MODELLING THE IMPACT OF ACID DEPOSITION ON THE HYDROCHEMISTRY OF THE LOCH DEE CATCHMENTS, S.W. SCOTLAND

David Allan Farley

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

1989

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MODELLING THE IMPACT OF ACID DEPOSITION ON THE HYDROCHEMISTRY OF THE LOCH DEE CATCHMENTS, S.W.SCOTLAND

by

David Allan Farley B.Sc

Thesis presented for Degree of
Philosophae Doctor.
University of St. Andrews

November 1988

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Thi crioch air an t-saoghal
Is thig crioch air daoin
Ach mairidh ceol is mairidh gaol
O mo run

I...DAVID...FARLEY......hereby certify that this thesis has been composed by myself, that it is a record of my own work, and that it has not been accepted in partial or complete fulfilment of any other degree or professional qualification.

Signed.. ..Date...29...November.....1988

I was admitted to the faculty of Science of the University of St.Andrews under Ordnance No12 on *1st October 1985* and as a candidate for the degree of Ph.D. in *February 1987*.

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Acknowledgements

Financial support for this research project was primarily provided by a Natural Environment Research Council research studentship. N.E.R.C. must also be thanked for the loan and installation of an Automatic Weather Station at Loch Dee. Additional funding to attend conferences in Norway and France was provided by the Surface Water Acidification Project, the North Atlantic Treaty Organisation and the Mai-Wong trust of St.Andrews. The work was undertaken whilst at the Department of Geography and Geology at the University of St.Andrews. I am especially grateful to my supervisors, Dr Werritty at St.Andrews and Dr Whitehead at the Institute of Hydrology for encouragement and advice throughout the course of the project and valuable comments and criticisms of a first draft of the thesis.

Many people have offered useful advice and assistance during the course of this research. I wish to thank the staff of the Solway River Purification Board in particular, the director Mr Welsh, the depute director Dr Tervert and the hydrologist Mr Burns, for providing much of the raw data used in this study and for a constant willingness to discuss ideas. Grateful thanks must also go to the staff of the University Computing Lab especially John Henderson for coping with my initial attempts to master FORTRAN and VMS , Hugh Weir for introducing me to EVE, and John Ball for advice with the Macintosh. I would also like to express thanks to Dr Grieve at Stirling University for helpful comments and advice with soil chemistry, Dr Neal at the Institute of Hydrology for discussions on hydrochemistry and Dr. Miller at Aberdeen University for information on forestry practices in Britain. I must also thank Dr Jarvis for help with constructing the soil solution samplers, the Department cartographers

Bert Bremner and Graeme Sandeman for lessons in diagram presentation and Colin Cameron the lab technician for practical advice with laboratory techniques.

Many friends at St.Andrews have provided help in many different ways from fieldwork to computing including: Alison, Bill, Graeme, Veena, Jill, Ian, Vanessa and Rachel. Thanks also to the Blackpool group whose many discussions on long distance trips started all this off, cheers Scoff, Deb, Mick,Moi, Scoo, Joe, Pam, Glen,Phil, Al and many others you know who you are. Most of all though considerable thanks and love to the family Gail, Les, Lauren, Alison, Roger and most of all Mum and Dad for much needed financial help and encouragement. This one's for you.

Abstract

This work describes an investigation into the impact of acid deposition on the hydrochemistry of the three main tributary catchments at Loch Dee in Southwest Scotland. The research covers two main objectives. First, the hydrochemical processes that determine the observed streamwater chemistry are examined empirically through the determination of the hydrochemical budgets for each sub-catchment. Second, the ability of the Integrated Lake Watershed Acidification Study model (ILWAS) to simulate the observed hydrochemical processes is evaluated. From the hydrochemical budgets two major factors are identified as responsible for the spatial variability in the streamwater chemistry at Loch Dee . These factors are the underlying geology and land-use management techniques. The role of afforestation is difficult to judge due to the immaturity of the forest. However, the budgets indicate that any influence is a result of the pre-afforestation ploughing and drainage rather than the presence of the trees. On a temporal basis the hydrochemical budgets show considerable variability on both a monthly and an annual timescale, with the variability in the streamwater outputs of bases and nutrients primarily related to the variability in precipitation quantity. The budgets also indicate that, particularly on an annual timescale, the dry deposition of sulphate and hence of acidity to the catchment varies considerably. Furthermore, on a monthly timescale, the temporal variation in the budgets indicates that the conservative ion chloride can be physically stored within the catchments. This finding has severe implications for the estimation of dry deposition inputs and for the utilisation of simple hydrochemical models.

The ILWAS model is generally able to simulate the hydrological response of both catchments. However, the chemical simulations of both catchments are considerably smoothed and bear little resemblance to the observed data. This failure is ascribed to the large number of input variables for which site-specific data are not available, together with the use of monthly averaged precipitation quality to drive the model. Sensitivity analysis of the model indicates that the most critical input variables are the soil depth and soil solution chemistry, and that the majority of the input variables can be considered as calibration parameters. Given the subsequent large number of calibration parameters it is suggested that a unique calibration of the model will rarely be possible. Consequently, it is concluded that the primary use of the ILWAS model will be as an explanatory tool for examining conceptual ideas about the hydrochemical processes that determine acidification. The model's value as a management tool to help mitigate the effects of anthropogenically derived changes in surface water chemistry will be extremely limited.

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1: INTRODUCTION

'Acid rain' is a very amorphous and emotional term that is widely used to describe the effects of anthropogenically derived pollutants which acidify atmospheric inputs to terrestrial ecosystems. The deleterious effects of acid rain near to pollutant source areas have been recognised for over a century (Franks 1983). However, during the 1970's and early 1980's new observations began to support the hypothesis that atmospheric acid deposition was responsible for the acidification and consequent fisheries decline in the surface waters of remote parts of North America, Scandinavia and Scotland at considerable distances from pollutant source areas (Jensen and Snekuik 1972, Schofield 1976, Almer et al. 1974, Gjessing et al. 1976, Seip and Tollan 1978, Johnson 1979, Likens et al. 1979, Overrein et al. 1980, Wright et al. 1980, Harriman and Morrison 1982). The areas vunerable to acidification all tend to have an excess of precipitation over evaporation and a slowly weathering bedrock, often crystalline metamorphic or igneous, underlying thin base-poor soils. These are environments which may be expected to produce acid soils and acidic surface waters naturally. Consequently, there has been an ongoing debate in both the popular and scientific press regarding the precise role that anthropogenically derived pollutants play in the acidification of upland surface waters. Several authors argue that the role of anthropogenic pollutant inputs is far overshadowed by natural acid-producing mechanisms in catchment soils, possibly intensified by land use changes (Rosenquist 1978, 1980, Krug and Frink 1983, Pennington 1984). Other authors have sought to demonstrate that elevated inputs of acidity derive directly from emissions produced by the combustion of fossil fuels (Davies et al. 1984, Battarbee et al. 1985, Flower et al. 1987).

In order to reconcile these competing hypothesis, and to permit action to be taken that may enable the observed acidification to be reversed, the complex interactions of the physical, chemical and biological processes that determine the surface water chemistry of a catchment must be understood. This complex interaction of processes has led to the development of two main methods of investigation in the study of surface water acidification; catchment studies and mathematical modelling. In response to the former method of investigation a number of multidisciplinary catchment studies have been initiated in the upland areas of the British Isles (eg Lynn Brianne, (Stoner et al. 1984) and Plynlimon, (Neal et al. 1986a) in Wales; Loch Ard, (Harriman and Morrison 1982,) and Loch Dee, (Burns et al. 1984) in Scotland). However, the spatial heterogeneity of the chemical processes within a catchment, in particular within the catchment soils, are such that these catchment studies can be very expensive, time consuming and logistically difficult to establish. Thus mathematical models have also been developed as an alternative approach to the study of catchment acidification.

Any action to predict future acidification trends or to reverse existing surfacewater acidification ultimately requires that the interaction of the physical, chemical and biological mechanisms that determine streamwater chemistry be understood. Consequently, attempts to study the complex interactions that determine streamwater chemistry have become increasingly focussed on the development of physically-based mathematical simulation models.

Such hydrochemical models are an important means of identifying and quantifying the processes within a catchment that may govern the response of surfacewater chemistry to acid deposition and/or land-use changes, and several such models of varying sophistication and complexity have been developed (eg the Titration model; Henriksen 1979, Birkenes ; Christophersen et al. 1982, ILWAS ; Chen et al. 1983, MAGIC ; Cosby et al. 1985, Time Series ; Whitehead et al. 1986).

1.1 *THESIS AIM and OBJECTIVES*

The aim of this research study is to use a mathematical simulation model as a tool for understanding the impact of acid deposition on the hydrochemical behaviour of an upland catchment in Southwest Scotland. Specifically within this overall aim the research has two main objectives;

a) to determine empirically the spatial and temporal variations in the major factors that govern the hydrochemical behaviour of upland catchments through the use of hydrochemical budgets, and to use the resultant knowledge as an aid to modelling such processes.

b) to evaluate the ability of the Integrated Lake Watershed Acidification Study model (ILWAS) to simulate and predict changes to the surfacewater chemistry of moorland and forested upland catchments in southwest Scotland.

In order to pursue these objectives access to a detailed and long-term hydrometeorological and hydrochemical database was required. Within Southwest Scotland such a database is only available for the Loch Dee experimental catchments. These catchments are the focus of a large multidisciplinary study initiated in 1980 into the effects of acid deposition and land-use change on streamwater chemistry. The project involves the Dept. of Agriculture and Fisheries, Scotland, the Scottish Development Department and the Forestry Comission, the total programme of research being co-ordinated and managed by the Solway River Purification Board. Other organisations which have made substantial inputs to the Project include the Institute of Hydrology and the Universities of St.Andrews, Stirling and London. The research reported in this project can be considered as a part of the Loch Dee project whose overall aims are to detemine the impacts of acid deposition and afforestation on surface water ecology at L:och Dee and to develop a management programme that will improve the the potential of Loch Dee as a trout fishery (Burns et al. 1982).

1.2 *THESIS STRUCTURE*

This thesis is structured so that the reader is firstly introduced to previously published work on the causes of surface water acidification (*Chapter 2*). This is then followed by a critical review of several different mathematical models that have already been used to simulate the effects of acid deposition, in particular, on surfacewater quality (*Chapter 3)*. This chapter also contains a detailed review of the conceptual basis and assumptions that underlie the ILWAS model. The characteristics of the study area, Loch Dee, including details of all the study sub-catchments are reported in *Chapter 4*. which also includes an account of the various methods and types of data collection used in the study.

In order to increase understanding of the processes that control streamwater chemistry at Loch Dee, the hydrochemical budgets of the three main sub-catchments are analysed in *Chapter 5*, on both an annual and a monthly basis. *Chapter 6* then examines the ability of the ILWAS model to simulate the observed flow and hydrochemistry of moorland and forested upland catchments. Subsequently, in *Chapter 7* a sensitivity analysis is performed on the major time-independent input parameters of ILWAS, in order to determine whether the input requirements of the model may be reduced. In conclusion *Chapter 8* provides an overall discussion of the hydrochemical behaviour of the study catchments and evaluates the ability of ILWAS to simulate, and predict changes to, this behaviour. The implications of this study for future hydrochemical modelling, in general as well as with ILWAS, are also evaluated.

2: ACIDIFICATION IN UPLAND BRITAIN - A REVIEW

2.1 *INTRODUCTION*

The aim of this review is to examine the various processes that may have resulted in the observed acidification of upland surface waters in Britain and to assess their relative importance. To this end the review shall firstly examine the natural mechanisms that influence the chemistry of water as it passes through the various transfer stages and storages within the hydrological system. This will then be followed by an examination of the possible impacts of anthropogenic factors (in particular atmospheric pollutant inputs and land-use changes) that may serve to increase the acidification rates associated with these natural regulating mechanisms of upland areas.

2.2 *NATURAL MECHANISMS REGULATING STREAMWATER ACIDITY*

2.2.1 *Atmospheric Mechanisms*

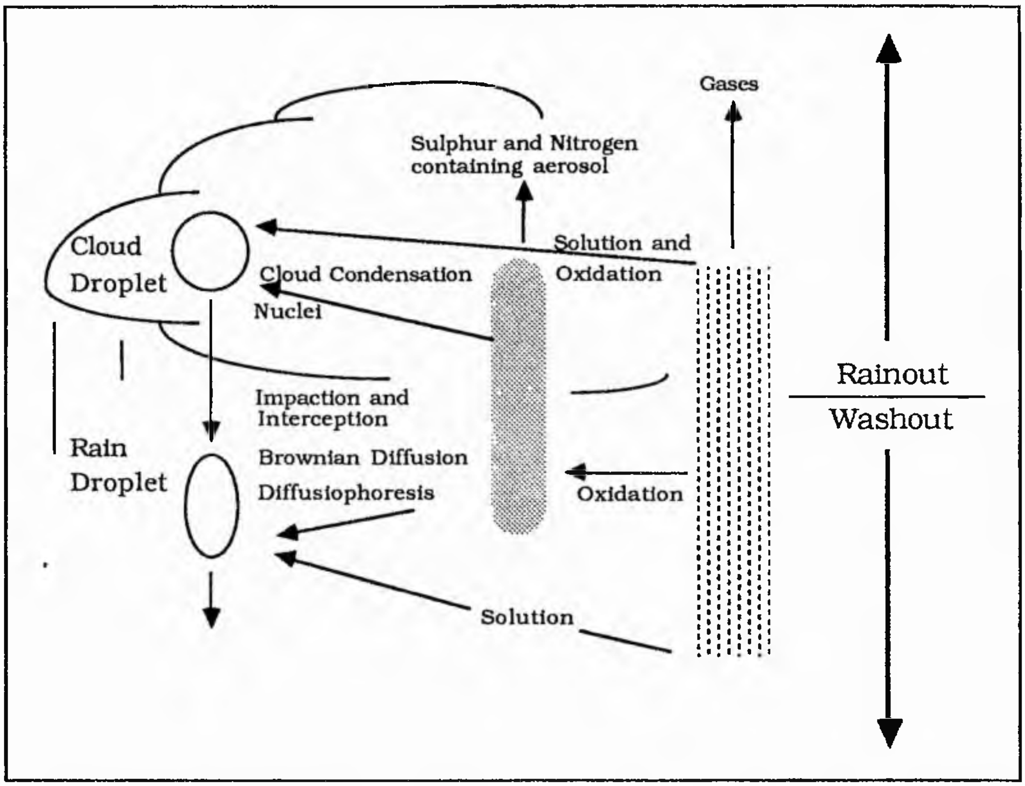
The amount of the different chemical species that the atmosphere is capable of depositing on an area is determined by two main factors, atmospheric material sources and atmospheric material deposition mechanisms

Non-anthropogenic material inputs to the atmosphere are derived from two main sources, the oceans and wind-blown terrestrial dust. Oceanic inputs are the major source of sodium, chloride, magnesium together with a large proportion of the sulphate input, particularly in maritime areas such as Northwestern Europe (Wright et al. 1980), whereas wind-blown terrestrial dust gives rise to calcium, magnesium, potassium and bicarbonate. Particulate and gaseous emissions, derived from biological decay mechanisms and volcanic eruptions, are the major sources of hydrogen ion, ammonium and nitrate. Consequently, the amount of individual chemical species in the atmosphere will vary from place to place, especially with proximity to the sea (Erikson 1960, Stevenson 1968) and the pattern of daily weather (Gorham 1958). Thus Stevenson's work (1968) shows the presence of a chloride gradient across the British Isles, with concentrations being greatest over the Northern and Western coasts. However, the strength of the gradient depends on prevailing meteorological conditions, hence the concentration of maritime species tends to be greatest in winter and lowest in summer (Sutcliffe and Carrick 1983), due to the increase in Westerly winds (Reid et al. 1981).

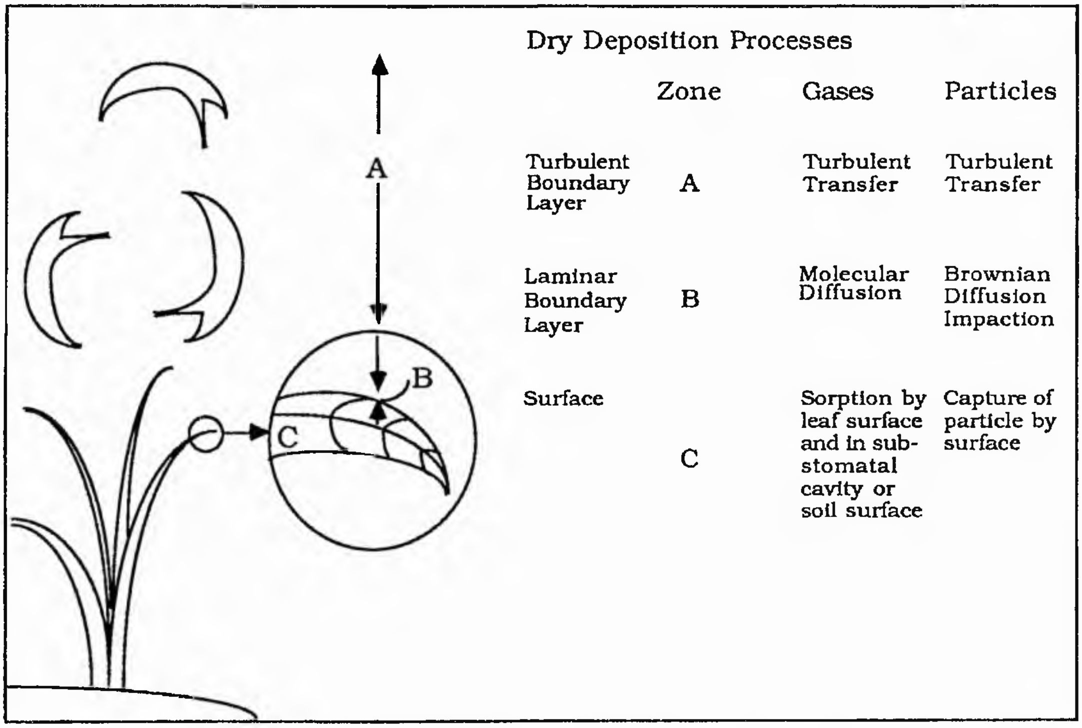
There are three main mechanisms by which chemical species may be removed from the atmosphere, i) *Wet deposition* which refers to ions reaching the surface in precipitation; ii) *dry deposition* which refers to the impaction and adsorption of gaseous and particulate matter by surfaces and iii) *occult deposition* which refers to the interception of water droplets in clouds and mist.

Wet deposition involves several vectors including rain, drizzle, snow, sleet and hail. However, in all these forms of precipitation two main processes operate, *rainout* and *washout* (Figure 2.1a). Rainout is the process by which atmospheric aerosols are brought into solution and removed from the atmosphere by acting as condensation nucleii

a) Wet Deposition Processes



b) Dry Deposition Processes



Dry Deposition Processes

	Zone	Gases	Particles
Turbulent Boundary Layer	A	Turbulent Transfer	Turbulent Transfer
Laminar Boundary Layer	B	Molecular Diffusion	Brownian Diffusion Impaction
Surface	C	Sorption by leaf surface and in sub-stomatal cavity or soil surface	Capture of particle by surface

Figure 2.1: The major (a)wet and (b) dry deposition processes after Fowler (1984)

for water vapour. Washout, in contrast, is the process by which falling water droplets 'scavenge' aerosols from the atmosphere during their descent. However, as Fowler (1980) emphasises, the distinction between the two processes is somewhat arbitary with both processes continuing to operate during the life of a particle. The differing contribution of these two processes may, however, result in the chemistry of different vectors varying. Thus Gorham (1958) suggests that snow has a lower scavenging efficiency than rain and consequently ion concentrations that are lower. However, Davies et al. (1984) in reporting on the occurrence of black acidic snow in the Cairngorms, attribute the high concentrations of particulate matter in the snowpack to efficient scavenging by snow as it descended.

Dry deposition refers to the sorption of gases and the settling of particulate matter under the influence of gravity onto terrestrial surfaces (Figure 2.1b). The majority of work in this area has been concerned with gaseous adsorption by vegetation covers, particularly grasses and trees. From these studies it has been noted that uptake rates to vegetation covers are dominated by surface factors such as stomatal resistance, with atmospheric factors such as windspeed and temperature stratification being of minor importance. This is especially true in forests where large surface roughness and associated atmospheric turbulence results in atmospheric resistance to transfer being negligible and surface processes almost totally controlling deposition rates (Fowler 1980, 1984). As sulphur dioxide is a soluble gas, rates of transfer will also be influenced by the moisture content on the adsorbing surface (Garland 1978). Work by Fowler (1978) shows that this is true for vegetation wetted by dew whilst dew is forming, however, once dew formation ceases then equilibrium is rapidly reached between gaseous sulphur dioxide and liquid sulphur dioxide in the dew film and adsorption ceases. Rain wetted vegetation in contrast shows little increase in deposition rates as the sulphur dioxide in the rain is already close to equilibrium with that in the air (Fowler and Cape 1983).

The distinction between wet and dry deposition is primarily dependent on collection procedures, thus Whitehead and Frith (1964) distinquish between samples collected during precipitation events (wet deposition) and those collected in between events (dry deposition). The practical difficulties of collecting separate wet and dry samples have lead to both often being collected together as bulk precipitation in continuously open collectors. However, problems with this approach are that the relative proportions of wet and dry deposition in the collector are unknown and that the amount of dry deposition collected will depend on the type of collector used. Thus collectors fitted with a gauze cover generally give higher concentrations of ions, a feature attributed to the increased filtering of dry and occult deposition (Miller 1984). The relative proportions of wet and dry deposition also vary with the amount of annual precipitation and distance from dry deposition sources. Thus work by Barrett et al. (1983) shows that dry deposition of sulphur exceeds wet deposition except for the remote high rainfall areas of the North and West.

Occult deposition refers to the deposition of solutes to the ground due to the direct impaction of cloud and mist droplets onto surfaces. These droplets can contain concentrations of ions higher by at least an order of magnitude than that associated with precipitation and it is suggested (Dolland et al. 1983) that this pathway could increase deposition estimates by up to 20 per cent from the values recorded in conventional bulk deposition gauges.

2.2.2 *Atmospheric Deposition-Vegetation Interactions*

There are three main processes by which vegetation may directly modify precipitation chemistry: i) increased concentrations due to *evapotranspiration* , ii) wash off of *intercepted deposition* and iii) *leaching of elements* from within the vegetation.

It is commonly estimated that of 30-40% of incoming precipitation is intercepted and evaporated from a coniferous forest in the western wetter parts of the British Isles and 10% from a heathland (Hornung 1984), thereby leading to a subsequent increase in concentrations of all chemical species. However, since all species are equally affected, this process is of minor importance in modifying the chemistry of incident precipitation compared with the other factors.

The concept of interception deposition was first identified by Mayer and Ulrich (1974) who used the term 'filter effect', referring to the process by which particulates and gases are removed from the atmosphere by vegetation. The rate of capture is dependent on windspeed and hence is enhanced in forests, due to the increased surface roughness in contrast to moorland areas where surface roughness is lower. Thus Miller and Miller (1980) assign the rapid build-up of sodium in peat soils at recently afforested sites in Eastern Scotland to the increased filtering action of the forest, and have further calculated that around 28% of the sulphur input to two Sitka spruce forests was the result of filtering. Likewise, Harriman and Morrison (1982) at sites around Loch Ard in the Southwest Grampians, assign the higher concentrations of species in streams draining afforested catchments to increased filtering by the forest, in contrast to the lower concentrations in streams draining adjacent moorland catchments . The filtering effect can also lead to the washdown of greatly enhanced levels of neutral salts, in particular sodium and magnesium chloride, which may be of importance in causing natural surges in streamwater acidity as the neutral salts exchange for hydrogen ions on the soil exchange complex (Wilklander 1975), a process discussed in more detail in Section 2.4.

Interception fluxes are very difficult to separate from the fluxes arising from cation exchange reactions on the canopy. These reactions can most readily be explained in terms of simple cation leaching, with base cations being leached out of the canopy and replaced by protons in precipitation. This process, assuming an ample supply of base cations to the leaf surface, will in theory result in a neutralisation of precipitation. Miller (1984) investigating conflicting reports on the effects of trees on throughfall acidity finds that old conifers acidified precipitation whereas deciduous trees, and to a certain extent young conifers, tended to neutralise. Cresser and Edwards (1987) suggest that this difference may be due to an insufficient replacement of base cations from the acidified soils under mature conifers to cope with the incident precipitation acidity.

Precipitation leaving the surface of vegetation does so in two forms as *stemflow* and *throughfall,* with ionic concentrations usually greater in stemflow, which is also generally more acidic. These two effects are probably the result of greater contact time and longer pathlengths together with the solution of organic compounds (Hornung 1984). The majority of precipitation leaving vegetation, however, occurs as throughfall, which due to cation exchange, is generally less acid than precipitation. For non-forest vegetation there are only limited data on throughfall quality, but Hornung (1984) reports data for bracken, gorse, heather and cotton grass which shows that in unpolluted areas these plant species all generally have a neutralising effect on precipitation. However, Clymo (1984) calculates that precipitation of pH 4.0 will be acidified to pH 3.7 after passing through a sphagnum canopy.

Overall, the evidence suggests that cation exchange reactions between precipitation and vegetation will generally result in the neutralisation of precipitation. However, the increased leaching of base cations and uptake of protons at the leaf surface requires an equivalent uptake of base cations and leaching of protons at the root zone thereby transferring precipitation acidity directly to the soil.

2.2.3. *Soil - Water Interactions*

The main inorganic buffering systems in soils have been summarised by Ulrich (1980) as follows:

Calcium Carbonate	pH8.0 - 6.2
Silicate	6.2 - 5.0
Cation Exchange	5.0 - 4.2
Aluminium	4.2 - 3.8
Iron	3.8 - 2.4

In areas of crystalline siliceous bedrock, typical of the British uplands, buffering systems are dominated by cation exchange reactions. These reactions together with anion adsorption, oxidation-reduction reactions and mineral weathering are the major processes determining soil-water interactions (Hornung 1984). Each of these will now be examined in turn.

2.2.3.1. Cation Exchange Reactions

Cation exchange reactions involve the exchange of cations between the soil solution and negatively charged sites on the surface of clay minerals. These reactions are very rapid and consequently are the most important influence on surface water quality in upland areas where soil weathering rates are very low (Rosenquist 1978, Seip 1980). The dominant exchange is that of base cations on the exchange complex for protons in solution, the base cations either being leached out of the profile along with associated anions or readsorped further down the profile. As a result of such processes, the balance of protons to base cations in input waters to the soil compared with the same balance in the soil solution will determine the extent to which the incoming waters are buffered. This balance is referred to as the 'lime potential' or acidity potential (Bache 1984). If the lime potential of the incoming solution is lower than than that of the existing soil solution, (as is common in circum-neutral mineral soils) then base cations will be removed from the exchange sites in return for protons from solution, thereby neutralising the soil solution and drainage waters. In contrast if the 'lime potential' of incoming water is higher than that of the soil solution, (as is often the case with organic soils and horizons), then base cations are removed from the solution in return for protons from the exchange sites, thereby acidifying the soil solution and drainage waters. If, however, the soil is an acid mineral soil typical of upland areas where exchange sites are dominated by exchangable aluminium as well as hydrogen, and, if the 'lime potential' of incoming waters is greater, then in these soils, the dominant exchange will be that of base cations in solution for aluminium on the exchange complex. However, this reaction not only acidifies drainage waters, as the aluminium is hydrolysed to aluminium hydroxide ions, it also results in the release of potentially toxic monomeric aluminium ions into drainage waters (Cronan and Schofield 1979, Bache 1984). This release of aluminium combined with the low pH and low calcium concentrations is now recognised as a major factor in the reduction of fish populations in acidified waters (Grahn 1980, Driscoll et al. 1980, Brown 1983). Exposure to aluminium species causes clogging of fish gills by mucus and respiratory stress eventually leading to death (Muniz and Leivenstad 1980), with inorganic aluminium species being far more toxic than organically complexed species. In contrast, elevated calcium concentrations may be important in reducing the stress on body salt regulation caused by low pH (Brown 1982, 1983, Sadler and Lynam, 1986).

Another important exchange mechanism, particularly in coastal areas, is the 'sea-salt effect' (Wilklander 1975), whereby large inputs of neutral salts such as sodium and magnesium chloride in precipitation and/or washoff of dry deposition from vegetation are adsorbed on to exchange sites with a consequent release of protons into the soil solution, thereby acidifying drainage waters. Although cation exchange reactions determine the relative amounts of each cation in the soil solution, the ability of these cations to be leached into drainage waters is controlled by the availability of balancing anions.

2.2.3.2 Anion Adsorbtion

The major inorganic anions in drainage waters are generally seen as chloride, nitrate and sulphate (Harriman and Wells 1982). Chloride is the most conservative ion and thus concentrations in drainage waters are determined on the basis of atmospheric seasalt input concentrations. Nitrate, whilst also exhibiting negligible uptake in soils, is subject to uptake by vegetation as shown by the very low nitrate concentrations in streamwaters during the growing season, especially in nitrogen stressed upland environments. Nitrate may, however, play an important role in driving cation exchange reactions during storms when it may be rapidly flushed through the soil (Edwards et al. 1984).

Sulphate, in contrast, is subject to specific adsorbtion on to the surface of the hydrated aluminium and iron oxides, a process that releases an equal quantity of hydroxyl ions. Since the pH of soils is buffered, the hydroxyl ions in turn react with the exchange complex and release protons in return for the adsorbtion of base cations (Cresser and Edwards, 1987). However, in highly organic soils or horizons the adsorbtion sites may be blocked by organic ligands or the influence of organic matter on the sesquioxides themselves (Johnson and Reuss 1984). Consequently, sulphate concentrations in drainage waters will depend on runoff patterns, with concentrations being greatest at high flow periods, when a major part of the flow is through the organic surface horizons (Feger and Brahmer 1987).

2.2.3.3 Oxidation-Reduction Reactions

If organic and inorganic sulphides and nitrides are present in the catchment soils, then the oxidation of these compounds which may develop as peats and organic surface horizons dry out during periods of drought, can result in the formation of sulphuric and nitric acids. The subsequent flushing out of these acids in the first drainage waters of the next storm event gives rise to highly acid pulses in catchment surface waters (Christophersen 1981, Hornung 1984)

2.2.3.4 Mineral Weathering

Mineral weathering proceeds primarily by hydrolysis reactions and involves the consumption of protons and the production of base cations. In the absence of anthropogenic inputs the primary source of protons is carbonic acid, produced as a by-product of plant respiration. The rate of consumption of protons and the production of base cations depends on the minerals present in the underlying bedrock from which the soil is derived. If calcite is present then protons will be rapidly consumed and the pH of the soil solution will rarely fall below 7. Alumino-silicate minerals will also decay in natural acids but generally at far slower rates. The dissolution rates of such minerals follows Bowen's reaction series, a typical alumino-silicate weathering reaction being the dissolution of K-Feldspar;

$$4KAlSiO_8 + 4H_2CO_3 + 18H_2O \text{ —> } 4K^+ + 4HCO_3^- + Al_4Si_4O_{10}(OH)_8 + 8H_4SiO_4 \quad (2.1)$$

Such reactions are generally capable of neutralising all natural acidity so that water flowing from soil mineral horizons will typically have a pH in the range 6-7. However, in the British uplands soils tend to have very thin mineral horizons with consequently a low supply of weatherable minerals. Thus weathering rates and the neutralisation ability of such soils decreases through time as the supply of weatherable minerals itself decreases as the weathering front advances into the underlying bedrock. Neutralisation rates are further reduced due to the high precipitation that prevails in upland areas. This high precipitation serves to increase initially the leaching rates of base cations and associated weathering rates so that the supply of base cations is reduced with time. The high precipitation rates when associated with rapid runoff rates may also increase the throughput of water through the soil. This will, in turn, reduce the contact time of the soil solution with mineral surfaces, so that weathering reactions are unable to proceed to equilibrium, thereby lowering the soils neutralisation capacity.

2.2.3.5 Soil Development in Upland Areas

Having examined the major processes governing soil-water interactions in upland areas it is useful to determine in general terms how acid soils may develop in the absence of anthropogenic influences. In such areas soil profile development is a consequence of the interaction of several factors, notably increasing wetness, time and the acidity of the underlying bedrock (Figure 2.2). If cations leached from exchange sites are replaced at a high rate then the base saturation and soil pH will remain high, resulting in the development of a typical brown earth profile. However, as discussed in the previous section the supply of base cations in upland areas is often insufficient to keep pace with leaching, and as a result soil base saturation and pH will fall. As soil acidity increases bacterial action is reduced and

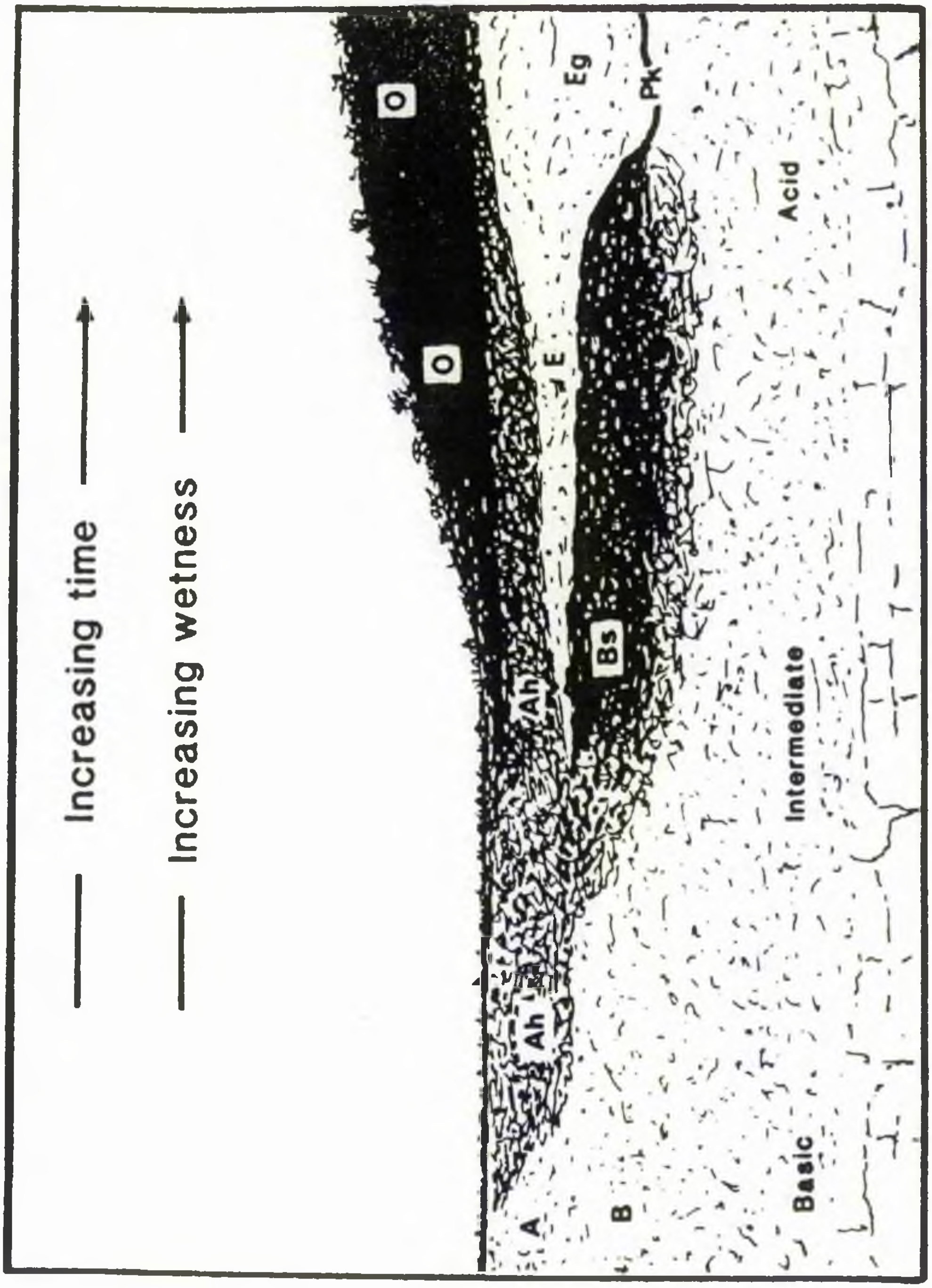


Figure 2.2: A generalised model of soil profile development in upland Britain. (O = organic horizon; Ah = A horizon with humus accumulation; E = leached horizon; Eg = Gleyed E horizon; Bs = B horizon with sesquioxide accumulation; Pk = placon or iron pan)

(after Cresser and Edwards 1987)

organic matter begins to accumulate in the surface horizons with the consequent encouragement of colonisation by acid tolerant vegetation ie *Calluna vulgaris* and conifers, which in turn produces an acid litter. As the pH of the surface horizon consequently falls the solubility of iron and aluminium species increases and these are translocated down the profile into the B horizon leading to the development of a podsolic profile. Eventually an iron pan is formed as the iron is precipitated out of solution into an impermeable band a few centimetres thick. This impermeable layer impedes drainage which may in turn result in an increase in the development of the organic layer until a hill peat is formed. Concomitant with this increase in soil acidity is a decrease in the buffering of drainage waters with the result that these become increasingly acidic. Thus in upland areas soil development may naturally lead to the acidification of surface waters.

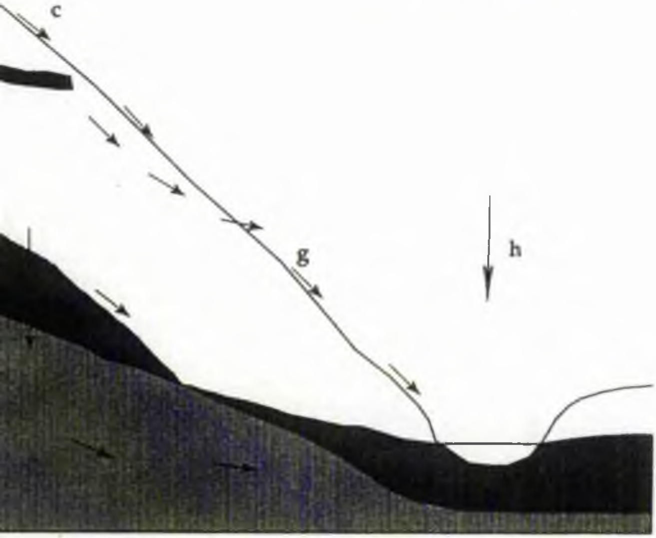
2.2.4 *Hydrological Pathways*

Differing hydrological pathways through a catchment can play an important role in determining surface water chemistry by influencing contact time with the soil and/or bedrock (Reid et al. 1981, Reynolds et al. 1986, Hornung et al. 1986, Bricker 1987). The major flowpaths through a typical upland catchment are shown in Figure 2.3. The particular flowpath taken at any time is determined by spatial and temporal variations in hydraulic conductivity. In dry periods flow is horizontally through the mineral soil horizons over the underlying rock surface or any impermeable horizon present. As precipitation commences soil moisture levels become recharged so that the low permeability deep soil layers rapidly become saturated followed by the higher permeability upper layers. Once a horizon is saturated lateral

Figure 2.3: The major pathways of water through an upland catchment

A Soil (unsaturated zone)
B Bedrock (unsaturated zone)
C Bedrock (saturated zone)

a Precipitation
b Throughfall
c Overland Flow
d Sub-surface flow
e Discontinuous indurated layers that effect flowpaths
f Macropores
g Return flow/Saturation overland flow
h Channel precipitation
i Groundwater flow



or throughflow commences, the volume of such flows depending on the horizon permeability. Consequently there are several types of throughflow which are characterised by their chemistry and frequency of occurrence, with flows from the deepest horizons having the highest solute concentrations due to their lower permeability and hence longer residence times (Hewlett 1967, Dunne 1978). As precipitation continues the soil infiltration capacity may be exceeded at the base of the slope and saturation overland flow will commence. The major component of this type of overland flow is return flow, i.e. flow that initially enters the soil at the top of a slope and on encountering a saturated wedge at the base of the slope is forced to return to the surface. Such return flow chemically equilibrates with the surface horizons; thus even though the flow may initially have equilibriated with the lower soil horizons, its final chemical composition will be similar to that of storm flow.

The solute composition of flow through soils can be further complicated by the presence of soil macropores or pipes, these being particularly common above impermeable layers such as ironpans (Jones 1979). They are thus often found in the organic surface horizons of upland podsols (Atkinson 1978, Newson 1984). Flow through such macropores may be very rapid, especially when the soil is close to or at saturation (Mosley 1982). The flow in such macropores typically has a low pH and low solute concentrations as it fails to have sufficient time to reach equilibrium with the horizon through which it passes (Bache 1984).

Stream solute concentrations are often explained using a simple two component mixing model, whereby solute concentrations are derived as the mixing of high concentration baseflow with low concentration stormflows (Pilgrim et al. 1979, Christophersen et al. 1982). However, Newson (1984) argues that such mixing models are too simplistic to describe accurately solute dynamics in upland areas as they fail to take into account soil structures such as macropores. Such models also have difficulty in describing the frequently observed increase in solute concentrations at the start of a storm. (Walling 1974, Walling and Foster 1975). Such increases are attributed to the 'new' low solute concentration water in precipitation displacing 'old' high concentration pre-event water from a saturated wedge in the soil (Anderson and Burt 1982, Bache 1984). This hypothesis is supported by tracer experiments performed by several authors (Dunne 1978, Overrein et al. 1981).

Another hydrological pathway of particular importance in many upland areas is snowmelt. Snowmelt particularly influences streamwater chemistry as a consequence of the fractionation of ionic species in the snow (eg Seip et al. 1980). Fractionation leads to highly elevated levels of pollutants and hydrogen ions in the initial meltwaters, with a consequent lowering of stream pH (Johannessen and Henriksen 1978, Johannes et al. 1981, Cadle et al. 1984). This initial 'acid flush' is favoured by a very rapid melt, poor soil buffering capacity (Morris and Thomas 1985) and by certain meteorological conditions (Tranter et al. 1986). However, Cresser and Edwards, (1987) argue from studies in the Glen Dye catchment in Northeast Scotland, that meltwaters are often in contact with the upper soil layers and it is the chemistry of these layers rather than the snow that determines the pH of drainage waters even if the melt is rapid. They further argue that 'acid flushes' are more likely to occur when soils are frozen confining flow to the very surface of the soil. Edwards et al. (1986) also report that the thawing of frozen soils may lead to an increased leaching of solutes, an effect attributed to the rupture of plant cells and soil microfauna as intracellular fluids expand on freezing.

The natural mechanisms regulating surface water quality reviewed above can clearly result in the production of acid soils and waters in upland catchments over both long and short timescales. Such mechanisms are postulated by Pennington (1984) as the primary cause of acidification in Cumbria. A major point of dispute in the acidification debate, however, concerns the degree to which anthropogenic influences may modify these natural regulating mechanisms to produce the observed patterns of present-day acidification of upland areas. Thus several authors (Rosenquist 1978, Krug and Frink 1983, Rowell and Wild 1985) argue that anthropogenically induced land-use changes, in particular coniferous afforestation, are the primary cause of acidification. Other authors such as Johnson et al. (1984) contend that it is the increased input of anthropogenically derived atmospheric pollutants, ie 'acid rain', that is of primary importance. In order to assess the relative importance of these two factors this review now examines the influence of anthropogenically derived atmospheric inputs on these natural water quality regulating mechanisms

2.3 *ANTHROPOGENICALLY -DERIVED ATMOSPHERIC INPUTS*

Whilst natural acidification processes can undoubtably result in the acidification of upland soils and waters, the focus of attention in the acid rain debate, in both the popular and scientific press, has been over the influence of atmospheric pollutant inputs from anthropogenic activities. This has arisen due to the perceived correlation of decreases in surface water pH with the increased use of fossil fuels.

2.3.1 *Pollutant Sources and Deposition*

The major pollutants involved in the acidification debate are sulphur and nitrogen oxides, the main sources being the burning of fossil fuels in power stations and the internal combustion engine. On a global scale it has been estimated that inputs of sulphur to the atmosphere from such anthropogenic sources are presently equal to those from natural sources (Granat et al. 1976). However, for nitrogen far less information is available and such a comparison is not possible at present. Once within the atmosphere various reactions lead to the conversion of sulphur dioxide, hydrogen sulphide, and nitrous oxides into sulphuric and nitric acids (Likens et al. 1972).

In the absence of these pollutants the dissociation of carbonic acid, will in theory, give rainwater a natural acidity of pH 5.6. In actuality, in remote temperate areas of the world the pH of rainfall is quoted as around 5.0 with individual episodes ranging from 4.5 - 5.6 (Galloway et al. 1982). Consequently the term 'acid rain' should refer to precipitation events that are more acidic than those found in remote areas. The influence of anthropogenically-derived pollutants on precipitation acidity in various parts of the industrialised world is reported by many authors (Anon 1971, Likens et al. 1976, Galloway et al. 1976, Martin 1979, Overrein et al. 1980), and the work by Vermulen (1978) in the Netherlands indicates that around 80 per cent of precipitation acidity can be attributed to sulphuric and nitric acids.

In the British Isles spatial trends in hydrogen ion concentrations show a West - East gradient across the country (Figure 2.4), as concentrations are lowest in Northwest Scotland and highest in the East Midlands and East Anglia (Barrett et. al. 1983). The latest Report of the U.K. Review Group on Acid Rain (Barrett et al. 1987) demonstrates that hydrogen ion concentrations in precipitation have decreased by around 25 per cent in the period 1981 - 1985 compared with the period 1978 - 1980. This report also indicates that similar spatial and temporal trends are shown by non-marine sulphate and nitrate concentrations.

Spatial trends in wet deposited acidity (Figure 2.5) are dominated by the pattern of rainfall amount as the variation in hydrogen ion concentration is far lower than that of rainfall quantity. Consequently the maximum rates of deposited acidity are found in the Lake District and West Central Highlands of Scotland where annual inputs can be greater than 5 kg ha^{-1}, and are similar to levels reported for Southern Scandinavia. Barrett et al. (1987) further note that temporal changes in levels of wet deposited acidity over the period 1978 - 1985 are difficult to assess due to intra-annual variability. They suggest, however, that there is some evidence for a decline in hydrogen ion and to a lesser extent sulphate inputs. This decline has been attributed to the reduction in sulphur dioxide outputs from power stations since

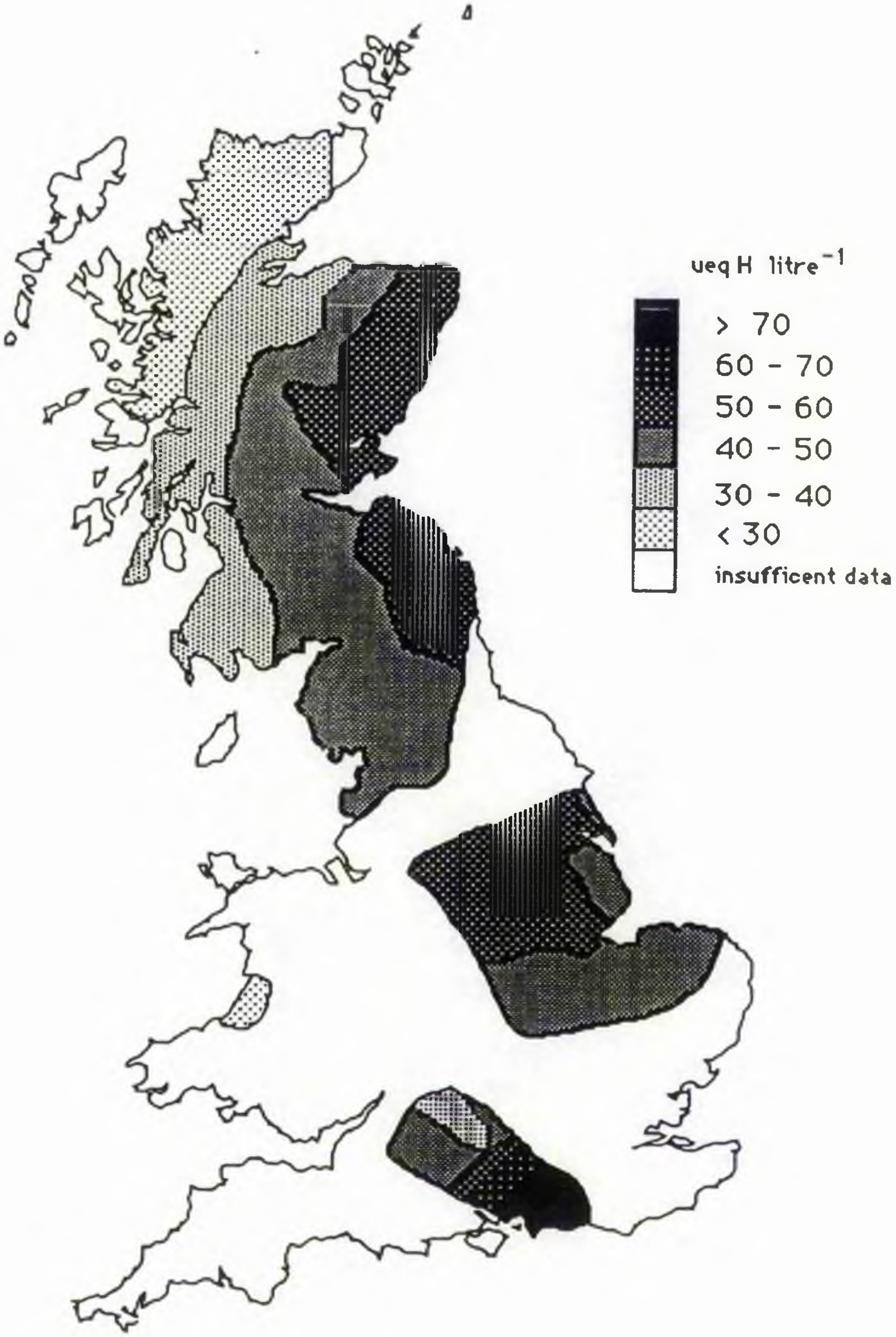


Figure 2.4: Spatial trends in H+ concentrations in precipitation over the United Kingdom 1978 - 1980.

