A (Eds.) _Ecological Impact of Acid Precipitation_. Proceedings of International Conference Sandefjord, Norway. p.250-251.

WRIGHT R.F, HARRIMAN R, HENRIKSEN A, MORRISON B and CAINES L.A 1980 Acid Lakes and Streams in the Galloway Area S.W Scotland. In Drablos D and Tollan A (Eds.) _Ecological Impact of Acid Precipitation_. Proceedings of International Conference Sandefjord, Norway. p.248-249.

YOUNG P.C 1970 An Instrumental Variable Method for Real-Time Identification of a Noisy Process. _Automatica_. Vol.6 p.271-287.

YOUNG P.C, SHELLSWELL S.H and NEETHLING C.G 1971 _A Recursive Approach to Time Series Analysis_. Technical Report CUED/B-Control/TR16, Dept. of Engineering, University of Cambridge.

APPENDIX A: Details of the Data Base.

INTRODUCTION.

This appendix lists the data files used in this thesis. The data are listed under 5 headings:

i. Weekly Chemical Data.

ii. Hourly Flow Data.

iii. Hourly PH Data.

iv. Hourly Conductivity Data.

v. Soil Experiment Data.

Each station has its own identification code, so that files beginning with a 1 signify White Laggan data, 3 Green Burn, 4 Dargall Lane and 5 Precipitation for stream discharge the identification codes are 108 for White Laggan, 110 for Green Burn and 111 for Dargall Lane.

For the weekly chemical files each line represents the full analysis undertaken on that sample for the date given. These weekly files contain all the data from the 1st. January 1980 to 25th. May 1984. Each analysis column is labelled in line one of each file, starting with the date in columns 1-6 (note the dates are reversed so that 25/5/1984 becomes 840525).

For the continuous (hourly files) the identification number is followed by a 3 letter abbreviation of the month followed by the year. Eg. White Laggan January 1984 PH becomes 1JAN84PH.DAT and Dargall Lane November 1983 flow becomes 111NOV83H.DAT.

I. Weekly Data.

```
BLCHEM.DAT;1        DLCHEM.DAT;8        GBCHEM.DAT;8        RNCHEM.DAT;8
WL1CHEM.DAT;8       WLCHEM2.DAT;1       WL3CHEM.DAT;1
```

II. Hourly Flow Data.

```
108APR82H.DAT;4     108APR83H.DAT;4     108APR84H.DAT;4     108AUG81H.DAT;4
108AUG82H.DAT;4     108AUG83H.DAT;4     108DEC81H.DAT;4     108DEC82H.DAT;4
108DEC83H.DAT;4     108FEB82H.DAT;4     108FEB83H.DAT;4     108FEB84H.DAT;4
108JAN82H.DAT;4     108JAN83H.DAT;4     108JAN84H.DAT;4     108JUL82H.DAT;4
108JUL83H.DAT;4     108JUN82H.DAT;4     108JUN83H.DAT;4     108MAR82H.DAT;4
108MAR83H.DAT;4     108MAR84H.DAT;4     108MAY82H.DAT;4     108MAY83H.DAT;4
108MAY84H.DAT;4     108NOV81H.DAT;4     108NOV82H.DAT;4     108NOV83H.DAT;4
108OCT81H.DAT;4     108OCT82H.DAT;4     108OCT83H.DAT;4     108SEP81H.DAT;4
108SEP83H.DAT;4     110APR84H.DAT;4     110DEC83H.DAT;4     110FEB84H.DAT;4
110JAN84H.DAT;4     110MAR84H.DAT;4     110MAY84H.DAT;4     110NOV83H.DAT;4
110OCT83H.DAT;4     111APR84H.DAT;4     111DEC83H.DAT;4     111FEB84H.DAT;4
111JAN84H.DAT;4     111MAR84H.DAT;4     111MAY84H.DAT;4     111NOV83H.DAT;4
111OCT83H.DAT;4     111SEP83H.DAT;4
```