(source Barrett et al. 1983)

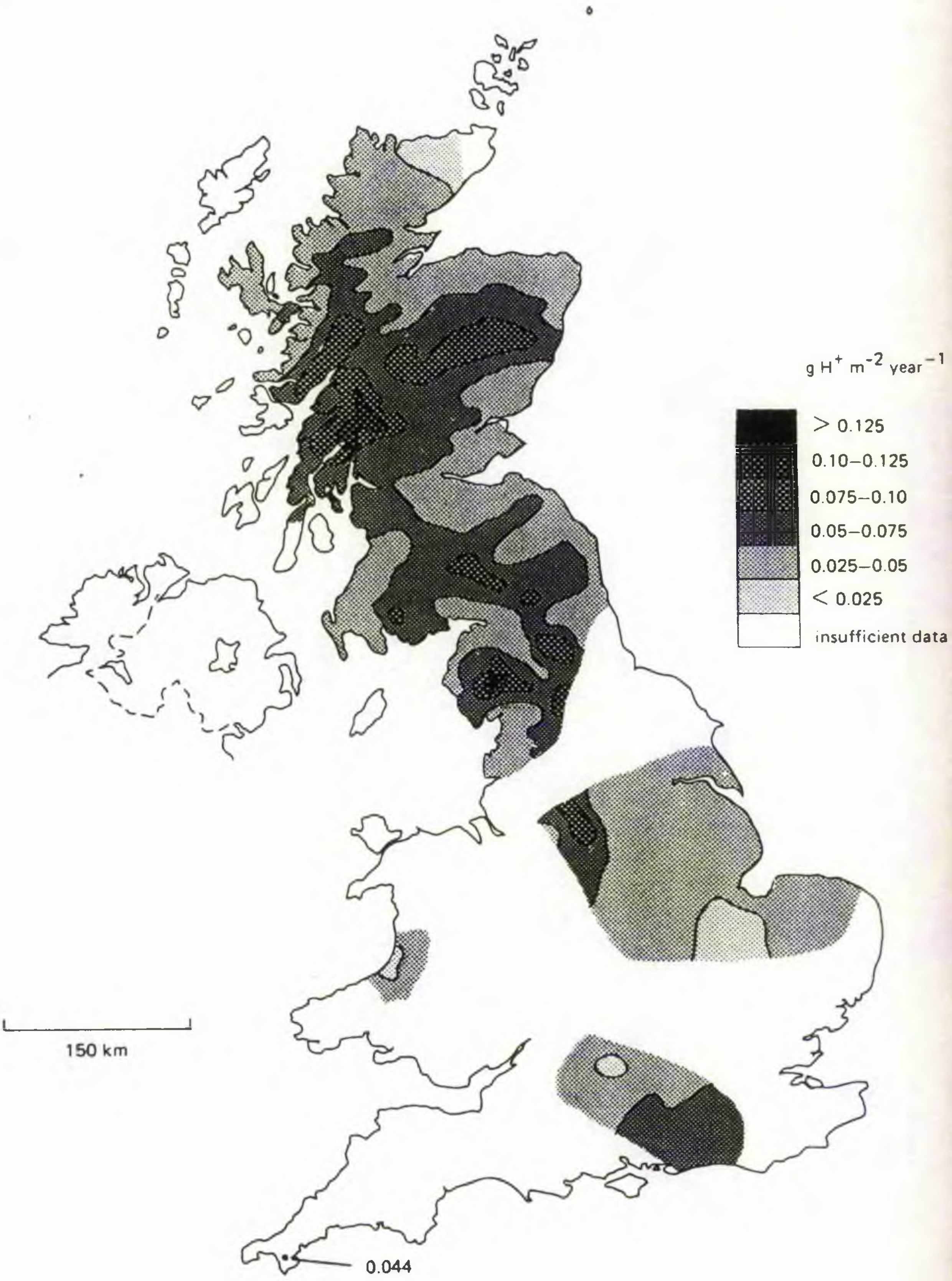


Figure 2.5: Wet Deposited acidity over the United Kingdom (1978-1980)

(source Barrett et al. 1983)

1979, primarily as a result of the recession in manufacturing output during the early 1980's (Department of the Environment 1986).

Anthropogenic inputs to the atmosphere also exhibit considerable seasonal variations in response to changes in energy consumption, emissions being far higher in the winter months. Such seasonal variations in emissions are reflected in precipitation quality, albeit with a time lag due to atmospheric dispersal processes, thus sulphate and acidity levels in precipitation are greatest in early spring (Figure 2.6).

Precipitation chemistry can also exhibit short term changes in composition related in particular to wind direction. At Eskdalemuir in Southern Scotland results cited by Barrett et al. (1987) show that the highest non-marine sulphate concentrations are associated with easterly air streams, where the air has passed over the main pollutant source areas of the United Kingdom and Western Europe. The greatest actual deposition at the same site is, however, associated with Westerly and South-Westerly air streams, again indicating the overriding influence of rainfall quantity on actual deposition. Consequently, precipitation composition may be highly variable between individual precipitation events. Thus Barrett et al.(1987) report that at Eskdalemuir in 1980 3.3% of the wet days gave rise to 30% of the total deposited acidity for that year. The authors also cite similar figures for several other sites in the British Isles and thereby conclude that acid deposition may be highly episodic over much of the country. Furthermore Barrett et al. (1987) also report that precipitation composition may be highly variable within an individual storm event and that there is commonly an inverse

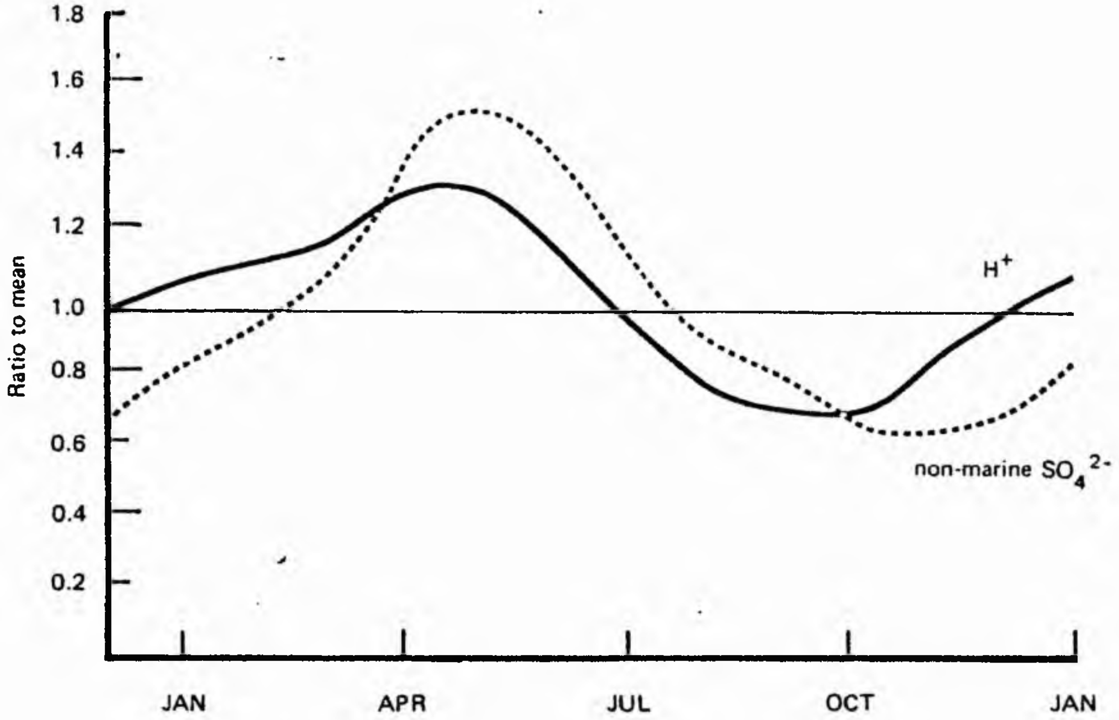


Figure 2.6: Seasonal variations in the concentration of H^+ and SO_4^{2-} concentations in Northern Britain 1978-1980.

(source Barrett et al. 1983)

correlation between ionic concentration and the rate of rainfall. However, they also note that this relationship may not occur during the passage of a frontal system, due to the involvement of different air masses within the duration of one precipitation event.

Dry deposition of hydrogen ions to the earth's surface does not directly occur, however, each molecule of dry deposited sulphur dioxide on oxidation to the sulphate ion produces two protons and is hence a contributing factor to deposited acidity. Over the United Kingdom Fowler (1984) calculates that dry deposition of sulphur dioxide is greatest over the source areas of the Midlands and Southeast and lowest in the North and West. A comparison of this pattern with that for wet deposited non-marine sulphate indicates that only in the extreme North and West are wet inputs of sulphur greater than dry inputs.

As reviewed in Section 2.2.1. occult deposition may considerably increase the input of chemical species to land surfaces in upland areas (Dolland et al. 1983). For Britain as a whole Barrett et al. (1987) calculate that the input of sulphate from this source may equal 10 per cent of that from wet and dry sources combined. In upland areas with high average sulphate concentrations this may rise further so that these inputs are a highly significant source of sulphate to catchments.

In upland parts of Britain another important depositional vector is snowfall. It is claimed that falling snow maybe a more efficient scavenger of nitrates than rain (Tranter et al. 1986) and the chemical composition of snowfall may vary to a different extent with altitude than rain (Davies et al. 1984). Given such findings, the relative contribution, of snow and rain to wet deposition inputs may have a considerable influence on the inputs of acidity to an area.

2.3.2. *Acid deposition - Vegetation Interactions*

Many of the processes involved in the interaction of precipitation and vegetation have been reviewed in Section 2.2.2. This section will therefore concentrate on the implications of anthropogenically increased acid deposition. As noted earlier hydrogen ions in precipitation may be exchanged at the leaf surface for base cations from within the vegetation. Work by several authors (Scherbatskoy and Klein 1983, Skiba et al. 1986) confirms that lowering the pH of simulated rain causes increased leaching of base cations, with the sum of base cations being equally balanced by the uptake of hydrogen ions. However, as previously noted, Miller (1985) reports that the extent of this neutralisation varies with age and species of the vegetation and that old conifers may actually accentuate the acidity of the precipitation further. If this acidification does occur the effects tend to be larger the more polluted a region has become (Cresser and Edwards 1987). However, even if cation exchange at the leaf surface significantly neutralises precipitation acidity, the amelioration is probably more significant for the ecological protection it provides to crops (Craker and Bernstein 1984), than for any beneficial effect on surface water as the cation exchange merely transfers the acidity to the rhizosphere. Furthermore, the increased concentration of base cations in throughfall may enhance soil solution and drainage water acidity due to the 'salt effect'. Thus work by Rosenquist (1978) shows that the leachate from acidic humus subjected to simulated 'coastal' and 'inland' precipitation is consistently 0.2 pH units lower for the 'coastal' rain.

In upland catchments susceptible to acidification, evidence increasingly suggests that anion uptake, as well as cation leaching, in vegetation may be of significance (Edwards et al. 1985). Nitrate uptake has been observed for both Sitka Spruce (Skiba et al. 1986) and moorland vegetation (Edwards et al. 1985). This uptake of nitrate is effectively a neutralising reaction (Van Breeman et al. 1983) of the form:

$$ROH + NO_3^- + H^+ \longleftrightarrow RNH_2 + 2O_2 \qquad (2.2)$$

However, when mineralisation and nitrification reactions eventually occur the hydrogen ions will be released along with the highly mobile nitrate anions and possibly transferred to drainage waters. Sulphate in comparison is not directly absorbed by vegetation but the increased interception deposition of pollutants will result in an increase in sulphate concentrations in throughfall and hence to the soil system.

2.3.3. *Acid Deposition - Soil Interactions*

The effect of increased precipitation acidity on soils will depend on the initial base saturation and cation exchange capacity of the soil in question (Hornung 1986). The main processes affected, however, will be cation exchange, anion adsorption and mineral weathering.

2.3.3.1. Cation Exchange

In acidic mineral soils typical of upland areas, where aluminium and exchangable hydrogen dominate the exchange complex, an increase in precipitation acidity will not only lead to a decrease in surface water pH but will also result in an increase in the release of potentially toxic aluminium into drainage waters (Cronan and Schofield 1979, Johnson et al. 1984, Bache 1984). In contrast, strongly acid organic soils or surface horizons, where the exchange complex is dominated by exchangable hydrogen, will be unable to buffer increased precipitation acidity at all and the acidity may be directly transferred to surface waters (Hornung 1984). The transfer of cation exchange products to surface waters is, however, dependent on the presence of an accompanying anion, the 'mobile anion' concept of Johnson and Cole (1977), Cronan et al. (1978) and Seip (1980). Consequently, anion adsorption rates in soils are also an important factor in determining the effect of acid deposition on drainage waters.

2.3.3.2. Anion Adsorbtion

Until the early 1980's sulphate had generally been regarded as subject to little long term adsorbtion in soils leading to the belief that the increase in sulphate deposition from 'acid rain' was primarily responsible for the acidification of surface waters (Seip and Tollan 1978, Wright and Henriksen, 1980). However, work in Scandinavia reported by Chester (1986), suggests that there could be an important storage of sulphate in the soil. This storage implies that if deposition of sulphate increases then initially adsorbtion will result in a non-proportional effect on runoff with a consequent lower than expected leaching of base cations, aluminium or hydrogen ions, as shown by the Reversing Acidification in Norway Study (RAINS) (Wright and Gjessing 1986) If deposition continues to increase so that the soil becomes saturated with respect to sulphate then an amount of sulphate equivalent to that input from the atmosphere will be released to surface waters. This sulphate will be accompanied by a reduction in alkalinity or an increase in cation concentrations depending on weathering rates and soil base status. The RAINS experiment has also shown that if the sulphate is reversibly absorbed in the soils then a decrease in the deposition of sulphate and hydrogen will not be initially reflected in drainage waters. The stored sulphate will continue to be leached out of the soil until the soil reaches equilibrium with the lower acidity of incoming precipitation.

In upland soils sulphate adsorbtion is generally associated with sesquioxides in the soil (Cresser and Edwards 1987). However, studies at Loch Gardsjon in Sweden (Chester 1986) suggest that the the vast majority of sulphur is stored in the form of basic aluminium sulphate, Jurbanite (Nilsson 1986):

$$AlOHSO_4 \dashrightarrow Al^{3+} + SO_4^{2-} + OH^- \qquad (2.3)$$

This reaction may be important in controlling both sulphate and aluminium leaching from soils and hence concentrations in drainage waters.

2.3.3.3. Mineral Weathering

As well as increasing cation exchange reactions, an increase in hydrogen ions in precipitation may also increase hydrolysis reactions and hence the release of base cations from silicate minerals and the neutralisation of drainage waters. If catchment soils or the underlying bedrock contain calcium carbonate then weathering reactions proceed relatively rapidly, and protons from precipitation are rapidly consumed and precipitation is neutralised. However, in upland areas subject to acidification, the mineralogy of soils and bedrock is dominated by alumino-silicate minerals whose weathering is extremely slow compared with cation exchange reactions. Consequently, release rates of base cations are far lower than the input of protons in deposition (Nilsson 1986). Thus although it has been calculated that there is sufficient calcium in a 1mm layer of granite to neutralise 200 years of precipitation at pH 4.3 (Bache 1984) many upland areas still have acid drainage waters. Increases in acid deposition also serve to change the type of mineral hydrolysis occurring as carbonic and organic acids in the soil are partially replaced by mineral acids from precipitation (Johnson 1984). If base cation release is insufficient to prevent rapid depletion of the soil exchange complex, this change may lead to the rapid development and breakdown of acid clays, which are naturally unstable, leading to the release of potentially toxic inorganic aluminium ions to drainage waters (Wilson 1986).

2.4 *LAND-USE CHANGES: EFFECTS ON UPLAND ACIDIFICATION*

Whilst there is a considerable body of evidence to support the contention that anthropogenically-derived atmospheric pollutants can result in the acidification of surface waters, several authors such as Krug and Frink (1983), argue that the effects of these pollutants are minor in comparison with the impact of land-use changes, and in particular coniferous afforestation.

2.4.1 *Coniferous Afforestation*

The association between coniferous afforestation and streamwater acidification is reported by several authors in upland Britain (Harriman and Morrison 1982, Stoner et al. 1984) and is described by Miller (1985) as a uniquely British feature of the acidification debate. Several general mechanisms have been put forward to account for the acidification of surface waters by forests: i) increased interception deposition, ii) changes to soil properties and iii) changes in soil hydrology.

The interception deposition mechanism has already been reviewed in Section 2.2.2 and it is sufficient to repeat that whilst coniferous afforestation will no doubt lead to an increase in solute inputs, the available evidence for the influence of this process on acidification is inconclusive since evidence exists for neutralisation as well as acidification below coniferous canopies (Miller 1985). In either situation there will be a net transfer of acidity to the soil, with possibly a consequent increase in drainage water acidification. Also if there is a significant increase in 'seasalt' interception, the 'salt effect' (Wilklander 1975) may lead to a temporary increase in drainage water acidity.

In terms of changes in soil properties the growth of coniferous forests will, over a few years, lead to the production of a highly acid litter layer and surface organic horizon, with a commensurate decrease in the pH of surface and litter flow (Hornung and Newson 1986). The development of this organic layer may also decrease the rate of flow into the subsoil, thereby increasing the acidity of runoff as an increasing proportion of flow is deflected through the acid surface horizons.

If the supply of mineral nitrogen in the soil is dominated by ammonium, as is generally the case in upland areas, then forests will remove an excess of base cations from the soil. This excess is then balanced by a flux of protons from the roots to the soil (Miller 1985). Cation exchange at roots is thus likely to be a soil acidifying process, a conclusion supported by an examination of available evidence by Miles (1978). This report suggests that the tendency to replace indigenous Beech and Oak forests with coniferous plantations has lead to a pH decline of 1 unit in the surface horizons of underlying soils. Nilsson et al. (1982) calculate that such soil acidification will be greatest during the early stages of forest development when humus build-up and cation accumulation are at their most rapid. If the trees are left on site, however, then much of the acidification will be temporary as the base cations return to the soil as the trees die and decompose. In contrast, removal of the trees will result in the soil acidification becoming permanent, the effect being greatest if the trees are young when felled. Nilsson et al. (1982) further argue that such root-generated acidity is unlikely to lead to surface water acidification due to the lack of a mobile anion. However, Hornung and Newson (1986) point out that the balancing anions may be supplied from increased interception deposition, particularly in the form of occult deposition.

Turning now to changes in soil hydrology, if waters are able to percolate to the base rich mineral soil then almost all soils will neutralise incoming precipitation (Bache 1984). Hence changes in the soil physical properties, associated with initial drainage improvements or with subsequent growth, such that drainage waters are less likely to enter the 'C' horizon, is the most attractive hypothesis to explain the effects of afforestation on streamwater acidification (Miller 1985). The presence of an initial drainage system established prior to planting will increase the rate at which water is evacuated from a catchment, particularly during storms (Robinson 1984). This drainage flow will be particularly acidified if the drains are covered in acidic litter deposits (Cresser and Edwards 1987). However, pre-afforestation ploughing may also breakup indurated horizons thereby increasing flow through the mineral horizons and hence reducing drainage water acidification. Improvements in drainage may also lead to the drying of anaerobic horizons allowing oxidation reactions to produce protons, typical reactions being:

$$4FeS + 9O_2 + 10H_2O \text{ <---> } 4Fe(OH)_3 + 4SO_4^{2-} + 8H^+ \qquad (2.4)$$

$$RNH_2 + 2O_2 \text{ <---> } ROH + NO_3^- + H^+ \qquad (2.5)$$

In the absence of an initial drainage network the hydrological effects of afforestation are contradictory. The greater interception and evapotranspiration from coniferous canopies (Calder and Newson 1979) are likely to reduce rapid throughflow (Cresser and Edwards 1987). However, in contrast the drying out of forest soils may be significant in the summer leading to the contraction of organic matter and the consequent development of macropore systems, which may also be produced by root development (Hornung et al. 1987). These macropores act as a pathway for rapid water transfer and consequently may lead to increased runoff acidity.

2.4.2 *Deforestation*

If,as alleged, afforestation is linked with streamwater acidification it may be expected that deforestation will result in an increase in stream pH. This arises because the removal of trees will result in a decrease in the interception deposition of pollutants and neutral salts which in turn will increase the pH of drainage waters (Miller 1985). Clearfelling may also lead to an increase in base cation concentration at depth as root uptake is reduced, thereby neutralising soil and hence drainage water acidity (Nilsson et al. 1982). On the other hand, removal of the trees will prevent the return of base cations, locked in the vegetation, to the soil as the trees die and decay, hence root-generated acidification will be permanent. Clearfelling will also reduce evapotranspiration and interception losses and thereby increase flow through the surface horizons so that runoff acidity may actually increase. If the trees are not totally removed then increased mineralisation and nitrification in the humus layer may lead to an increase in the flux of sulphate, nitrate and associated cations through the soil and a possible increase in drainage water acidity (Rosen and Lindmark-Thelin 1987). The effects of deforestation will also depend on the vegetation which colonises the area afterwards, if such vegetation is an acidophilic moorland vegetation such as *Calluna vulgaris,,* then the catchment acidification may be little changed (Krug and Frink 1983). Overall the impact of deforestation on streamwater acidity is far from clear, much depending upon the manner of deforestation and local site factors.

2.4.3 *Heather Burning and Forest Fires*

The burning of moorland vegetation in order to encourage young growth for hunting and shooting is a common practice in much of upland Britain. The effects on stream acidification may be considerable especially in the short term (Starr 1985). A particularly fierce fire may have a beneficial effect on stream acidification by returning base cations in the plant ash to the soil surface layers and, if the organic horizons are destroyed, by reducing the input of organic acids to the soil. Rosenquist (1981) reports that after a particularly fierce fire in Norway where the humus layers were totally lost, the pH of streams in the burnt area was 1-3 units higher than those in the surrounding unburnt area. The reduction in surface vegetation by burning will, however, also reduce evapotranspiration and interception rates and thereby increase flow through the surface horizons and the acidity of runoff. Runoff acidity may also be increased if the burn modifies soil structure so that the surface layers remain hydrophobic for several months. Hence the influence of fires on stream acidification is complex as the liming effect of the plant ash is mitigated to a varying extent by modifications to hydrological pathways.

2.4.4. *Fertiliser Inputs*

The addition of fertilisers to upland catchments is generally associated with commercial afforestation as the areas are too marginal for agriculture which would necessitate fertiliser application. The use of nitrogen fertilisers is generally accepted as leading to soil acidification at locations where the soil has a low buffering capacity and/or lime has not been added. This acidification occurs as the ammonium in the added fertilisers is nitrified, with each mole of ammonium producing two moles of hydrogen (van Breeman and Jordens 1983), typical reactions for urea and anhydrous ammonium are;

$$(NH_2)_2CO + 4O_2 \longrightarrow 2NO_3^- + 2H^+ + H_2CO_3 \qquad (2.6)$$

$$NH_3 + 2O_2 \longrightarrow NO_3^- + H^+ + H_2O \qquad (2.7)$$

It has been estimated that the addition of protons in an application of 100 Kg of ammonium-N per hectare may be 1.4 times that in 1000mm of rain at pH 4.0 (Cresser and Edwards 1987). In lowland agricultural areas the potential acidification is neutralised by the addition of lime to the soil which retains base saturation and pH. However, as upland afforested catchments are rarely, if ever, limed (Department of the Environment 1976) the use of fertilisers is another possible contributing agent to surface water acidification in these areas.

2.5 *ASSESSMENT OF ACIDIFICATION HYPOTHESES*

The crucial problem in assessing the relative importance of the competing hypothesis that seek to explain upland acidification is the lack of reliable long term records on pH changes. However, recent studies using different methods in Britain and Scandinavia have begun to produce quantified pH trends with time. In Sweden, Hallbacken and Tamm (1986) compare pH changes over the rotation period of a tree crop at the present day with results from a similar study performed in 1927 at the same location and using the same techniques. In both the 1927 and 1980's studies no change in the 'C' horizon pH is found relating to the stand age. However, compared with the 1927 results the 1980's results show a decline in 'C' horizon pH of 0.6 units. The authors attribute this decline to the impact of acid rain combined with biological acidification.

In Britain the U.K. Acid Waters Review Group (Warren et al. 1987) performed a 'cusum' analysis of long-term records of pH measurements in surface waters in order to determine if any long-term trends exist. They note, however, that the available pH records are generally inadequate for the detection of long-term trends (>10 year) in acidity due to changes in analytical techniques and the irregularity of sampling frequency. Within these constraints they report that an acidification trend was only observable at six of the seventy five sites for which data was supplied. It should, however be noted that areas likely to be most susceptible in this regard (eg. Southwest Scotland and the Highlands of Scotland) did not make returns to this survey.

Due to the increased concern that acidification may adversely affect the biological status of surface waters, the U.K. Acid Waters Review Group (1987) also compare Salmon catch records from Scotland for the decades 1952-61, 1962-71 and 1972-81, in order to see if any long-term trends were evident. The results show that of the 54 statistical catch districts on the mainland, 7 showed a severe decline in catch (>50%), 12 a decline in catch and 35 no decline in catch, with areas of the greatest decline tending to be mainly in the Southwest of the country (Figure 2.7). However, whilst no significant relationship was found between catches and rainfall pH or bedrock geology, a significant relationship is found with coniferous afforestation, so that all eleven districts with greater than 20% afforestation show a decline in catch.

Figure 2.7: Salmon catch trends for the 54 statistical catch districts in mainland Scotland (1952 - 1981).

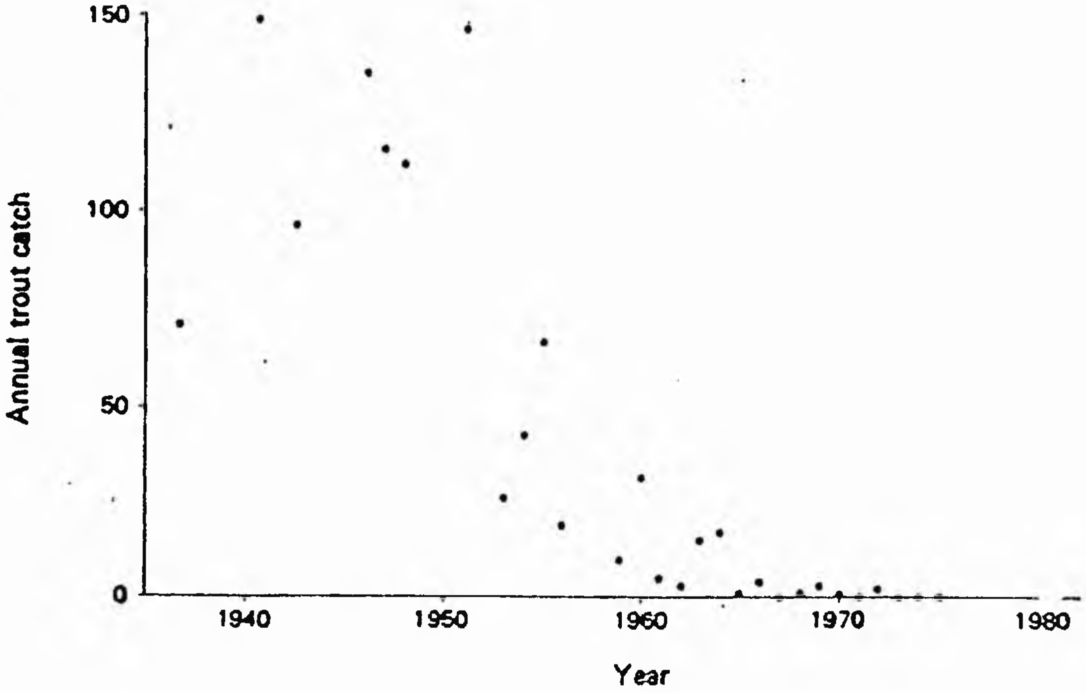


Figure 2.8: Fisheries catch records for Loch Fleet (1935 - 1985)

(after A.W.R.G. 1986)

However, the strongest evidence of progressive damage to fish stocks is from two unafforested lochs (Loch Enoch and Loch Fleet) in Galloway. The fisheries records from Loch Fleet in particular, clearly reveal a progressive decrease in catches over the last few decades to the stage where the Loch now appears effectively fishless (Figure 2.8). Thus on the basis of the available evidence the U.K. Acid Waters Review Group (1987) concludes that surface water acidification in Britain is localised in occurrence, but in such areas as it does occur, rates of acidification appear to be increasing. At the time of the review the Group considered the evidence insufficient to relate this acidification to any causal mechanism.

By far the most detailed pH reconstruction work has been that performed by Battarbee and his co-workers (Battarbee et al. 1985 and Flower et al. 1987) analysing the diatom content of ^{210}Pb dated sediment cores. This work has enabled the pH history of several lochs in the Galloway region of Scotland to be reconstructed, thus enabling the relative merits of the competing acidification hypotheses to be substantiated for this area.

In this work Flower et al. (1987) reconstructs pH trends for three afforested sites (Lochs Dee, Grannoch and Skirnow) which are compared with those for three unafforested sites (Round Loch of Glenhead, Loch Enoch and Loch Valley) (Figure 2.9). The results show that after long periods of stability all three unafforested sites have been acidified by 1 pH unit since the mid-late 19th century. In contrast the afforested Loch Dee catchment is much less acidic at present and acidification has proceeded at a much slower rate overall, probably because a part of this catchment is underlain by non-granitic

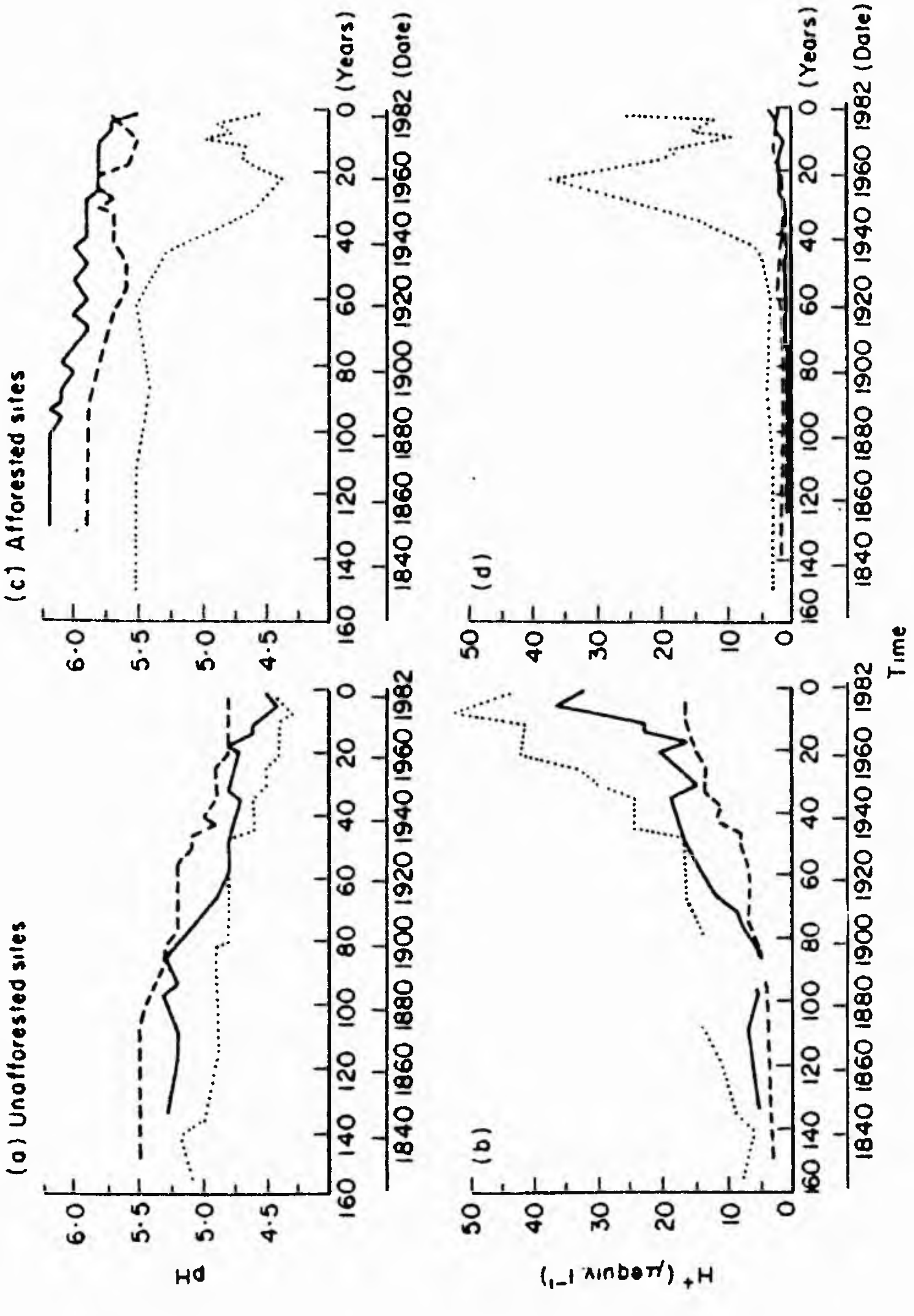


Figure 2.9: Lake water acidity changes in Galloway reconstructed by diatom analysis of sediments cores for three unafforested catchments (left), Loch Enoch (....), Loch Valley (____) and Round Loch of Glenhead (---) and three afforested catchments (right), Loch Grannoch (...), Loch Dee (___) and Loch Skirrow (---), as pH (a,c) and H+ concentration (b,d).

(after Flower et al. 1987)

sedimentary rocks whereas the other sites are underlain by granitic or metamorphosed rocks. Loch Skirnow like Loch Dee also experienced only mild acidification until the 1940's at which point the pH began to actually increase. The other afforested catchment Loch Grannoch experienced no decline in pH until the 1920's at which point a rapid decline occurred.

These results indicate that in the Galloway area the recently observed acidification has not been due to natural acidifying processes, coniferous afforestation or longer term land-use changes. Each of these alternative hypothesis can be systematically excluded. Thus, the recent acidification of all six lochs precludes the possibility that long term natural processes is a cause as Pennington (1984) has suggested for the Lake District. Afforestation is also not responsible as not only did the forested catchments become acidified before afforestation commenced in the area, the unafforested lochs are equally or more acidic. However, at Loch Grannoch the period of maximum acidity is closely associated with afforestation and it is therefore possible that for this site afforestation has accentuated a pre-existing trend of acidification. The long-term replacement of grassland by moorland vegetation, with the commensurate development of an acid humus due to land-use change, has also been hypothesised as a cause of acidification (Rosenquist 1978, Krug and Frink 1983). However, pollen analysis of the sediment cores from Loch Enoch (Battarbee et al. 1985) indicates that proportions of *Calluna* pollen, show a gradual decrease as the proportions of *Gramineae* pollen increases, rather than increasing as might be expected if the land-use change hypothesis was correct. In the same work the authors report that trace metal concentrations have increased since the 1850's in the sediment cores and this correlates with the onset of acidification. Increases in trace metal concentrations in rural lakes are often attributed to the deposition of atmospheric contaminants (Galloway et al. 1982) and are associated with the acidification of surface waters (Wright and Henriksen 1978).

2.6 *CONCLUSION*

For the Galloway area the sediment core evidence clearly indicates that the acidification of surface waters is primarily a result of anthropogenically derived acid deposition and that alternative explanations, as presently formulated, are not substantiated. In more recent work Battarbee and his co-workers have extended this sediment core work to the Highlands and Islands of Scotland, the English Lake District and Pennines and upland Wales (Battarbee et al. 1988) . This later work clearly indicates that the onset of surface water acidification in the upland areas of Britain occurs after 1800AD and coincides with the presence of trace metal contamination and high concentrations of carbonaceous particles, derived from fossil fuel combustion, in the sediment cores. This work also indicates that at all the afforested study sites, except for Loch Fleet in Galloway, acidification began before afforestation. and that in many of the study catchments land-use changes have led to a decline in moorland vegetation, rather than the reverse. Consequently, it can be concluded that although natural processes and land-use changes will cause upland areas to become acidified, the combustion of fossil fuels is the primary cause of the recent increase in catchment acidification rates in upland Britain.

3: MODELLING ACIDIFICATION OF SURFACE WATER
A REVIEW

3.1 *INTRODUCTION*

The complex nature of the physical, biological and chemical processes that govern the acidification of surface waters together with the cost and practical difficulties of setting up catchment studies has led to the development of several computer-based mathematical simulation models. These models all share two main aims: i) to increase our theoretical understanding of the processes that govern water quality in acidified catchments and ii) to provide realistic predictions, over varying timescales, of the impact of acid deposition on surface water quality. However, despite sharing the same aims the models range dramatically in scope and sophistication from ones which are simple and empirical to ones which are highly complex and process-orientated. In this review several models will be examined; commencing with a relatively simple empirical titration model and followed by several models of increasing complexity based on a systems approach.

3.2 *EMPIRICAL TITRATION MODELS*

The most widely known of this group of models is that originally developed by Henriksen (1979) and expanded by Henriksen (1980, 1982), Wright (1983) and Henriksen and Wright (1983). The model is used as a simple 'early warning' indicator in order to identify the first stages of surface water acidification and to predict possible future responses to changes in acid deposition levels. The model is based on two main premises; the concept of alkalinity and the electo-neutrality or ion balance principle. The electo-neutrality equation used is based on the sum of major ions, corrected for sea-salt inputs, equaling the sum of major anions, corrected for sea-salt inputs:

$$[H^+] + [Ca^{2+}] + [Mg^{2+}] + [Al^{3+}] = [SO_4^{2-}] + [HCO_3^-] \qquad (3.1)$$

It is further assumed that concentrations of sodium, ammonia, nitrate, potassium and organic species are negligible and that $[Al^{3+}]$ represents all the positively charged aluminium species. On the basis of this the alkalinity or is defined as;

$$Alk = [HCO_3^-] - [H^+] - [Al^{3+}] = [Ca^{2+}] + [Mg^{2+}] - [SO_4^{2-}] \qquad (3.2)$$

Following from this Henriksen (1980) defines acidification as pre-acidification alkalinity minus present day alkalinity. As few measurements of past alkalinity levels exist, the model derives a value on the basis of a regression relation between non-marine divalent ions and alkalinity from present day pristine environments;

$$Alk = 0.93\,(Ca^{2+} + Mg^{2+})^* - 14 \qquad (3.3)$$

where $(Ca^{2+} + Mg^{2+})^*$ is the non-marine
divalent ion concentration (ueq/l)

The constants in this relationship, which may vary from area to area, are seen as compensating for the background non-marine sulphate and the species considered as negligible in equation (3.1).

In the initial versions of the model, based upon regression relationships between species in present-day waters, acidification was assumed to be essentially a large scale titration of an alkaline solution with a sulphuric acid solution. However, Reuss et al. (1986) argue that these observed relationships only serve to support the charge balance principle, since with this approach it is not possible to determine whether or not an increase in sulphate deposition will lead to an increase in divalent ion concentrations or a reduction in alkalinity. An extended version of the model (Henriksen 1982) was developed to cope with these problems. In this it is assumed that acidification is directly proportional to increases in non-marine sulphate, and that the effects of acid deposition are reversible and independent of sea-salt inputs. Thus the extended model involves the calculation of the proportion of the change in non-marine sulphate concentrations that is accounted for by a change in divalent ion concentrations and leaves alkalinity unchanged. This proportion is termed the 'F' factor, where 'F' is defined as;

$$'F' = [Ca^{2+} + Mg^{2+}] \ / \ [SO_4^{2-}] \qquad (3.4)$$

As the major assumption of the model is that acid precipitation is the major cause of surface water acidification, determination of the 'F' factor is critical in the utilisation of the model. Henriksen (1982) calculates the 'F' value by assuming that alkalinity is equal to the background non-marine sulphate concentration. The calculated value will, however, be very sensitive to changes in the background non-marine sulphate concentration. (Wright and Henriksen 1983). Consequently whilst the value of 0.2 derived for southern Norway is probably reasonable for pre-industrial times in susceptible areas, it will probably be too low for other less susceptible regions (Reuss et al. 1986). Reuss et al. further contend that the 'F' value may change over time as a result of changes in soil base saturation. The model further assumes that seasalts "follow" each other through the catchment. Whilst in the short term the assumption may not hold due to the "sea-salt effect" discussed in Chapter 2, over the longer periods with which the model is generally concerned the assumption is realistic.

Overall the major advantage of this model is its simplicity which enables an estimate of the effects of increased acid deposition to be gained from relatively simple chemical analyses of surface waters.

3.3 *SYSTEMS BASED MODELS*

An alternative modelling strategy to that of Henriksen's is to use a systems-based approach. Models using this approach require two main sets of inputs (Figure 3.1), first a theoretical knowledge of the physical, chemical and biological processes occurring in a catchment and second detailed field observations with which to calibrate and validate the model (Whitehead et al. 1986). The relative extent to which these sets of inputs are known gives rise to two main systems-based modelling approaches, systems synthesis and systems analysis.

Systems synthesis models require a detailed knowledge of the major system processes and the theoretical behaviour of such processes. As the complexity of a catchment's hydrochemical processes prevents precise mathematical representation, at present systems synthesis models assume that these processes can be spatially and/or temporally aggregated. Despite this aggregation, however, the model still attempts to reproduce the deterministic behaviour of the catchment hydrochemical processes. Systems analysis models, in contrast, take a "black-box" approach with catchment processes represented by mathematical functions and do not attempt to replicate the complex deterministic behaviour of catchment processes. A major technique in this approach is the use of time series analysis.

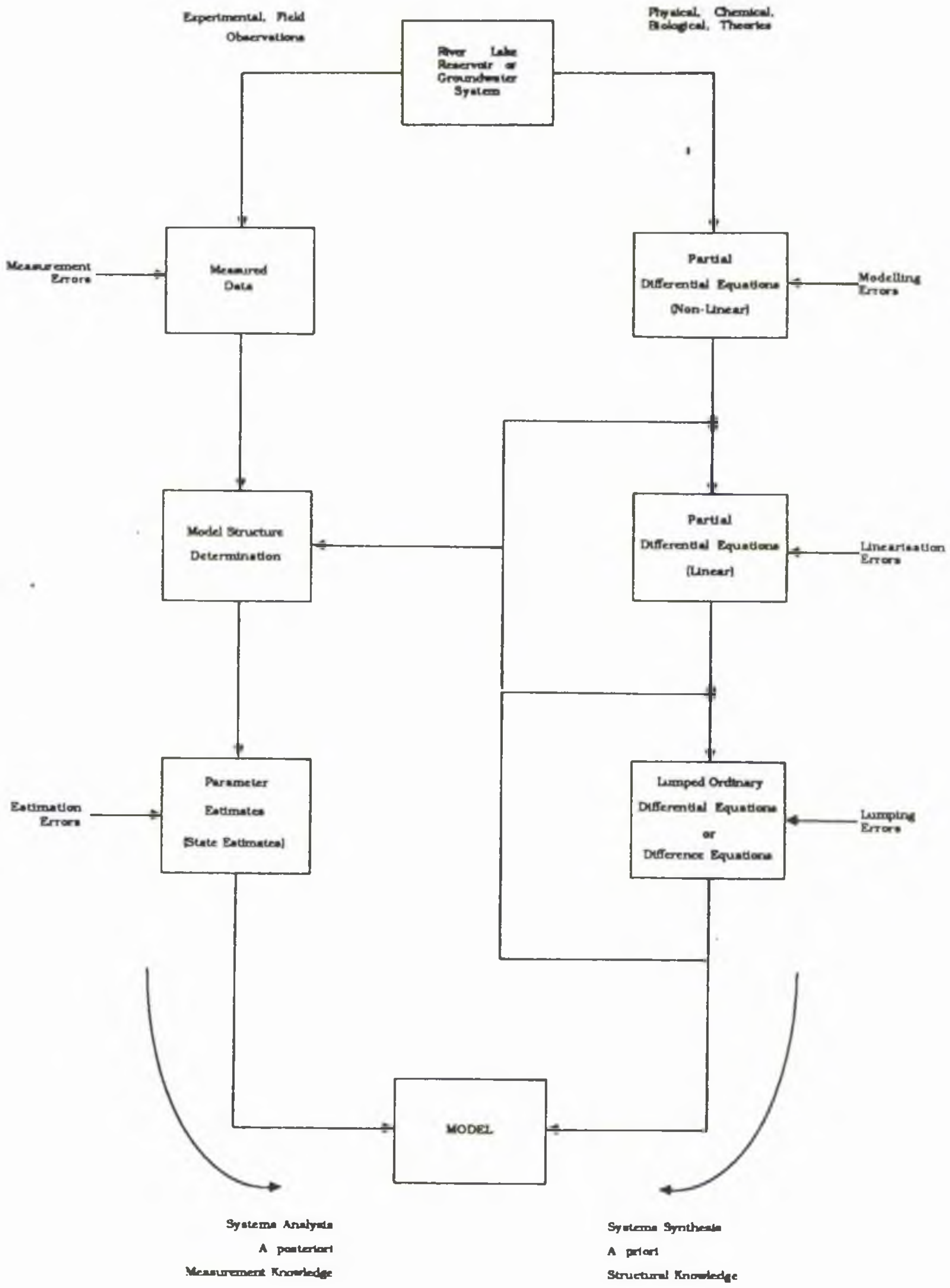


Figure 3.1: The combination of theoretical knowledge and field data in the development of modelling strategies.

(after Whitehead et al. 1985)

3.3.1 *Time Series Modelling*

The time series approach in systems analysis produces an empirical input-output or 'black box' model on the basis of statistical inference derived directly from the observed data. Such models are based on the assumption that a "law of large systems" (Young 1978) applies. As such, they are especially useful where system processes are particularly complex and where the overall input-output budget of the system is of major importance (Whitehead et al. 1986). Such criteria makes this modelling strategy especially useful for analysing the change in the pH of surface waters as a result of increased acid deposition.

The general form of a simple single input-output time series model consists of two parts, a deterministic process model and a stochastic noise model (Figure 3.2). The system output (Y_t) is considered to result from the deterministic input (U_t), which is responsible for most of the output variation, together with a stochastic input (a_t) which accounts for the inevitable uncertainties in the relationship. Consequently the observed output at time, t, Y_t is the sum of the outputs from the deterministic model (X_t) and the stochastic model (e_t) at the same instance, i.e:

$$Y_t = X_t + e_t \tag{3.5}$$

Both X_t and e_t are generated by autoregressive moving average (ARMA) discrete time series models (Box and Jenkins 1970) where the autoregressive term represents memory and correlation between the output data sequence and the moving average term represents the contribution of the input at each time step. The general form of the deterministic model is:

$$A|z^{-1}|\ X_t = B|z^{-1}|\ U_t \tag{3.6}$$

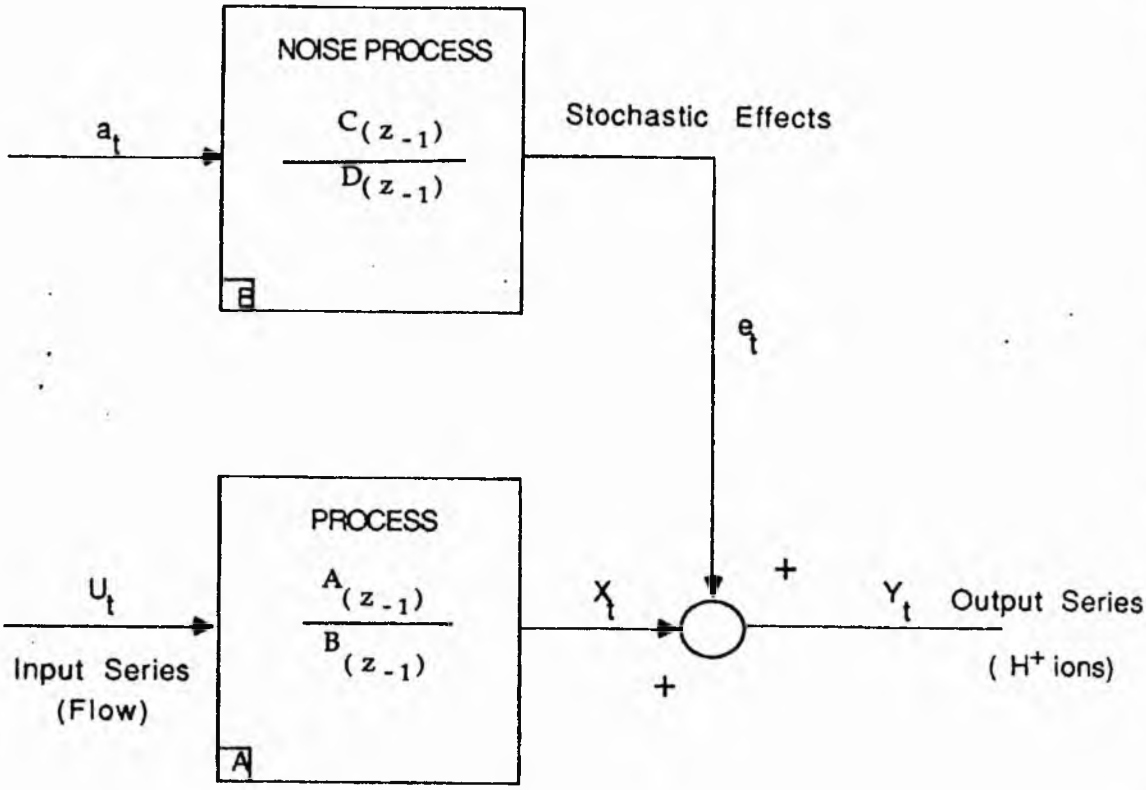


Figure 3.2: An Input - Output time series model

where z is a backward shift operator , so that, $z^{-1}X_t = X_{t-1}$ and $A|z^{-1}|$ and $B|z^{-1}|$ are both polynomials in z^{-1}. Consequently as a difference equation the model takes the form:

$$X_t = -a_1X_{t-1} - a_2X_{t-2} \ldots -a_nX_{t-n} + b_0U_t + \ldots + b_nU_{t-n} \qquad (3.7)$$

The stochastic model is of a similar form so that the full transfer function model is:

$$Y_t = [A(z^{-1})/B(z^{-1})]U_t + [C(z^{-1})/D(z^{-1})]a_t \qquad (3.8)$$

The system output (Y_t) is consequently seen as dependent on past values of the output (Y_t) as well as past and present input values(U_t), together with past and present values of a hypothetical white noise input (a_t)

Such time series techniques have been applied to a variety of environmental situations, however, the models produced by Whitehead et al. (1986) are the first examples of the application of such techniques to the study of surface water acidification. In the models produced by Whitehead et al. (1986) the system output (Y_t) represents the hydrogen ion concentration in streamwater and is related to the previous day's hydrogen ion concentration and runoff by the two parameters A and B. The two parameters are estimated from the observed data by the use of a recursive instrumental variable algorithm. Consequently, variability in the parameter values through the analysis time period can be examined in order to investigate the catchment processes that influence acidification.

The application of time series techniques at Loch Dee in Scotland, Plynlimon in Wales and Birkenes in Norway indicates that such models can accurately simulate hourly, daily and weekly timescales. As the authors note, however, the accuracy is reduced as the data sampling timescale increases relative to the catchment response time. A further weakness of time series models is due to the fact that the model parameters are constantly updated from the observed data. Consequently, the models are unable to simulate long term changes in streamwater chemistry in response to changes in deposition loadings or catchment land-use. However, the time series technique may be very useful in an initial analysis of a catchment, eg identifying the major processes that determine streamwater chemistry, prior to more detailed process-based modelling studies. This role is illustrated particularly well by the analysis of streamwater chemical data at Birkenes by Beck et al. (1987).

3.3.2 *Systems Synthesis Models*

The vast majority of acidification models are based on the system synthesis approach, such models include the "Birkenes" model (Christophersen et al. 1982, Seip et al. 1986), "MAGIC" (Cosby et al. 1985a, 1985b), "ILWAS" (Chen et al. 1983, Goldstein et al. 1984), "Trickle Down" (Schnoor et al. 1984 Schnoor and Stumm 1985;), "Pulse" (Bergstrom et al. 1985) and "RAINS" (Alcamo et al. 1985). Whilst these models show considerable variation in modelling philosophy and structure there is, however, a considerable convergence of thought concerning the key processes. Thus to a greater or lesser extent all the models accept the importance, through the charge balance principle, of the anion mobility concept (Seip et al. 1980), cation exchange and the dissolution of aluminium in determining short-term solution chemistry together with the importance of mineral weathering in determining the longer term response. This section of the review will focus on three such models namely, "MAGIC", "Birkenes" and "ILWAS". The "MAGIC" and "Birkenes" models will be examined initially as they are not only the two most widely adopted acidification models, but are also the only systems synthesis models to have been applied to catchments in upland Britain. The "ILWAS" model will then be examined in considerable detail as an evaluation of this model, as a tool for studying acidification at Loch Dee in Southwest Scotland, forms the bulk of the work in this thesis.

3.3.2.1 "MAGIC" (Model of Acidification of Groundwater In Catchments)

The main objectives in the development of this model were twofold. The first objective was to develop a relatively simple process-orientated model which could accurately simulate the chemical behaviour of catchments so as to enable long-term predictions of the effects of acid deposition to be made. The second objective was to determine the extent to which spatially distributed physical and chemical processes in a catchment can be "averaged" or lumped without affecting a model's ability to reproduce a catchments behaviour (Cosby et al. 1985a). The conceptual basis of the model lies in the research reported by Reuss and Johnson (1985) whereby soil system processes are described by equilibrium reactions involving the dissolved and adsorbed phases of ions in the soil-soilwater system, together with the effects of carbonic acid resulting from the elevated carbon dioxide levels in the soil. Soil chemical processes simulated in the "MAGIC" chemical module thus comprise the following; i)cation exchange in soils, ii)aluminium mobilisation and solubility, iii)carbonic acid dissociation, iv)anion retention in soils and v)mineral weathering.

Cation exchange reactions between the soil and soilwater are assumed to involve only the four base cations (sodium, potassium, calcium and magnesium) and aluminium. In these reactions the total cation charge in solution is determined by the anions in solution through the charge balance principle, whilst the relative amount of each cation on the exchange complex is determined by the use of ion exchange equilibria. The general form of such exchange equilibria is:

$$K_{a,b} = (A^{a+})^{b} / (B^{b+})^{a} \qquad (3.9)$$

where $K_{a,b}$ is the activity ratio for two positively charged ions A and B with valences a^+ and b^+ respectively and the brackets represent ion activities in solution (Bolt 1967). As the value of $K_{a,b}$ is dependent on the fraction of each ion on the exchange complex, this particular form of exchange equilibria restricts simulations to the short term (ie weeks to months) where changes in the exchange fraction will not be significant. Consequently, in order to evaluate the effect of changes in the amount of an ion on the exchange complex, "MAGIC" makes use of a modified form of the Gaines-Thomas exchange coefficient (Gaines and Thomas 1953), for example the equilibrium expression for the calcium - sodium exchange reaction:

$$S_{CaNa} = \frac{\{Na+\}^2 \quad E_{Ca}}{\{Ca^{2+}\} \quad E_{Na}^2} \qquad (3.10)$$

where the braces represent the aqueous activities, E_{Na} and E_{Ca} the equivalent fraction of the exchange site occupied by the respective ions, and S is the selectivity coefficient. As the selectivity coefficients represent cation exchange reactions "lumped" over the entire catchment, their values may be estimated either from field data or via model calibration.

Aluminium solubility reactions in the model are based on the assumptions that there is an equilibrium between Al^{3+} in the soil solution and a solid phase of $Al(OH)_3$ and that as solution concentrations of H^+ and Al^{3+} vary the reversible reaction

$$3H^+ + Al(OH)_3 = Al^{3+} + 3H_2O \qquad (3.11)$$

occurs instantaneously. The equilibrium expression for this reaction is;

$$\{Al^{3+}\}/\{H^+\}^3 = K_{Al} \qquad (3.12)$$

As with the cation selectivity coefficients, K_{Al} is a "lumped" value assumed to be representative of the entire catchment, and consequently is also a model parameter estimated with each application. The model also includes solution phase reactions of Al^{3+} with sulphate and fluoride ions, the equilibrium constants for these reactions are, however, seen as unvarying in different applications.

Inorganic carbon reactions included in the model involve the hydration of carbon dioxide to produce carbonic acid together with the subsequent breakdown of the carbonic acid and the production of carbonate, bicarbonate and hydrogen ions. The model also assumes that the soil water is in equilibrium with carbon dioxide in the soil-air with the partial pressure of carbon dioxide being a model calibration parameter.

The above three processes form the equilibrium part of the model (Cosby et al. 1985a). Whilst this is a useful tool for short term predictions, (i.e. weeks), the aim of "MAGIC" is to predict the long term effects (i.e. decades) of acid deposition on streamwater chemistry. Consequently, this equilibrium model is coupled to a dynamic model (Cosby et al. 1985b) based on the input-output mass balance of ions in the catchment.

The mass balance is applied for each major base cation and strong acid anion in the form of a dynamic mass balance equation;

$$DX_t / dt = Fx + Wx - Q*(X) \qquad (3.13)$$

where X_t is the total amount of the ion (x) in the catchment; Fx is the atmospheric flux to the catchment; Wx is the mineral weathering flux; (X) is the ion concentration in streamwater and Q is stream discharge. The atmospheric and mineral weathering fluxes are both model inputs. An upper limit to the weathering rates is provided by the observed net catchment losses. The actual rates used in the model are chosen by a trial and error procedure until the model accurately reproduces observed stream concentrations and adsorbed values of base cations. The strong acid anions, with the exception of sulphate, are assumed to have no adsorbed phase. Sulphate adsorption is determined by a further sub-model (Cosby et al. 1984), based on a simple non-linear Langmuir isotherm of the form:

$$E_s = E_{mx} * (SO_4^{2-}) / (C + (SO_4^{2-})) \qquad (3.14)$$

where E_s is adsorbed sulphate, (SO_4^{2-}) is the dissolved sulphate concentration, E_{mx} is the maximum adsorption capacity of the soils and C is the half-saturation constant. Such a non-linear process leads to a decrease in the response time of the system to changes in atmospheric deposition, as the amount of adsorbed sulphate is increased.

In contrast to the complexity with which catchment chemistry is described the model's description of catchment hydrology is very simple using average hydrological conditions such as mean annual precipitation and streamwater flow volumes. In its original form as applied at White Oak Run in Virginia U.S.A., a catchment is represented in the model by two compartments, one describing soil processes and the other stream processes (Figure 3.3). However, if a catchment's soils show a distinct separation of A and B horizons, with different processes in the two horizons, the model may be expanded to include two soil compartments. In the same manner, in regions where snowmelt is an important hydrological component, another compartment may be added to represent snow accumulation and melt processes.

At White Oak Run the model faithfully reproduced present-day water chemistry and gave plausible values for the model parameters. Over the longer term the model also indicated the importance of sulphate saturation in soils in determining the response of streamwaters to changes in sulphate deposition. As the authors noted, however, verification of the model would require years/decades of catchment monitoring. Alternatively model verification maybe accomplished through the reconstruction of past water chemistry and comparing the results with historical records.

Accurate data of past water chemistry is in general severely limited. At Loch Dee in Galloway, however, a palaeoecological analysis of sediment cores (Battarbee et al. 1985, Flower et al. 1987) has enabled the pH record of the surface waters to be reconstructed for several hundred years. Consequently "MAGIC" was applied to one of the sub-catchments at Loch Dee, the moorland Dargall Lane, by Cosby et al. (1986a). This location was also studied in order to assess how well the

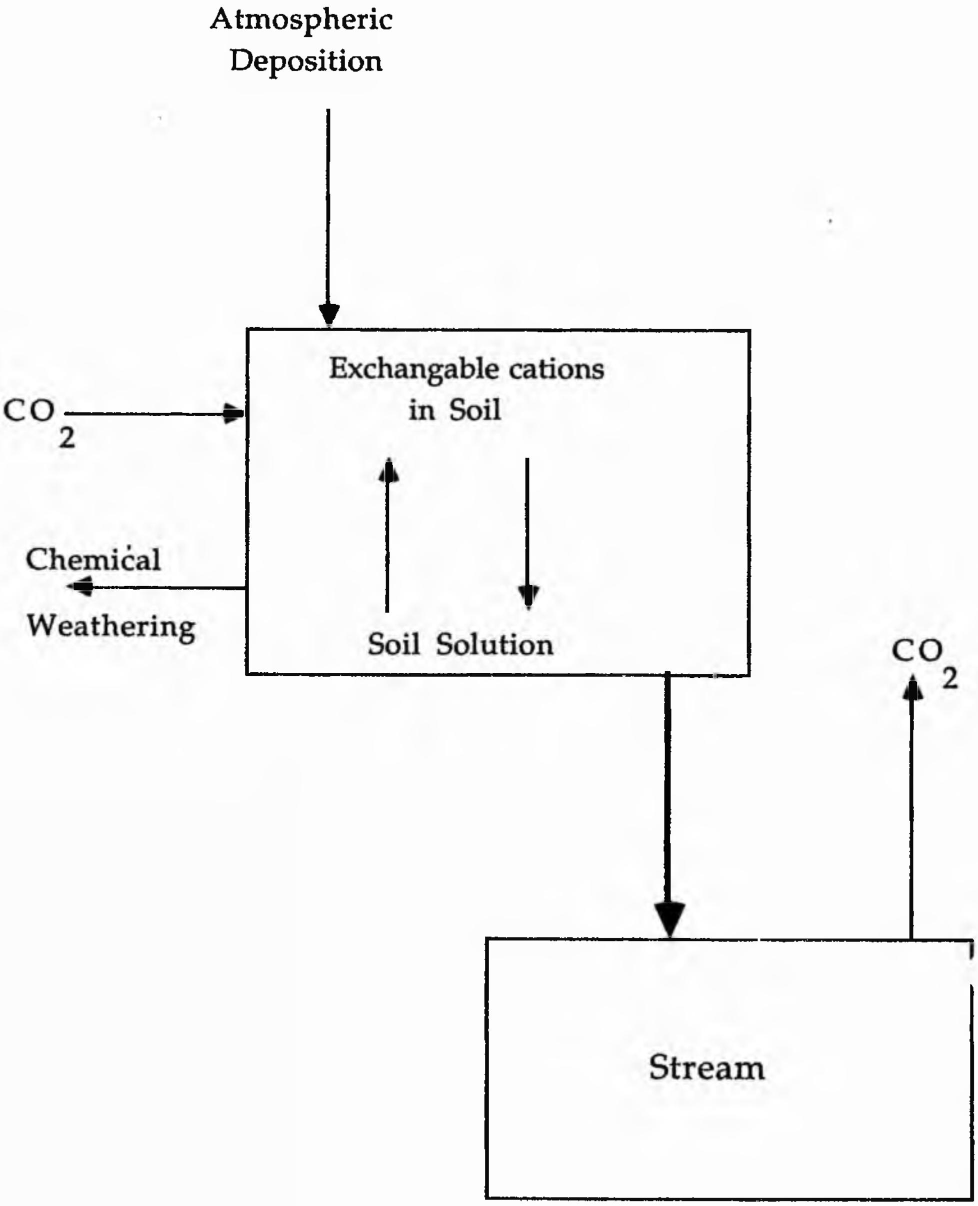


Figure 3.3 Schematic view of MAGIC (Model for Acidification of Groundwater in Catchments).

(after Cosby et al. 1985a,b)

model would perform in an area subject to high seasalt inputs. The simulations indicate that the conceptual basis of the model is well founded with the model predictions of past pH closely following the historical reconstruction of Battarbee et al. (1987). Furthermore, the model was also able successfully to cope with the high levels of seasalt inputs. Later work at Loch Dee (Neal et al. 1986) involved the use of "MAGIC" as a tool to investigate the effects of coniferous afforestation and/or acidic deposition on streamwater acidity. In this work the influence of the trees was confined to increased dry and occult deposition and no allowance was made for biomass uptake and changes in hydrological pathways. Despite these limitations the simulations indicated that coniferous afforestation can have a significant deleterious effect on streamwater acidity. Furthermore, the results indicated that any reduction in acidic deposition would have to be significantly greater for forested than moorland catchments, if any increase in streamwater acidity is to be prevented.

A further recent extension of "MAGIC" has been the use of Monte-Carlo techniques to reduce the uncertainty in parameter estimation (Cosby et al. 1986b, Musgrove et al. 1988a). The use of such techniques indicates that "MAGIC" maybe a useful tool for examining long-term regional scale as well as catchment scale responses to acid deposition (Musgrove et al. 1988b).

3.3.2.2 "The Birkenes model"

Whereas "MAGIC" is primarily concerned with the long term response of catchments to acid deposition, the "Birkenes" model, (Christophersen and Wright 1981, Christophersen et al. 1982), was developed in order to determine if the short-term response of streamwater chemistry to acid deposition could be adequately explained by a small number of physical processes.

The basis of the model is the hydrological submodel (Figure 3.4) which is a modification of the two reservoir system developed by Lundquist (1977). In this model the upper reservoir may be considered as pipeflow or fast throughflow which enters the streams directly and consists of water that is mainly in contact with the humus and upper soil horizons. The lower reservoir, in turn, provides baseflow and represents water that is mainly in contact with the deeper mineral soil.

The chemistry component of the model is built on top of the hydrological model and consists in turn of two sub-models for sulphate dynamics and cation partitioning. There are two major assumptions in the chemistry model; firstly that sodium and chloride follow each other through the system and take no part in determining the concentrations of other species in the stream and secondly that concentrations of potassium, ammonium, nitrate, bicarbonate and organic anions can be ignored as they account for only a few percent of the ionic sum at Birkenes (Christophersen et al. 1982). The model chemistry is consequently implicitly based on the mobile anion concept (Seip 1980), with concentrations of the remaining cations hydrogen, calcium, magnesium, and aluminium balanced by concentrations of sulphate.

The sulphate sub-model (Christophersen and Wright 1981, Christophersen et al. 1982) attaches chemical processes involving

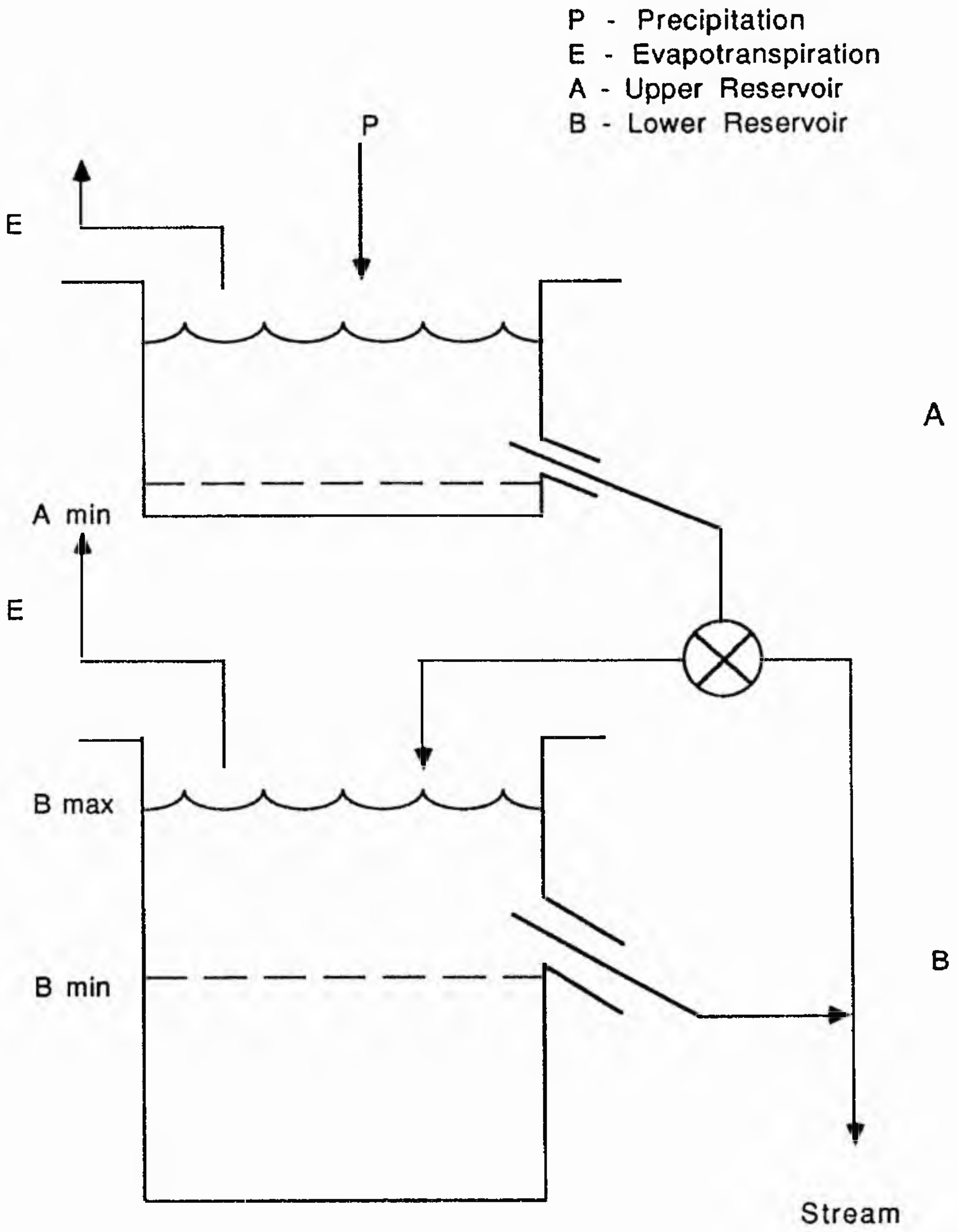


Figure 3.4: Schematic Diagram of the "Birkenes" Model

sulphate to the two compartment hydrological model. In the upper reservoir it is assumed that all sulphate of atmospheric origin remains water soluble. It is further assumed that sulphate concentrations in drainage waters from the reservoir (C_a) are directly proportional to the amount of water-soluble sulphate on the solid phase (F_a), such that essentially a linear sulphate adsorption isotherm is obtained i.e.

$$C_a = K_a F_a \tag{3.15}$$

Mineralisation of sulphate in the upper reservoir during dry periods is also included in the model by allowing F_a to increase by a fixed amount for each day the reservoir is empty.

In the lower reservoir the only process considered is adsorbtion/desorbtion. In contrast to the upper reservoir a more complex non-linear adsorbtion isotherm is used of the form;

$$dC_b/dt = k_b(C_{eq} - C_b) \tag{3.16}$$

where k_b is the adsorbtion rate coefficient, C_{eq} is the equilibrium concentration and C_b is the concentration of sulphate in drainage water from the lower reservoir. Consequently, concentrations are assumed to fall exponentially towards a fixed equilibrium value. Also in order to prevent unrealistic buildup of sulphate concentrations in dry periods, when evapotranspiration occurs, sulphate is removed from solution and transferred to the solid phase.

The cation sub-model is linked to the sulphate sub-model by the assumption that the sulphate concentration in each reservoir is balanced by the total concentration of hydrogen, calcium, magnesium, and aluminium and that the reservoirs are ideally mixed.

Aluminium concentrations in the model are produced by a gibbsite equilibrium equation of the type used in "MAGIC" eq.(3.12), together with a correction term to account for aluminium complexes with fluoride and organic compounds. The divalent cations calcium and magnesium are assumed to vary together and consequently are summed and lumped together as M^+. The relationship between $[H^+]$ and $[M^+]$ in the upper reservoir is, as in "MAGIC", governed by cation exchange and is modelled by an equation of type eq.(3.9). The adsorbed ion concentrations in the soil, however, are assumed to be constant thereby leading to a constant selectivity coefficient or lime potential (Bache 1984). In the lower reservoir the partitioning between $[H^+]$ and $[M^+]$ is assumed to be determined by mineral weathering. This is seen as a simple exponential decrease in $[H^+]$ balanced by a commensurate increase in $[M^+]$.

This separation of cation exchange and mineral weathering into separate reservoirs, however, is criticised by Reuss et al. (1986) who suggest that it would be more realistic to incorporate both processes in each reservoir. However, a different chemistry in each reservoir may not always be necessary, as exemplified at Storgama in Norway where Christophersen et al. (1984) find that the incorporation of cation exchange in each reservoir was adequate. In order to reproduce the observed data at Storgama and to allow predictions of the effects of acid deposition, the model was modified in several ways. These were the inclusion of a snow reservoir, the addition of the anions nitrate and bicarbonate so that the charge balance equation is extended as follows;

$$H^+ + 2M^{2+} + 3Al^{3+} = 2SO_4^{2-} + NO_3^- + HCO_3^- \qquad (3.17)$$

and by the inclusion, in the upper reservoir, of a relationship between solution concentrations of bicarbonate and carbon dioxide of the form;

$$[H^{+}][HCO_3^{-}] = K{*}P_{co} \quad (\lg K = -7.71 \text{ at } 5.0° \text{ C}) \qquad (3.18)$$

where P_{co} is the partial pressure of carbon dioxide.

Several other modifications have been made to the model in the course of its application at other sites. Thus Rustad et al. (1986) in an application at Harp Lake in Canada modify the hydrological model to include a 'piston flow' component, whereby in certain circumstances water from the upper reservoir displaces a equal amount from the lower reservoir. The inclusion of this process serves only to alter the streamwater chemistry as the total discharge remains constant. In the same work the chemical model is also directly modified to include organic acids and their dissociation with increasing pH.

More recently attention has become focused on the possible role of high seasalt inputs in short term streamwater acidification. Consequently Grip et al. (1985), in studies of several Swedish catchments, further extends the model by the inclusion of the chloride anion. At Plynlimon in Wales, however, Neal et al. (1988) find that the model is unable successfully to reproduce chloride dynamics. Consequently, several methods are suggested by which the model structure could be modified, if chloride dynamics are to be successfully reproduced. The main suggestions are to include a representation of a dynamic interchange of water between the upper and lower reservoirs and/or a semi-mobile chloride store in the upper reservoir.

A particular advantage of the "Birkenes" model is that it can serve as a management tool, in that it enables an account of the response of streamwater chemistry to changes in physical and chemical processes within a catchment to be made. Thus Whitehead et al. (1986) use the model to assess the influence of hydrological changes, such as may be associated with coniferous afforestation, on streamwater acidity. Then, on the basis of the model predictions, they are able to suggest methods by which the impact of such changes could be reduced.

The apparent success of the "Birkenes" model in the prediction of observed streamwater chemistry at several differing sites in Northwest Europe and North America would appear to support the contention that the model processes are able to explain the major trends in streamwater chemistry. As the model parameters need to be recalibrated for each site, however, the apparent agreement between the observed and predicted chemistry may only be taken as an indication of the generality of the processes incorporated in the model.

3.3.2.3 ILWAS (the Integrated Lake Watershed Acidification Study) model

The ILWAS model was developed as part of a detailed investigation into surface water acidification in the Adirondack mountains of New York State and is probably the most detailed acid deposition model developed to date (Chen et. al. 1983, 1984, Goldstein et al. 1984, Gherini et al. 1985). It consists of a hydrological sub-model coupled to a chemical sub-model with both of the sub-models in turn divided into a number of modules, so as to describe more accurately spatial heterogeneity within a catchment. Consequently ILWAS is far less "lumped" than either "MAGIC" or "Birkenes", with the catchment divided both vertically and horizontally into a number of homogeneous compartments.

Horizontally a catchment is divided into land sub-catchments, stream segments and, if present, a lake (Figure 3.5). The land sub-catchments are determined on the basis of their topography, vegetation, soils and underlying bedrock and the stream segments on the basis of length, depth, typical cross section and a stage-flow relationship. The land sub-catchments are also vertically segmented into a number of compartments that represent the canopy, snowpack and up to 5 soil layers (Figure 3.6). Each of these compartments is treated mathematically as a continuously stirred tank reactor (CSTR), with concentrations of all species determined by the application of mass concentration, equilibrium and kinetic principles. A lake, if present, is also sub-divided horizontally into a number of mixed layers to allow the calculation of temperature and water quality profiles.

Inputs to the model are both time-dependent and time independent. Time dependent inputs include daily precipitation, maximum and minimum daily temperatures, monthly averaged precipitation quality and wet bulb temperatures. Time independent inputs include constants and parameters to describe the physical, chemical and biological processes that occur within the catchment. Amongst such inputs are the catchment's physical dimensions, ground slope, slope aspect, canopy type (% coniferous, deciduous or open), leaf area index, soil horizon depths, hydraulic conductivities, mineral composition, base saturation indices and cation exchange capacities. On the basis of these inputs the model computes daily

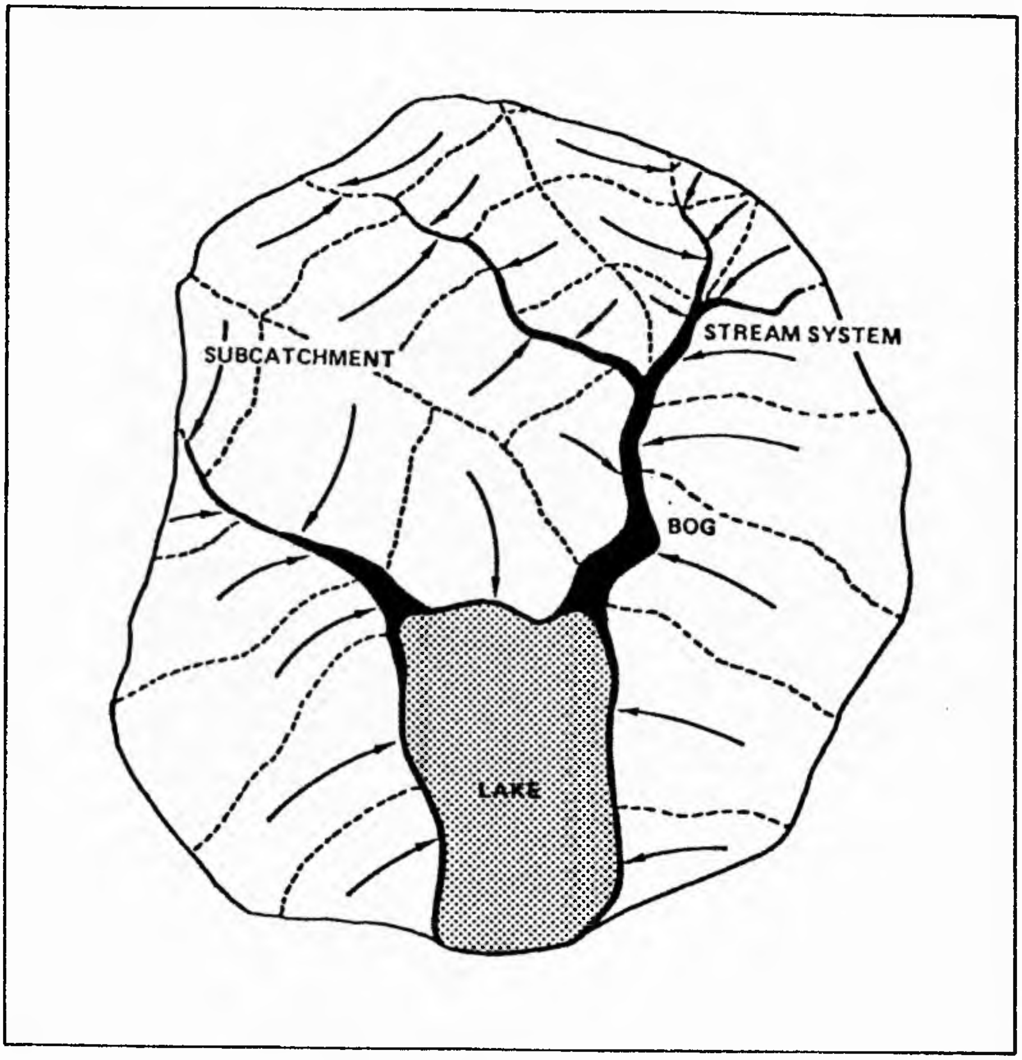


Figure 3.5: The horizontal segmentation of a catchment as in a generalised "ILWAS" simulation.

(source: Chen et al. 1983)

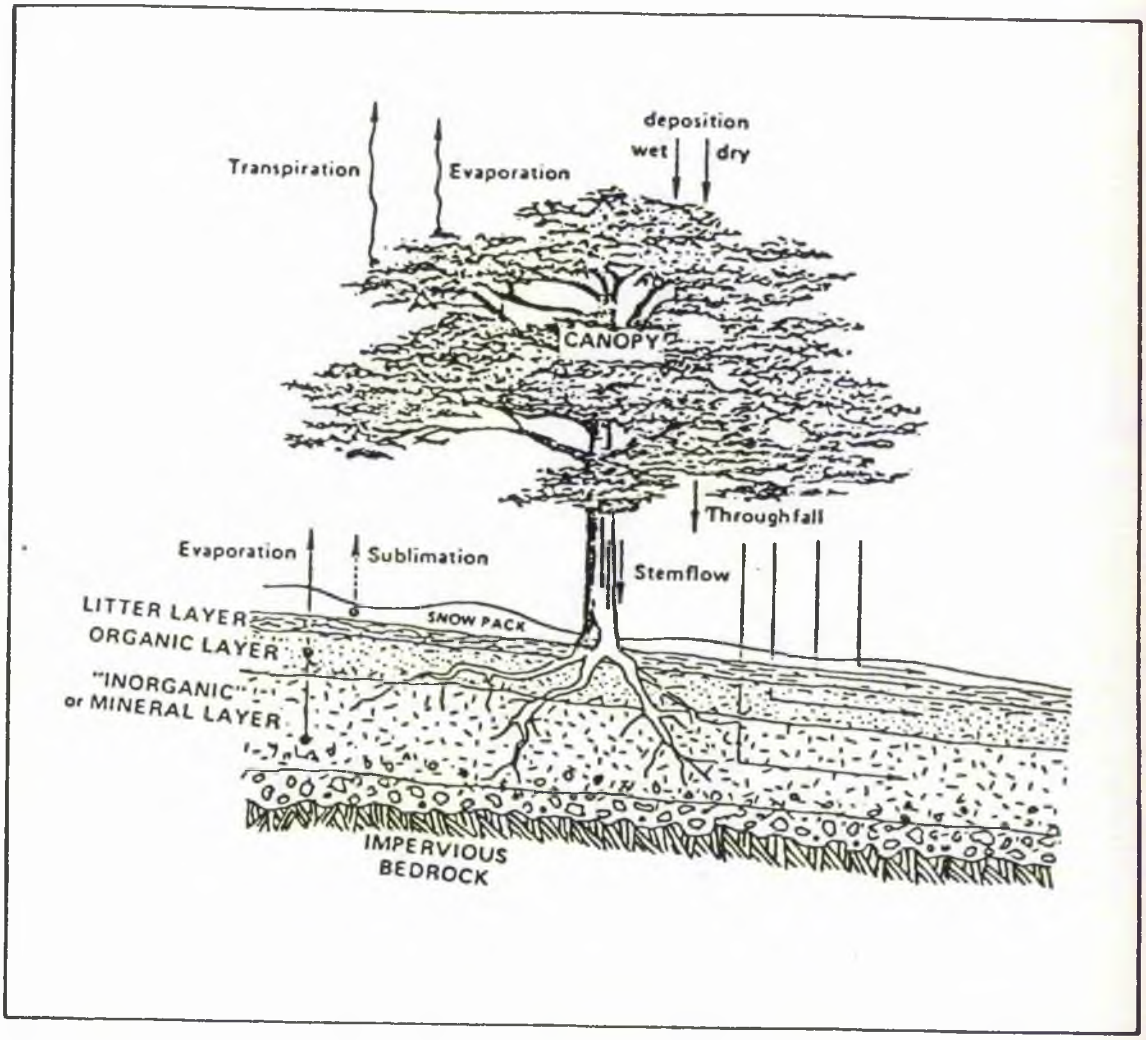


Figure 3.6: The vertical segmentation of a catchment as in a generalised "ILWAS" simulation.

(source: Chen et al. 1983)

flows and water balance and associated chemical fluxes throughout the catchment system. In the following section of the review the formulations underlying firstly, the hydrological sub-model and secondly the chemical sub-model will be examined, followed by a review of the solution techniques used in linking the two sub-models.

A) The hydrological sub-model

The hydrological component of the ILWAS model is far more complex than that of any of the other models reviewed. In the simulation of water routing through a catchment five basic processes are considered;

i) Interception and Evapotranspiration
ii) Snow Accumulation and Melting
iii) Soil and Ground Water Hydraulics
iv) Stream Hydraulics
v) Lake Hydraulics

In the hydrological model precipitation is separated into rainfall and snowfall components, on the basis of a snow fractionation temperature (a model input parameter) and the ambient air temperature. Thus precipitation at periods when the air temperature is above the fractionation temperature is seen as rain. Snowfall is assumed to reach the ground without interception whereas rainfall is assumed to be intercepted onto the vegetation canopy. The rainfall interception (Is) is seen as being related to the leaf area index (LAI) of the canopy as follows:

$$Is = [\, LAI_{(month)} \,/\, LAI_{(max)} \,] * D_{max} \qquad (3.19)$$

where D_{max} is defined as the potential interception storage for the month where LAI is maxima. Subsequently throughfall is assumed to occur when rainfall exceeds the canopy interception capacity. Daily potential evapotranspiration (P.E.) is determined as the product of the mean air temperature, an evapotranspiration function based on the catchment latitude (Hargreaves 1974), a humidity correction function together with global and seasonal calibration parameters and is consequently a major calibration parameter. In ILWAS P.E. is assumed to be firstly satisfied from canopy interception storage. If, however, this is insufficient then the unsatisfied P.E. is removed from the soil layers on the basis of root distribution. Within any soil layer it is further assumed that all moisture above field capacity is available for evapotranspiration and that below field capacity actual evapotranspiration is exponentially reduced to zero moisture capacity.

Snow accumulation in the model is determined by a mass balance approach, with dissipation of the resultant snowpack controlled by sublimation together with rain and temperature induced melting. Both the rain and temperature melt rate coefficients are input calibration parameters whereas the sublimation rate is assumed to be constant. Water released by melting, rather than directly draining from the snowpack, is assumed to be held in the pack until capillary storage is exceeded.

The description of soil and ground water hydraulics involves the separation of a catchment soil system into several soil layers. Each soil layer in turn is described by a volumetric soil moisture content, a saturated moisture content, field capacity and hydraulic conductivity. On entry to a layer water is assumed either to increase soil moisture content, to be lost in evapotranspiration, to percolate to the horizon below or to become lateral flow to a stream or lake segment. The water balance of any particular layer is subsequently derived as follows:

$$A_jZ_j * d0_j/dt = A_jP_{j-1} - A_j E_{pj} - P_j A_{j+1} - L_j \qquad (3.20)$$

where A_j = the area of layer j; Z_j = thickness of layer j; 0_j = average volumetric water content of layer j; A_{j+1} = the surface area of layer j+1; P_{j-1} = percolation from layer j-1; E_{pj} = actual evapotranspiration from layer j; P_j = percolation from layer j to the layer below; and L_j = lateral flow from layer j. This means that the moisture content of a layer is equal to the moisture input from the layer above, minus outflow from the layer as evapotranspiration, percolation and lateral flow.

Both vertical and lateral flows are essentially modelled by the use of a Darcian approach. Two simplifying assumptions, however, are made with regard to unsaturated flow, first that the unsaturated hydraulic conductivity varies linearly between field capacity and saturation and second that the unsaturated pressure gradient term may be neglected. On this basis the percolation rate of any layer is assumed to be zero at and below field capacity and to increase linearly with the soil moisture content up to the saturated hydraulic conductivity. Likewise lateral flow is determined as the product of the hydraulic conductivity, soil layer width, hydraulic gradient and an effective saturated depth, where the effective saturated depth is assumed to be zero at field capacity and increase linearly to the layer depth at saturation.

Equation (3.20) is solved for each layer in turn from the top down. If, however, the percolation flux downwards is greater than the capacity of the underlying layer an iterative correction is made in the overlying layer. Consequently, if the entire profile is saturated, or if the infiltration capacity is limited by the saturated hydraulic conductivity, water is assumed to accumulate on the soil surface. Surface runoff is subsequently calculated by the use of Manning's flow equation together with a water balance equation.

Flow dynamics in each stream segment are determined by the Muskingum routing technique where stream inflow minus outflow, or stream storage, is seen as equal to the change in stage (Figure 3.7), consequently:

$$I - O = d(A_S D) / dt \qquad (3.21)$$

Thus as inflow (I) to the most upstream segment is known and as the outflow (O) and surface area (A_S) are functions of water depth (D), an input parameter, the solution of Eq. (3.21) provides the segment depth, surface area and outflow. As outflow from each upstream segment becomes the inflow to the next downstream segment, the routing of water through the catchment can be calculated.

Discharge from a lake, if present, is derived from a simple water balance equation of the form

$$dV / dt = P + G + S - E - O \qquad (3.22)$$

where V = lake volume; P = Precipitation or snowmelt rates on the lake surface; G = Groundwater seepage into the lake; S = Streamflow input to the lake; E = Evaporation from the lake; and O = lake discharge.

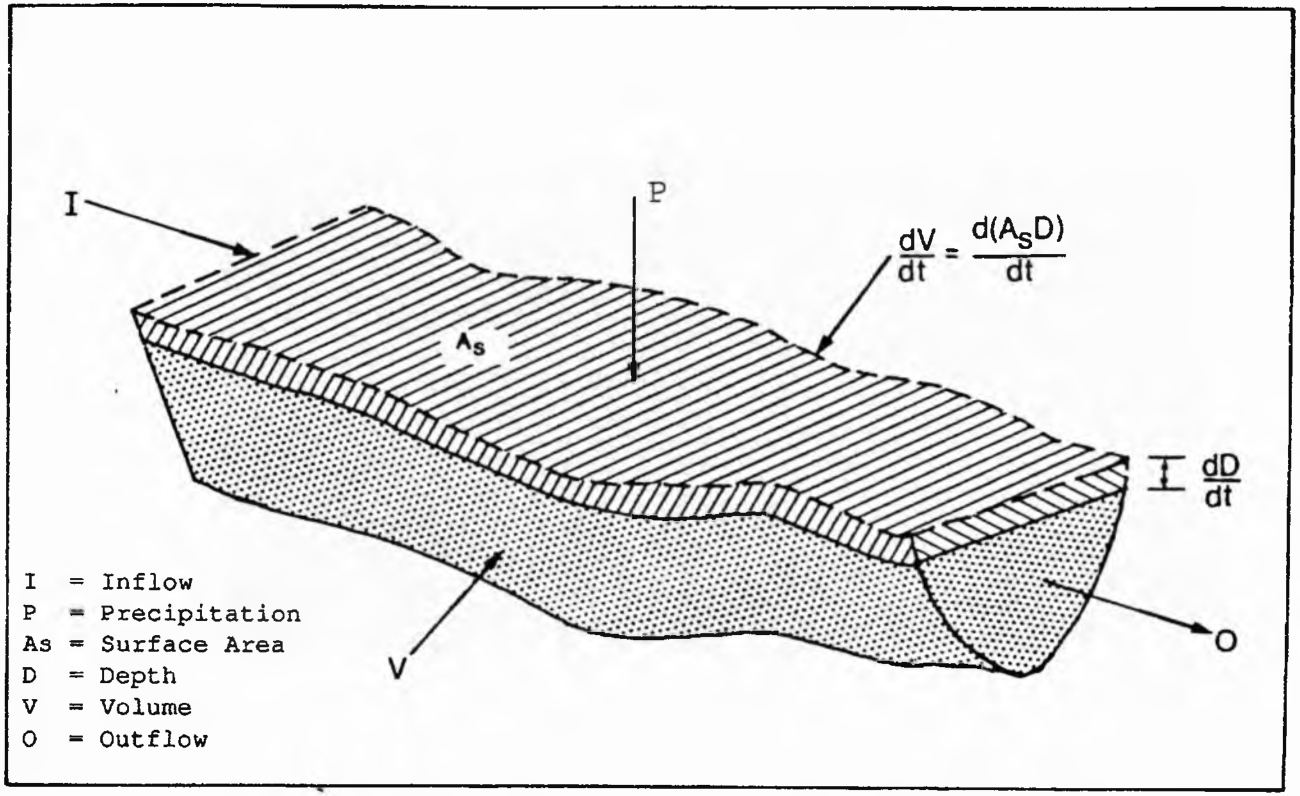


Figure 3.7: Stream segment flow dynamics as simulated by the "ILWAS" model.

(source: Chen et al. 1983)

Lake volume and discharge are user-defined functions of stage. Evaporation is a function of water temperature, air temperature, humidity, solar radiation and wind speed (all model inputs). Since all the other terms are known Eq. (3.22) can be solved for lake stage and subsequently lake discharge.

B) The Chemistry Sub-model

Within the chemistry sub-model the water quality parameter of greatest interest is the hydrogen ion concentration. In the model it is assumed that hydrogen ion concentrations cannot be predicted from either a mass balance procedure or from the sulphate budgets alone. Consequently, it is assumed that the most appropriate method for the determination of hydrogen ion concentrations is through the use of alkalinity. In ILWAS alkalinity includes the carbonate system, the monomeric aluminium system and its organic complexes, together with dissolved organic carbon and water itself. Thus alkalinity is defined as:

$$\begin{aligned} \text{Alk} &= [OH^-] - [H^+] \\ &+ [HCO_3^-] + 2[CO_2] \\ &+ [H_2R_1^-] + 2[HR_1^{2-}] + 3[R_1^{3-}] \\ &+ [Al(OH)^{2+}] + 2[Al(OH)_2] + 3[Al(OH)_3] + 4[Al(OH)_4^-] \\ &+ 3[AlR_1] + [AlR_2^{2+}] + 2[Al(R_2)^{2+}] + 3[Al(R_2)_3] \\ &= -\text{ mineral acidity} \qquad (3.23) \end{aligned}$$

where [ ] is the molar concentration of the species and H_2R, HR ,and R are disassociated species of an analogue organic acid.

The model, however, also includes a mathematically equivalent form of alkalinity derived from the above together with the electroneutrality condition of the solution. This derivation defines alkalinity as the sum of the total non-hydrogen cations multiplied by the individual free cation charges at the equivalence point (ΣCb ueq/l), minus the sum of the total strong acid anions multiplied by the individual free anion charges at the equivalence point (ΣCa ueq/l) i.e.,

$$\text{Alk} = (\Sigma\text{Cb} - \Sigma\text{Ca}) \qquad (3.24)$$

The hydrogen ion concentration is subsequently derived from the solution alkalinity together with the adjusted concentrations of total inorganic carbon (T.I.C), total aqueous aluminium (T.Al) and total organic acid (Rt), which are all determined by the model through the use of mass balance procedures.

Like the "Birkenes" model, ILWAS simulates both equilibrium and rate limited reactions, however, unlike "Birkenes", both processes are allowed to occur in the same compartment during the same time-step. Equilibrium reactions, as in "MAGIC" and "Birkenes", are represented by equations of type Eq. (3.9). Although the actual form varies with a particular reaction, the rate limited reactions are all represented by similar rate expressions (Figure 3.8).

Canopy processes that may be simulated by the model include dry deposition, foliar exudation, nitrification together with the oxidation of SO_2 and NO_x (Figure 3.9). Dry deposition is determined as a function of the LAI, ambient air quality, a species deposition velocity and a collection efficiency parameter. Foliar exudation involves two assumptions; first that exudation rates are proportional to the leaf chemical composition, and second that any imbalance between base cation and strong acid anion exudation produces a net release of

RATE LIMITED REACTIONS (SLOW REACTIONS)

$$A \xrightarrow{R} B$$

ILWAS EXAMPLES

$R_1 = -\frac{d[A]}{dt} = k[A]$	LITTER DECAY
$R_2 = -\frac{d[A]}{dt} = k[A][H^+]^a$	Mineral Weathering
$R_3 = \frac{d[B]}{dt} = k([B]_E - [B])$	RATE LIMITED APPROACH TO EQUILIBRIUM
$R_4 = \frac{V_{MAX}[A]}{K_M + [A]}$	NITRIFICATION

Figure 3.8: The form of several rate limited reactions as represented in "ILWAS"

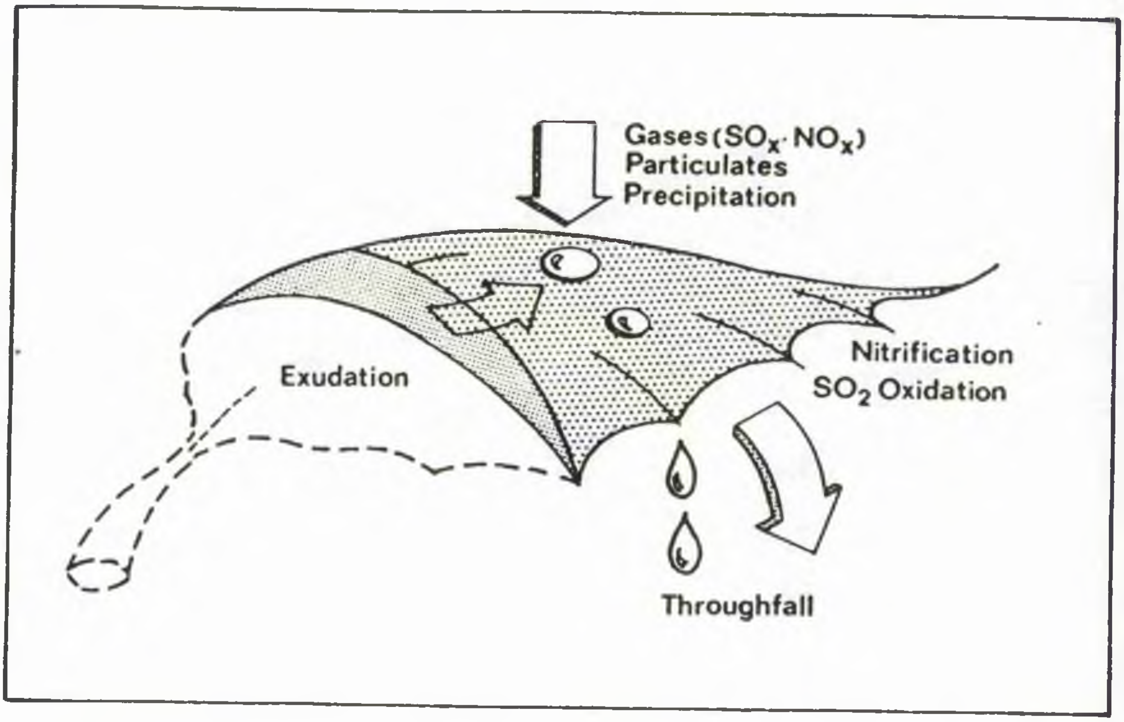


Figure 3.9: The canopy processes simulated by the "ILWAS" model.