III. Hourly PH Data.

```
1APR81PH.DAT;4      1APR82PH.DAT;4      1APR83PH.DAT;4      1AUG81PH.DAT;4
1AUG82PH.DAT;4      1DEC82PH.DAT;4      1DEC83PH.DAT;4      1FEB81PH.DAT;4
1FEB82PH.DAT;4      1FEB83PH.DAT;4      1JAN83PH.DAT;4      1JAN84PH.DAT;4
1JUL81PH.DAT;4      1JUL82PH.DAT;4      1JUL83PH.DAT;4      1JUN82PH.DAT;4
1JUN83PH.DAT;4      1MAR81PH.DAT;4      1MAR82PH.DAT;4      1MAR83PH.DAT;4
1MAR84PH.DAT;4      1NOV82PH.DAT;4      1NOV83PH.DAT;4      1OCT81PH.DAT;4
1OCT82PH.DAT;4      1SEP81PH.DAT;4      1SEP82PH.DAT;4      3AUG83PH.DAT;4
3DEC83PH.DAT;4      3FEB84PH.DAT;4      3JAN84PH.DAT;4      3JUL83PH.DAT;4
3MAR84PH.DAT;4      3NOV83PH.DAT;4      3OCT83PH.DAT;4      3SEP83PH.DAT;4
4AUG83PH.DAT;4      4DEC83PH.DAT;4      4FEB84PH.DAT;4      4JAN84PH.DAT;4
4JUL83PH.DAT;4      4MAR84PH.DAT;4      4NOV83PH.DAT;4      4SEP83PH.DAT;4
5APR81PH.DAT;1      5APR83PH.DAT;1      5AUG83PH.DAT;1      5DEC83PH.DAT;1
5FEB84PH.DAT;1      5JAN84PH.DAT;1      5JUL83PH.DAT;1      5JUN81PH.DAT;1
5JUN83PH.DAT;1      5MAR84PH.DAT;1      5MAY83PH.DAT;1      5NOV81PH.DAT;1
5NOV83PH.DAT;1      5OCT81PH.DAT;1      5OCT83PH.DAT;1      5SEP83PH.DAT;1
```

IV. Hourly Conductivity Data.

```
110FEB84H.DAT;4     1APR81CH.DAT;4      1APR82CH.DAT;4      1APR83CH.DAT;4
1AUG81CH.DAT;4      1AUG82CH.DAT;4      1AUG83CH.DAT;4      1DEC81CH.DAT;4
1DEC82CH.DAT;4      1DEC83CH.DAT;4      1FEB81CH.DAT;4      1FEB82CH.DAT;4
1FEB83CH.DAT;4      1FEB84CH.DAT;4      1JAN82CH.DAT;4      1JAN83CH.DAT;4
1JAN84CH.DAT;4      1JUL81CH.DAT;4      1JUL82CH.DAT;4      1JUL83CH.DAT;4
1JUN81CH.DAT;4      1JUN82CH.DAT;4      1JUN83CH.DAT;4      1MAR81CH.DAT;4
1MAR82CH.DAT;4      1MAR83CH.DAT;4      1MAR84CH.DAT;4      1MAY81CH.DAT;4
1MAY82CH.DAT;4      1MAY83CH.DAT;4      1NOV81CH.DAT;4      1NOV82CH.DAT;4
1NOV83CH.DAT;4      1OCT81CH.DAT;4      1OCT82CH.DAT;4      1OCT83CH.DAT;4
1SEP81CH.DAT;4      1SEP82CH.DAT;4      1SEP83CH.DAT;4      3DEC83CH.DAT;4
3FEB84CH.DAT;4      3JAN84CH.DAT;4      3JUL83CH.DAT;4      3MAR84CH.DAT;4
3NOV83CH.DAT;4      3OCT83CH.DAT;4      3SEP83CH.DAT;4      4AUG83CH.DAT;4
4DEC83CH.DAT;4      4FEB84CH.DAT;4      4JAN84CH.DAT;4      4JUL83CH.DAT;4
4MAR84CH.DAT;4      4NOV83CH.DAT;4      4OCT83CH.DAT;4      4SEP83CH.DAT;4
```

V. Soil Experiment Data.

```
                                        SOIL1A.DAT;1        SOIL1B.DAT;1
SOIL1C.DAT;1        SOIL2A.DAT;1        SOIL2B.DAT;1        SOIL2C.DAT;1
SOIL3A.DAT;2        SOIL3B.DAT;1        SOIL3C.DAT;2        SOIL4A.DAT;1
SOIL4B.DAT;1        SOIL4C.DAT;1
```

WHITE LAGGAN MEAN DAILY FLOW