(source: Chen et al. 1983)

alkalinity. Nitrification of ammonia on the canopy is assumed to follow the following stoichiometric equation:

$$NH_4 + 2O_2 <\text{---}> NO_3^- + 2H^+ + 2H_2O \qquad (3.25)$$

thus for each equivalent of ammonia oxidised, two equivalents of strong acid are produced. Likewise any sulphur dioxide or nitrogen oxides deposited on the canopy are assumed to be rapidly converted to sulphate and nitrate, with the consequent production of acidity (or consumption of alkalinity).

Snowpack chemistry is derived by the use of a mass balance approach, with ion concentrations in the pack derived as a function of snowfall, dry deposition onto the pack and the oxidation of sulphur dioxide, nitrous oxides and ammonium. The leaching of species from the pack is assumed to follow an exponential path. Consequently leaching rates are modelled by the use of a simple first order differential equation, whereby each volume of melt removes its own solute content together with a fraction of the solutes in the snowpack.

The simulation of soil processes is the most complex part of the ILWAS model. As with "MAGIC" and "Birkenes" cation exchange, anion adsorption, carbon dioxide exchange, aluminium dynamics and mineral weathering are all included. The ILWAS model, however, also includes litterfall and decay, nutrient uptake, root respiration and nitrification (Figure 3.10).

Litter is assumed to be deposited onto the upper soil layer at rates which are dependent on canopy type and the time of year. On deposition to the surface, it is further assumed that a small proportion of the chemical species in the litter are immediately released into

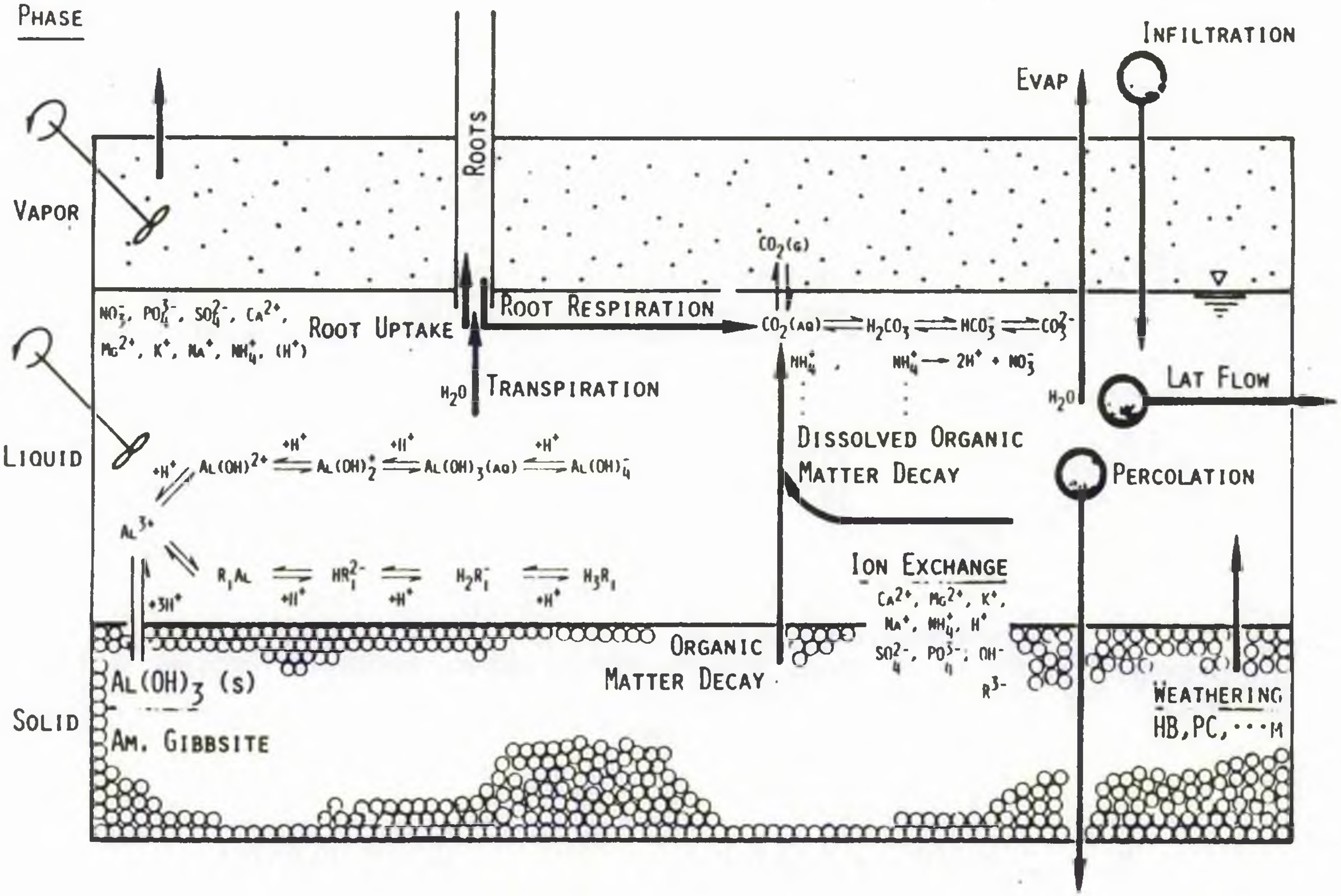


Figure 3.10: The major soil chemistry processes simulated within the "ILWAS" model.

solution, with the proportion leached determined as a user-defined input. The majority of the litter, however, is allowed to undergo four stages of decomposition;

Litter ---------> Fine Litter (3.26)

Fine Litter ---> Humus and Cations (3.27)

Humus -------> Fulvic acid + NH_4 + SO_4^{2-}+ H^+ + CO_2 (3.28)

Fulvic acid --> CO_2 + NH_4 + SO_4^{2-}+ H^+ (3.29)

with each stage of decay represented by a rate expression with a first order dependency on the reactant concentration or mass.

Nutrient uptake is assumed to occur in order to support vegetation growth and to meet the requirements of leaf exudation. Uptake rates are assumed to vary with the seasonal growth pattern and for different species depending on the vegetation composition. The nutrients are withdrawn from the soil layers in relation to root distribution. If, however, there is a deficit of any species in a layer, uptake of all species is assumed to be proportionally reduced. It is further assumed that the vegetation has an equal preference for ammonium and nitrate and that as soil solution concentrations of ammonium are generally low, nitrogen demand will be satisfied by nitrate. As uptake rates of base cations and strong acid anions may differ, an imbalance in solution alkalinity may also occur. Consequently, in order to maintain solution electroneutrality it is assumed that the difference is made up by either hydrogen or hydroxyl ions, thereby producing or consuming alkalinity.

Root respiration is modelled on the basis that it is responsible for the increased concentration of carbon dioxide in the soil solution relative to the atmosphere. Consequently, root release of carbon dioxide is assumed to be fractionated into proportions associated with basal metabolism and active growth. The simulated carbon dioxide produced is dissolved into solution following Henry's law, so that the gas phase diffusion of carbon dioxide is proportional to the difference in the partial pressure of carbon dioxide between the layers. On dissolution the carbon dioxide is assumed to hydrate with the production of hydrogen ions, which are then able to drive cation exchange and weathering reactions.

Nitrification in the soil leads to the production of nitrate and hydrogen ion together with the consumption of alkalinity. In ILWAS nitrification is assumed to follow a Michaelis-Menten rate expression where the oxidation rate is seen as constant at high levels of ammonia and linearly dependent on ammonia concentrations at low concentrations.

Anion adsorbtion in the model involves the simulation of sulphate, phosphate and organic acids in the form of non-competitive reversible equilibrium processes. Sulphate and phosphate adsorbtion are both represented by a linear isotherm similar to that used for sulphate in the upper reservoir of the "Birkenes" model, Eq. (3.15). However, sulphate adsorbtion may alternatively be simulated by a non-linear isotherm as used in "MAGIC". In either case, the adsorbtion coefficient may be varied for each ion in each soil layer. Organic acid adsorbtion is based on the assumption that the analogue organic acid disassociates as a function of pH and temperatures, so that at higher pH more of the organic acid is adsorbed. The adsorbtion is consequently simulated by the following isotherm:

$$(Csol = (K\ /\infty) * Csorbed \text{ with } \infty = \infty_1 + 2\infty_2 + 3\infty_3 \qquad (3.30)$$

where ∞_i's are the ionisation constants which are a function of the solution pH and temperature.

As in "Birkenes" and "MAGIC" cation exchange in ILWAS is simulated by competitive reversible exchange reactions of the type Eq. (3.9). In ILWAS, however, the exchange of all the major cations, hydrogen, sodium, potassium, calcium, magnesium, ammonium, and aluminium is simulated and two different exchange expressions are used, with calcium the reference cation in both. The exchange of cations of equal valency is represented by a mass action equilibrium equation of the type Eq.(3.9), whereas exchange of divalent and monovalent cations, is represented by a Gapon expression similar to equation type Eq.(3.10). The selectivity coefficients are derived from a submodel from input values for solution concentrations and exchangable ions.

Mineral weathering reactions in ILWAS are assumed to be a function of the mass of mineral present and the hydrogen ion concentration. The amount of mineral weathered is calculated by a rate limited equation of the type shown in Figure 3.8, whilst the quantity of hydrogen ions consumed and base cations produced is determined through the mineral specific weathering stoichiometry.

The aluminium system simulated in ILWAS (Figure 3.11) is the most detailed of all the models and includes both equilibrium and rate limited reactions. It is assumed that if the solution is in equilibrium with gibbsite, or any other $Al(OH)_3$ solid, then gibbsite dissolution and precipitation may be represented by an equilibrium reaction of form Eq.(3.9). The same type of reaction is also assumed

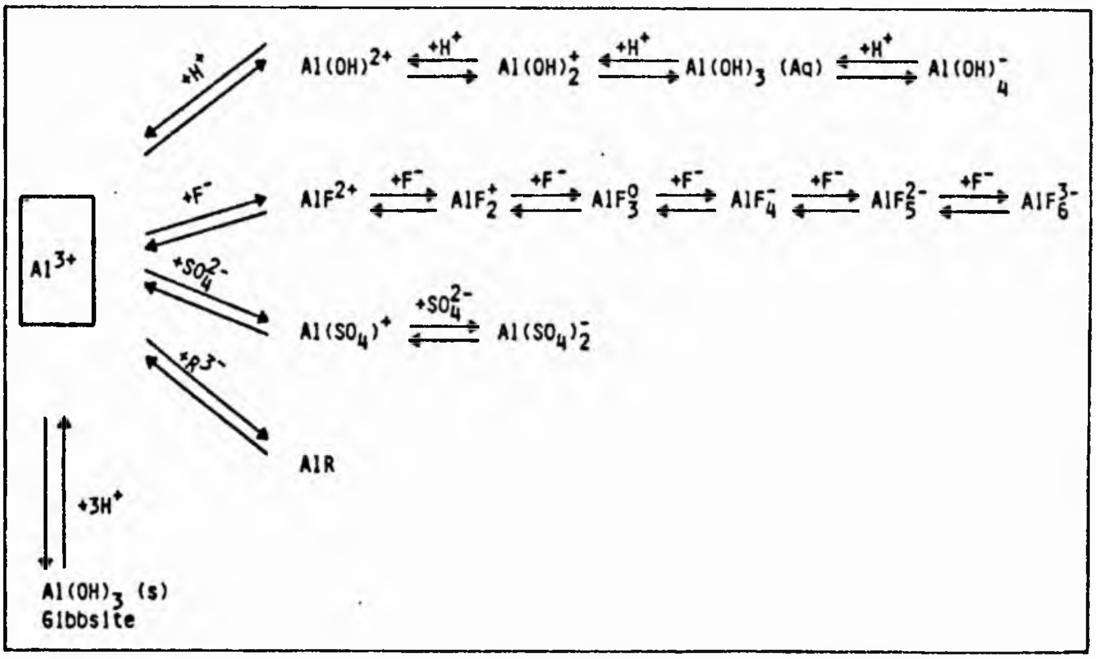


Figure 3.11: The aluminium chemistry system simulated by "ILWAS".

appropriate to represent the protonation and complexation reactions of Al^{3+} with an organic acid ligand, sulphate, and fluoride. However, if the solution is under or over saturated with respect to gibbsite solubility, a mass action rate expression of the following form is assumed to represent the change in solution concentrations:

$$R = k([Al_{Tsat}]_e - [Al_T]) \qquad (3.31)$$

where k = the specific reaction rate coefficient; $[Al_{Tsat}]_e$ = the total concentration of aluminium in solution, including complexes, if the solution is in equilibrium with gibbsite, and $[Al_T]$ the actual monomeric aluminium concentration, including complexes.

Streamwater chemical processes considered by ILWAS are very straight forward, with streamwater solute concentrations of all constituents, except carbon dioxide, calculated by a mass balance dilution method. Carbon dioxide concentrations, in contrast, are assumed to follow rate limited equilibria with atmospheric concentrations.

Solute concentrations in lake water are also derived layer by layer by the use of a mass balance equation. For the lake, however, the mass balance is calculated in combination with the heat budget, inflow distribution and outflow withdrawal. The concentration is subsequently derived for each constituent in all layers, one constituent at a time. Subsequently the dissolved ions in each layer are equilibriated and the lake pH determined.

c) Solution techniques

In ILWAS a catchment is represented by a series of continuously stirred tank reactors (CSTRs), Figure 3.12. Within a simulation timestep the model first solves the hydraulic equations that determine the flow between the CSTRs and the water volume within each CSTR. The model then proceeds to simulate chemical processes within each CSTR, the outflow concentrations of one CSTR becoming the inflow concentration to the next CSTR.

Within any one CSTR the order that the processes occur in any one timestep is shown schematically in Figure 3.13. At the start of a timestep the initial solute concentration (C_i) is equal to the initial mass of the solute (M_i) divided by the initial liquid volume (V_i). The first step that occurs is the addition of rate limited reaction products (e.g., weathering) to the solution so that a new unequilibriated solute mass (M^*) exists. Next external inputs are added so that both the solution volume and the solute mass are increased to (V) and (M) respectively. The solution, solid and gas phases are subsequently equilibriated with the production of a new solute mass (M_e), where (M_e) equals the solution volume (V) divided by the equilibrium solute concentration (C_e). Finally, a volume of water equal to the average outflow rate over the timestep is removed from the reactor thereby leaving the final solution volume (V_f) and solute mass (M_f) in the reactor.

The ILWAS model as noted was developed on the basis of studies in the Adirondacks in the U.S.A. For these sites there is some published material on verification of the model. This material is,

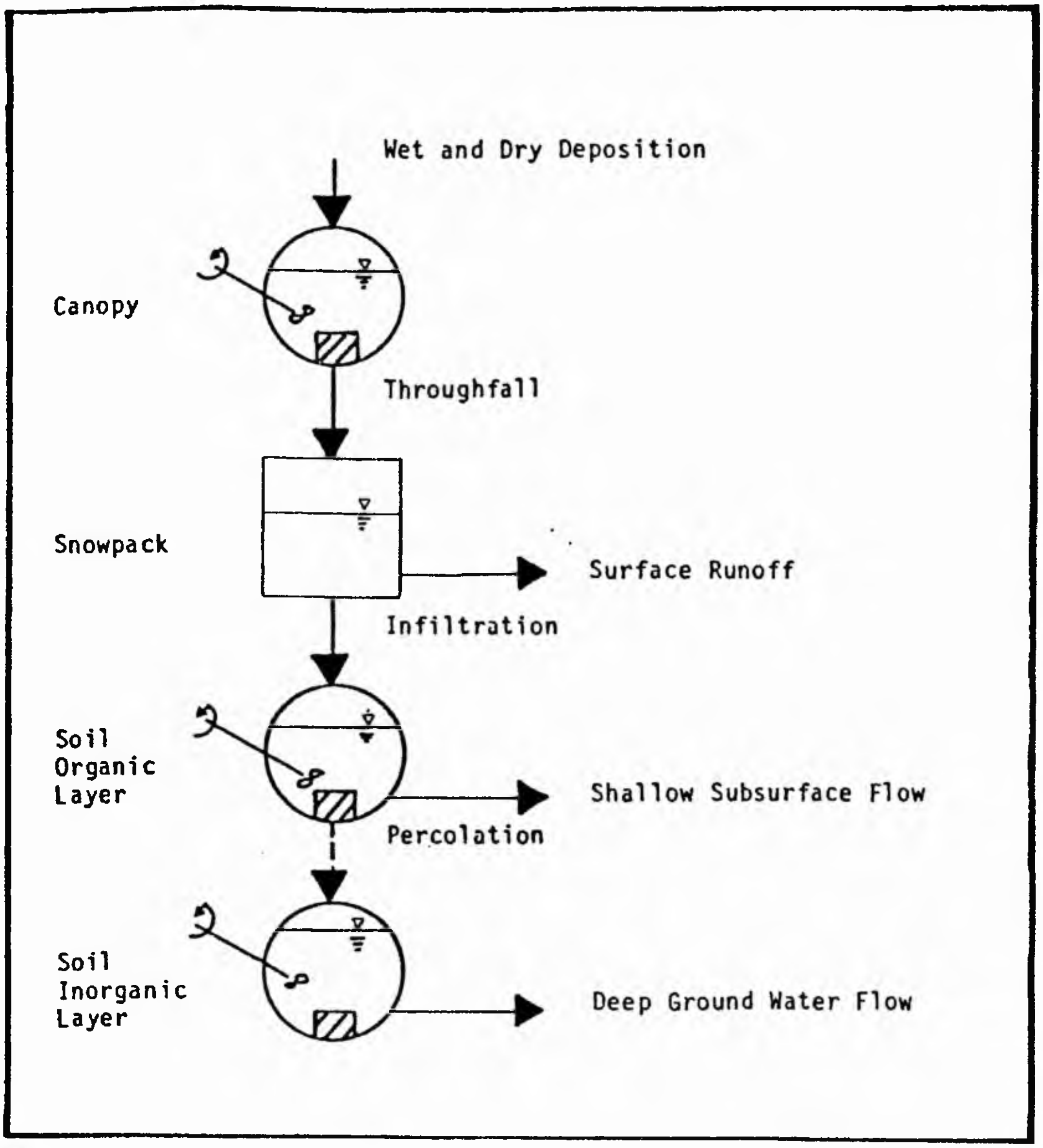


Figure 3.12: The "ILWAS" representation of a catchment as a series of C.S.T.R's (Continuously Stirred Tank Reactors).

(source: Chen et al. 1983)

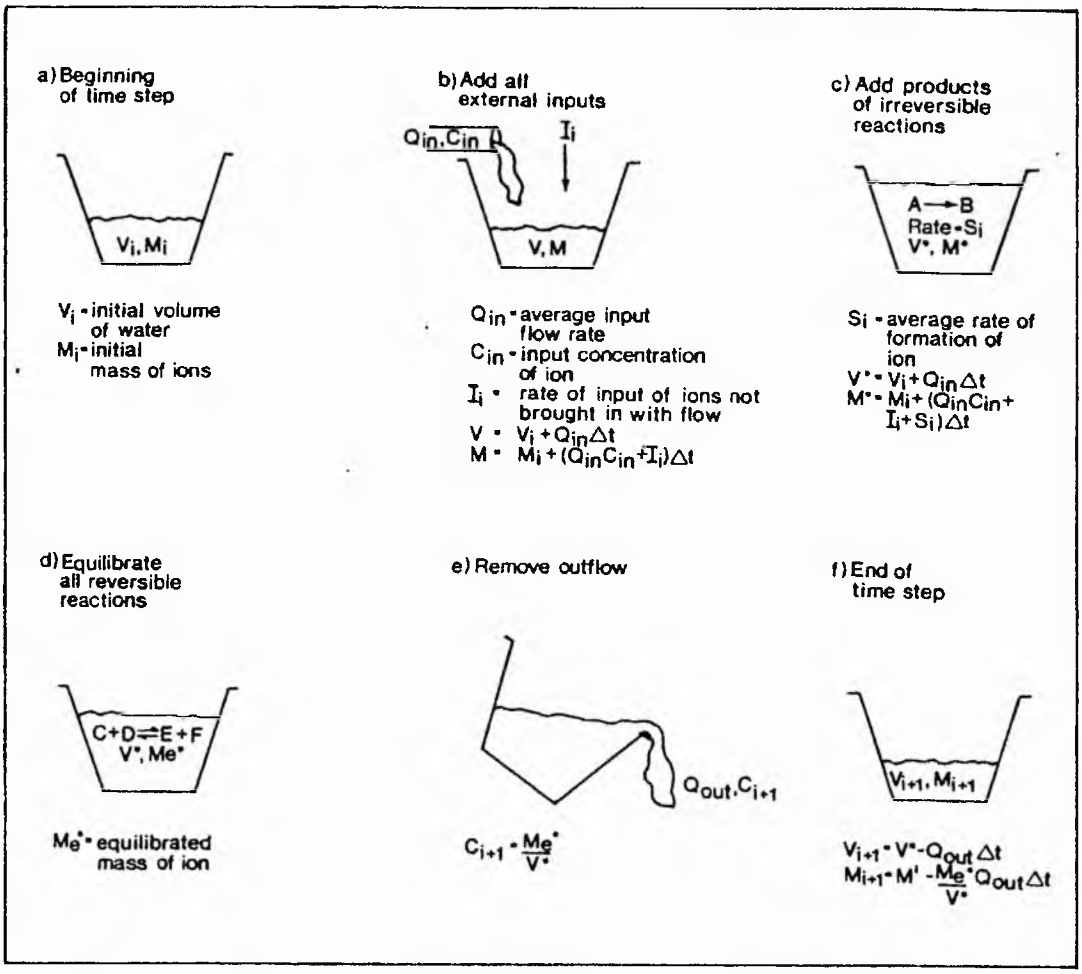


Figure 3.13: The processes occuring within any one C.S.T.R. over a single time step.

(source: Chen et al. 1983)

however, limited to discharge comparisons (Chen et al. 1982) together with alkalinity and pH at the Panther Lake outflow (Gherini et al. 1985). Whilst these studies indicate the ability of the model to reproduce the major features, this can not be considered a critical test of the model (Reuss et al. 1986).

Given this lack of material on verification and in order to assess the model's performance and applicability to other catchments outside the Adirondacks, it was decided to apply ILWAS to the Loch Dee experimental catchments in Southwest Scotland in order to evaluate it away from its test-bed and to ascertain it's more general applicability.

THE STUDY AREA

4.1 *INTRODUCTION*

Towards the end of the 1970's the acidification of surface waters became widely recognised as a major environmental problem in the Galloway hills of Southwest Scotland. This acidification was attributed to the atmospheric deposition of hydrogen and sulphur and/or land use change, in particular the replacement of hill sheep grazing by coniferous afforestation. Concern about the perceived problem led to the establishment of the Loch Dee project in 1979 as a cooperative investigation between the SRPB, the Department of Agriculture and Fisheries for Scotland (DAFS) and the Forestry Commission. The project, as initiated, had two major objectives:

"(a) to assess the combined and individual effects of acid precipitation and coniferous afforestation on surface water ecology; and

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

(Burns et al.1984 pg146)

4.2 *SITE DESCRIPTION*

Loch Dee (NX470790) is situated in the Galloway Hills of Southwest Scotland (Figure 4.1) approximately 40km east and 35km north of the Mull of Galloway. This westerly location with the consequent influence of Atlantic frontal systems results in a mean annual rainfall of 2200mm (1941-70) (Burns et al. 1984). The majority of the catchment lies to the south of the loch and consists of three main sub-

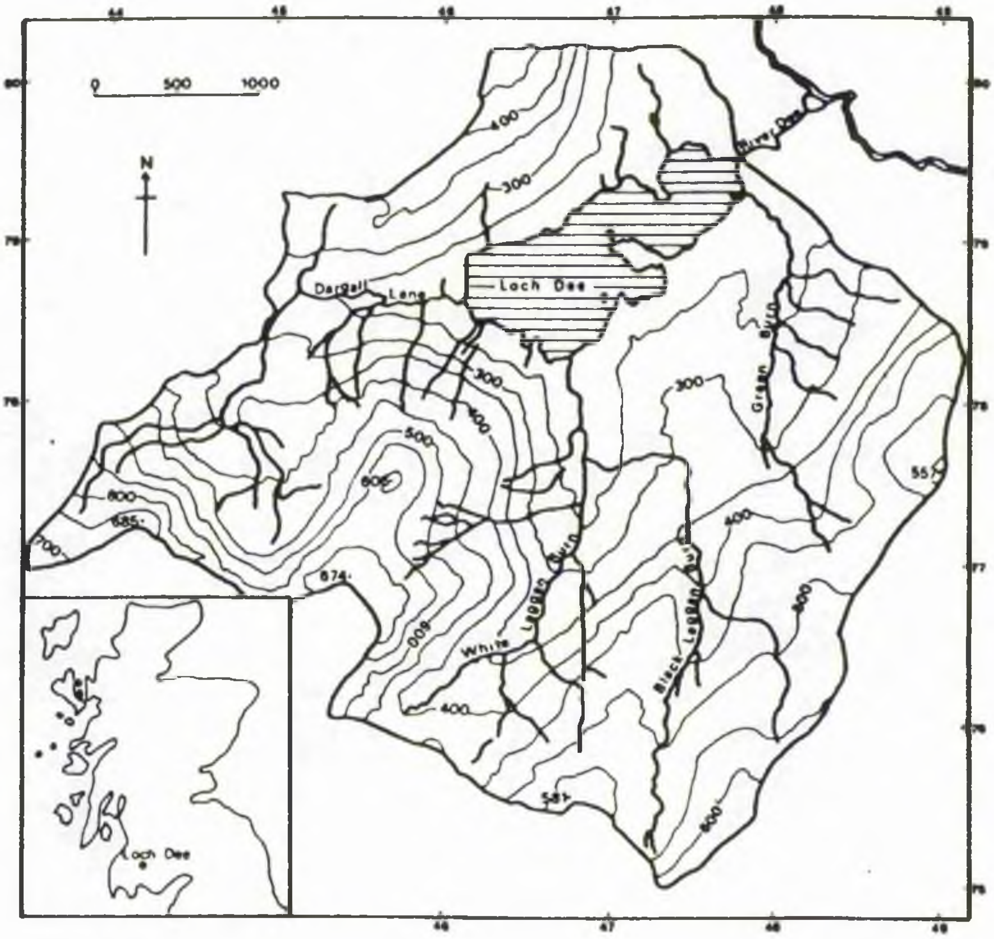


Figure 4.1: Location of the study area: the Loch Dee catchment

catchments, 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. The natural catchment area of the Loch Dee basin is 13.5km^2 of which the loch surface occupies 1.0km^2. This has been increased, however, to 15.6km^2 by the 1939 diversion of the headwaters of the Glenhead Burn, which formerly flowed into Loch Trool, and which now flows into the Dargall Lane as part of the Galloway Hydro-electric power scheme.

Catchment altitudes vary from 225m on the loch shore to 716m on Lamachlan at the head of the Dargall Lane, with almost two thirds of the catchment above 300m (Figure 4.1). The most rugged topography, with steep slopes and rocky outcrops, form the southern boundary of the Dargall Lane catchment and the watershed between the Dargall Lane and the White Laggan Burn. The remainder of the catchment is far gentler in relief with more rounded hills, especially in the Green Burn catchment.

4.2.1 *Solid Geology*

The solid geology of the catchment (Figure 4.2) is dominated by intrusive igneous rocks of the Loch Doon complex to the north and sedimentary rocks to the south. The igneous rocks of the Loch Doon complex are described by Brown et al. (1979) as decreasing in acidity from granites at the centre to hypersthene diorites and quartz monzonites at the margins. The sedimentary rocks consist of Ordovician and Silurian greywackes, shales and mudstones, the majority of which lie within the 2km wide metamorphic aureole of the igneous complex. These metamorphic rocks are more resistant

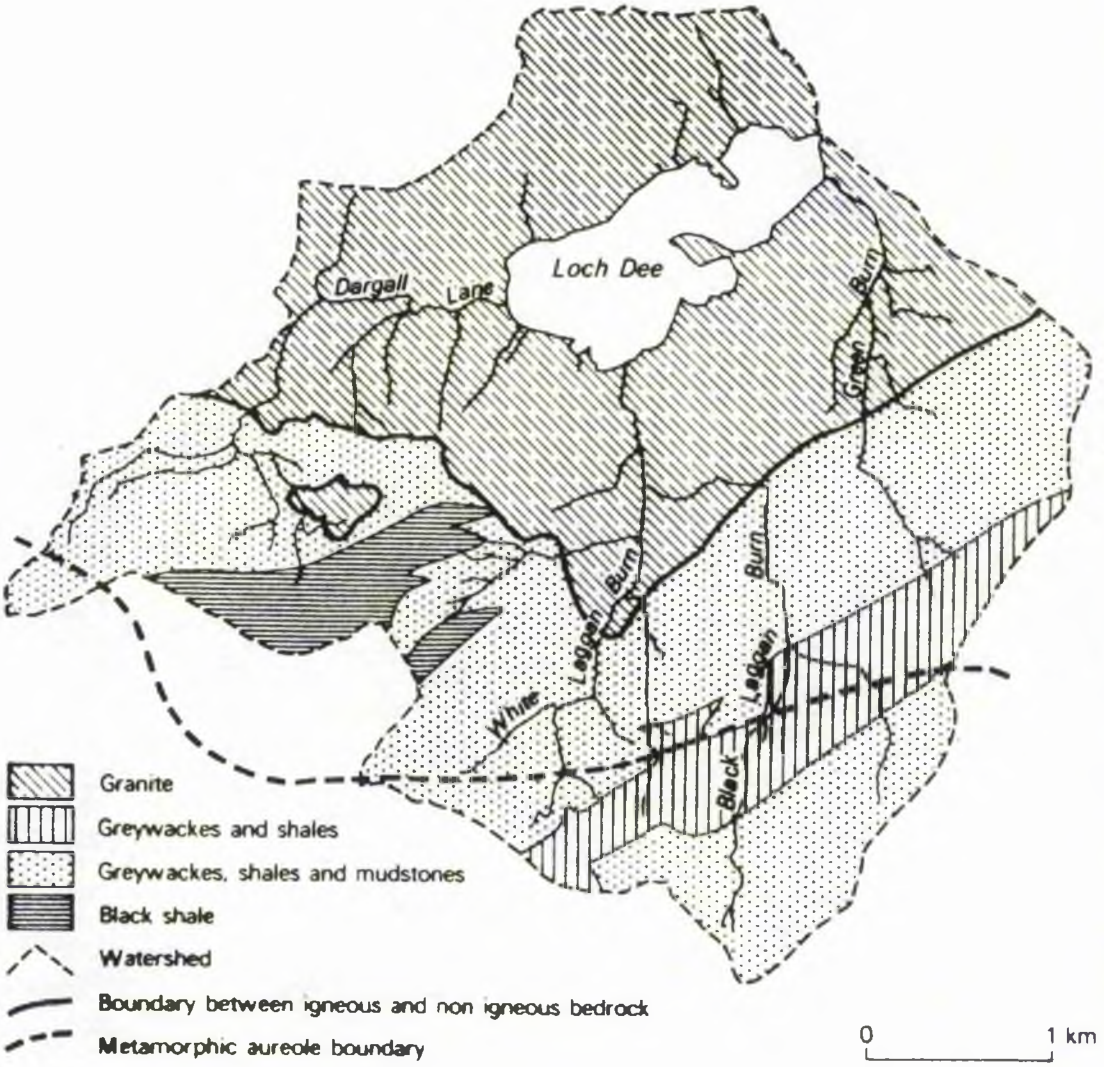


Figure 4.2: The Solid Geology of the Loch Dee Catchment

than the igneous rocks, thereby accounting for the ridge of high ground at the southern end of the catchment.

The northernmost half of the Loch Dee catchment lies within the hypersthene diorite/quartz monzonite margin of the complex. Most of the the southern half of the catchment consists of Ordovician greywackes, shales and mudstones, the majority of which lie within the metamorphic aureole, except for the headwaters of the White and Black Laggan Burns. There is also a band of Silurian greywackes and shales that runs through the headwaters of the Green Burn and into the White Laggan. In the Green Burn these are within the metamorphic aureole but pass beyond the aureole in the Black and White Laggan catchments. Further sediments of Silurian age occur at the head of the Dargall Lane in the form of an area of metamorphosed pyritic black shales.

The sedimentary rocks are described by Bown (1973) as having a chemical composition which differs little from those recorded for the acid igneous rocks in the northern part of the catchment. Despite the fact that the sedimentary rocks are more resistant than the granite to physical weathering their chemical breakdown is more rapid.

4.2.2 *Drift Geology and Soils*

The drift cover of the catchment is predominantly of Lateglacial origin consisting of lodgement tills and morainic ridges of poorly consolidated sands and gravels. Soils developed over the drift cover are dominated by blanket and basin peats which reach over a metre in thickness on the gentle slopes. On the lower slopes of the catchment

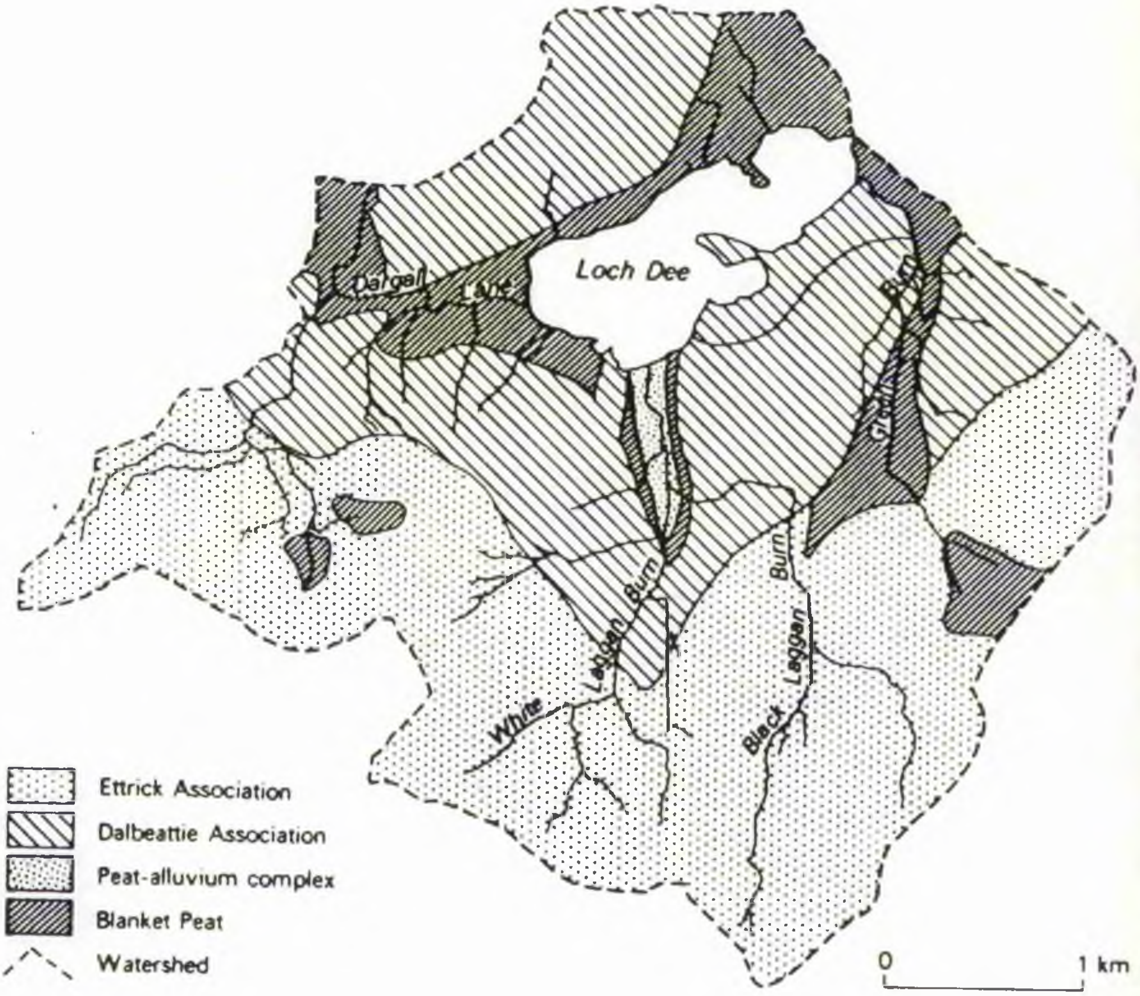


Figure 4.3: The major soil groups within the Loch Dee catchment (after Bown 1973)

there is a limited degree of podsolisation and these soils are also dominated by thick organic horizons. Bown (1973) divides the soils into two main associations, the Dalbeattie and the Ettrick, as shown in Figure 4.3. The parent material for the Dalbeattie association is the Loch Doon granite, whereas the greywackes, shales and mudstones form the parent material for the Ettrick association. From figure 4.3 the soil associations appear to be well developed across the catchment, more detailed site investigation suggests, however, that peat deposits are far more extensive than figure 4.3 implies.

4.2.3 *Land-use and Vegetation*

Land-use in the catchment is limited to sheep grazing and forestry. Prior to afforestation, vegetation in the Loch Dee area was dominated by a dry grass and heather moorland community on the steeper well drained slopes and bracken and *Molinia* communities on the lower slopes (Tivy 1954). The land capability classification, prior to afforestation, is described as land classes 6 and 7 so that land use is restricted to rough grazing and forestry (Bown 1973).

Between 1973 and 1982 the Forestry Commission have pursued a planting programme in the catchment, so that 28 % of the catchment is now afforested (Figure 4.4). Sitka spruce (*Picea sitchensis (Bong.)Carr.*) is the principal species planted, with small pockets of Lodgepole pine (*Pinus contorta Dougl. var. latifolia)*, Norway spruce (*Picea abies* (L.) *Karst.*) and Scots pine (*Pinus sylvestris L*).

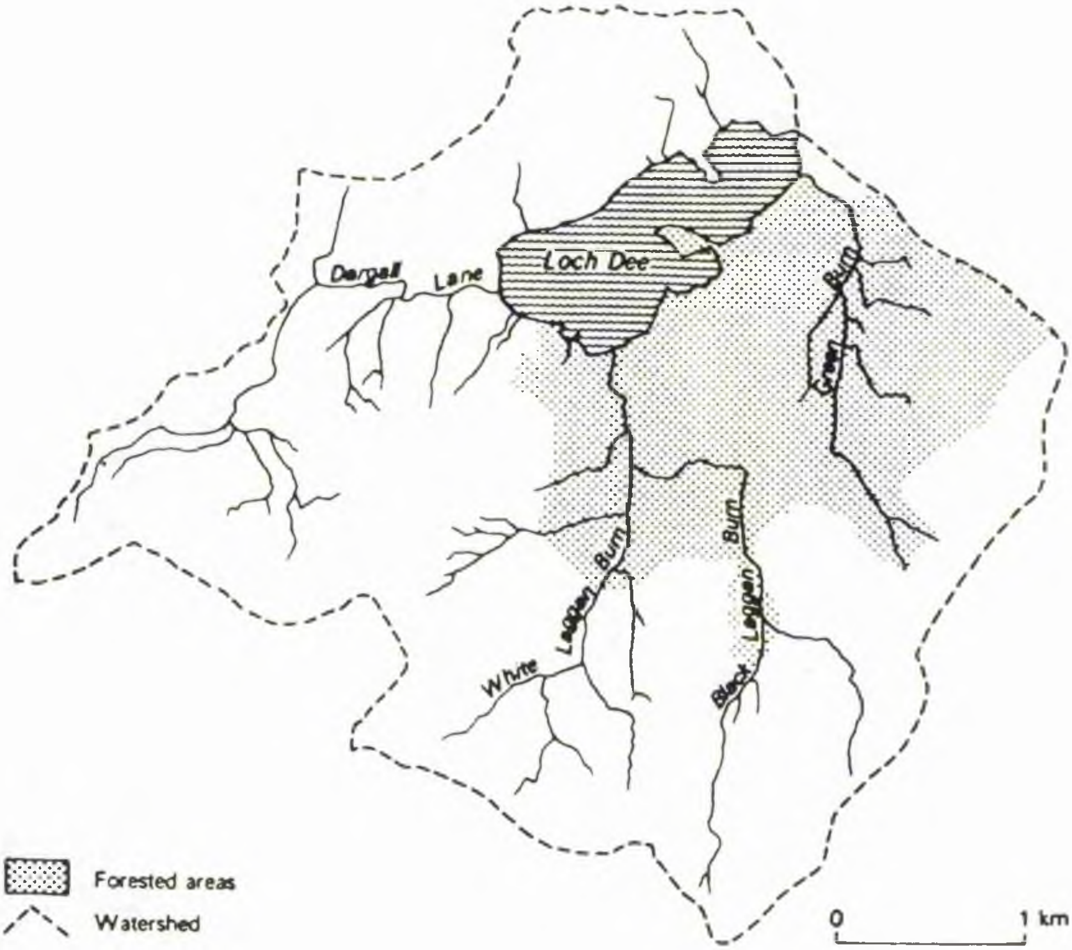


Figure 4.4: Location of the afforested area within the Loch Dee catchment.

4.3 *THE THREE SUB-CATCHMENTS*

The sections that follow will describe the catchment hydrology and catchment water quality in each of the three main sub-catchments together with the land-use and land management practices that have been pursued on each since afforestation.

4.3.1 *The Dargall Lane Burn*

The gauged area of the Dargall Lane catchment, with the inclusion of that part of the catchment that formly drained into the Glenhead Burn just upstream of the gauging station, is 2.1km^2. Topographically the catchment has a typical corrie form, with steep cliff-like slopes surrounding a semi-enclosed valley floor (Plate 4.1). The lower slopes and floor of the corrie are mantled by an accumulation of peat which can reach a thickness of 1.5m. The average gradient of the catchment is 11.6° (Little 1985), this gradient is, however, broken by a steep section where water leaving the corrie falls over a rock step into the lower catchment. The stream channel, incised into the peat, varies in width from 1-2m and has a bed of well-rounded boulders and cobbles (200-300mm), which are liable to move in spate conditions (Burns et al. 1984).

The Dargall Lane catchment is open moorland and will be left uncultivated by the Forestry Commission until the 1990's, in order to act as the control catchment in the Loch Dee Project study. The catchment vegetation over much of the catchment is typical of upland moorland areas and consists of *Sphagnum, Molinia* and *Gramineae*

Plate 4.1: A general view of the Dargall Lane catchment showing the steep corrie walls surrounding the shallow valley bottom

Plate 4.2: The Green Burn catchment looking upstream away from the Loch

communities. *Calluna* and *Erica spp.* and *Aquilinium pteridium* become more important, however, in the lower part of the catchment.

4.3.2 *The Green Burn*

The area of the Green Burn catchment to the gauging station is 2.5km^2. Topographically the catchment is far gentler than the Dargall Lane (Plate 2) with an average gradient of 7.2° (Little 1985). The stream channel is similar to the Dargall Lane in that it is incised into peat over much of its length and in that it has a cobble and boulder bed. The channel is, however, generally wider than the Dargall Lane at 2-3m and at several sites, usually at bends, the bed is overlain by gravel.

Upstream of the sampling station 70% of the catchment was planted with Sitka spruce *(Picea sitchensis)* between 1973 and 1975. This afforestation occurred up to an altitude of 460m at a stocking density of 7000 trees per acre (Kite 1984). Prior to planting catchment drainage was improved by ploughing. The resultant furrows now form a dominant part of the catchment drainage system with some of the major ditches connecting directly with the Green Burn channel. At the present time, 15 years after planting, the trees are about 3m in height and the canopy is just beginning to close (Plate 3).

4.3.3 *The White Laggan*

The total area of the White Laggan catchment to the gauging station, including its tributary the Black Laggan, is 5.7 km^2. The catchment forms the head of a glacial valley and with an average slope of 10.4°

Plate 4.3 Typical coniferous vegetation in the Green Burn

Plate 4.4: The White Laggan catchment looking upstream

(Little 1985) is topographically more akin to the Dargall Lane catchment than the Green Burn (Plate 4).

The main stream channels are incised into peat in the upper catchment and alluvial deposits in the lower catchment. In the lower reaches the width of the channels are 4m and 3m for the White Laggan and Black Laggan respectively. The beds of both channels are composed of gravel and cobbles, however, the cobbles in the Black Laggan are far more angular than those of the White Laggan (Burns et al. 1984).

As a result of afforestation in 1975 30% of the catchment, primarily in the Black Laggan sub-catchment, has been planted with Sitka spruce. Outside the afforested area vegetation is dominated by *Molinia* and *Sphagnum* in the upper catchment and *Calluna* and *Erica spp.* and *Aquilinium pteridium* in the lower catchment.

In 1979 the conifers were cut back approximately 100m from the main channel for 1km upstream from the loch. The cut back area was subsequently replanted with hardwoods such as, alder (*Alnus glutinose*) , birch (*Betula spp.*) , willow (*Salix sp.*) and rowan (*Sorbus aucuparia L.*) in order to conform with the 'buffer zone' concept of Mills (1980) (Plate 5). Mills also suggests that forest drains should finish short of water courses in order to prevent high sediment loads entering streams and to enhance the infiltration of precipitation. Consequently, the ditches in the replanted area that connected directly with the stream channel were infilled.

Plate 4.5: A view across The "Buffer Zone" of the White Laggan catchment

Plate 4.6 Limestone addition to the White Laggan Burn Loch Dee

In a further attempt to reduce the acidity of the White Laggan Burn (and thereby Loch Dee) calcium, in the form of queen scallop shells and powdered limestone, has been added to the White Laggan catchment on several occasions since 1980 (Plate 6). Precise details of the type and location of such applications are given in table 4.1.

4.4 *CATCHMENT HYDROLOGY*

For the period 1980-1985 rainfall totals to the catchment have ranged from 96-131% of the 1941-1970 period average of 2232mm recorded by the Loch Dee gauge (Welsh and Burns 1987). Based on a comparison of rainfall totals from rain gauges on the valley floor and on the valley slopes, Welsh and Burns further report that there appears to be a general 6% increase in rainfall per 100m increase in altitude. The higher level gauge, however, tends to show a reduced catch in winter months, which the authors attribute to snow and high winds. A comparison of runoff from the catchment with rainfall, adjusted for the altitudinal increase, indicates an annual loss due to evaporation of around 375mm (Table 4.2). This figure compares well with the 400mm figure suggested by the Meteorological Office map of average annual potential evaporation for areas such as Loch Dee (Welsh and Burns 1987).

Flow duration curves for the three sub-catchments and the loch outlet, over the common period of record (1984-85), calculated by the Solway River Purification Board on the basis of mean daily flows are shown in Figure 4.5. The four curves are broadly similar, with the White Laggan Burn and Green Burn showing the greatest similarity, possibily due to the influence of forest drainage in both sub-

Date	Location	Type	Quantity (tonnes)
Spring 1980	Burn at road bridge	Scallop shells	5
Autumn 1980	Burn at road bridge	Scallop Shells	5
Spring 1981	Burn at road bridge	Powered Limestone	10
Autumn 1981	Lower Catchment	Powdered Limestone	80
Winter 1982	Lower 1Km of Burn	Limestone Chips	80
Spring 1983	Burn at road bridge	Powered Limestone	75
Spring 1985	Burn at road bridge	Powered Limestone	100

Table 4.1: Limestone Applications to the White Laggan Catchment

Year	Rainfall (mm)	Runoff (mm)	AE/T (mm)
1983	2560	2188	372
1984	2508	2134	394
1985	2827	2471	356
Mean	2632	2258	374

Table 4.2: Annual Rainfall, Runoff and Actual Evapotranspiration (AE/T) from the Loch Dee catchment 1983-1985.

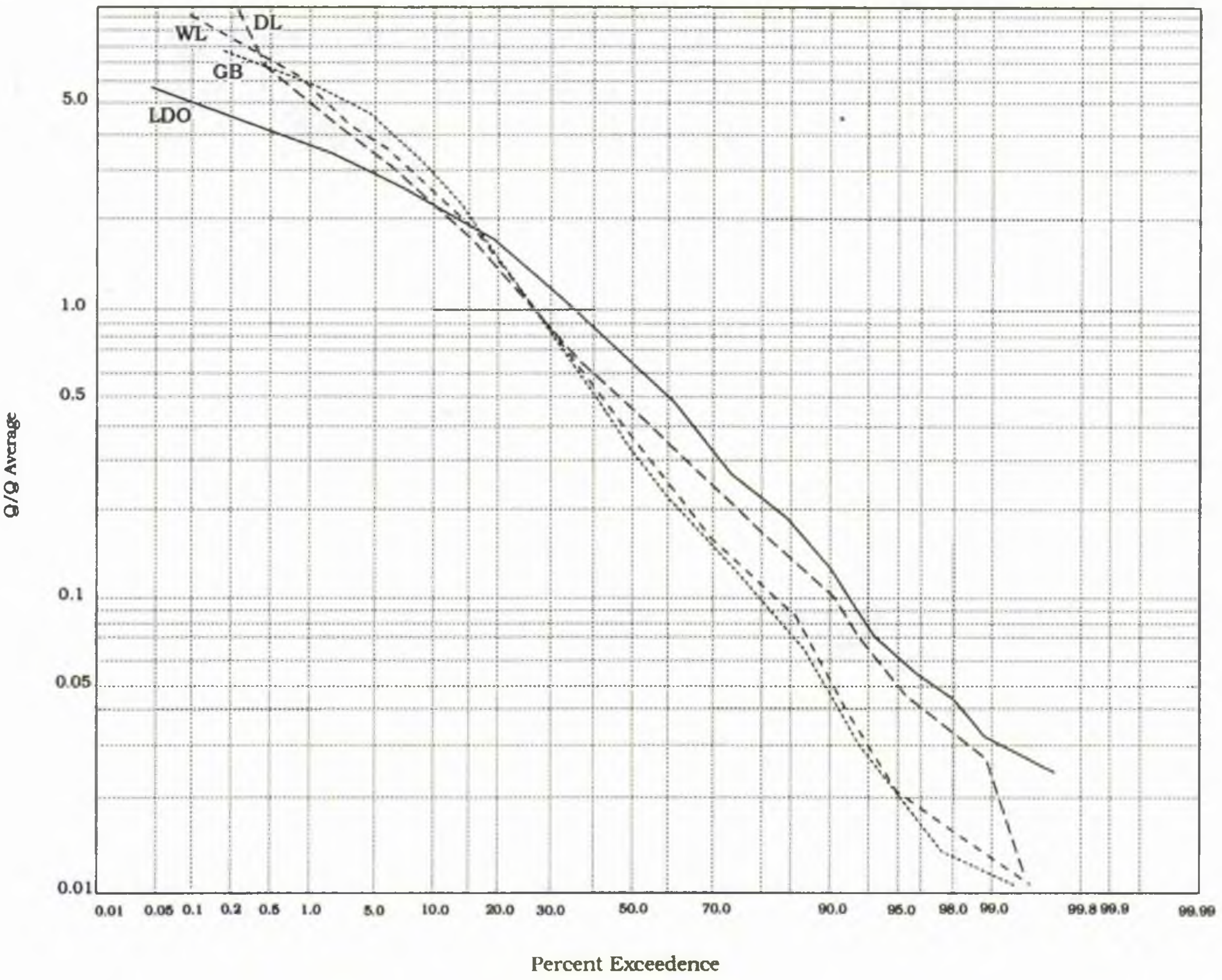


Figure 4.5 Flow duration curves for the Loch Dee outlet (LDO), the White Laggan Burn (WL), the Dargall Lane Burn (DL) and the Green Burn (GB).

catchments. The curve for the Dargall Lane Burn is generally parallel to those of the Green Burn and White Laggan Burn except for a sharp upward inflexion at high flows. This upward inflexion is attributed by Welsh and Burns (1987) to a period of high snowmelt at the end of 1984 which produced exceptionally high flows. At the lower end of the curve the 95% exceedance flow for the Dargall Lane ($0.055m^3 s^{-1}$) is about double that of the Green Burn ($0.035m^3 s^{-1}$). This difference is possibly due to the thick accumulations of peat on the valley floor. Thus Langan (1986) suggests that the peat serves to retain and gradually release a high proportion of stormwater runoff.

In a comparative unit hydrograph study at Loch Dee (Harper 1984) the hydrological differences between the afforested and non-afforested sub-catchments are further emphasised. Table 4.3 shows the percentage runoff from the three sub-catchments at various time periods based on the proportional catchment average unit hydrograph. The afforested catchments of the White Laggan and Green Burn show a proportionally greater evacuation of stormflow than the non-afforested Dargall Lane. This is attributed to the faster routing of stormwater through the forest ditches than in the unploughed Dargall Lane, where the lower drainage density together with the thick peat accumulations on the valley floor results in runoff taking longer to leave the catchment. The greater drainage density of the Green Burn and White Laggan catchments, due to the forest drainage, also results in greater peak flow values per unit area for these sub-catchments (Table 4.4). However, table 4.4 also shows that the average time to peak runoff is lower for the unditched Dargall Lane (2.5 hrs) than the extensively ditched Green Burn (2.8 hrs), a

	% Runoff after first :				
	5 hours	7 hours	10 hours	20 hours	24 hours
White Laggan	49.4	64.8	78.8	93.9	96.9
Dargall Lane	32.7	49.0	63.5	89.1	94.0
Green Burn	43.7	65.8	80.7	93.9	97.1

Table 4.3 Percentage Runoff Evacuated from the Loch Dee Sub-catchments after different periods of time (data derived from the catchment average unit hydrograph).

Source : Harper (1984)

Catchment	Time to peak (hrs)	Peak flow (m^3 s^{-1} km^{-2})
White Laggan	2.3	0.77
Dargall Lane	2.5	0.57
Green Burn	2.8	0.72

Table 4.4 Major parameters of the proportional catchment average unit hydrographs

Source : Harper (1984)

feature which Harper attributes to the far steeper slopes of the Dargall Lane.

4.5. *CATCHMENT WATER CHEMISTRY*

In an initial study of the water chemistry at Loch Dee, Burns et al. (1984) report that precipitation quality at Loch Dee is correlated with wind direction. The most acid episodes are associated with easterly and south-easterly airstreams and the least acid with westerly airstreams. The authors also report that streamwater quality in the three sub-catchments is very similar with low base cation and nutrient content.

A more detailed baseline study of the water quality at Loch Dee has been undertaken by Langan (1986). In this study the author identifies five main factors that interact to control water quality at Loch Dee namely; atmospheric inputs, weathering, ion exchange, biology and flow. Langan indicates that buffering of precipitation is greatest in the White Laggan and least in the Dargall Lane. The higher acidity of the Dargall Lane is attributed to a greater dependence on atmospheric inputs, due to the interaction of slow chemical weathering and base cation release with the peats. Langan further suggests that the lower acidity of both the White Laggan and Green Burn is due to the forest ditches, which result in an increased exposure of the underlying mineral soil to percolating waters and hence to an increase in base cation release. The overall lower acidity of the White Laggan is, however, attributed at least in part to the liming programme carried out in this sub-catchment.

Langan (1987) also investigats the importance of episodic precipitation events on streamwater quality. Consequently two types of storms with differing effects on streamwater quality are identified. The first type of storm results in the well known dilution of major ions and an attendant increase in streamwater acidity. This in turn rapidly decreases as the precipitation ceases. In contrast the second type of storm is characterised by a high pH and conductivity due to a high loading of seasalts. Such storms are believed to be responsible for the most acid streamwater events experienced at Loch Dee. With such 'seasalt' storms there is not only to an increase in stream acidity but also an increase in conductivity, as the sodium in precipitation is exchanged within the catchment soils for hydrogen ions. Furthermore the resultant increase in acidity decreases at a far lower rate, than with the normal non sea-salt storm, as cation exchange continues within the soils for some hours after the precipitation event finishes.

A detailed investigation of variations in baseflow quality at Loch Dee has been undertaken by Welsh and Burns (1987). In this study the authors report that the major control on baseflow quality is the underlying lithology. Thus waters that drain the black shales have acidity levels up to two pH units lower than waters that drain the unmetamorphosed sedimentary rocks, this being due to the oxidation of the pyrites within the shales. As almost all the sedimentary rocks are found at the head of the White and Black Laggan Burns, the authors suggest that this greater buffering is responsible for the lower acidity of the White Laggan Burn than either the Green Burn or the Dargall Lane.

The variability in water quality between the three streams is also shown by an examination of continuous pH data (Burns and Lees 1987). These data indicate that the Green Burn has the lowest mean annual pH (4.8), compared with a pH of 4.9 for the Dargall Lane and a pHof 5.5 for the White Laggan Burn. The Green Burn also shows the most variable range of pH. Storm response is especially dramatic as pH can fall by two units within hours as a result of the high number of forest ditches in this catchment.

4.6 *DATA COLLECTION*

As part of the Loch Dee project a comprehensive hydrological and hydrochemical monitoring programme has been established in each of the three catchments (Figure 4.6) Precipitation inputs are determined on both a continuous and monthly basis by the use of two pairs of raingauges at 235m and 408m O.D in the Black Laggan sub-catchment. The lower pair consists of an autographic gauge (Munro 0.2mm tipping bucket) (Plate 7) together with a standard Meteorological Office 5 inch check gauge . The upper system is similar except that the autographic gauge is a 0.5mm tipping bucket. There is also an extra Meteorological Office monthly check gauge at 323m O.D in the Green Burn Sub-catchment.

Streamflow has been continuously determined in the White Laggan Burn since March 1980 and in the Green Burn and Dargall Lane since the summer of 1983, by float-operated continuous recorders (Ott R20, plate 8). The control weir on the Dargall Lane is a natural outcrop of large boulders. On the White Laggan Burn and Green Burn, however, there are no suitable natural sites and the controls

Plate 4.7: The lower autographic rainfall gauge used at Loch Dee

Plate 4.8: One of the Ott stage recorders used at Loch Dee

Plate 4.9: The bulk precipitation collector at Loch Dee

Plate 4.10: The continuous recorders for pH and Conductivity

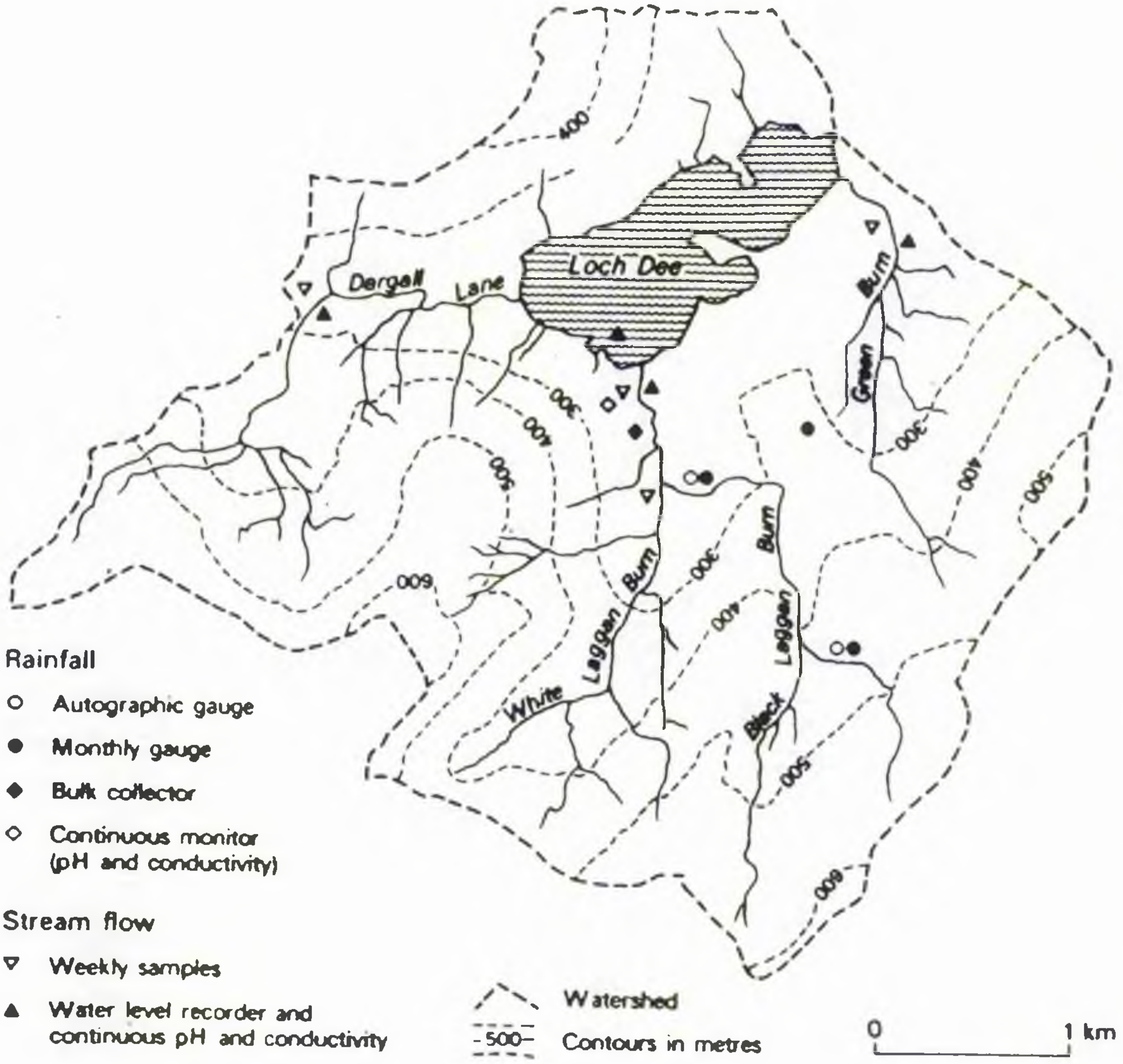


Figure 4.6: The hydrometeorological and hydrochemical monitoring network at Loch Dee.

consist of hardwood crests with a downstream apron of large stones. The cross-sections of each stream are rated by regular current meter gauging, on a weekly basis where possible.

Water quality of both precipitation and streamwater is monitored on both a continuous and, where possible, a weekly basis. The weekly samples have been taken since early 1980 from a bulk precipitation collector (Plate 9) and from the White Laggan Burn, Green Burn and Dargall Lane tributaries. These samples are collected in 1 litre polypropelene bottles and returned to the laboratory at Dumfries within 24 hours of collection.

Laboratory analysis is undertaken by the staff of the Solway River Purification Board in Dumfries and involves the determination of a wide range of water quality parameters. The sample pH was determined by the use of a Walden Precision Apparatus CD390 pH meter, together with a Russell CE7L gel-filled combination electrode and the conductivity by the use of a Chandos Intercontinental A21/d meter. The anions chloride, nitrate, sulphate and phosphate were determined by ion chromatography on a Dionex QIC and alkalinity by titration with sulphuric acid to an end point pH of 4.5. Reactive silicate concentrations were determined by the use of a Technicon autoanalyser and values for the major cations and trace elements were determined by spectrophotometry; sodium and potassium by flame emission and calcium and magnesium by atomic absorption. In both spectrophotometric methods the samples were analysed after the addition of strontium so as to miminise interference effects. Total aluminium, iron, manganese and zinc were also determined by atomic absorption following evaporative concentration in 8%

hydrochloric acid. All the metals were determined on a Varion model 1275 atomic absorption spectrophotometer.

The pH and conductivity of bulk precipitation and streamflow are also recorded on a continuous basis. The precipitation monitoring system (designed by the SRPB) involves the collection of precipitation by 400mm polypropylene funnels from where it is passed through a polypropylene 'U' tube within which are contained permanently immersed electrodes. The pH and conductivity are recorded by a PHOx series 47 and series 52 meters respectively onto Rustrak strip chart recorders (Plate 10). Continuous monitoring of streamwater pH and conductivity has been maintained since 1981 in the White Laggan Burn and July 1983 in the Green Burn and Dargall Lane. The system is very similar to the precipitation system with electrodes permanently immersed in the stream attached to the same type of meters and recorders hosed in weatherproof boxes on the streambank (Plates 11). On the White Laggan Burn and Dargall Lane the instruments are located next to the gauging station, whereas on the Green Burn the instruments are 150m upstream.

A Didcot Automatic Weather Station, on loan from the Natural Environment Research Council equipment pool, has also been operational at Loch Dee since October 1986, and produces hourly records of precipitation, wind speed, wind direction, solar radiation, net radiation together and dry bulb temperatures (Plate 12).

Plate 4.11: The electrodes for continuous monitoring of stream pH and Conductivity

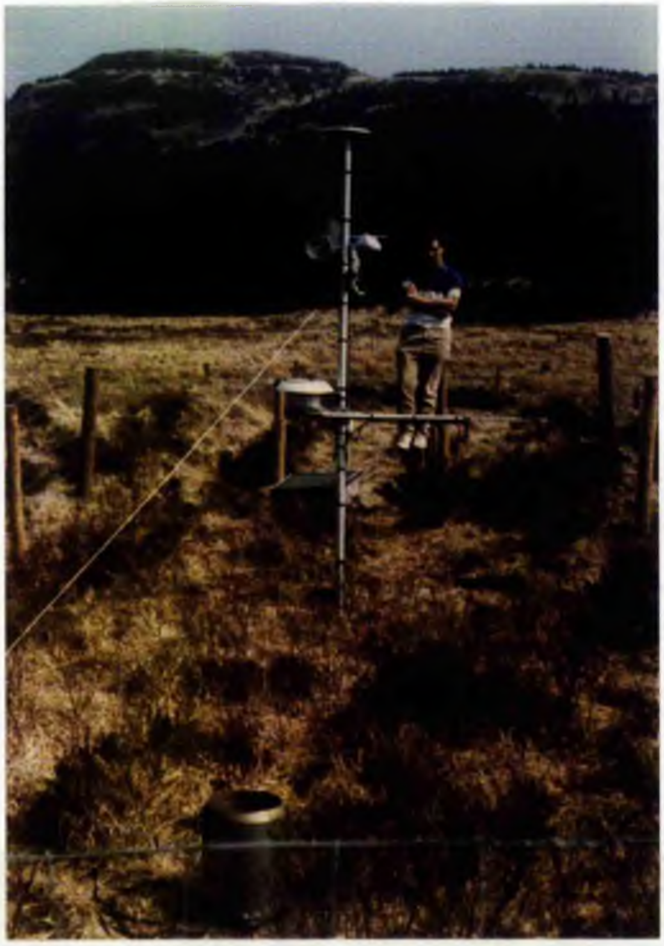


Plate 4.12: The Didcot Automatic Weather Station in use at Loch Dee

5: HYDROCHEMICAL BUDGETS at LOCH DEE

5.1 *INTRODUCTION*

The determination of hydrochemical budgets for a catchment is a useful tool for the study of the biogeochemical processes occurring within that catchment. Such budgetary studies can also be useful in assessing the possible response of the catchment system to changes in external factors such as acid deposition and land management practices. In the context of the overall modelling study the objectives of the research reported in this chapter were three-fold;

a) to determine the influence of acid deposition and afforestation on the solute chemistry of the Loch Dee catchments.

b) to provide an understanding of the processes that govern streamwater chemistry at Loch Dee and to aid thereby the application of the ILWAS model at this site.

c) to obtain data against which the ILWAS model could be successfully calibrated.

5.2 *DATA REDUCTION*

All the weekly chemical data were initially subject to an ion balance to establish basic quality control. At this stage problems with sulphate determinations during 1982 became apparent and thus no results are reported for that year. For all other years samples with an ion balance greater than +/-10% were rejected.

Estimates of annual input loadings (kg ha^{-1} yr^{-1}) were initially calculated as the product of the volume-weighted mean annual concentration of each element in the collector (mg l^{-1}) and the total annual precipitation (cm). Total annual precipitation was calculated separately for each sub-catchment using a height-weighted method which assumes a linear increase in precipitation, at the Loch Dee sites, of 6% per 100m increase in altitude (Welsh and Burns 1987). However, the determination of inputs solely from bulk precipitation data probably underestimates the additional input of elements through dry deposition. Consequently, to improve the accuracy of the input loadings dry deposition rates for the major cations were estimated by assuming that chloride is chemically conservative within the sub-catchments, so that the annual net output of chloride is balanced by dry deposition. The dry deposition rates of the major cations were then calculated following Clarridge (1970), who demonstrated that the ratios of the major cations to chloride in dry deposition is identical to those in the bulk collector. Thus the dry deposition rates of the major cations were determined by multiplying the ionic ratios to chloride in precipitation by the net chloride output (Wright and Johannessen 1980).

Annual solute outputs (kg ha^{-1} yr^{-1}) were determined using rating curves for those ions which registered a statistically significant relationship ($p>0.95$) between flow and concentration (Table 5.1). The resulting daily solute outputs were derived as the product of the mean daily flow and the associated concentration divided by the appropriate sub-catchment area. When summed these values produce the annual output for each ion. This output value was then corrected for statistical bias using the procedure developed by Ferguson (1987). As

Chemical species	Equation	R^2	s.e.e
White Laggan Burn			
H^+	$H = 3.63\ Q^{0.53}$	0.65	0.303
Ca^{++}	$Ca = 52.48\ Q^{-0.16}$	0.55	0.096
Mg^{++}	$Mg = 57.54\ Q^{-0.09}$	0.46	0.098
Al	$Al = 18.20\ Q^{0.20}$	0.41	0.177
SiO_2	$Si = 2.67\ Q^{-0.11}$	0.35	0.107
Dargall Lane Burn			
H^+	$H = 23.44\ Q^{0.69}$	0.73	0.279
Ca^{++}	$Ca = 26.30\ Q^{-0.22}$	0.59	0.098
Mg^{++}	$Mg = 38.91\ Q^{-0.10}$	0.33	0.084
Al	$Al = 38.02\ Q^{0.32}$	0.60	0.134
SiO_2	$Si = 3.03\ Q^{-0.14}$	0.43	0.090
Green Burn			
H^+	$H = 22.89\ Q^{0.91}$	0.88	0.206
Ca^{++}	$Ca = 39.81\ Q^{-0.17}$	0.47	0.102
Mg^{++}	$Mg = 48.98\ Q^{-0.14}$	0.44	0.098
Al	$Al = 40.32\ Q^{0.25}$	0.54	0.158
SiO_2	$Si = 3.54\ Q^{-0.19}$	0.55	0.107

Table 5.1: Regression relationships between concentration (ueq/l) and discharge (Q, m^3/s) which are statistically significant at $p>0.95$.

<u>Equation:</u>

$Q_{DL} = 0.361\ Q_{WL}^{\ 0.79}$ $R^2 = 0.96$ s.e.e = 0.084

$Q_{GB} = 0.431\ Q_{WL}^{\ 1.02}$ $R^2 = 0.98$ s.e.e = 0.096

Table 5.2: Regression relationships between mean daily flows on the Dargall Lane (Q_{DL}) and Green Burn (Q_{GB}) and mean daily flows on the White Laggan (Q_{WL}). (Flow measured in m^3/s)

the Dargall Lane and Green Burn have only been gauged since July and September 1983 respectively, retrodictive models to produce mean daily flows for earlier periods were developed. These models took the form of regression equations in which the mean daily flows in each of the Green Burn and Dargall Lane were regressed against the equivalent flow on the White Laggan over the common period of record. The resulting equations and associated goodness-of-fit values are reported in Table 5.2 and graphed in Figures 5.1 and 5.2. On the basis of these models the mean daily flows for the Green Burn and Dargall Lane for 1981 and 1983 were simulated using the gauged flows on the White Laggan for those years. For elements where the rating relationship was not statistically significant (i.e. those not reported in Table 5.1) the annual output values (kg ha^{-1} yr^{-1}) were produced as the product of the flow weighted mean annual solute concentrations (mg l^{-1}) and the total annual discharge (m^3 s^{-1}) divided by the sub-catchment area (m^2).

Monthly inputs to both the Dargall Lane and Green Burn were determined in a similar manner to the annual inputs. Thus monthly inputs (kg ha^{-1}) were derived as the product of the volume weighted monthly concentration (mg l^{-1}) of each element in the bulk collector and the total monthly precipitation (cm). As with the annual data the total monthly precipitation was derived separately for both sub-catchments and a linear increase in precipitation of 6% per 100m increase in altitude was assumed. In contrast to the annual loadings, however, it did not prove possible to make an allowance for the dry deposition of the major cations. This was due to an apparent storage of chloride within each sub-catchment in various months, a feature which will be discussed in more detail in section 5.4.

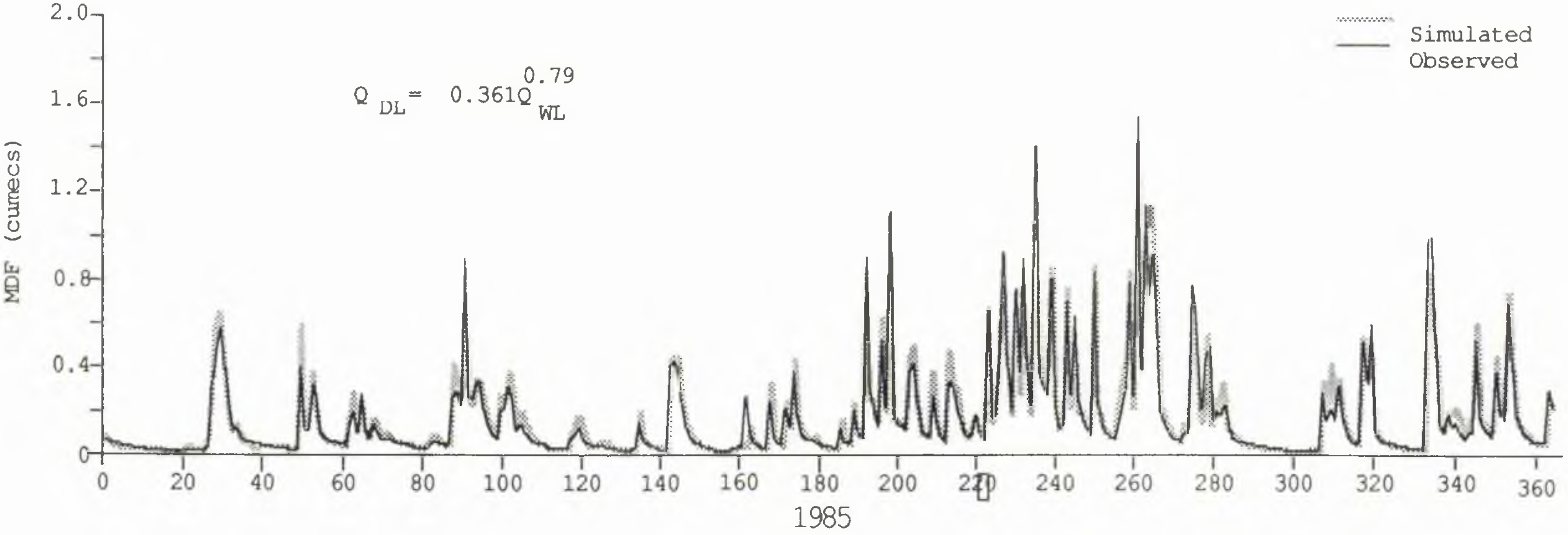


Figure 5.1 Simulated and Observed Flows - Dargall Lane 1985

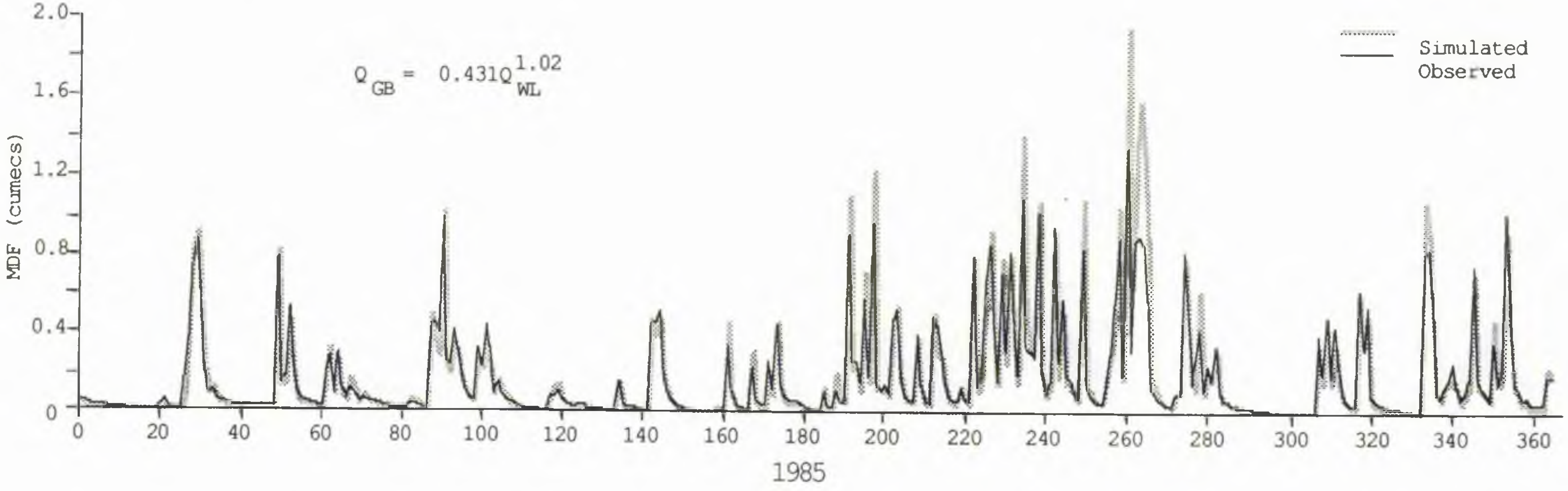


Figure 5.2 Simulated and Observed Flows - Green Burn 1985

Monthly outputs (kg ha^{-1}) from both sub-catchments were derived as the product of the flow-weighted monthly solute concentration (mg l^{-1}) and the total monthly flow (m^3 s^{-1}), divided by the area of the sub-catchment (m^2). This relatively straight-forward method was chosen in order to facilitate comparisons with predicted output budgets to be produced by the ILWAS model.

5.3 *ANNUAL HYDROCHEMICAL BUDGETS*

5.3.1 *Results*

5.3.1.1 Mean Annual Concentrations

Table 5.3 shows the mean annual concentrations for precipitation inputs to the White Laggan, Dargall Lane and Green Burn for 1981 and 1983-85, the results being reported in micro-equivalents per litre to facilitate comparison with other studies. The table shows that precipitation chemistry in each year is dominated by seasalts, with the sodium : chloride and magnesium : chloride ratios similar to those found in seawater. However, the actual concentrations of seasalts show considerable variation between years, with the highest values in 1984 being almost double those of 1985. In comparison the inter-annual variations of the other chemical species are far lower. Furthermore, the highest concentrations for most other species are in 1981, with the exception of sulphate where the highest concentration occurs in 1983. When the seasalt contributions are removed, sulphate is left as the dominant species in precipitation, excess sulphate concentration being greatest in 1983 and lowest in 1985.

	1981	1983	1984	1985
H	20.54	11.68	18.83	15.45
NH_4	26.85	24.24	22.06	23.02
Na	99.90	119.80	145.20	80.30
K	5.38	4.82	5.07	2.07
Ca	8.62	7.54	6.61	5.63
Mg	23.65	26.53	30.14	14.84
Al	5.12	4.09	5.66	5.21
Fe	N.D.	4.79	2.68	2.79
Mn	0.49	0.43	0.57	0.30
Zn	1.00	1.67	0.85	0.45
Cl	117.60	140.30	172.30	91.50
HCO_3	1.42	2.13	1.78	1.11
SO_4	51.80	57.15	52.20	42.31
SO_4**	39.69	42.70	34.45	32.89
NO_3	4.00	3.51	3.77	3.26
PO_4	1.61	0.71	1.25	0.62
*SiO_2	0.01	0.03	0.02	0.02

N.D. = not determined
* (mg/l)
SO_4** = Non Seasalt SO_4

Table 5.3: The mean annual solute concentrations (ueq/l) in precipitation at Loch Dee 1981, 1983/85.

The chemical composition of the runoff in the three streams, like that for precipitation, is dominated by sodium, chloride and sulphate (Table 5.4). However, concentrations of all species, other than hydrogen, ammonium and zinc, are far higher in the streamwaters than in the precipitation and are much less variable from year to year. Each year the Dargall Lane is the most acidic stream and the White Laggan the least acidic, reflecting the calcium concentrations which are consistently highest in the White Laggan and lowest in the Dargall Lane. Likewise magnesium and sulphate concentrations are both lowest in each year in the Dargall Lane. However, whereas magnesium concentrations are consistently highest in the Green Burn, sulphate concentrations are higher in the White Laggan than the Green Burn in both 1981 and 1983. Nitrate concentrations in contrast are consistently highest in the Dargall Lane, whereas the lowest concentrations are found in the Green Burn in 1983 and 1984. Concentrations of the trace metals; aluminium, iron, manganese and zinc are all very low but tend to be greatest in the Green Burn and lowest in the White Laggan, with the exception of zinc where the highest concentrations tend to occur in the Dargall Lane.

5.3.1.2 Spatial Variations in the Hydrochemical Budgets

Having examined the input and output concentrations of individual chemical species, the annual hydrochemical budgets within each sub-catchment are now analysed, initially in terms of spatial variation between sub-catchments and then in terms of contrasting years. The mean annual input loadings, outputs and net catchment losses, for each of the sub-catchments, over the period of study are shown in table 5.5. Mean annual inputs of all chemical species are

	White Laggan				Dargall Lane				Green Burn			
	1981	1983	1984	1985	1981	1983	1984	1985	1981	1983	1984	1985
H	3.18	1.11	1.40	0.87	8.37	5.61	6.18	4.26	4.97	3.59	3.74	1.84
NH_4	1.39	1.40	1.46	1.85	0.60	1.55	1.30	2.00	0.44	1.68	1.18	1.74
Na	154.71	195.04	205.39	154.76	144.91	185.55	193.30	159.41	148.00	188.22	205.47	155.48
K	8.17	7.63	7.56	8.14	9.55	6.95	8.80	9.20	8.54	8.78	8.73	8.71
Ca	72.16	86.85	86.57	76.99	47.34	54.20	54.17	47.95	58.80	77.52	68.02	60.92
Mg	69.39	74.90	78.99	65.74	50.61	55.44	58.76	48.56	70.64	83.15	83.28	66.04
Al	9.43	8.72	9.93	14.83	20.23	15.46	14.84	19.08	21.72	16.49	18.39	22.29
Fe	N.D.	2.68	1.38	1.35	N.D.	3.91	1.64	1.78	N.D.	5.97	5.08	5.65
Mn	0.48	0.48	0.46	0.49	0.86	0.86	0.81	0.88	1.43	1.30	1.24	1.45
Zn	0.24	0.21	0.21	0.25	0.41	0.29	0.28	0.40	0.31	0.31	0.18	0.14
Cl	180.50	223.60	244.80	178.16	162.90	217.42	228.80	177.94	164.20	215.50	244.20	173.61
HCO_3	54.87	52.21	59.87	58.81	28.27	26.16	29.68	33.40	48.30	56.28	72.77	59.05
SO_4	92.60	89.94	98.94	85.53	87.62	80.76	76.33	80.23	92.19	92.87	94.05	86.45
NO_3	5.37	6.60	5.76	5.28	7.41	6.90	6.72	7.20	6.03	4.68	5.28	6.99
PO_4	0.60	0.27	0.45	0.27	0.08	0.17	0.10	0.27	0.07	0.23	0.16	0.18
SiO_2*	3.01	3.00	3.38	3.10	3.70	3.80	3.50	3.60	4.69	4.50	4.37	4.32

Table 5.4: The mean annual solute concentrations (ueq/l) in the Loch Dee catchments 1981, 1983/85.

greatest for the Dargall Lane and least for the Green Burn, reflecting the variations in the amount of precipitation received by each of the three sub-catchments. As with the solute concentrations, input loadings to each of the sub-catchments are dominated by sodium, chloride and sulphate. These same three species together with silica also dominate the solute outputs. Net sub-catchment losses were calculated as the difference between stream outputs and the total of wet and dry deposition. All three sub-catchments are net sources of silica, calcium, magnesium, potassium, sodium, bicarbonate, sulphate and nitrate and net sinks for hydrogen, ammonium and phosphate. However, variations exist between the three sub-catchments in the extent to which the various species are lost or gained. Thus whilst hydrogen is retained to a greater extent in the White Laggan than the Green Burn and Dargall Lane, calcium and magnesium are lost from all three in an inverse manner (ie White Laggan highest and Dargall Lane lowest). Silica, sodium, aluminium and sulphate losses are all greatest from the Green Burn and lowest from the White Laggan. Losses of both nitrate and potassium are greatest from the Dargall Lane. However, whereas nitrate losses are lowest from the Green Burn, potassium losses are lowest from the White Laggan. The trace metals iron, manganese and zinc show a particularly complex pattern, with zinc and manganese both being stored in the White Laggan sub-catchment and released from the other two sub-catchments whereas iron is stored in both the Dargall Lane and White Laggan sub-catchments.

	INPUTS			OUTPUTS			BALANCE		
	W.L.	D.L.	G.B.	W.L.	D.L.	G.B.	W.L.	D.L.	G.B.
H	0.48	0.49	0.46	0.05	0.30	0.29	-0.43	-0.19	-0.17
NH_4	9.54	9.73	9.16	0.47	0.47	0.37	-9.07	-9.26	-8.79
Na	86.42	95.34	82.69	86.61	96.81	84.46	0.19	1.47	1.77
K	5.65	6.16	5.39	6.66	8.37	7.24	1.01	2.21	1.85
Ca	4.95	5.36	9.29	24.78	17.73	21.16	19.83	12.37	16.48
Mg	9.71	10.69	10.69	15.91	13.51	15.33	6.20	2.82	6.04
Al	1.27	1.29	1.22	3.63	6.12	6.43	2.36	4.83	5.21
Fe	1.72	1.76	1.66	0.70	0.99	2.15	-1.02	-0.77	0.49
Mn	0.34	0.35	0.33	0.29	0.58	0.80	-0.05	0.23	0.47
Zn	0.12	0.12	0.11	0.16	0.28	0.17	-0.04	0.16	0.06
Cl	155.79	171.96	149.16	155.79	171.96	149.16	0	0	0
HCO_3	2.75	2.81	2.64	67.91	44.43	70.33	65.16	41.62	67.69
SO_4	68.90	70.00	65.68	94.59	96.36	93.45	25.69	26.36	27.77
NO_3	6.37	6.49	6.11	7.67	10.82	6.62	1.30	4.32	0.51
PO_4	0.95	0.97	0.91	0.27	0.11	0.10	-0.68	-0.86	-0.81
SiO_2	0.55	0.56	0.54	60.82	89.95	96.24	60.27	89.39	95.61

W.L. = White Laggan D.L. = Dargall Lane G.B. = Green Burn

Table 5.5: The mean annual loadings, outputs and hydrochemical balances (Kg/ha/yr) for the White Laggan, Dargall Lane and Green Burn 1981, 1983/85.
(Dry deposition of major cations allowed for by assuming that chloride is chemically conservative within the catchments)

5.3.1.3 Annual Variability in the Hydrochemical Budgets

Tables 5.6-5.8 show the calculated deposition, outputs and catchment losses of all the species examined in each of the three sub-catchments for each study year. The budgets of the major species of interest are also presented diagramatically as figures 5.3-5.5, in order to aid interpretation. From table 5.6 it can be seen that the input loadings of all the major chemical species vary from year to year in all three sub-catchments. The seasalt inputs of sodium and chloride show this temporal variation particularly well, deposition of both being highest in 1984 and lowest in 1981 (Figure 5.3). The hydrogen ion, in contrast, has the highest deposition rate in 1981 and then shows a dramatic fall to 1983 followed by a slight increase in 1984. Nitrate exhibits the same pattern as hydrogen except the decline in deposition from 1981 to 1983 is much less pronounced. Sulphate, however, shows a consistent decrease throughout the period, as does potassium. All species, except magnesium, exhibit the same temporal patterns in all three sub-catchments. Magnesium loadings, whilst broadly similar to sodium loadings, are lowest to all three sub-catchments in 1985. They are highest to the to the Dargall Lane and the Green Burn sub-catchments in 1983, and to the White Laggan sub-catchment in 1981.

Streamwater solute outputs (Table 5.7 and Figure 5.4) also exhibit an annual variability, although in each year outputs from each of the sub-catchments are dominated by sodium, chloride, sulphate and silica. The annual variability in the output of sodium and chloride reflects the pattern of precipitation loadings, which were highest in 1984 and lowest in 1981. Hydrogen ion outputs from all three sub-catchments are also highest in 1984 and lowest outputs in 1983 and 1985. In

	White Laggan				Dargall Lane				Green Burn			
	1981	1983	1984	1985	1981	1983	1984	1985	1981	1983	1984	1985
Ppt (mm)	3122	2648	2594	2924	3181	2698	2643	2979	2995	2541	2489	2806
H	0.65	0.31	0.49	0.46	0.66	0.32	0.50	0.46	0.62	0.30	0.47	0.44
NH_4	11.74	8.99	8.01	9.43	11.96	9.16	8.17	9.61	11.26	8.63	7.69	9.05
Na	81.92	86.75	90.16	86.86	79.25	97.52	112.33	92.27	74.02	84.27	94.36	78.12
K	7.50	5.94	5.35	3.81	7.25	6.67	6.65	4.05	6.78	5.77	5.59	3.43
Ca	6.14	4.76	3.58	5.31	5.94	5.38	4.42	5.68	5.55	4.65	3.71	4.81
Mg	10.26	10.16	9.90	8.52	9.93	11.42	12.34	9.05	9.27	9.88	10.36	7.65
Al	1.43	0.97	1.31	1.36	1.45	0.99	1.34	1.39	1.37	0.93	1.25	1.31
Fe	N.D.	2.36	1.29	1.52	N.D.	2.41	1.32	1.55	N.D.	2.27	1.24	1.46
Mn	0.42	0.31	0.41	0.24	0.43	0.32	0.41	0.25	0.40	0.30	0.39	0.23
Zn	0.10	0.15	0.13	0.10	0.11	0.15	0.13	0.10	0.10	0.14	0.12	0.09
Cl	148.75	156.70	165.04	152.67	143.91	176.14	205.63	162.17	134.41	152.21	172.73	137.30
HCO_3	2.70	3.44	2.82	2.05	2.76	3.51	2.87	2.09	2.59	3.30	2.70	1.97
SO_4	77.67	72.68	65.83	59.42	79.14	74.06	66.26	60.55	74.52	69.74	62.39	57.01
NO_3	7.74	5.76	6.06	5.91	7.89	5.87	6.18	6.02	7.43	5.53	5.82	5.67
PO_4	1.59	0.60	1.03	0.57	1.62	0.61	1.05	0.58	1.53	0.57	0.98	0.55
SiO_2	0.31	0.79	0.52	0.58	0.32	0.81	0.53	0.60	0.30	0.76	0.50	0.56

N.D. = not determined

Table 5.6: Annual precipitation and input loadings (Kg/ha/yr) to the Loch Dee catchments 1981, 1983/85
(Dry deposition of major cations allowed for by assuming that chloride is chemically conservative within the catchments).

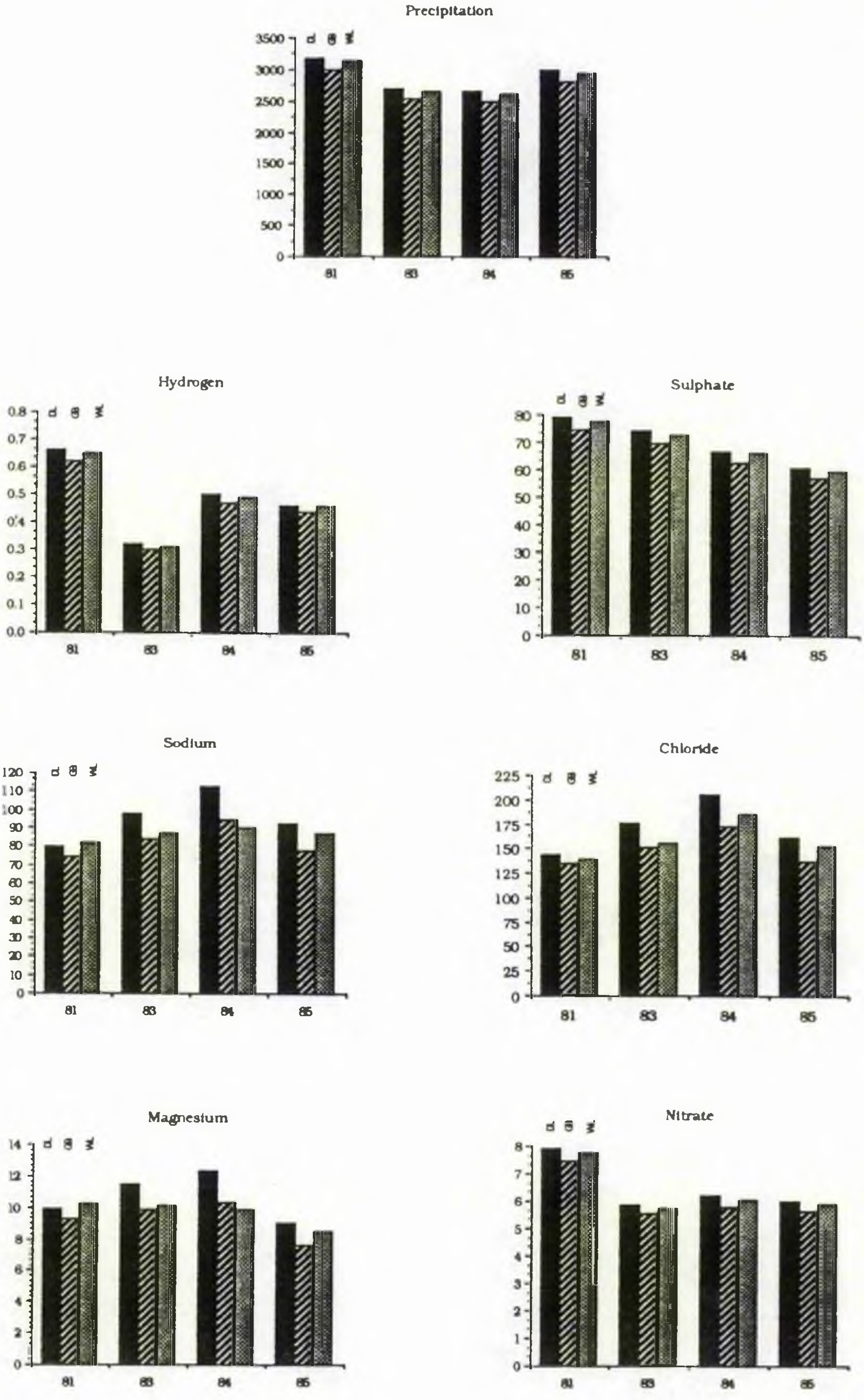


Figure 5.3: Inputs of Precipitation (mm) and Major Ions (kg/ha) to the Dargall Lane, Green Burn and White Laggan Burn 1981, 1983/85.

	White Laggan				Dargall Lane				Green Burn			
	1981	1983	1984	1985	1981	1983	1984	1985	1981	1983	1984	1985
Runoff(mm)	2357	2004	1928	2451	2491	2261	2534	2570	2308	2007	1995	2230
*H	0.05	0.04	0.08	0.03	0.32	0.20	0.48	0.20	0.30	0.24	0.40	0.24
NH_4	0.45	0.39	0.39	0.63	0.21	0.50	0.46	0.72	0.14	0.47	0.33	0.54
Na	82.65	88.61	89.99	85.17	82.99	97.45	112.62	94.18	78.54	86.18	94.22	79.71
K	7.43	5.90	5.62	7.69	9.30	6.21	8.72	9.24	7.71	6.84	6.81	7.59
*Ca	26.27	24.06	21.98	26.80	18.28	16.96	17.37	18.31	22.65	20.22	19.75	22.03
*Mg	17.08	14.80	14.16	17.60	13.87	12.78	13.32	14.07	16.44	14.61	14.30	15.96
*Al	4.02	3.01	3.17	4.30	6.04	4.74	7.04	6.64	6.40	6.08	6.25	6.99
Fe	N.D.	0.99	0.49	0.61	N.D.	1.36	0.77	0.85	N.D.	2.21	1.88	2.35
Mn	0.31	0.26	0.24	0.33	0.59	0.54	0.56	0.62	0.91	0.71	0.68	0.89
Zn	0.18	0.11	0.13	0.20	0.33	0.22	0.23	0.34	0.19	0.16	0.16	0.18
Cl	148.75	156.70	165.04	152.67	143.91	176.14	205.63	162.17	134.41	152.21	172.73	137.30
HCO_3	77.80	62.95	44.16	86.71	42.97	36.46	45.90	52.37	68.03	68.39	64.56	80.35
SO_4	103.36	85.37	90.35	99.27	104.85	88.62	92.92	99.04	102.22	88.85	90.11	92.60
NO_3	7.87	8.09	6.79	7.91	11.45	9.77	10.56	11.46	8.63	5.78	6.53	5.54
PO_4	0.44	0.17	0.27	0.21	0.06	0.12	0.06	0.20	0.05	0.14	0.10	0.12
*SiO_2	65.85	57.11	54.74	67.56	94.00	88.29	90.70	94.63	112.08	92.93	90.51	100.90

N.D. = not determined
* Determined using rating equations

Table 5.7: Mean annual solute outputs (Kg/ha/yr) from the three sub-catchments at Loch Dee.

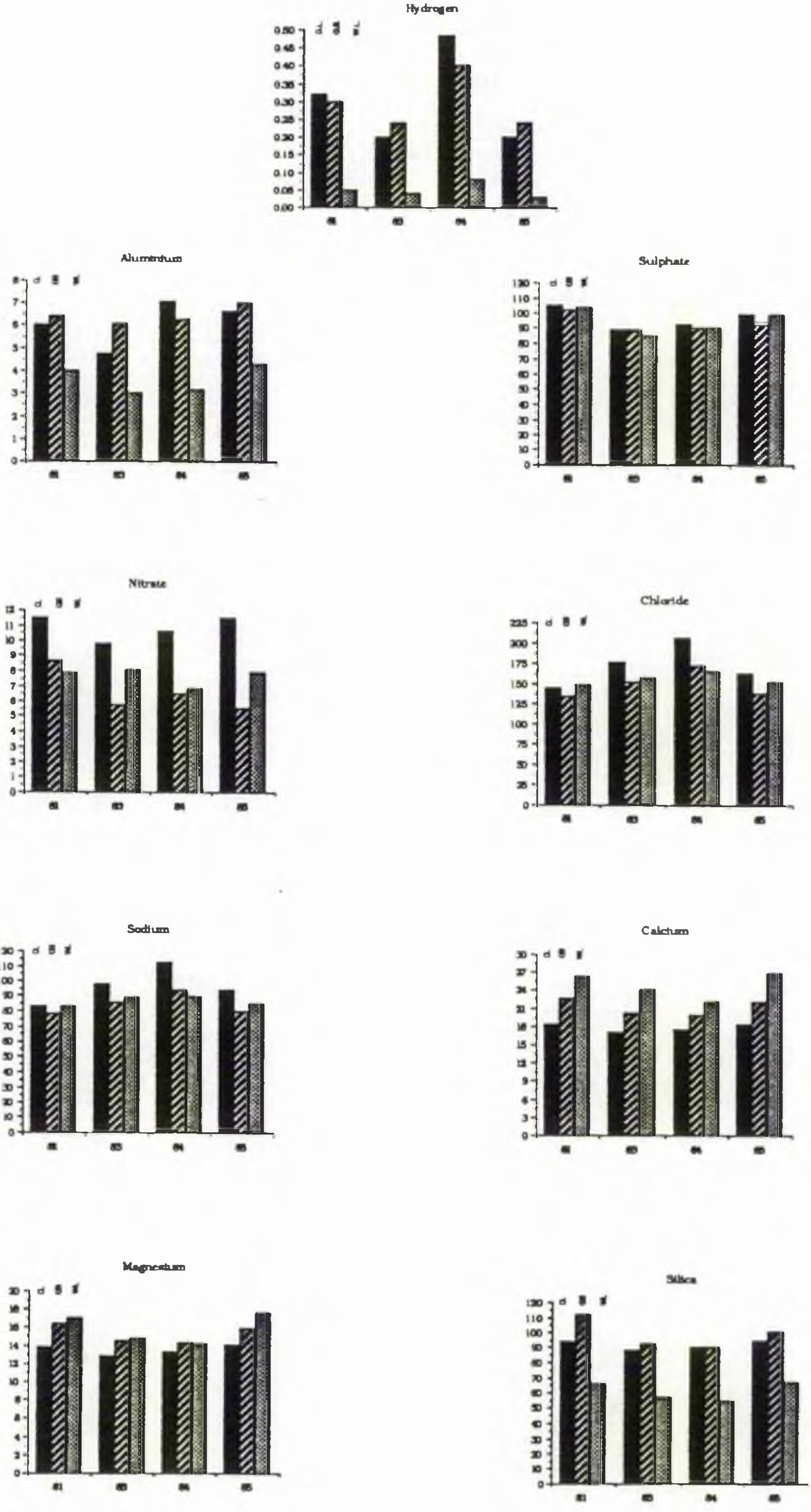


Figure 5.4: Major Ion Outputs from the Dargall Lane, Green Burn and White Laggan Burn for 1981, 1983/85.

contrast, sulphate outputs in all three sub-catchments are highest in 1981, fall to a nadir in 1983 and then increase through 1984 to 1985. Nitrate outputs follow a more complex pattern, outputs from the Green Burn being highest in 1981, fall in 1983, rise again in 1984 before reaching the lowest value in 1985. From the Dargall Lane nitrate outputs also fall from 1981 to 1983, however, the outputs continue to rise through 1984 to reach a maximum in 1985. In contrast nitrate outputs from the White Laggan increase from 1981 to 1983 and fall to a minimum in 1984. Like nitrate, outputs of other chemical species also tend to vary spatially as well as temporally. Thus whilst aluminium outputs are lowest from all three sub-catchments in 1983, they are highest from the Green Burn and White Laggan in 1985 compared with 1984 from the Dargall Lane. Silica outputs also show a spatial as well as temporal variation. Thus outputs from both the White Laggan and Dargall Lane are greatest in 1985 and lowest in 1983, whereas Green Burn outputs are greatest in 1981 and lowest in 1984. Similarly calcium, magnesium and potassium outputs are highest in either 1981 or 1985 and lowest in either 1983 or 1984.

The net catchment losses (Table 5.8 and Figure 5.5) show that in each year all three sub-catchments were net sources of calcium, magnesium, aluminium, bicarbonate, sulphate, nitrate and silica. Losses of calcium and magnesium from the White Laggan and Green Burn sub-catchments follow a similar pattern, with both being greatest in 1985 and higher in 1981 than in either 1983 or 1984. Losses from the White Laggan are, however, greater in all years than from the Green Burn. In contrast, losses of calcium and magnesium from the Dargall Lane follow a different pattern, thus calcium losses are greatest in 1984 and lowest in 1983 whereas magnesium losses are greatest in 1985 and

	White Laggan				Dargall Lane				Green Burn			
	1981	1983	1984	1985	1981	1983	1984	1985	1981	1983	1984	1985
H+	-0.60	-0.27	-0.41	-0.43	-0.34	-0.12	-0.08	-0.26	-0.32	-0.06	-0.07	-0.20
NH_4	-11.29	-8.60	-7.62	-8.80	-11.73	-8.65	-7.75	-8.88	-11.12	-8.16	-7.36	-8.51
Na	0.73	1.86	-0.17	-1.69	3.74	-0.07	0.29	1.94	4.52	1.91	-0.14	1.59
K	-0.07	-0.04	0.27	3.88	2.05	-0.46	2.07	5.27	0.93	1.07	1.22	4.16
Ca	20.13	19.30	18.40	21.49	12.34	11.58	12.95	12.63	17.10	15.57	16.04	17.22
Mg	6.82	4.64	4.26	9.08	3.94	1.36	0.98	5.02	7.17	4.73	3.94	8.31
Al	2.59	2.04	1.86	2.94	4.59	3.75	5.70	5.25	5.03	5.15	5.00	5.68
Fe	N.D.	-1.37	-0.80	-0.91	N.D.	-1.01	-0.61	-0.69	N.D.	-0.06	0.64	0.89
Mn	-0.11	-0.05	-0.17	-0.09	0.16	0.22	0.15	0.37	0.51	0.41	0.29	0.66
Zn	-0.08	-0.04	-0.00	-0.10	0.22	0.07	0.10	0.24	0.09	0.02	0.04	0.09
Cl	0	0	0	0	0	0	0	0	0	0	0	0
HCO_3	75.10	59.51	41.34	84.66	40.21	32.95	43.03	50.28	65.44	65.09	61.86	78.38
SO_4	25.69	12.69	24.52	39.85	25.71	14.56	26.66	38.49	27.70	19.11	28.72	35.59
NO_3	0.13	2.33	0.73	2.00	3.56	3.90	4.38	5.44	1.20	0.25	0.71	2.12
PO_4	-1.15	-0.43	-0.76	-0.36	-0.95	-0.48	-0.98	-0.36	-1.48	-0.43	-0.88	-0.43
SiO_2	65.54	56.32	54.22	66.98	91.68	85.60	88.24	92.01	108.42	89.39	87.30	97.32

N.D. = not determined

Table 5.8: Net hydrochemical balances (Kg/ha/yr) from the three sub-catchments at Loch Dee.

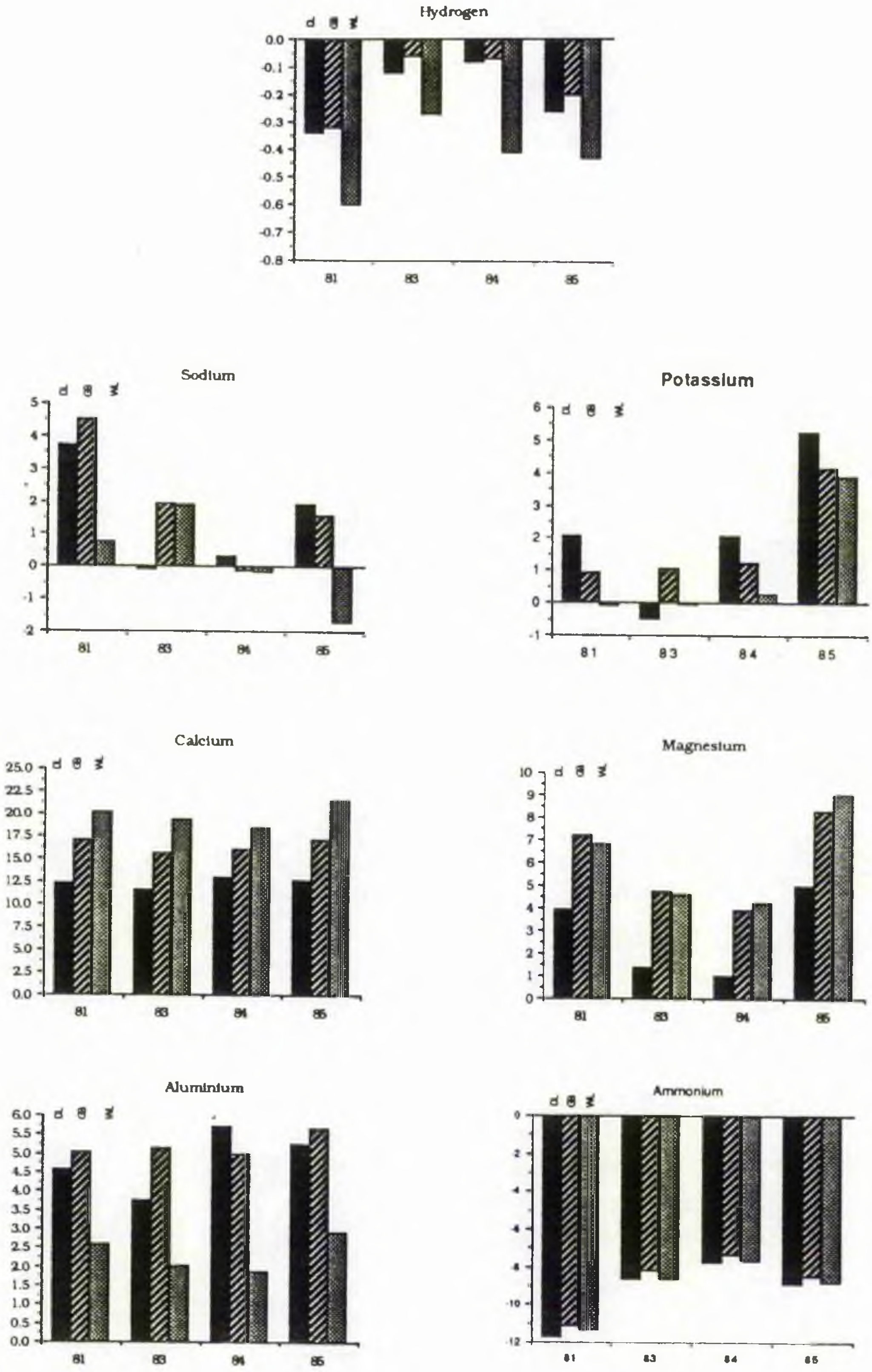


Figure 5.5a: The Hydrochemical Balance (Kg/ha) for the Major Cations for the Dargall Lane, Green Burn and White Laggan Burn, for 1981, 1983/85

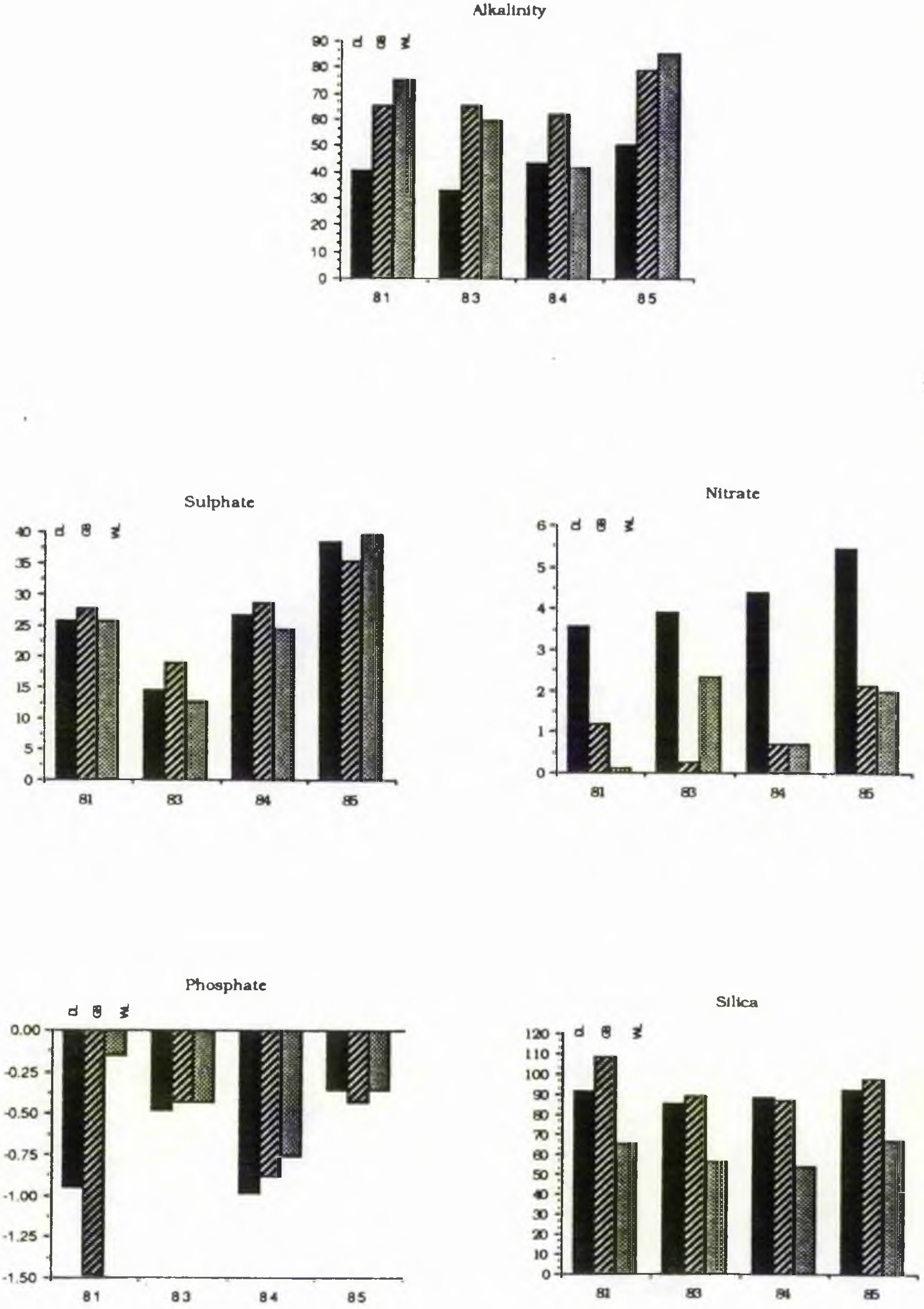


Figure 5.5b: The Hydrochemical Balance (Kg/ha) for the Major Anions and Silica for the Dargall Lane, Green Burn and White Laggan Burn, for 1981, 1983/85

least in 1984. Furthermore, in each of the study years losses of both species are greatest from the White Laggan sub-catchment and least from the Dargall Lane sub-catchment. Aluminium losses from the Green Burn and White Laggan are greatest in 1985 and lowest in 1984 whereas from the Dargall Lane aluminium losses are greatest in 1984 and lowest in 1983. Sulphate losses from all three sub-catchments follow the same pattern with losses being greatest in 1985 and lowest in 1983. Losses in 1981 and 1984 are intermediate but similar in value. Nitrate losses in contrast are highest from the Green Burn and Dargall Lane in 1985 compared with 1983 from the White Laggan. The lowest nitrate losses occur in 1981 from the White Laggan and Dargall Lane sub-catchments and 1983 from the Green Burn. Net losses of silica from both the White Laggan and Dargall Lane are greatest in 1985 but are lowest in 1983 from the Dargall Lane and 1984 from the White Laggan. In contrast silica losses from the Green Burn are greatest in 1981 and lowest in 1984.

Table 5.8 also shows that all three sub-catchments are net sinks for hydrogen, ammonium and phosphate. Hydrogen ions are gained by each sub-catchment in the same temporal pattern, the gains being greatest in 1981 and falling to 1985 apart from a slight increase in 1984. Ammonium gains are also greatest in 1981 but fall to 1984 before rising again in 1985. Phosphate uptake follows the same temporal pattern as for hydrogen ions in the Green Burn and White Laggan sub-catchments. In the Dargall Lane sub-catchment, however, the increase in uptake in 1984 is greater with the highest uptake occurring in that year.

For the trace metals, iron, manganese and zinc each catchment is either a net source or sink. Thus iron uptake occurs for the three years 1983-85 in the White Laggan and Dargall Lane, but only in 1983 in the Green Burn. Similarly manganese and zinc are uptaken each year in the White Laggan sub-catchment but output each year from the Green Burn and Dargall Lane

Sodium and potassium show particularly complex temporal and spatial patterns, with each sub-catchment a net source or sink in different years. Thus for sodium, in 1981 all three sub-catchments are net sources, but in 1983 the Dargall Lane becomes a sink for sodium whilst the White Laggan and Green Burn remain sources. In 1984 the situation reverses and the Dargall Lane becomes a net source and the other two sub-catchments net sinks. Finally in 1985 the Green Burn and Dargall Lane are net sources and the White Laggan becomes a net sink.

5.3.2 *Discussion*

5.3.2.1 Spatial Variability

Analysis of the mean sub-catchment losses indicates that the release of the major cations is lowest in the moorland Dargall Lane sub-catchment. These low values are a result of the rugged topography and general lack of a minerogenic soil in the catchment. Precipitation is initially routed through the thick organic surface horizons of the peaty soils on the steep valley slopes with little opportunity for the release of base cations. The flow is then retarded by the thick peats of the valley bottom, the peats containing minimal minerogenic material and thus contributing few base cations to the flow. The consequent slight neutralisation of acidic precipitation, (streamwater pH being only slightly higher than the pH of precipitation), together with the high net output of aluminium indicates that the dominant exchange process is that of protons in solution for aluminium on the exchange complexes within the soils. This leaching of potentially toxic aluminium ions into streamwaters has been reported from several areas receiving acidic precipitation (Johnson et al. 1968, Cronan and Schofield 1979, Neal et al. 1986a).

In contrast the 70% afforested Green Burn sub-catchment, whilst showing a similar release of aluminium as that recorded in the Dargall Lane, exhibits a far greater release of base cations, bicarbonate and silica. This complex hydrochemical response is likely to be a result of the pre-afforestation draining and ploughing rather than the presence of the trees, which were planted in the early 1970's and whose canopy is only just starting to close. The increased drainage density that has occurred due to the land preparation procedures has resulted in a more rapid stormflow from the sub-catchment (Harper 1984), thereby leading to a reduction in the opportunity for neutralisation of acidic precipitation. The consequent high acidity of the stormflow, as in the Dargall Lane, leads to the mobilisation of aluminium into the streamwaters. However, the greater total organic carbon content of the Green Burn compared with the Dargall Lane (Harriman and Morrison 1985) suggests that a larger proportion of this aluminium will be in a non-labile organic form, a hypothesis supported by the higher observed fish population in the Green Burn (Harriman and Morrison 1985). During low flow periods, however, the flow in the ditches is through the basal part of the peat profile and any associated minerogenic soil which will have been exposed by the draining operations. Consequently, there is far greater opportunity for neutralisation reactions to proceed during low flows thereby increasing the leaching of bases and nutrients into the streamwater (cf results on the Plynlimon catchments in central Wales by Neal et al. 1985, 1986a). As yet there is only slight evidence of the filtering effect of forests identified by Harriman and Morrison (1981), (ie a generally slightly higher net output of sulphate from the Green Burn than from the other two sub-catchments), since the forest is still relatively immature.

On the basis of the foregoing comments the White Laggan Burn whose catchment is 30% forested and 70% moorland could be expected to have a chemistry combining the responses of both other streams. In reality the greater uptake of hydrogen and release of calcium and magnesium gives the White Laggan Burn the highest pH of all three streams. This higher release of bases and consequent buffering of precipitation is primarily due to the head of the White Laggan catchment being underlain by unmetamorphosed sedimentary rocks, a lithology absent from the other catchments. Probably of secondary importance is the addition of limestone to the catchment since 1981 (Table 4.1). The presence of these unmetamorphosed rocks and the lower amount of pre-afforestation ditching together with the higher uptake of protons and lower net output of aluminium implies that the dominant neutralisation reaction in this sub-catchment is the cation exchange of bases on the soil exchange complexes for protons in the soil solution. This exchange occurs at all flow levels in the Dargall Lane in comparison with the Green Burn where the same reactions only occur at low flow levels. This is in contrast with the previously noted exchange reaction of protons for aluminium which occurs at all flow levels in the Dargall Lane and under high flow conditions in the Green Burn.

Net sulphate outputs from the White Laggan are not only lower than from the Green Burn, as would be expected with the lower proportion of forest, but are also lower than from the unforested Dargall Lane sub-catchment. This is probably due to the presence of a band of pyritic black shales in the upper headwaters of the Dargall Lane sub-catchment (Figure 4.2), which upon oxidation will produce sulphate. Overall, across all these catchments, after allowance is made for the slight increase in excess sulphate concentrations due to either forest filtering or to oxidation of pyritic bedrock, the annual net output of sulphate is approximately 25 kg ha^{-1}. This value represents unmeasured dry/occult deposition of sulphate to the area and is similar to that reported by Barrett et al. (1983) for dry deposition in the Galloway Hills. If it is assumed that all the unmeasured deposition of sulphate occurs as gaseous sulphur dioxide then this corresponds to an unmeasured atmospheric input of acidity of 0.53 (kg ha^{-1} yr^{-1}). Upon oxidation to sulphate each molecule of dry deposited sulphur dioxide represents a potential gain to the system of two protons. This figure represents approximately 55% of the net hydrogen ion input to the catchments.

5.3.2.2 Annual Variability

As well as the above noted spatial variability in the annual hydrochemical budgets at Loch Dee, temporal variations are also seen in both annual inputs and outputs. During the study period sulphate loadings to the catchment declined steadily (cf I.T.E. data for Scotland, Fowler et al. 1986). This decline reflects the reduction in power station emissions resulting from the recession in manufacturing output during the early 1980's (Department of the Environment 1986). However, this decline is nor recorded in the net sulphate outputs, which are below average in 1983 and above average in 1985. This indicates that either unmeasured dry/occult deposition of sulphate varies annually to a greater extent than wet deposition or that sulphate is stored in the catchment in some years and released later. However, the high organic matter content together with the low proportion of aluminium and ferrous oxides in the soils of the Loch Dee catchments probably precludes the adsorbtion of sulphate to any significant extent. This suggests that the dry/occult deposition of sulphate and thereby the possible unmeasured input of acidity do vary considerably from year to year.

Apart from sulphate the greatest variation in input loadings is in the amount of seasalt deposition, with the higher seasalt years being those with the lower annual precipitation (Table 5.6). Over the short time period of an individual storm Langan (1987) has described the cation exchange process of sodium for hydrogen which takes place within the Loch Dee soils during precipitation events with a high concentration of seasalts. However, over the longer period of an annual budget there is little evidence of this process being important (cf Brakke et al. 1987) since the adsorbed seasalts are re-exchanges for protons and released back into solution during subsequent non-seasalt storms. Over far longer periods of several decades, however, Neal et al. (1986b) postulate that increases in seasalt concentrations associated with forest filtration effects could significantly depress streamwater pH levels.

Outputs of bases and nutrients generally appear higher in the "wet" years 1981 and 1985 than in the "dry" years 1983 and 1984. This observation can be explained by the higher precipitation in the wet years leading to an increase in percolation through the thick surface organic layers into the underlying mineral soil with its greater supply of weathered material. This observation is also supported by the higher outputs of silica in these two years, the silica being more likely to have been leached from the mineral soil than from the peat.

5.3.2.3 Comparisons with other British Sites

The mean solute loadings to the Loch Dee catchments are broadly similar to those reported for other sites in Galloway and for Plynlimon in central Wales (Table 5.9). The higher seasalt loadings at Loch Dee in comparison with the other Galloway sites arise because of the lower amounts of rainfall at the other sites and because the values at Loch Dee include an estimate for dry deposition. The Loch Dee values are, however, very similar to those reported by Neal et al. (1985) for Plynlimon where an estimate of the dry deposition of major cations was also included. In comparison the 1985 sulphate loadings to both Loch Dee and neighbouring Loch Fleet are higher than at Plynlimon. This may possibly reflect the different sources of air pollution in southwest Scotland and central Wales respectively. Whereas the former area receives pollution inputs from the industrial areas of the Midlands and north of England (Burns et al. 1984), the latter area is upwind of such sources.

	Loch Dee* (1981)	Glentrool[(a)] (1979)	Cairnsmore of Fleet[(a)] (1979)	Loch Dee* (1985)	Loch Fleet[(b)] (1985)	Afon Haffren[(c)] (1985)
H	0.64	0.30	0.80	0.45	0.31	0.38
Na	78.40	43.00	54.00	85.75	29.57	71.70
K	7.15	4.00	5.00	3.76	1.70	3.07
Ca	5.88	4.00	7.00	5.27	3.49	3.98
Mg	9.82	4.00	7.00	8.41	3.71	9.00
Al	1.42	-	-	1.35	-	0.26
Cl	142.36	63.00	92.00	150.71	51.79	129.00
SO_4	77.11	58.00	94.00	58.99	48.17	34.40
NO_3	7.69	7.00	14.00	5.87	3.36	12.00
Precip (mm)	3099	1500	2000	2903	2180	1950

* Mean of inputs to 3 sub-catchments
(a) Burns et al. (1984)
(b) C.E.R.L.
(c) Neal et al. (1985)

Table 5.9: A comparison of annual input loadings (Kg/ha/yr) for Loch Dee with several other sites in upland Britain.

	White Laggan	Dargall Lane	Green Burn	Narrator[(a)]	Glendye[(b)]	Afon Haffren[(c)]
Na	0.11	1.47	1.97	6.70	9.00	-6.30
K	1.01	2.21	1.85	3.10	2.90	-0.02
Ca	19.83	12.37	16.48	11.30	17.00	8.00
Mg	6.20	2.82	6.04	2.30	5.00	2.90
SiO_2	60.27	89.39	95.61	92.60	82.40	22.60

(a) Williams et al. (1986)
(b) Reid et al. (1981)
(c) Neal et al. (1985)

Table 5.10: A comparison of catchment losses (Kg/ha/yr) for Loch Dee with several other sites in upland Britain.

When the net solute losses from the Loch Dee catchments are compared with losses from other catchments in Dartmoor, Wales and northern Scotland (Table 5.10), a clear similarity can be seen with all being dominated by high losses of silica. The only observable contrast is the lower rate of release of sodium and the corresponding higher rate of release of magnesium from the Loch Dee and Afon Hafren catchments than from the Narrator and Glen Dye catchments. These differences may reflect variations in the relative quantities of sodium and magnesium which can be weathered from the underlying bedrock.

5.4 *MONTHLY BUDGETS*

In contrast to the annual hydrochemical budgets the mean monthly hydrochemical budgets have only been determined for the Dargall Lane and Green Burn sub-catchments and only over the period 1983-1985. The rationale for these restrictions was connected with the modelling study. Firstly, these two sub-catchments were those where the modelling studies would be initially applied. Secondly this time period was the one over which the model calibration and verification would be performed.

5.4.1 *Results*

5.4.1.1 Mean Monthly Ion Concentrations

The volume-weighted mean monthly ion concentrations in precipitation together with the flow-weighted mean monthly ion concentrations for the Dargall Lane and Green Burn are shown in

a) Precipitation

Month	Ion											
	H^+	NH_4^+	Na^+	K^+	Ca^{++}	Mg^{++}	Al^{+++}	Cl^-	HCO_3^-	SO_4^{--}	NO_3^-	PO_4^-
Jan	10.19	0.15	4.60	0.19	0.16	0.46	0.038	7.89	0.11	2.65	0.18	0.29
Feb	38.03	0.51	4.26	0.14	0.17	0.48	0.044	8.35	0.08	3.60	0.45	0.006
Mar	18.02	0.58	3.88	0.18	0.21	0.37	0.056	6.43	0.09	3.01	0.28	0.022
Apr	12.04	0.31	1.84	0.10	0.09	0.16	0.044	3.20	0.12	1.94	0.19	0.026
May	26.22	0.64	1.34	0.08	0.15	0.16	0.081	2.23	0.08	2.99	0.46	0.012
Jun	11.36	0.34	0.80	0.09	0.14	0.12	0.078	1.48	0.06	2.32	0.21	0.006
Jul	13.65	0.38	1.27	0.08	0.12	0.12	0.075	1.83	0.06	2.62	0.24	0.021
Aug	6.40	0.47	0.86	0.09	0.15	0.15	0.046	1.69	0.09	1.75	0.17	0.009
Sep	7.57	0.29	1.96	0.16	0.14	0.22	0.059	3.84	0.05	2.02	0.13	0.030
Oct	11.15	0.35	4.56	0.19	0.17	0.51	0.066	8.25	0.07	3.15	0.16	0.016
Nov	19.71	0.19	2.67	0.10	0.09	0.21	0.047	4.15	0.14	2.47	0.25	0.028
Dec	15.55	0.24	3.55	0.21	0.11	0.38	0.063	6.11	0.08	2.32	0.18	0.006

b) Dargall Lane Burn

Month	Ion											
	H^+	NH_4^+	Na^+	K^+	Ca^{++}	Mg^{++}	Al^{+++}	Cl^-	HCO_3^-	SO_4^{--}	NO_3^-	PO_4^-
Jan	10.79	0.01	5.74	0.29	0.49	0.68	0.158	10.42	1.61	3.18	0.40	0.002
Feb	16.82	0.01	5.92	0.39	0.83	0.72	0.288	11.08	1.18	3.54	0.75	0.005
Mar	12.81	0.02	5.58	0.44	0.97	0.64	0.293	9.54	1.26	4.64	0.54	0.016
Apr	7.47	0.02	5.61	0.41	0.93	0.57	0.258	8.07	1.94	4.36	0.71	0.001
May	2.33	0.02	4.24	0.51	1.27	0.61	0.163	7.65	2.82	4.46	0.61	0.001
Jun	4.77	0.02	4.97	0.60	1.58	0.74	0.153	6.43	1.91	4.25	0.60	0.010
Jul	5.92	0.02	3.25	0.42	1.08	0.63	0.110	5.41	2.04	3.50	0.35	0.021
Aug	6.40	0.04	2.54	0.32	1.10	0.59	0.230	4.12	1.82	3.64	0.22	0.001
Sep	8.10	0.02	3.10	0.30	0.59	0.49	0.219	5.66	1.98	4.07	0.41	0.010
Oct	16.10	0.01	5.16	0.23	0.53	0.55	0.242	9.27	1.27	4.32	0.40	0.006
Nov	8.69	1.33	3.64	0.25	0.82	0.48	0.212	6.33	2.25	4.61	0.41	0.005
Dec	10.48	0.97	4.43	0.27	0.80	0.63	0.227	7.89	1.51	4.66	0.48	0.014

c) Green Burn

Month	Ion											
	H^+	NH_4^+	Na^+	K^+	Ca^{++}	Mg^{++}	Al^{+++}	Cl^-	HCO_3^-	SO_4^{--}	NO_3^-	PO_4^-
Jan	13.32	0.02	4.76	0.49	1.01	0.86	0.209	9.11	2.87	4.13	0.59	0.018
Feb	20.98	0.02	5.31	0.47	1.16	0.97	0.198	9.69	2.63	4.04	0.71	0.006
Mar	9.30	0.02	4.81	0.36	1.08	0.94	0.332	8.14	2.68	4.50	0.86	0.011
Apr	11.95	0.03	4.70	0.38	1.14	0.84	0.239	8.92	2.65	4.50	0.67	0.009
May	2.96	0.03	4.24	0.31	1.42	1.19	0.193	7.50	4.36	4.29	0.18	0.001
Jun	3.45	0.02	4.27	0.18	1.44	1.14	0.149	7.16	4.92	4.58	0.08	0.011
Jul	5.50	0.07	3.91	0.29	1.39	1.06	0.242	5.47	4.63	4.11	0.02	0.004
Aug	11.08	0.03	2.60	0.20	0.87	0.69	0.348	3.99	3.13	3.71	0.01	0.001
Sep	8.59	0.02	3.40	0.22	1.27	0.88	0.262	5.71	2.85	4.54	0.06	0.008
Oct	26.51	0.02	4.16	0.29	1.14	0.89	0.362	7.64	1.78	4.70	0.05	0.010
Nov	11.26	0.01	3.77	0.37	1.13	0.83	0.243	6.83	2.86	4.53	0.25	0.006
Dec	12.09	0.01	4.35	0.41	1.17	0.86	0.265	7.85	2.47	4.40	0.44	0.008

Table 5.11 The mean monthly concentrations (mg/l except H which is reported as ueq/l) for a) Precipitation, b) The Dargall Lane and c) The Green Burn for 1983 - 1985

Table 5.11. The initial monthly concentration data from which the means were derived is detailed in Appendix 1.1.

From Table 5.11 it can be seen that for the seasalts, sodium and chloride a clear seasonal pattern exists for both species with precipitation concentrations far greater in the winter (Oct - Mar) half of the year. The actual peak concentrations are found in January and the lowest concentrations in August. Hydrogen ion concentrations also share this seasonal pattern, however, the peak hydrogen ion concentration occurs in February. Calcium, magnesium and potassium concentrations all also show some evidence of a seasonal pattern with concentrations generally higher in the winter than summer period. In contrast, for both sulphate and nitrate concentrations there is little evidence of any seasonal pattern. However, whereas for sulphate the peak precipitation concentration occurs in February and the minimum in August, for nitrate the highest concentration occurs in May and the lowest in September.

Mean monthly output concentrations in both streams are in general considerably dampened in comparison with precipitation concentrations. This damping, over the monthly timescale, is particularly evident for the seasalt concentrations in both the Dargall Lane and Green Burn. However, despite the damping, seasalt concentrations in both streams still exhibit a clear seasonal pattern with higher concentrations in the winter/spring period. Hydrogen ions, whilst also exhibiting generally higher concentrations in the winter period, show a far greater range of concentrations in both streams than in precipitation. Nitrate concentrations in the Green Burn also show this seasonal pattern with concentrations far higher in the period Jan-April than in the summer. In the Dargall Lane, however, this pattern is modified with concentrations greater in the spring/summer period than the autumn/winter period. By contrast sulphate concentrations in both streams show no evidence of a seasonal pattern with peak concentrations occuring in March in the Dargall Lane and September in the Green Burn. Magnesium, and to a greater extent calcium concentrations, in both streams do show a seasonal trend in concentration, however, the pattern is the reverse of that for the seasalts, with concentrations of both ions greater in the summer months than the winter.

5.4.1.2 Mean Monthly Hydrochemical Budgets

For the study period, the mean monthly input loadings of precipitation and all determined chemical species, to the Dargall Lane and Green Burn sub-catchments are tabulated in Tables 5.12a and 5.13a respectively. To aid interpretation input loadings of precipitation and the major chemical species to both sub-catchments are also shown graphically in Figures 5.6 and 5.7. From these tables and figures it can be seen that the loadings of all the species are far lower in the summer period than for the rest of the year, clearly reflecting the far lower precipitation input at this time of the year. In the same manner the peak inputs of all the determined species, except for the hydrogen ion, occur in October, the month with the highest mean precipitation input for the study period. Hydrogen ion inputs in contrast are greatest in February, a month when precipitation inputs are lower than for all other months except May. The tables also show that whereas input loadings in the winter are dominated by the seasalts, sodium and

a) Precipitation and Loadings : Dargall Lane

Month	Precip (mm)	Ion											
		H^+	NH_4^+	Na^+	K^+	Ca^{++}	Mg^{++}	Al^{+++}	Cl^-	HCO_3^-	SO_4^{--}	NO_3^-	PO_4^-
Jan	313.8	0.032	0.47	14.44	0.60	0.56	1.43	0.12	24.77	0.33	8.32	0.56	0.02
Feb	136.6	0.052	0.69	5.82	0.19	0.23	0.66	0.06	11.40	0.11	4.92	0.61	0.03
Mar	232.8	0.042	1.34	9.02	0.42	0.48	0.87	0.13	14.96	0.21	7.00	0.66	0.05
Apr	157.6	0.019	0.48	2.90	0.15	0.14	0.25	0.07	5.05	0.19	3.06	0.30	0.02
May	110.5	0.029	0.71	1.48	0.09	0.17	0.18	0.09	2.46	0.09	3.30	0.51	0.01
Jun	140.7	0.016	0.48	1.13	0.12	0.20	0.14	0.11	2.08	0.09	3.27	0.29	0.05
Jul	146.4	0.020	0.56	1.86	0.11	0.18	0.17	0.11	2.68	0.09	3.89	0.35	0.03
Aug	218.6	0.014	1.02	1.89	0.20	0.33	0.32	0.10	3.70	0.19	3.83	0.36	0.02
Sep	303.4	0.023	0.88	5.98	0.47	0.43	0.66	0.18	11.66	0.16	6.12	0.38	0.09
Oct	376.2	0.042	1.31	17.15	0.70	0.65	1.91	0.25	31.03	0.28	11.83	0.60	0.08
Nov	212.9	0.042	0.40	5.69	0.21	0.19	0.44	0.10	8.83	0.29	5.25	0.53	0.06
Dec	314.9	0.049	0.76	11.17	0.65	0.33	1.18	0.20	19.23	0.27	7.31	0.58	0.02
Annual	2664.4	0.380	9.10	78.53	3.91	3.91	8.21	1.52	137.85	2.12	68.10	5.73	0.48

b) Flow and Outputs : Dargall Lane

Month	Flow (mm)	Ion											
		H^+	NH_4^+	Na^+	K^+	Ca^{++}	Mg^{++}	Al^{+++}	Cl^-	HCO_3^-	SO_4^{--}	NO_3^-	PO_4^-
Jan	361.0	0.039	0.04	20.73	1.08	1.77	2.45	0.57	37.61	5.82	11.46	1.44	0.01
Feb	184.1	0.031	0.02	10.89	0.71	1.52	1.33	0.53	20.40	2.17	6.51	1.38	0.01
Mar	187.2	0.024	0.03	10.45	0.82	1.81	1.19	0.55	17.85	2.36	8.75	1.01	0.03
Apr	147.2	0.011	0.03	8.26	0.61	1.37	0.83	0.38	11.88	2.85	6.41	1.05	0.00
May	85.9	0.002	0.02	3.64	0.49	1.08	0.52	0.14	6.57	2.42	3.83	0.52	0.00
Jun	104.8	0.006	0.02	4.27	0.63	1.66	0.78	0.16	6.74	2.00	4.45	0.64	0.01
Jul	118.2	0.007	0.02	3.84	0.50	1.27	0.74	0.13	6.39	2.41	4.14	0.41	0.02
Aug	187.3	0.012	0.04	4.78	0.59	2.06	1.11	0.43	7.71	3.41	6.81	0.41	0.00
Sep	295.0	0.024	0.06	9.19	0.89	1.76	1.45	0.65	16.78	5.87	12.04	1.22	0.03
Oct	322.6	0.052	0.03	16.63	0.73	1.72	1.78	0.78	29.92	4.10	13.94	1.28	0.02
Nov	184.0	0.016	0.03	6.69	0.46	1.51	0.89	0.39	11.64	4.13	8.47	0.75	0.01
Dec	276.9	0.029	0.04	12.26	0.76	2.21	1.73	0.63	21.86	4.18	12.89	1.33	0.04
Annual	2454.2	0.320	0.37	111.63	8.27	19.74	14.80	5.34	195.35	41.72	99.70	11.44	0.18

c) Balances : Dargall Lane

Month	Ion											
	H^+	NH_4^+	Na^+	K^+	Ca^{++}	Mg^{++}	Al^{+++}	Cl^-	HCO_3^-	SO_4^{--}	NO_3^-	PO_4^-
Jan	0.007	-0.43	6.30	0.48	1.19	1.02	0.45	12.84	5.42	3.14	0.88	-0.01
Feb	-0.021	-0.67	5.07	0.53	1.29	0.67	0.48	9.00	2.06	1.59	0.76	-0.02
Mar	-0.018	-1.30	1.43	0.41	1.33	0.32	0.42	2.88	2.15	1.75	0.36	-0.02
Apr	-0.008	-0.50	5.36	0.46	1.23	0.58	0.31	6.83	2.67	3.35	0.75	-0.02
May	-0.027	-0.70	2.17	0.39	0.92	0.34	0.06	4.12	2.33	0.52	0.01	-0.01
Jun	-0.011	-0.46	3.14	0.51	1.45	0.64	0.05	4.66	1.91	1.18	0.35	-0.04
Jul	-0.013	-0.54	1.98	0.39	1.09	0.58	0.02	3.71	2.32	0.25	0.06	-0.01
Aug	-0.002	-0.98	2.89	0.39	1.72	0.79	0.32	4.02	3.22	2.99	0.05	-0.02
Sep	-0.001	-0.83	3.21	0.42	1.33	0.79	0.47	5.11	5.71	5.91	0.84	-0.06
Oct	-0.010	-1.28	-0.52	0.02	1.07	-0.14	0.53	-1.11	3.82	2.12	0.68	-0.06
Nov	-0.026	-0.37	1.00	0.25	1.32	0.45	0.28	2.81	3.84	3.22	0.22	-0.05
Dec	-0.020	-0.72	1.09	0.11	1.87	0.55	0.43	2.63	3.91	5.58	0.75	0.02
Annual	-0.060	-8.73	33.10	4.36	15.83	6.59	3.82	57.50	39.60	31.60	5.71	-0.30

Table 5.12: The mean monthly a) Precipitation and Loading, b) Flow and Outputs and c) Balances for the Dargall Lane 1983 - 1985. (Precipitation and Flow in mm, Loadings, Outputs and Balances as Kg/ha)

a) Precipitation and Loadings : Green Burn

Month	Precip (mm)	Ion											
		H^+	NH_4^+	Na^+	K^+	Ca^{++}	Mg^{++}	Al^{+++}	Cl^-	HCO_3^-	SO_4^{--}	NO_3^-	PO_4^-
Jan	295.4	0.030	0.44	13.59	0.56	0.55	1.35	0.11	23.32	0.31	7.84	0.52	0.02
Feb	128.6	0.049	0.65	5.48	0.18	0.21	0.62	0.05	10.79	0.11	4.63	0.58	0.03
Mar	219.2	0.039	1.26	8.49	0.39	0.46	0.82	0.12	14.08	0.20	6.59	0.62	0.04
Apr	148.4	0.017	0.45	2.73	0.14	0.13	0.23	0.07	4.76	0.18	2.88	0.28	0.02
May	104.1	0.027	0.67	1.39	0.09	0.16	0.17	0.08	2.31	0.08	3.11	0.48	0.01
Jun	132.5	0.015	0.45	1.08	0.11	0.19	0.14	0.11	1.96	0.08	3.08	0.27	0.04
Jul	137.8	0.019	0.53	1.75	0.10	0.17	0.16	0.10	2.52	0.08	3.66	0.33	0.02
Aug	205.8	0.013	0.96	1.78	0.19	0.31	0.30	0.10	3.48	0.18	3.80	0.34	0.02
Sep	285.6	0.021	0.83	5.63	0.44	0.41	0.62	0.17	10.98	0.15	5.77	0.36	0.08
Oct	354.2	0.039	1.24	16.15	0.66	0.61	1.80	0.23	29.21	0.26	11.13	0.57	0.07
Nov	200.5	0.040	0.37	5.36	0.20	0.18	0.41	0.10	8.31	0.27	4.94	0.50	0.05
Dec	296.4	0.046	0.71	10.51	0.61	0.31	1.11	0.19	16.10	0.26	6.88	0.54	0.02
Annual	2508.2	0.365	8.57	73.94	3.67	3.69	7.73	1.43	129.78	2.16	64.11	5.39	0.42

b) Flow and Outputs : Green Burn

Month	Flow (mm)	Ion											
		H^+	NH_4^+	Na^+	K^+	Ca^{++}	Mg^{++}	Al^{+++}	Cl^-	HCO_3^-	SO_4^{--}	NO_3^-	PO_4^-
Jan	225.0	0.030	0.04	10.71	1.09	2.27	1.94	0.47	20.49	6.45	9.30	1.33	0.04
Feb	171.5	0.036	0.03	9.11	0.80	1.98	1.66	0.34	16.62	4.50	6.93	1.21	0.01
Mar	171.9	0.016	0.03	8.28	0.61	1.86	1.62	0.57	14.00	4.61	7.73	1.48	0.02
Apr	117.1	0.014	0.03	5.50	0.45	1.33	0.98	0.28	10.44	3.10	5.27	0.78	0.01
May	67.4	0.002	0.02	2.86	0.21	0.96	0.80	0.13	5.06	2.94	2.89	0.12	0.00
Jun	86.8	0.003	0.02	3.39	0.16	1.25	0.99	0.13	6.21	4.27	3.97	0.07	0.00
Jul	90.8	0.006	0.06	3.13	0.26	1.26	0.96	0.22	4.96	4.20	3.73	0.00	0.01
Aug	153.3	0.017	0.04	4.00	0.31	1.34	1.06	0.53	6.12	4.80	5.69	0.02	0.00
Sep	244.2	0.021	0.05	8.31	0.53	3.11	2.15	0.64	13.96	6.96	11.06	0.14	0.02
Oct	316.5	0.084	0.05	13.17	0.92	3.61	2.80	1.16	24.17	5.64	14.88	0.15	0.03
Nov	168.6	0.019	0.01	6.36	0.63	1.90	1.40	0.41	11.52	4.82	7.63	0.42	0.01
Dec	264.4	0.032	0.03	11.49	1.07	3.09	2.28	0.70	20.75	6.53	11.64	1.16	0.02
Annual	2077.5	0.278	0.41	86.32	7.04	23.96	18.64	5.58	154.13	58.83	90.74	6.88	0.17

c) Balances : Green Burn

Month	Ion											
	H^+	NH_4^+	Na^+	K^+	Ca^{++}	Mg^{++}	Al^{+++}	Cl^-	HCO_3^-	SO_4^{--}	NO_3^-	PO_4^-
Jan	0.000	-0.40	-2.88	0.53	1.72	0.58	0.36	-2.83	6.13	1.46	0.80	0.02
Feb	-0.013	-0.62	3.63	0.62	1.76	1.06	0.29	5.89	4.39	2.30	0.63	-0.02
Mar	-0.023	-1.23	-0.21	0.22	1.40	0.80	0.44	-0.08	4.41	1.14	0.86	-0.02
Apr	-0.003	-0.43	2.77	0.32	1.19	0.75	0.21	5.68	2.93	2.39	0.50	-0.01
May	-0.025	-0.65	1.49	0.12	0.79	0.63	0.03	2.74	2.86	-0.21	-0.36	-0.01
Jun	-0.012	-0.43	2.33	0.05	1.06	0.85	0.08	4.25	4.18	0.90	-0.20	-0.04
Jul	-0.015	-0.47	1.38	0.16	1.09	0.81	0.08	2.43	4.11	0.07	-0.33	-0.02
Aug	0.004	-0.91	2.21	0.13	1.04	0.76	0.45	2.64	4.62	2.08	-0.32	-0.02
Sep	-0.000	-0.78	2.68	0.09	2.70	1.52	0.47	2.98	6.82	5.31	-0.22	-0.06
Oct	0.450	-1.19	-2.98	0.26	3.00	1.00	0.92	-5.04	5.38	3.75	-0.42	-0.04
Nov	-0.021	-0.36	1.00	0.43	1.72	0.99	0.32	3.21	4.55	2.69	-0.08	-0.04
Dec	-0.014	-0.68	0.98	0.46	2.78	1.17	0.51	2.65	6.27	4.76	0.61	0.00
Annual	-0.076	-8.16	12.38	3.87	20.27	10.91	4.15	24.35	56.67	26.63	1.49	-0.25

Table 5.13: The mean monthly a) Precipitation and Loading, b) Flow and Outputs and c) Balances for the Green Burn 1983 - 1985. (Precipitation and Flow in mm, Loadings, Outputs and Balances as Kg/ha)

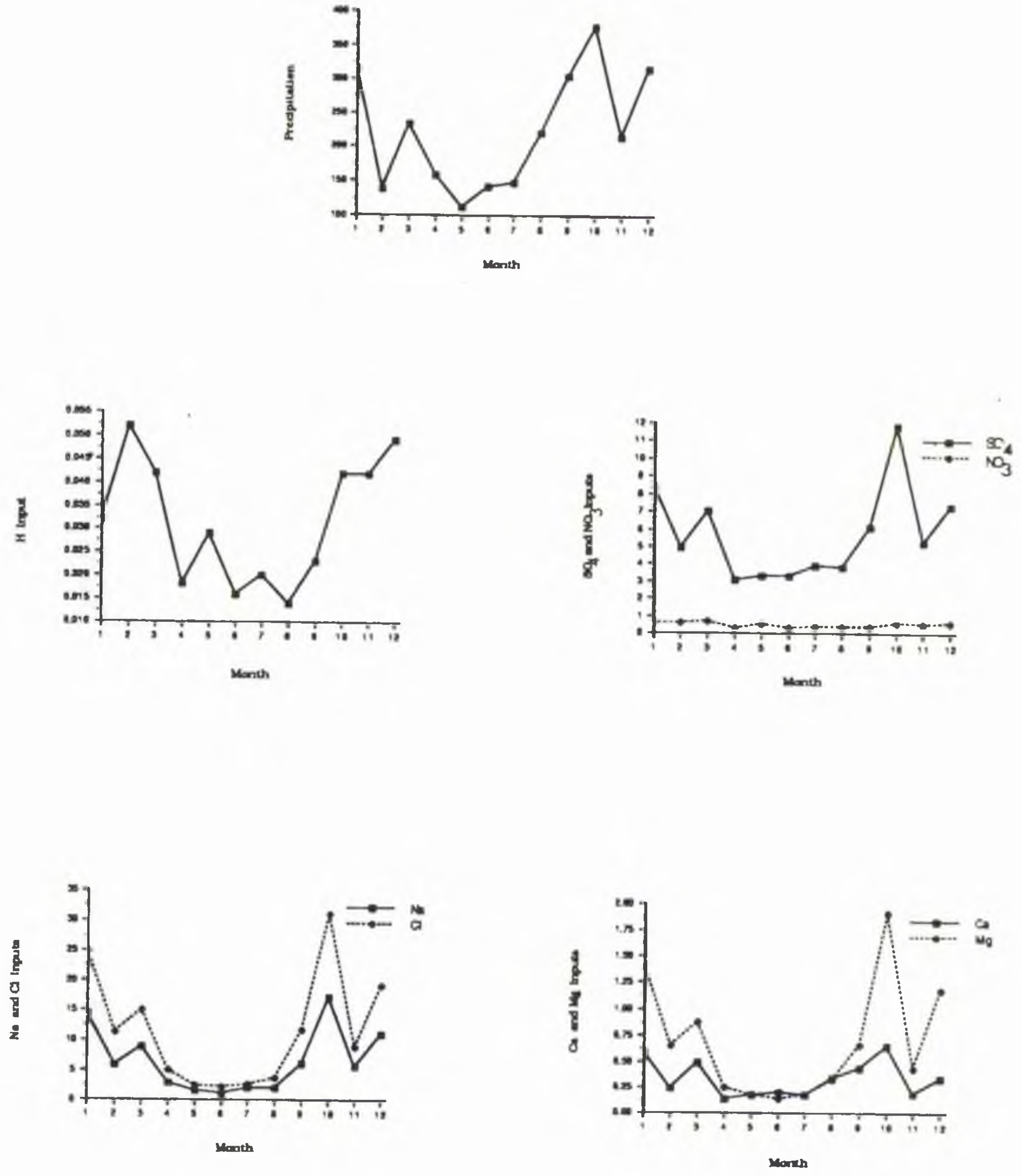


Figure 5.6: Mean Monthly Precipitation and Solute Inputs (Kg/ha) to the Dargall Lane 1983 - 1985.

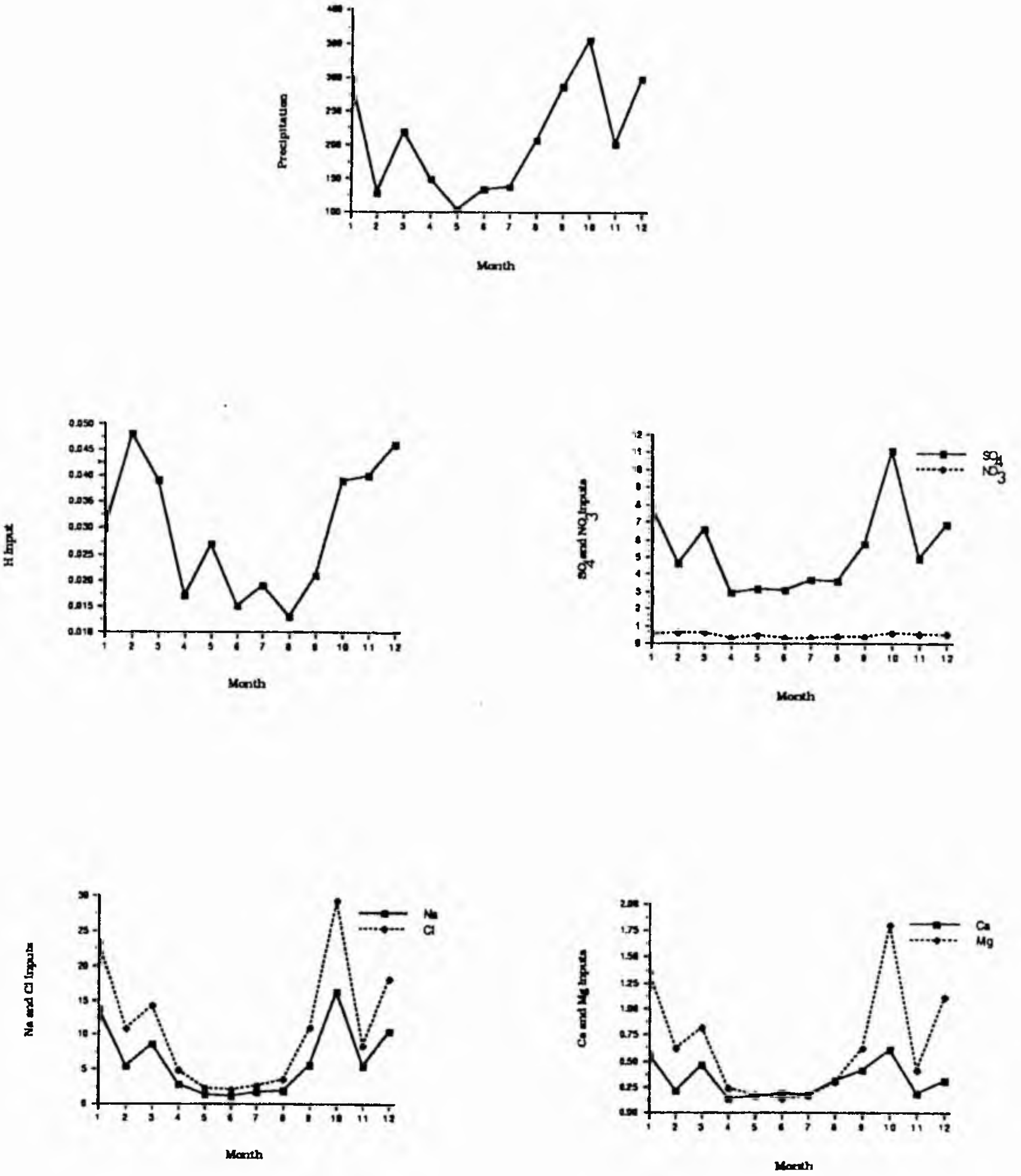


Figure 5.7: Mean Monthly Precipitation and Solute Inputs (Kg/ha) to the Green Burn 1983 - 1985.

chloride, in the summer months sulphate loadings are the dominant input.

The mean monthly flow and hydrochemical outputs from the Dargall Lane and Green Burn sub-catchments are tabulated in tables 5.12b and 5.13b respectively. As with input loadings, outputs of the major chemical species and the mean monthly flow are also shown graphically in Figures 5.8 and 5.9. The tables and figures show that the mean monthly flows in both streams follow the same seasonal pattern as precipitation, with the exception of the high mean flow from the Dargall Lane in January. For both sub-catchments a relationship between flow and solute outputs can be seen for outputs of sodium, chloride, magnesium hydrogen and sulphate from both sub-catchments. As with input loadings the solute outputs are dominated by the seasalts and sulphate, with seasalt outputs especially dominant in the winter months. Potassium and nitrate outputs from both sub-catchments also exhibit higher outputs in winter than summer. However, for these two species the pattern has less resemblance to the flow regime and is more clearly a seasonal feature. The only observable difference in this monthly pattern in terms of solute outputs from the two sub-catchments occurs for calcium. Thus calcium outputs from the Dargall Lane sub-catchment are lowest in May and highest in December and show no clear relationship to flow.

The net monthly mean hydrochemical balances for the two sub-catchments are also presented in both a tabular and graphical form in Table 5.12c and Figure 5.10 for the Dargall Lane and Table 5.13c and Figure 5.11 for the Green Burn. The tables and figures show that for each month both the sub-catchments are net sources of potassium,

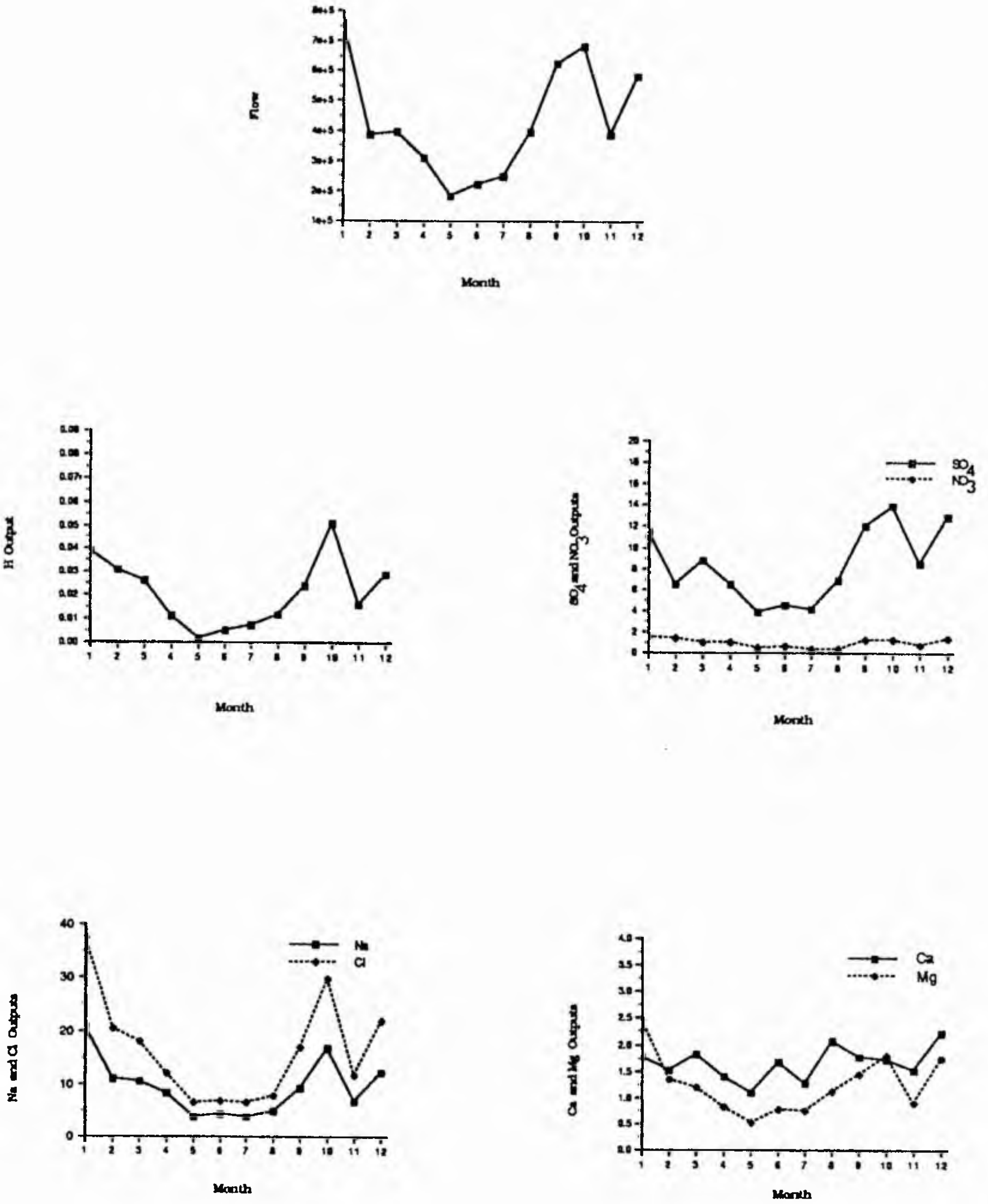


Figure 5.8: Mean Monthly Flow (m^3) and Solute Outputs (Kg/ha) from the Dargall Lane 1983 - 1985

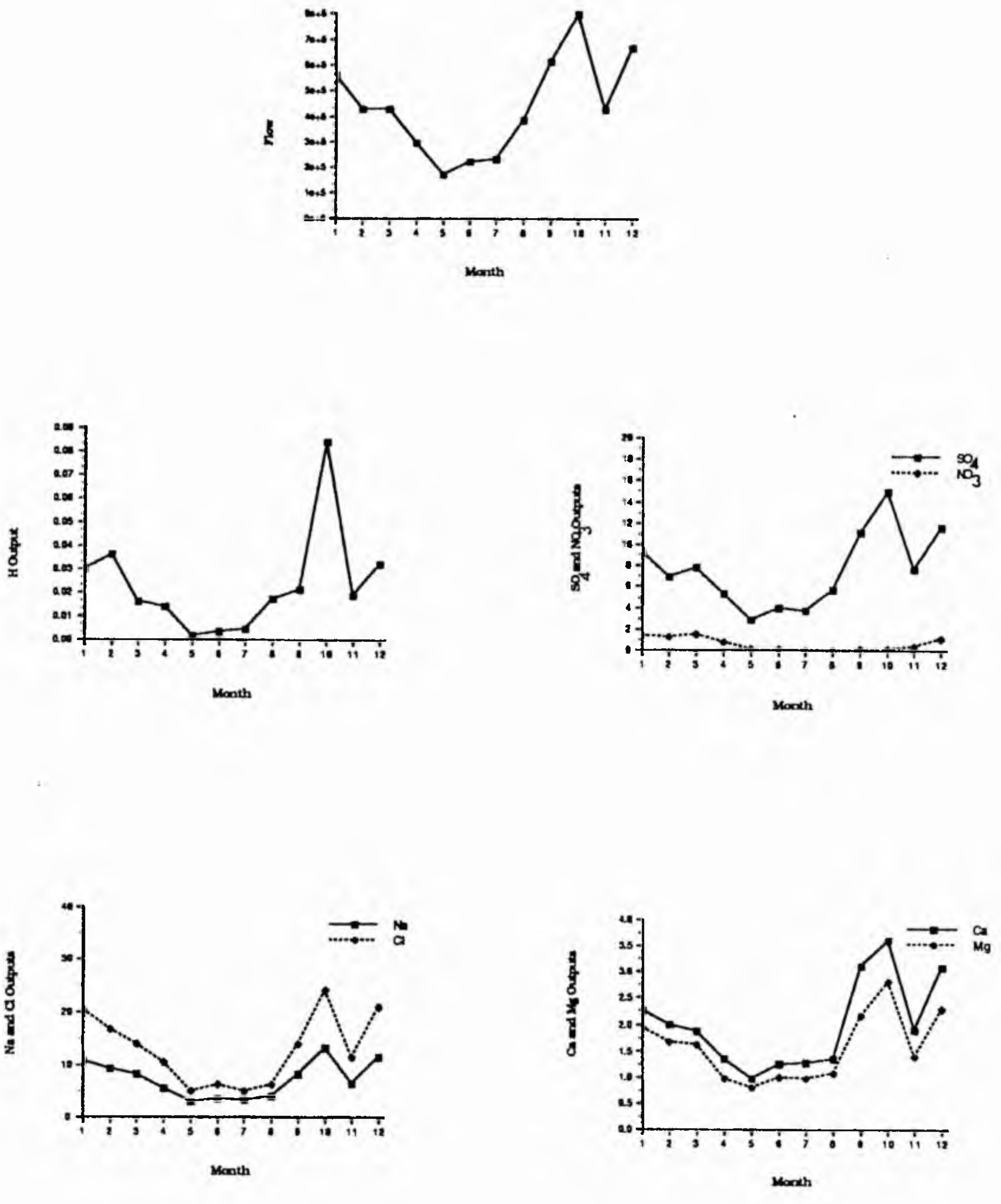


Figure 5.9: Mean Monthly Flow (m^3) and Solute Outputs (Kg/ha) from the Green Burn 1983 - 1985

calcium, aluminium, and bicarbonate and net sinks for ammonium. With the Dargall Lane also being a net source of sulphate and nitrate and the Green Burn a net source of magnesium. For the other species the sub-catchments are either a net source or sink in different months. In the Dargall Lane, the seasalts, sodium and chloride together with magnesium, show this latter pattern with a small net input of all three species occurring in October (Figure 5.10). In contrast, in the Green Burn there is a substantial net input of both sodium and chloride in January and October, together with a much lower net input of both ions in March. However, there is no net input of magnesium in the Green Burn in any month (Figure 5.11). It is this apparent net input of chloride in both sub-catchments that has rendered estimates of the mean monthly dry deposition input of major cations impossible to perform. Figures 5.10 and 5.11 also show that for both sub-catchments evidence of a seasonal pattern to the net outputs is far less clear than for the input loadings and the outputs. The figures also show that the monthly pattern for the hydrogen ion balance is similar in both sub-catchments with the greatest net outputs occurring in October and the greatest net input in May. By comparison there is some evidence for a seasonal pattern to the net outputs of sulphate and aluminium from both sub-catchments. Net outputs of both species are lowest in the period May - July, to the extent of a small net input of sulphate in the Green Burn during May, and greatest in September and October for sulphate and aluminium respectively. Net outputs of nitrate show a similar pattern with outputs generally lower in the summer than the rest of the year, particularly in the Green Burn where net input occurs from April to November. In contrast the calcium balance for both sub-catchments shows generally higher net outputs in summer than

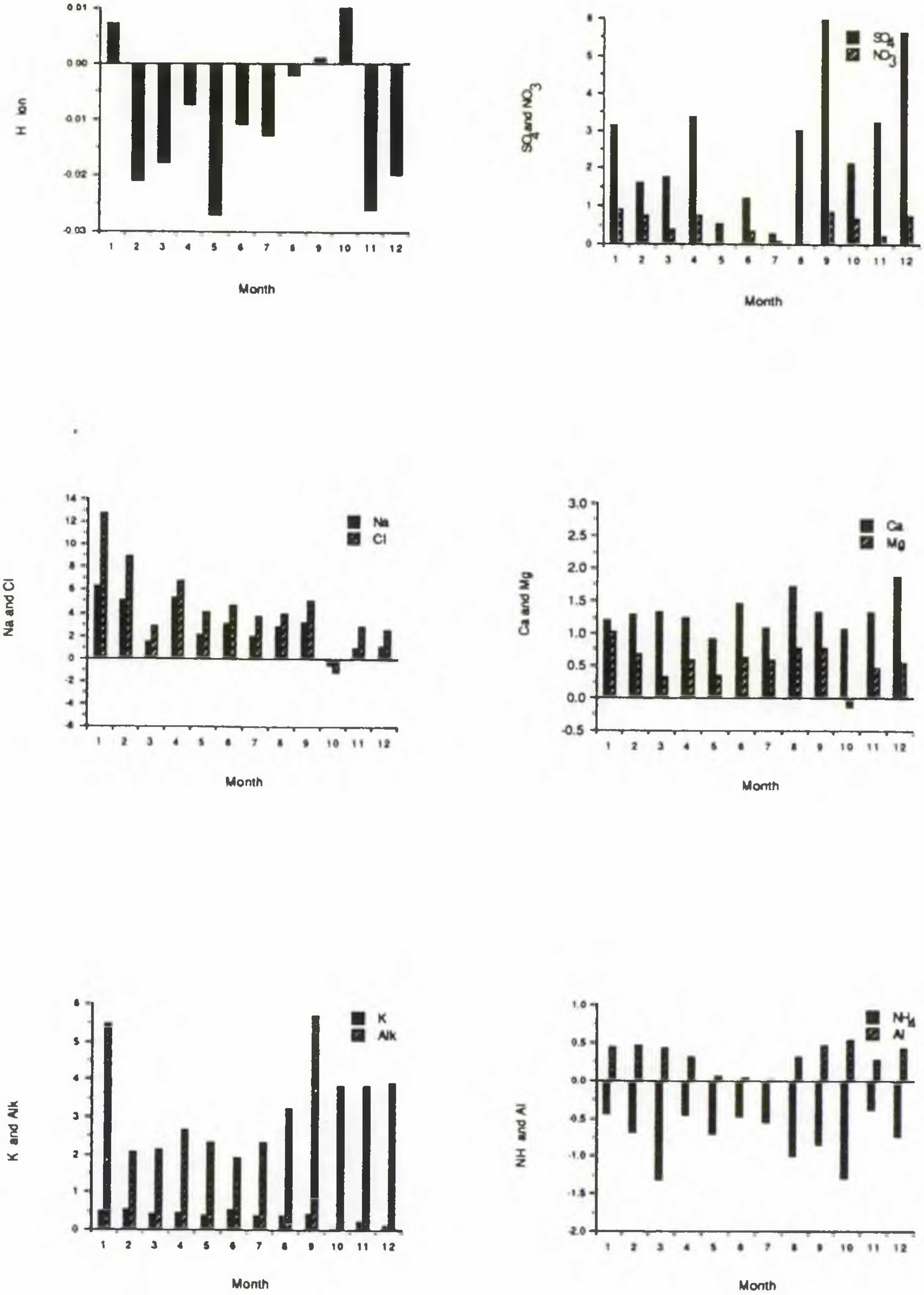


Figure 5.10: Mean Monthly Hydrochemical Balance (Kg/ha) for the Dargall Lane 1983 - 1985.

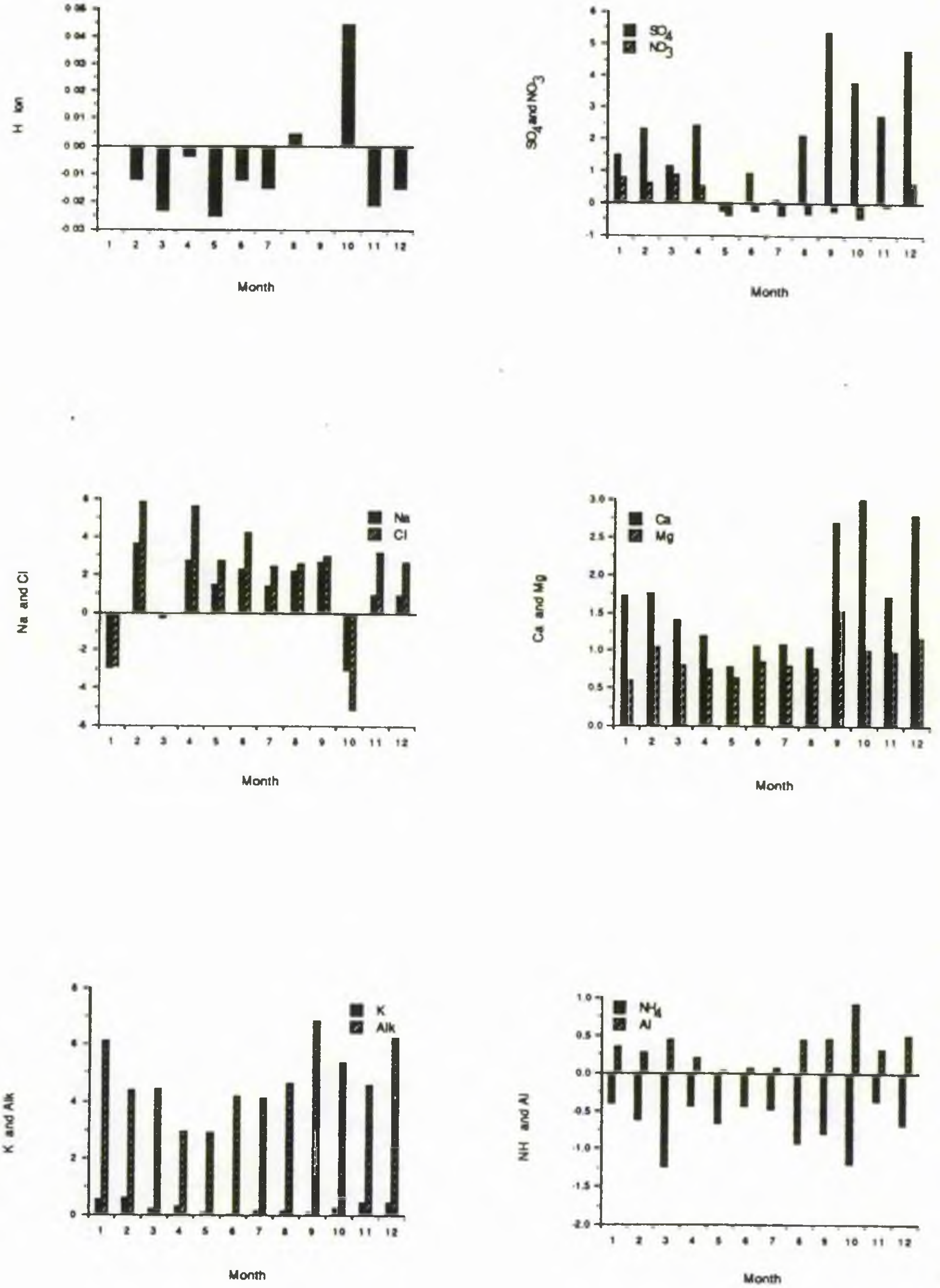


Figure 5.11: Mean Monthly Hydrochemical Balance (Kg/ha) for the Green Burn 1983 - 1985.

winter, although the peak net output occurs in December from the Dargall Lane and October from the Green Burn.

5.4.2 *Discussion*

Analysis of the mean monthly solute inputs indicates that solute loadings are dominated, particularly in the winter, by the seasalts sodium and chloride, a feature typical of maritime areas (cf Stevenson 1968, Walling and Webb 1981). These high seasalt loadings are a consequence of entrainment of these ions from seaspray into the atmosphere by the strong westerly winds associated with the Atlantic frontal systems that track across Galloway in the winter (Barrett et al.,1987). In summer the change in the atmospheric circulation pattern typically results in anticyclonic conditions over Britain. This change consequently leads to a reduction in wind speed and hence in the amount of seasalts entrained and blown inland. Furthermore, the associated increase in South and South-Easterly winds may be responsible for the the relative increase in the importance of sulphate in the loadings during the summer, the prevailing wind blowing over the pollution source areas of the Midlands and North-West rather than the Irish Sea (cf Burns et al. 1984). The actual amounts of sulphate deposited, however, decrease in summer as a majority of the sulphate input is also of a maritime origin (Table 5.3).

The seasalts, sodium and chloride, are also the dominant ions in the streamwater solute outputs. This dominance clearly indicates the importance of atmospheric inputs in the determination of streamwater quality in the Loch Dee area. There is, however, damping in the range of seasalt outputs compared with the inputs, particularly

		Dargall Lane	Green Burn
Cl^-	loading output	2.08 - 31.03 6.39 - 37.61	1.96 - 29.21 4.96 - 24.17
Na^+	loading output	1.13 - 17.15 3.64 - 20.73	1.06 - 16.15 3.13 - 13.17

Table 5.14 The range of mean monthly sodium and chloride loadings and outputs (Kg/Ha/Yr) for the Dargall Lane and Green Burn 1983-85.

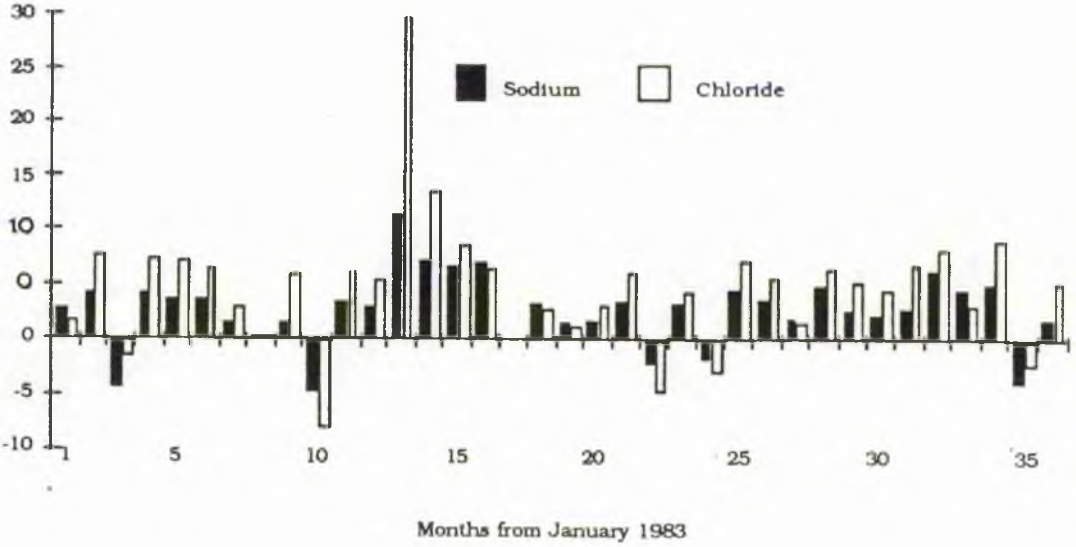
	1983		1984		1985	
Month	D.L.	G.B.	D.L.	G.B.	D.L.	G.B.
Jan	360.7	339.6	420.3	395.7	160.3	150.9
Feb	100.2	94.4	209.9	197.6	99.6	93.7
Mar	346.4	326.1	145.7	137.2	206.3	194.2
Apr	121.8	114.7	132.8	125.0	218.3	205.5
May	158.4	149.1	25.2	23.8	148.0	139.3
Jun	140.8	132.6	133.1	125.3	148.3	139.6
Jul	65.2	61.3	80.9	76.2	293.1	275.9
Aug	50.3	47.3	103.1	97.1	502.5	473.0
Sep	254.2	239.3	228.8	215.4	427.1	402.1
Oct	564.9	531.8	413.4	389.2	150.3	141.5
Nov	107.7	101.4	279.1	268.2	251.9	237.2
Dec	334.4	314.8	279.6	263.2	330.6	311.2

Table 5.15 Monthly Precipitation Input (mm) to the Dargall Lane (D.L.) and Green Burn (G.B.) sub-catchments 1983- 1985.

in the Green Burn (Table 5.14). Such damping indicates that complex flow routing occurs in both sub-catchments and it is noteworthy that this feature is also identified by Neal et al. (1988) in the Afon Hafren and Afon Hore catchments at Plynlimon. For these sites it is suggested that the damping indicates either a rapid mixing of rainfall inputs with stored inputs, or large stores of water in the catchment. The later possibility is also invoked by Reynolds et al. (1988) to explain similar chloride damping at a different catchment, the Afon Cyff, in Plynlimon.

At Loch Dee the presence of large water stores is suggested by the observed net input of seasalts during certain months in both the Dargall Lane and Green Burn sub-catchments. As noted in section 5.3 Langan (1987) identifies the exchange of sodium in precipitation for hydrogen ions on the soil exchange complexes during high seasalt storm events at Loch Dee. However, over the annual timescale, there is no evidence of this process being an important element in the budgets (see Section 5.3.1). Furthermore, such ion exchange does not account for the apparent net input of chloride reported above, which is commonly considered to be a chemically conservative ion which does not partake in ion exchange and mineral equilibria reactions. Thus the apparent "uptake" of chloride is more probably a physical feature due to the storage of water within the catchment soils. The storage of chloride is also a more common event than is suggested by the mean monthly hydrochemical balances as is shown by extracting the seasalt/monthly hydrochemical balances for the full three year period of record from Appendix 1.1 and plotting these data in Figure 5.12. From this it can be seen that a net input of seasalt is more common in the Green Burn than the Dargall Lane and that storage occurs more

a) Dargall Lane



b) Green Burn

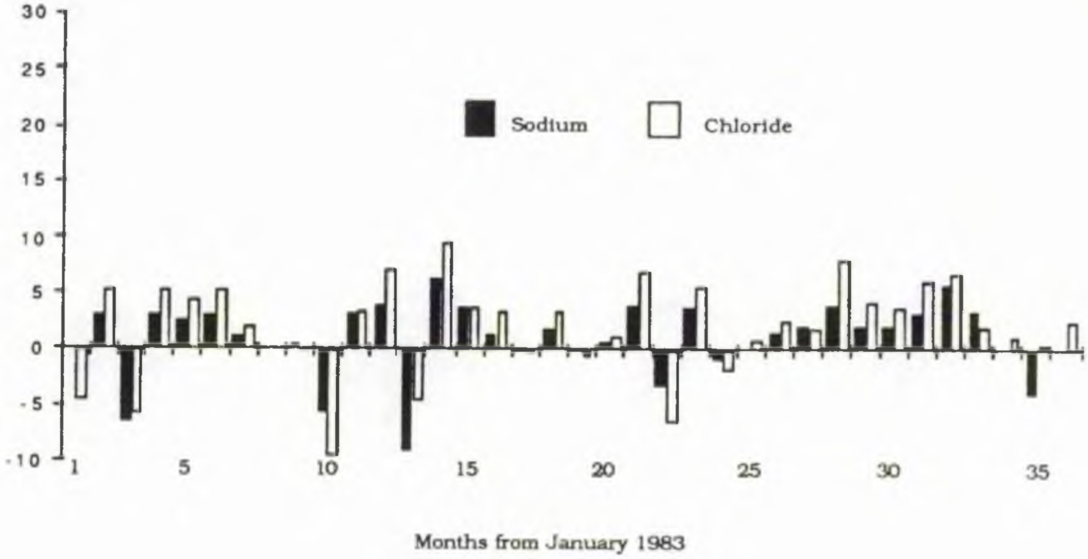


Figure 5.12: The Mean Monthly Hydrochemical Balance (Kg/ha) for Na^+ and Cl^- in a) the Dargall Lane and B) the Green Burn for 1983 - 1985

often in the "drier" years 1983 and 1984 than in the "wetter" 1985. The "uptake" of chloride in the Green Burn for month 13 (Jan 1984) in contrast to the net chloride loss from the Dargall Lane in the same month is probably the result of a rare severe snowfall over the upper parts of the Dargall Lane catchment in that month and the inclusion in the monthly water balance of several exceptionally large flows due to the snowmelt, but not the water input of the unmeasured snowfall (SRPB pers. comm.). Consequently the input loadings of solute species to the Dargall Lane catchment in January 1984 are probably underestimated and it is possible that "uptake" of both sodium and chloride may have occurred in the Dargall Lane catchment in this month.

If the seasalt balances are compared with the measured monthly precipitation (Table 5.15) it can be seen that in the Dargall Lane high storage rates coincide with months of high precipitation. The storage may therefore be due to precipitation water not directly entering the stream but instead pushing a wedge of "old" water out of the catchment soils and into the stream whilst the "new" precipitation water, with its associated chemical load is stored in the soils. Such a physical process is a form of the 'piston'-flow described by Hewlett (1961) and is identified by several authors using oxygen isotope tracers (cf Rodhe 1981, Sklash et al. 1986). In the Green Burn, however, storage also occurs in months where precipitation is very low. In such months storage may be simply due to a majority of the precipitation satisfying the soil moisture deficit.

Despite the uncertainty surrounding the exact process by which chloride storage may occur, the phenomenon has several important consequences. In the area of budgetary studies, the dry deposition contribution to the budget of other species is often estimated from the multiplication of net chloride outputs by the ionic ratios to chloride in precipitation. Chloride storage, as noted above, will prevent this procedure from being used, particularly at lower than annual timescales. Secondly, chloride storage may have important consequences for hydrochemical modelling studies for, as Neal et al. (1988) have commented, if we are unable to describe accurately the hydrochemical response of chloride, the simplest ion, then fundamental questions arise as to how we may describe the response of far more chemically active species.

Together with the occurrence of seasalt storage another major feature of interest in the monthly budgets is the peak in the net sulphate outputs that occur in September from both the Dargall Lane and Green Burn sub-catchments. An autumnal peak is also identified at Birkenes in Norway (Christophersen and Wright 1981) and may be explained by the flushing of sulphate accumulated in the soil during the summer. This accumulation occurs either as a result of water loss from evapotranspiration or from the oxidation of organic sulphur materials during dry periods (cf Christophersen and Wright 1981).

The seasonal effect of vegetation on the hydrochemical budgets is shown by the outputs of the major nutrient species, nitrate and potassium with net outputs of both species lower in the summer growing season than the winter. The influence of the forest in the Green Burn is also evident with outputs of both species lower than from the moorland Dargall Lane. For nitrate the summer net input suggested by the budgets implies that afforestation has led to the Green

Burn being nitrogen stressed during the growing season. Consequently, it may be that for afforestation to reach its full potential in areas such as Loch Dee nitrogen fertilisers will have to be applied at greater rates, with attendant risks for water pollution.

5.5 *CONCLUSIONS*

Spatial variations in the hydrochemical budgets of the study sub-catchments at Loch Dee are related to differences in the underlying geology and land-use management practices. The role of afforestation is difficult to judge as the plantations are less than fifteen years old. At present the influence of afforestation is primarily a result of the pre-afforestation ploughing which, in the Green Burn, serves to increase the output of acidity and aluminium during high flows and the output of base cations and silica during low flows. However the Green Burn is less inimical to fish populations than the equally acidic Dargall Lane suggesting that more of the aluminium is in an organic form. The effectiveness of catchment and forestry management techniques in reversing the effects of acid precipitation and coniferous afforestation are also difficult to judge. The White Laggan Burn, where these techniques have been applied, has both acidity and aluminium levels far lower than in the neighbouring catchments. However, the influence of the limestone inputs is difficult to separate from the contrasts in the underlying geology and the hardwoods of the buffer zone are still too immature to have registered any realistic influence. Consequently, the impact of the amelioration techniques on the water quality of the White Laggan Burn is difficult to assess at present, but they are likely to be of much lower significance than the presence of the unmetamorphosed sediments in the headwaters.

On a annual basis temporal variations in catchment losses of bases and nutrients tend to be complex, but can generally be related to the amount of precipitation; this possibly indicates a greater flow through the lower mineral soil in wetter years. In contrast, sulphate losses tend to vary independently of the amount of precipitation thereby supporting the view that the dry deposition of sulphate and attendant inputs of acidity vary considerably from year to year. On the monthly timescale the storage of chloride within the catchments indicates that present descriptions of the hydrochemical behaviour of catchments are inadequate, a conclusion that has serious implications for short term budgetary studies and for simulation modelling of hydrochemical processes.

6: THE ILWAS MODEL : CALIBRATION AND VERIFICATION

6.1 *INTRODUCTION*

Simulation modelling is a vital tool for understanding the present effects of anthropogenic influences such as acid deposition on catchment ecosystems. However, a further and possibly more important use of simulation modelling is for predicting the possible future impacts of changes in such anthropogenic influences on an ecosystem. As outlined in Chapter 3 several different models have been developed in order to increase our awareness of anthropogenic impacts on catchment ecosystems. One such model is the ILWAS model developed by workers at EPRI in the U.S.A. on the basis of research in the Adirondack mountains of New York State (Chen et al. 1983, Gherini et al. 1984, Goldstein et al. 1985). At the present time there is no published information on the behaviour of this model outside its development ground, consequently in this project it was decided to evaluate the performance of the model at Loch Dee.

Thus the aim of the research reported in this chapter was twofold; firstly, to calibrate the ILWAS model against observed hydrochemical data for 1983 from the moorland Dargall Lane and 70% afforested Green Burn sub-catchments and secondly, to determine if the resultant optimum calibrations could be verified by simulations of the observed hydrochemical behaviour of the two streams for 1984 and 1985.

At this stage it must be emphasised that a considerable number of simulation runs (over fifty) were required in order to identify the hydrological variables of major importance in determining the hydrochemical behaviour of the study sub-catchments. The identification of the major variables in the chemical module of the model (Section 6.2.2) also required a similarily large number of simulation runs. Furthermore, once the major variables had been identified at least five, and more often ten simulation runs per variable, were required in order to derive the optimal value for a variable in each study sub-catchment simulation. Furthermore, for catchment segmentation of the order used in this study, a three year simulation run would take about thirty minutes of C.P.U. time on a VAX 11/785 minicomputer, a timespan that in real time could often extend over several hours. Consequently, in order to increase the number of simulation runs possible in any period, a number of command level procedures were derived for the VAX system that enabled several simulation runs to be completed in succession. The large size of the model source and executive files, which together take up over 1000 blocks of disc space on the VAX, should also be noted. Indeed if the input and output datafile requirements are included then, for catchment systems similar in size to those reported in this study, the total file space required can extend to over 50,000 blocks.

6.2 *SYSTEM SEGMENTATION*

The first stage in using the ILWAS model is to represent the spatial heterogeneity of the study catchment. This is accomplished by dividing the catchment horizontally and vertically into a number of compartments. Horizontally, the catchment is divided into a number of land sub-catchments and stream segments. The land sub-catchments are derived initially from catchment topography so

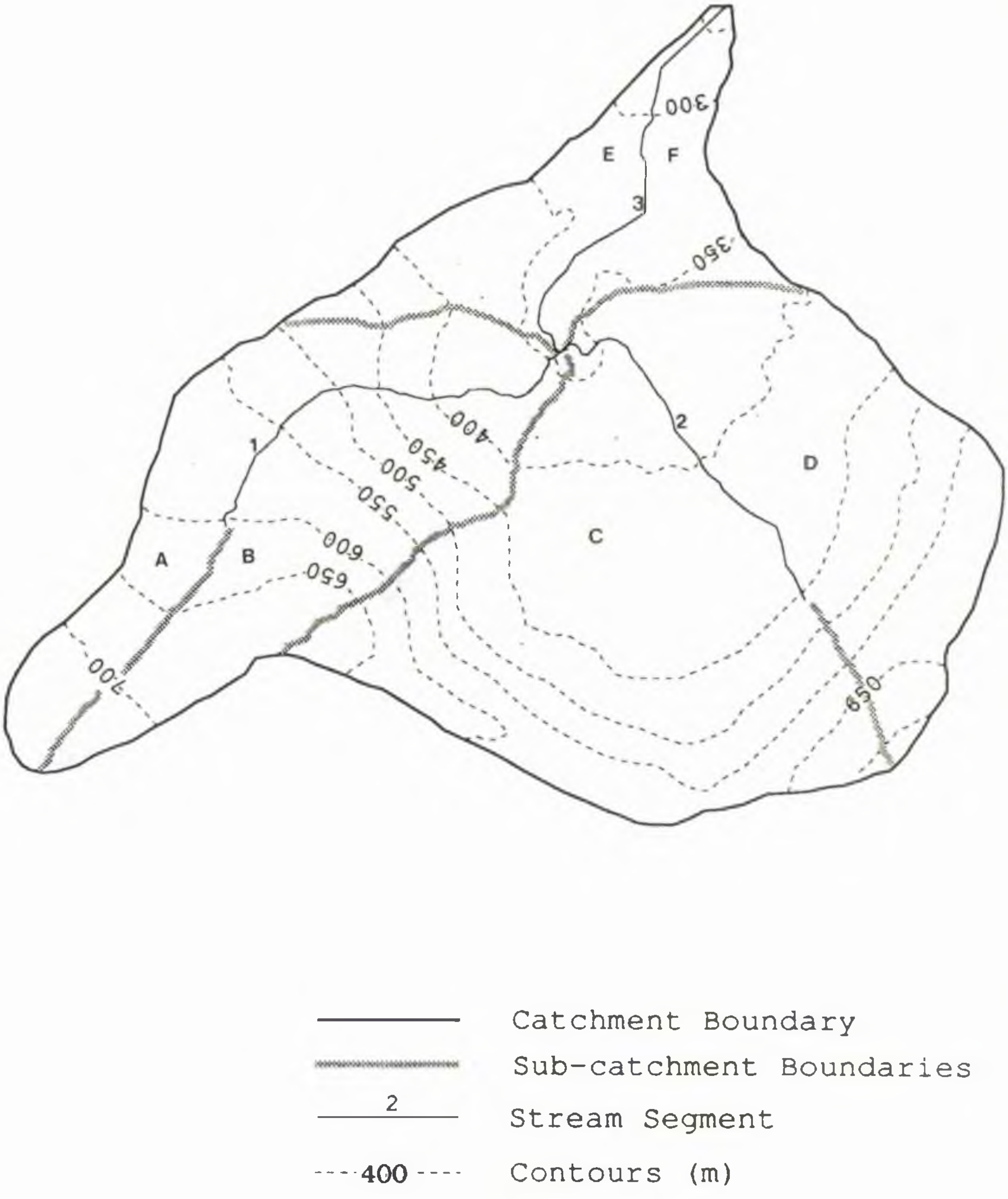


Figure 6.1: Horizontal segmentation of the Dargall Lane catchment
(A-F are the sub-catchments and 1-3 the stream segments used in the ILWAS representation of the catchment).

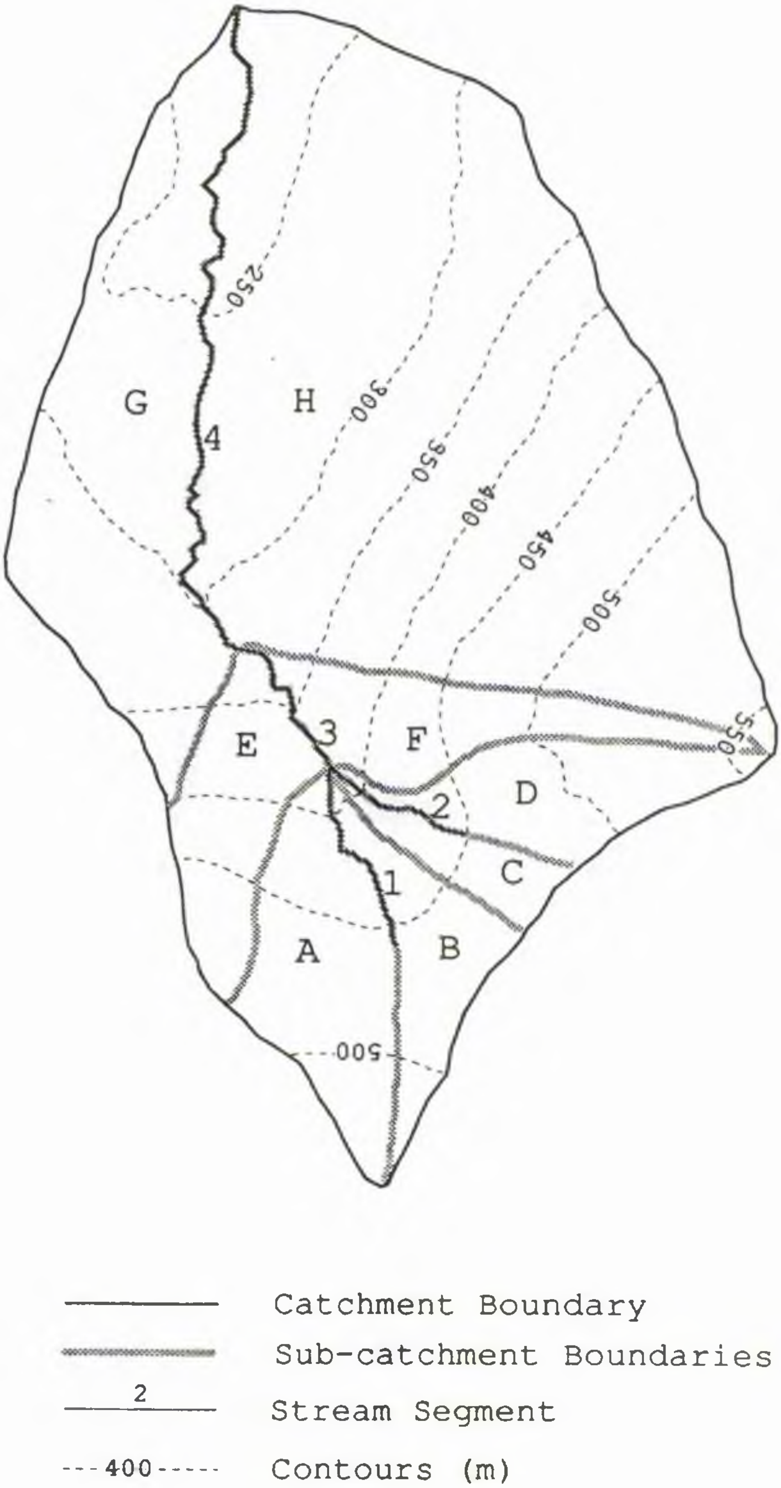


Figure 6.2: Horizontal segmentation of the Green Burn catchment.
(A-H are the sub-catchments and 1-4 are the stream segments used in the "ILWAS" representation of the catchment.

that each sub-catchment has uniform slope and aspect and drains directly into a stream segment. These sub-catchments are then combined, where possible on an understanding of how surface and sub-surface flows may occur in the catchment, so as to reduce the number of sub-catchments to the lowest number that can realistically represent the catchment. Each of the resultant sub-catchments may also have different percentages of coniferous and deciduous trees, and open areas. The stream segments are then derived with two aims; firstly, to represent the major tributaries in the catchment and secondly, to accept flow from the resultant sub-catchments. The resultant land sub-catchments and stream segments for the Dargall Lane and Green Burn are shown in Figures 6.1 and 6.2 respectively.

The vertical division of each of the land sub-catchments is mainly determined by the model structure and consists of modules that represent the canopy, snowpack, where present, and soil horizons. The only user-defined decision is to determine the number of soil layers to be used in the simulation. The model is able to deal with a maximum of five soil layers. Given the general lack of detailed soil information available for the Loch Dee catchments the decision was taken to use only two layers for both the Dargall Lane and Green Burn simulations. Thus one layer was used to represent the upper organic horizon and the other to represent the lower mineral soil.

6.3 *HYDROLOGICAL CALIBRATION AND VERIFICATION*

With the study catchments divided both horizontally and vertically the next step in the utilisation of ILWAS is to calibrate the hydrological sub-model. This calibration will be performed first for the Dargall Lane sub-catchment and then for the Green Burn sub-catchment.

6.3.1 *The Dargall Lane Burn*

The first stage in the calibration of the hydrological sub-model is to derive values for the time-dependent input variables that drive the model and the time-independent variables that describe the catchment hydrological system. The time-dependent input variables consist of daily values for precipitation quantity, maximum and minimum temperatures, wet bulb temperatures and wind speed together with mean monthly values for air pressure and cloud cover. Time-independent variables describe the major physical characteristics of each land sub-catchment, i.e. area, width, aspect, percentage of each canopy type, together with a precipitation weighting factor that allows for the influence of altitude on precipitation quantity. Other variables similarly describe the major physical features of each stream segment, i.e. initial depth, axial length, up-stream and down-stream bed height, Muskingum routing coefficients and a stage-surface area relationship. The values of these variables for each sub-catchment and stream segment are shown in Tables 6.1 and 6.2 respectively.

	Sub-Catchments					
	A	B	C	D	E	F
Area (m^2)	227850	358550	723500	456200	139800	157500
Mean Slope (m/m)	0.270	0.270	0.250	0.240	0.110	0.110
Mean Width (m)	141.0	352.0	634	423.0	176.0	176.0
Aspect (degrees)	30°	45°	355°	310°	90°	270°
Canopy Type	Moorland (100%)	Moorland (100%)	Moorland (100%)	Moorland (100%)	Moorland (100%)	Moorland (100%)
Precipitation Weighting	1.3	1.3	1.2	1.2	1.1	1.1

Table 6.1: The major physical parameters of the land sub-catchments used in the ILWAS representation of the Dargall Lane catchment

	Stream Segment		
	1	2	3
Depth (m)	0.306	0.204	0.460
Length (m)	979.0	716.0	1060.0
KR	0.011	0.014	0.022
KX	0.250	0.250	0.25
Bed Height Upstream (m)	610.0	510.0	345.0
Bed Height Downstream (m)	345.0	345.0	245.0
Stage - Surface Area (m/m^2)	0.0 - 0.0 10.0 -15380.0	0.0 - 0.0 10.0 - 15380.0	0.0 - 0.0 10.0 - 15380.0
Upstream sub-catchments	A, B	C, D	E, F
Upstream segments	-	-	1, 2

Table 6.2: The major physical parameters of the stream segments used in the ILWAS representation of the Dargall Lane catchment

(KR and KX are Muskingum routing coefficients)

Month	Leaf Area Index (cm^2/cm^2)		Relative Humidity (%)
	Conifers	Moorland	
Jan	12.0	0.5	87
Feb	12.0	0.5	84
Mar	12.0	0.5	88
Apr	12.0	0.6	81
May	13.0	0.7	81
Jun	14.0	0.8	80
Jul	15.0	0.8	79
Aug	15.0	0.8	80
Sep	15.0	0.7	87
Oct	15.0	0.7	87
Nov	14.0	0.6	90
Dec	13.0	0.5	91

Table 6.3: The monthly leaf area indicies for coniferous and moorland vegetation, together with the monthly relative humidities used in the ILWAS representation of the Dargall Lane and Green Burn catchments.

	Sub-Catchments A - D		Sub-Catchments E - F	
	Layer 1	Layer 2	Layer 1	Layer 2
Thickness(cm)	60.0	40.0	60.0	60.0
Initial Moisture Content	0.41	0.36	0.50	0.36
Field Capacity	0.39	0.25	0.39	0.35
Saturated Moisture Content	0.55	0.43	0.55	0.50
Permeability (cm/day)				
Horizontal	1.00E5	1.00E3	1.00E5	1.00E3
Vertical	1.00E5	1.00E3	1.00E5	1.00E3
% Roots	80.0	20.0	80.0	20.0
Initial Temperature (°C)	8.0	5.0	8.0	5.0

Table 6.4: The physical data used for the two soil layer ILWAS representation of the Dargall Lane catchment. (Initial Moisture Content, Field Capacity and Saturated Moisture Content are all expressed as a fraction of the soil volume)

In addition to describing the physical characteristics of each sub-catchment and stream segment, values are also required to describe the major hydrological processes in the canopy, snowpack (where present) and soils of each sub-catchment. For the canopy the major data requirements are for the monthly relative humidity and the monthly leaf area index for each canopy type (Table 6.3). For the snowpack, values are required for a snowmelt rate coefficient (cm $°C^{-1}$ day^{-1}), the snowpack sublimation rate and the moisture field capacity of the snowpack. At Loch Dee, however, there are no data available for these variables. Fortunately the presence of a substantial snowpack is very rare at Loch Dee, consequently the decision was taken to utilise the data from the Adirondack application of the model (EPRI pers. comm.). The input data for the catchment soils consist of the horizon thickness, initial soil moisture content, field capacity, saturated moisture content, horizontal and vertical permeability, root distribution and initial temperature.

With the values for the major input variables determined, the model was calibrated by comparing the model results with observed data. The first step in this procedure was to perform a global calibration to ensure that the simulated and observed total annual outflows were equal. This was achieved by altering the value of an evapotranspiration calibration parameter, thereby adjusting the annual predicted evaporation, until the predicted and observed cumulative outflows were equal. The next step was to calibrate the daily flow peaks and troughs, this was achieved by a trial and error procedure which identified the major calibration parameters as the horizontal permeability, the saturated moisture content and the field capacity of each soil horizon. These variables were subsequently adjusted until the root mean square error (RMSE) of the predicted and observed Mean Daily Flows (M.D.F.s) time series were minimised. The resultant optimum values for the saturated mosture content, field capacity and hydraulic permeability, together with the utilised values for the other soil variables, are shown in Table 6.4. With the derivation of the optimum values for the hydrological input variables in the two soil layer representation of the Dargall Lane sub-catchment, the resultant predicted M.D.F.s for 1983 are plotted against the observed M.D.F.s for the same year in Figure 6.3. However, from Figure 6.3 it can be seen that the hydrograph recessions are very poorly reproduced (eg Julian Date 100-150). Furthermore, the simulation was unable to be improved by any further adjustment of the calibration parameters.

A possible reason for this failure to reproduce the hydrograph recessions was the selection of only two soil layers. In order to take into account possible permeability changes caused by the presence of an iron pan in the mineral soil on the slopes or the thickness of the peat in the valley bottom, it was decided to increase the number of soil layers represented in the model from two to three by splitting the mineral soil layer in two. Thus for the slope sub-catchments (A-D) layer 1 represents the organic horizon, layer 2 the horizon above the iron pan and layer 3 the horizon below the iron pan. In contrast for the valley floor sub-catchments layers 1 and 2 both represent the thick peat and layer 3 represents the thin mineral soil under the peat. The optimum values for the soil variables, in the three horizon representation of the Dargall Lane, are shown in Table 6.5.

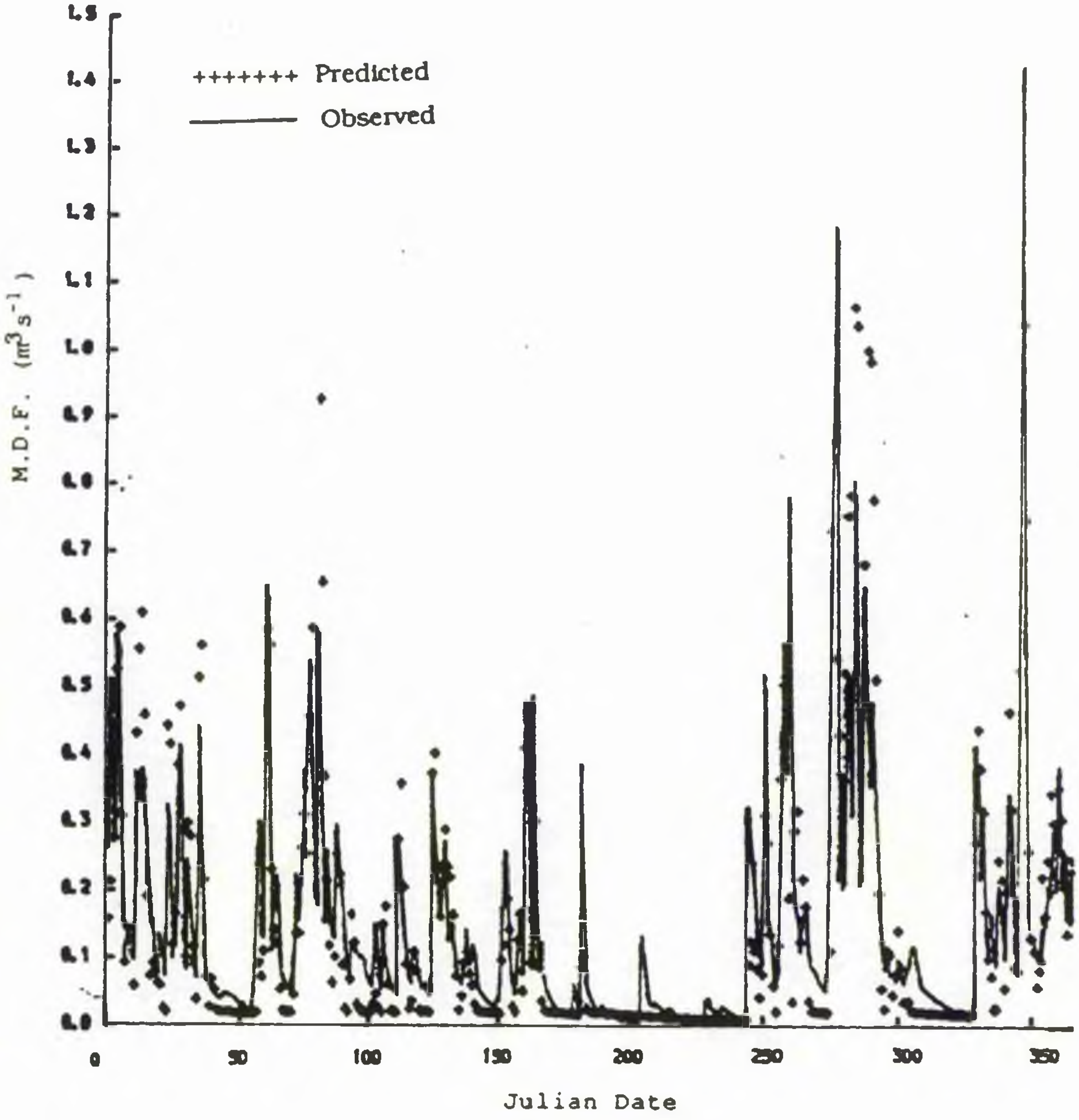


Figure 6.3: Simulated and Observed M.D.F's for the two soil layer representation of the Dargall Lane 1983.

	Sub-Catchments A - D			Sub-Catchments E - F		
	Layer 1	Layer 2	Layer 3	Layer 1	Layer 2	Layer 3
Thickness(cm)	60.0	15.0	25.0	60.0	40.0	20.0
Initial Moisture Content	0.41	0.36	0.20	0.50	0.38	0.20
Field Capacity	0.39	0.25	0.20	0.39	0.25	0.20
Saturated Moisture Content	0.55	0.43	0.35	0.55	0.50	0.35
Permeability (cm/day)						
Horizontal	1.00E5	9.00E3	1.00E3	1.00E5	9.00E3	1.00E3
Vertical	1.00E5	9.00E3	1.00E3	1.00E5	9.00E3	1.00E3
% Roots	80.0	20.0	0.0	80.0	20.0	0.0
Initial Temperature (°C)	8.0	5.0	5.0	8.0	5.0	5.0

Table 6.5: The physical data used for the three soil layer ILWAS representation of the Dargall Lane catchment.
(Initial Moisture Content, Field Capacity and Saturated Moisture Content are all expressed as a fraction of the soil volume)

	1983	1984	1985
RMSE.	0.1073	0.3141	0.1336
Actual Total Flow (m^3)	4748112	5321808	5397408
Predicted Total Flow (m^3)	4752522	4488686	5468009
Layer 1 (% of Total)	3128623 (65.83)	2929698 (65.27)	3585255 (66.57)
Layer2 (% of Total)	1304421 (27.45)	1231214 (27.43)	1552305 (28.39)
Layer3 (% of Total)	319478 (6.72)	327774 (7.30)	330449 (6.04)

Table 6.6: The observed and ILWAS predicted annual flows for the Dargall Lane 1983 - 1985.

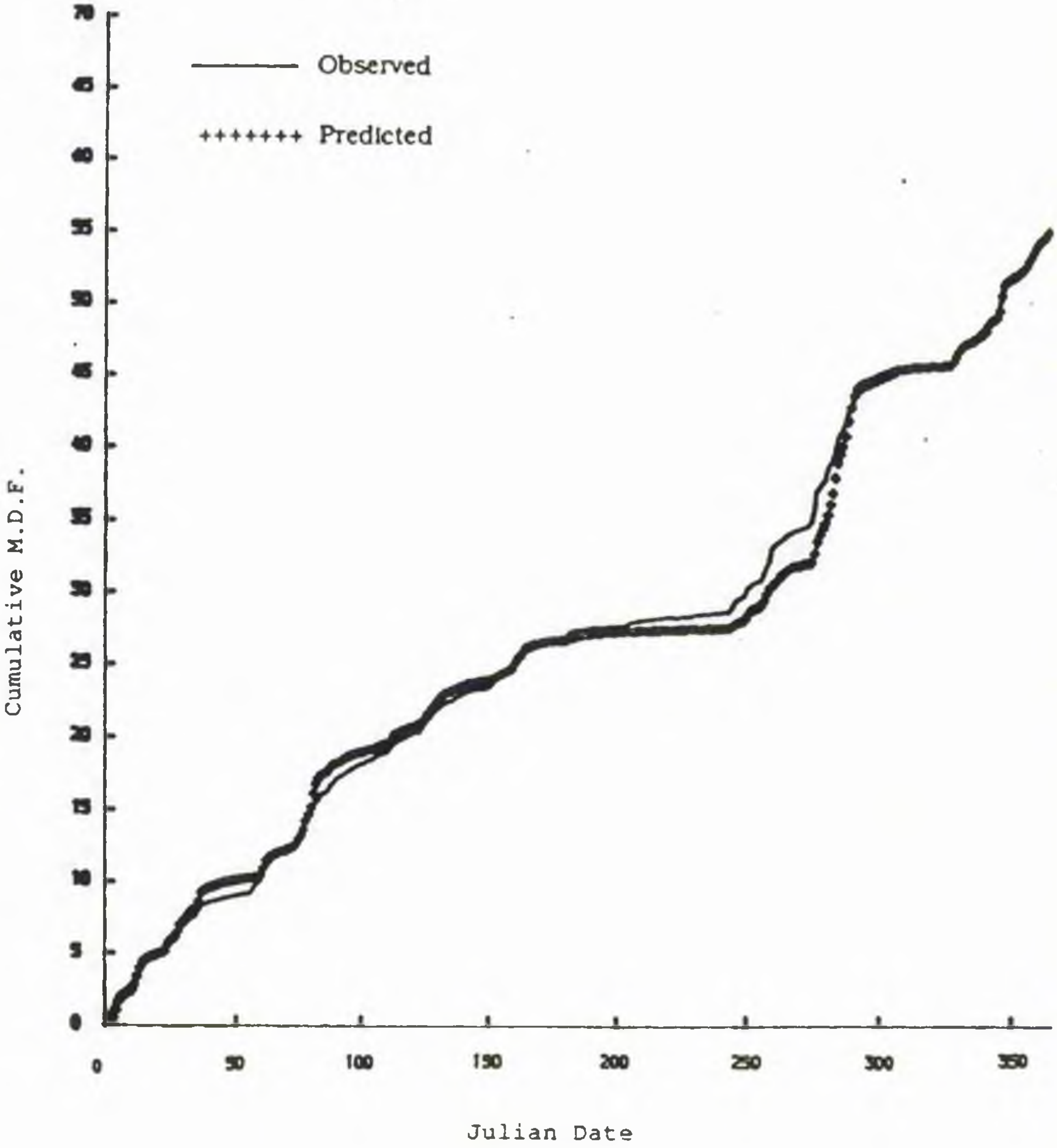


Figure 6.4: Simulated and Observed Cumulative M.D.F.s ($m^3 s^{-1}$) for the Dargall Lane 1983.

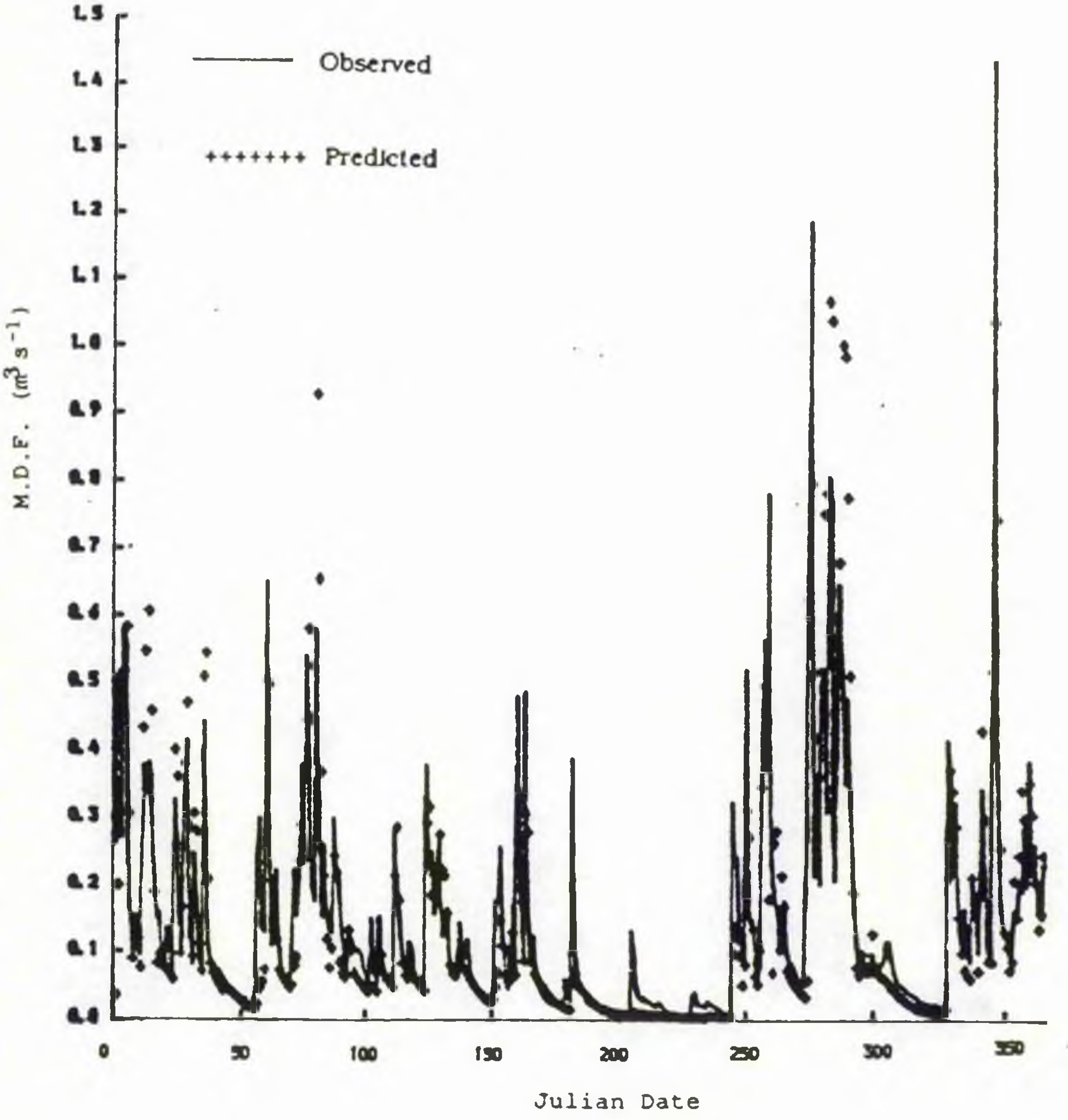


Figure 6.5: The Simulated and Observed M.D.F.s ($m^3 s^{-1}$) for the Dargall Lane 1983.

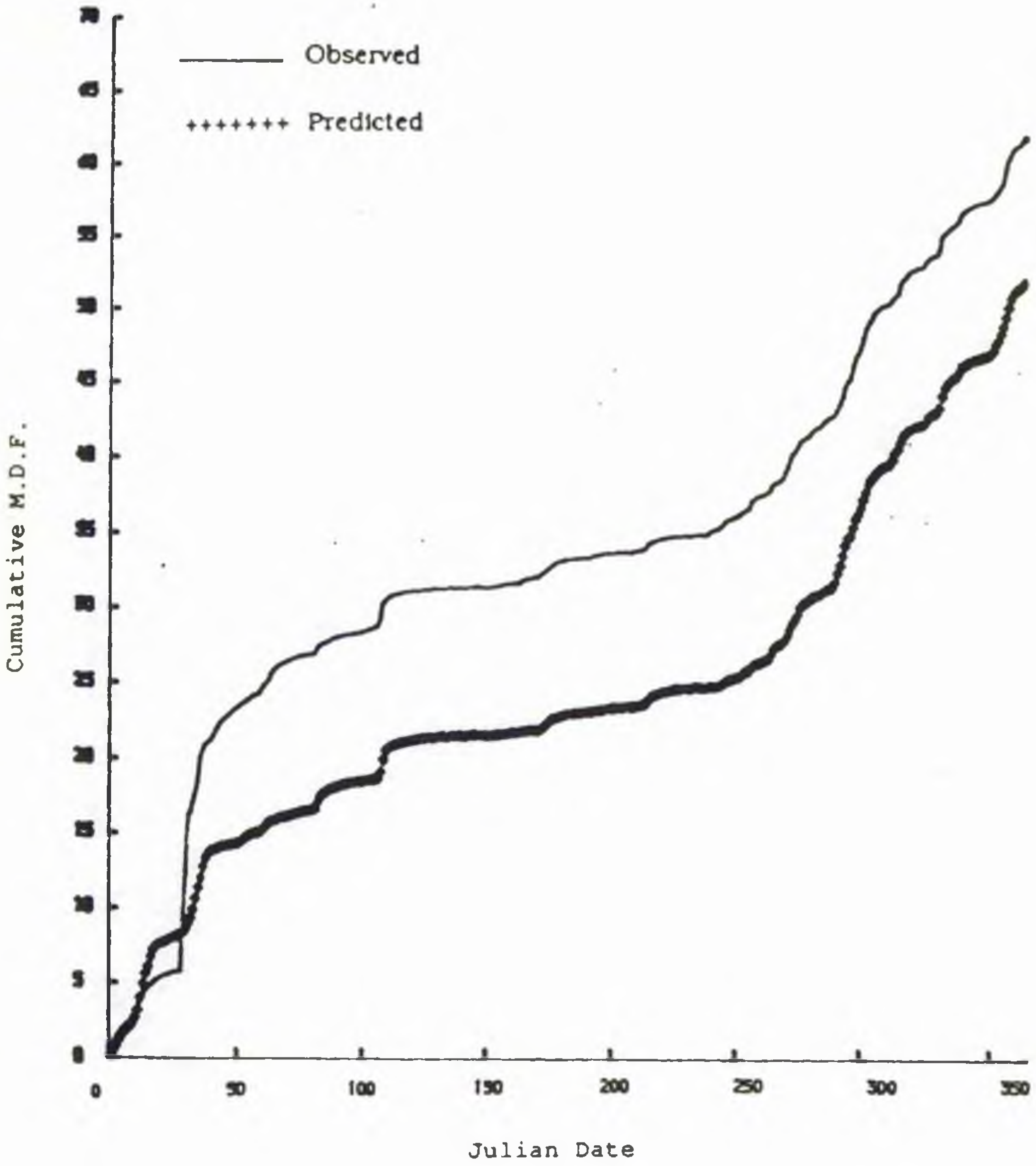


Figure 6.6: Simulated and Observed Cumulative M.D.F.s ($m^3 s^{-1}$) for the Dargall Lane 1984.

As with the two soil layer version of the model the three layer model was initially calibrated globally so that the predicted and observed cumulative annual outflows were equal (Figure 6.4). It can be seen that a generally good match is obtained between the predicted and cumulative M.D.F.s apart from a period in mid-summer (days 200-250) when the model simulation underestimates the observed flow. An instantaneous calibration of the hydrographs was then performed by adjustment of the values for the soil parameters in each layer, again on a trail and error basis, until the RMSE between the predicted and observed M.D.F.s was minimised. The final optimum values for the various soil parameters in each horizon are shown in Table 6.6., with the optimum fit between the predicted and observed M.D.F.s presented graphically in Figure 6.5. It can be seen that as with the plot of cumulative outflows a reasonable agreement exists between the simulated and observed individual M.D.F.s. Again the main difference between the simulated and observed plots is for the hydrograph peaks in the summer months (days 200-250) which the model totally fails to reproduce, the model instead predicting a continuous recession in flow throughout the summer period. It can also be seen that the model flow simulation has difficulty in reproducing the hydrograph peaks at the start of the year and during the autumn. Thus the simulated peaks at these times tend to be overestimated.

Despite these problems it was considered that a reasonable agreement had been established between the simulated and observed hydrographs for the calibration year. Consequently, the model was used to simulate runoff from the Dargall Lane in 1984 and 1985 in order to verify the calibration. Figure 6.6 shows the simulated and observed cumulative outflow for 1984. The initial impression is of a very poor match as the model totally fails to reproduce a large increase in runoff at the end of January 1984. If, however, allowance is made for this exceptionally large runoff event then a generally close agreement exists between the simulated and observed cumulative flows throughout the rest of 1984. This conclusion is supported by the individual M.D.F.s for 1984 (Figure 6.7). Here it can be seen that apart from the large runoff events from days 30-40, the model generally simulates the observed hydrographs well. The only other exceptions are a hydrograph peak around day 160 which the model misses altogether and a tendency to underestimate the hydrograph peaks in the later part of the year (days 290-350).

For the final verification year, 1985, the plot of simulated and observed cumulative outflow (Figure 6.8) shows a very good correspondence apart from the period around day 90 where the model tends to overestimate runoff. The comparison of the individual M.D.F.s for this year, (Figure 6.9) shows that as in the calibration year 1983 and the initial verification year 1984 the model is able to reproduce the recession curves of individual hydrographs well but has more trouble with the hydrograph peaks. Thus the model has a tendency to overestimate peak flows at the start and end of the year (days 25-60 and 330-355) and to underestimate peak flows during the summer period (days 190-260).

The major results from the comparison of the simulated and observed M.D.F.s for all three years are also shown in Table 6.6. The simulated and observed total outflows (m^3) and the RMSEs between

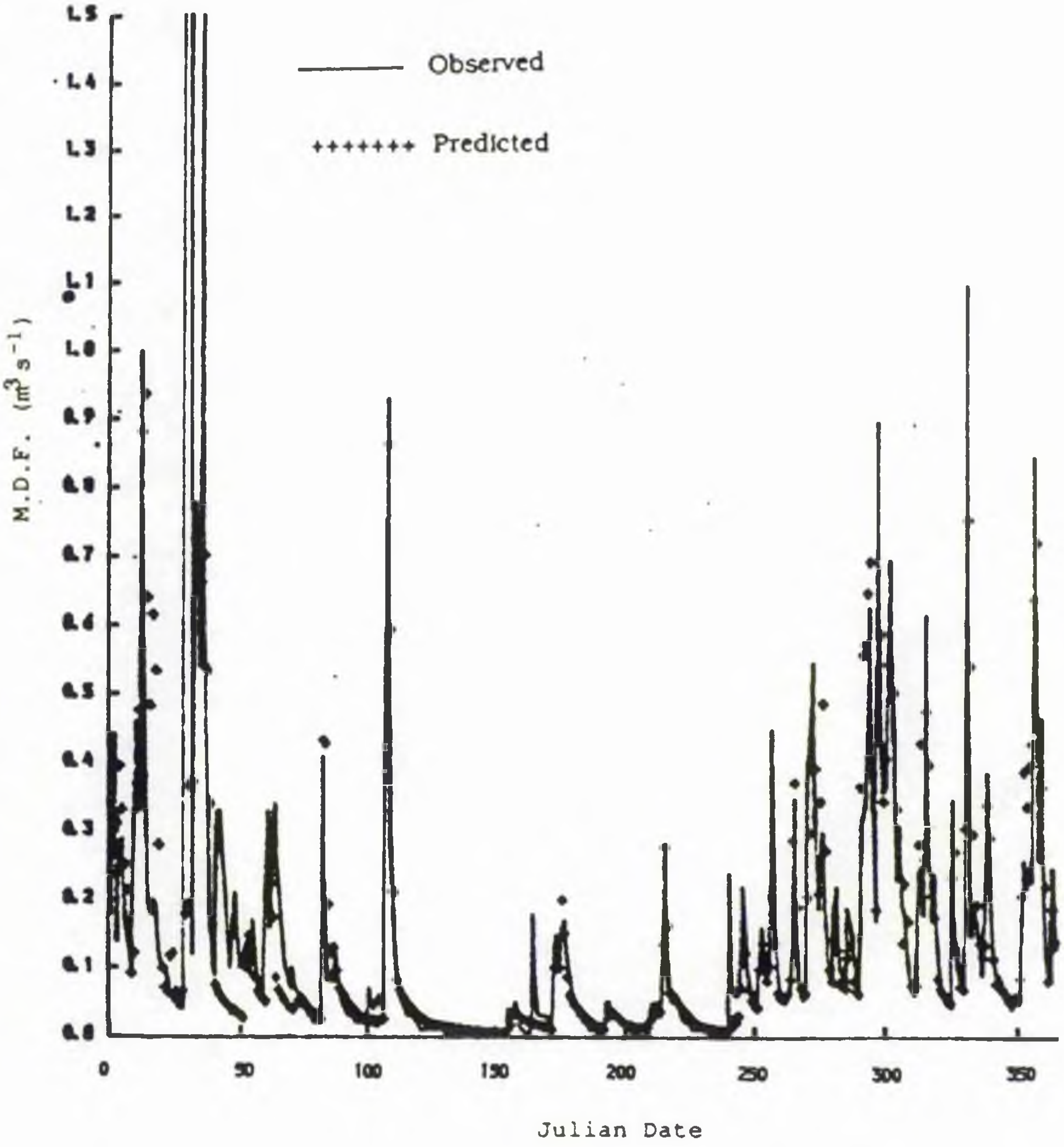


Figure 6.7: The Simulated and Observed M.D.F.s ($m^3 s^{-1}$) for the Dargall Lane 1984.

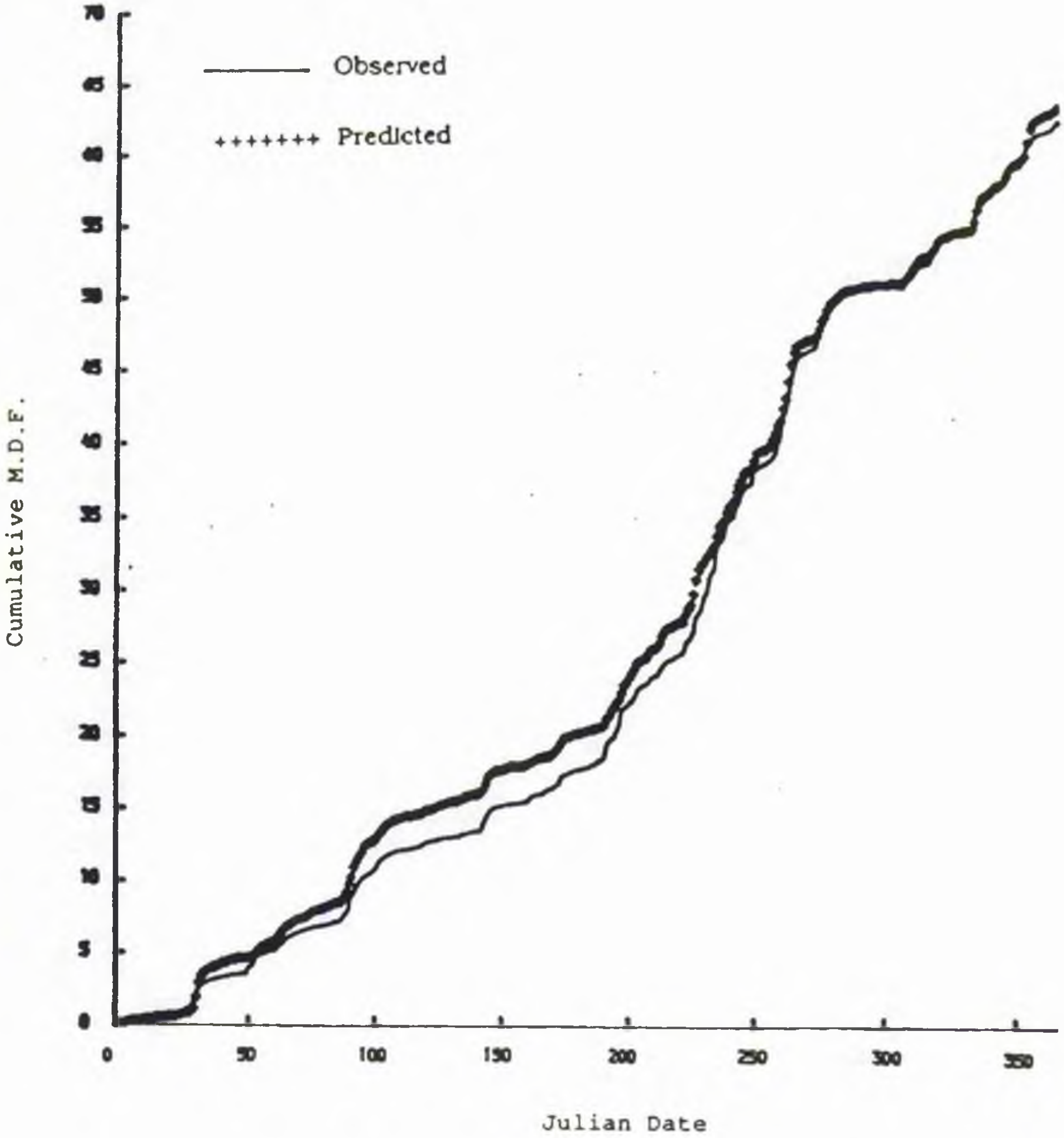


Figure 6.8: Simulated and Observed Cumulative M.D.F.s ($m^3 s^{-1}$) for the Dargall Lane 1985.

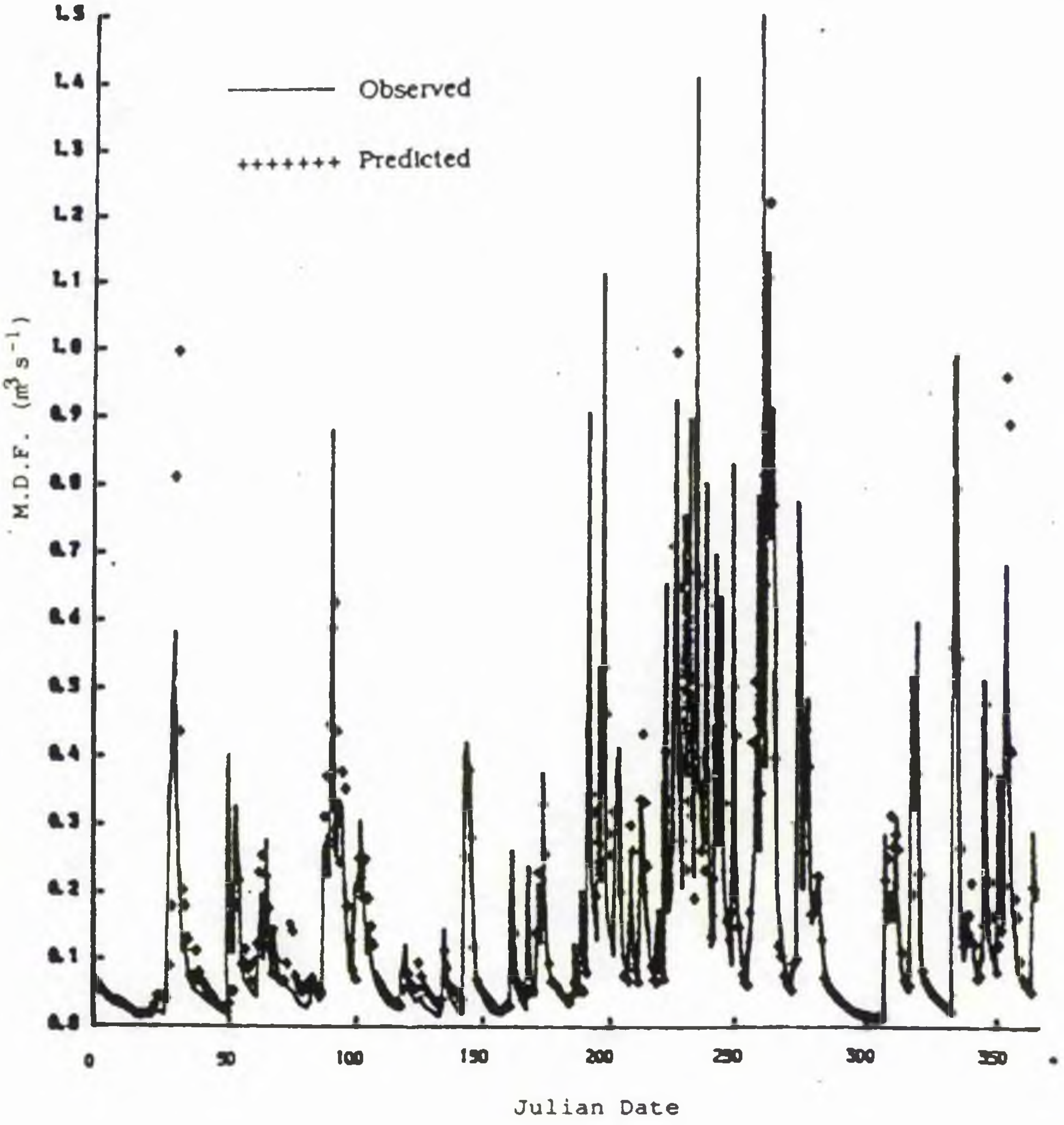


Figure 6.9: The Simulated and Observed M.D.F.s ($m^3 s^{-1}$) for the Dargall Lane 1985.

the simulated and observed flow time series and the predicted total outflows through each soil layer (as represented in the model) are presented in this table. The large underestimation of runoff in 1984, due to the model's failure to reproduce the runoff events of days 30-40, can be clearly seen, together with the very good estimations for 1983 and 1985. The table also shows that the simulated runoff in each year is dominated by flow through the upper organic horizon (>65%). Furthermore, it can be seen that there is very little variation in the relative proportions of simulated runoff through each layer in each of the three study years

6.3.2 *The Green Burn*

As for the Dargall Lane simulation the first stage in the Green Burn simulation was to derive values for the model inputs. The time-dependent inputs used were the same as in the Dargall Lane simulation. For the time-independent variables the major differences were for the physical descriptions of the land sub-catchment and stream segments and in the soil parameters Tables 6.7, 6.8 and 6.9). The values for the physical variables that describe the sub-catchment and stream segments are shown in Tables 6.7 and 6.8 respectively. For the soils the Green Burn simulation was initially set up with a simple two soil layer representation of the catchment (Table 6.9).

Calibration was performed on the same basis as for the Dargall Lane. Firstly , a global calibration was performed to ensure that the simulated and cumulative outflows were equal. Again this was accomplished by adjustment of the annual predicted

	Sub-Catchments							
	A	B	C	D	E	F	G	H
Area (m)	191570	115070	66470	127400	119210	132120	607840	1343750
Mean Slope (m/m)	0.144	0.144	0.162	0.189	0.266	0.218	0.066	0.174
Mean Width (m)	250.0	120.0	140.0	180.0	220.0	160.0	400.0	900.0
Aspect (degrees)	15°	320°	300°	260°	10°	270°	35°	325°
Vegetation (%):								
Coniferous Forest	20	24	28	10	68	45	98	81
Moorland	80	76	72	90	32	55	2	19
Precipitation Weighting	1.2	1.20	1.20	1.20	1.20	1.20	1.10	1.15

Table 6.7: The major physical parameters of the land sub-catchments used in the ILWAS representation of the Green Burn catchment

	Stream Segment			
	1	2	3	4
Depth (m)	0.306	0.204	0.460	0.500
Length (m)	1140.0	580.0	290.0	1560
KR	0.011	0.011	0.022	0.022
KX	0.25	0.25	0.25	0.25
Bed Height Upstream (m)	460.0	450.0	380.0	320.0
Bed Height Downstream (m)	360.0	380.0	320.0	230.0
Stage - Surface Area (m/m^2)	0.0:0.0 10.0:15380.0	0.0:0.0 10.0:15380	0.0:0.0 10.0:15380	0.0:0.0 10.0:15380
Upstream sub-catchments	A, B	C, D	E, F	G, H
Upstream segments	-	-	-	-

Table 6.8: The major physical parameters of the stream segments used in the ILWAS representation of the Green Burn catchment

(KR and KX are Muskingum routing coefficients)

	Layer 1	Layer 2
Thickness(cm)	60.0	40.0
Initial Moisture Content	0.41	0.36
Field Capacity	0.39	0.25
Saturated Moisture Content	0.50	0.43
Permeability (cm/day)		
Horizontal	1.00E5	9000.0
Vertical	1.00E5	9000.0
% Roots	80.0	20.0
Initial Temperature	8.0	5.0

Table 6.9: The physical data used for the two soil layer ILWAS representation of the Green Burn catchment. (Initial Moisture Content, Field Capacity and Saturated Moisture Content are all expressed as a fraction of the soil volume)

	1983	1984	1985
RMSE.	0.1399	0.1485	0.1479
Actual Total Flow (m^3)	5016989	4987182	5575996
Predicted Total Flow (m^3)	4961791	4592107	5776181
Layer 1 (% of Total)	4173059 (84.10)	3888991 (84.69)	4881202 (84.51)
Layer2 (% of Total)	788732 (15.90)	703116 (15.31)	894979 (15.49)

Table 6.10: The observed and ILWAS predicted annual flows for the Green Burn 1983 - 1985.

evapotranspiration. Secondly, with a reasonable match between the simulated and observed cumulative flows obtained, the fine structure of the hydrograph was calibrated by a trial and error procedure until the RMSE of the simulated and observed series was minimised. As for the Dargall Lane the major calibration parameters at this stage were identified as the horizontal permeability, the saturated moisture content and the field capacity of each soil horizon.

For the two soil layer representation of the Green Burn in the 1983 calibration period the correspondence between observed and simulated cumulative flows is shown in Figure 6.10. If Figure 6.10 is compared with Figure 6.4 it can be seen that the correspondence is, infact, rather better than for the three soil layer representation of the Dargall Lane, with only a slight mismatch in the early spring (day 100) and early autumn (day 300). The plot of the individual M.D.F.s (Figure 6.11) shows a far better match than for the two soil layer representation of the Dargall Lane (figure 6.3), with the recession periods particularly well reproduced. The M.D.F.s show even a slightly better match than with the three soil layer representation of the Dargall Lane (Figure 6.5), the three soil layer representation of the Dargall Lane is the one referred to in the rest of the text unless otherwise stated. The main discrepancy between the simulated and observed series occurs, as for the Dargall Lane, during the summer period (days 170-240) when the model is unable to reproduce any of the hydrograph peaks, instead producing a continuous recession. Furthermore, as with the Dargall Lane simulation, the Green Burn simulation also has a tendency to overestimate the hydrograph peaks in the early autumn (days 270-300).

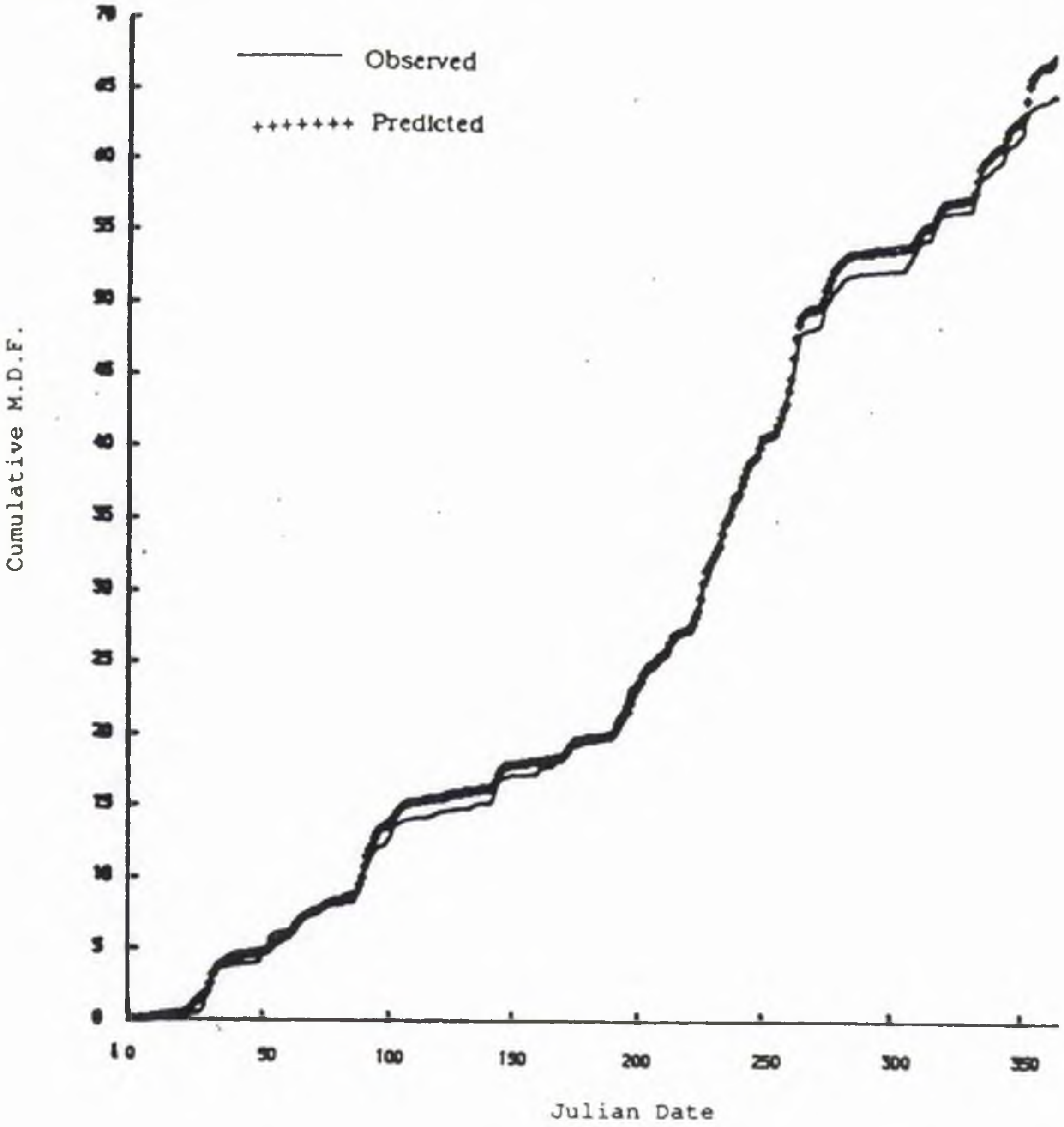


Figure 6.10: Simulated and Observed Cumulative M.D.F.s ($m^3 s^{-1}$) for the Green burn 1983

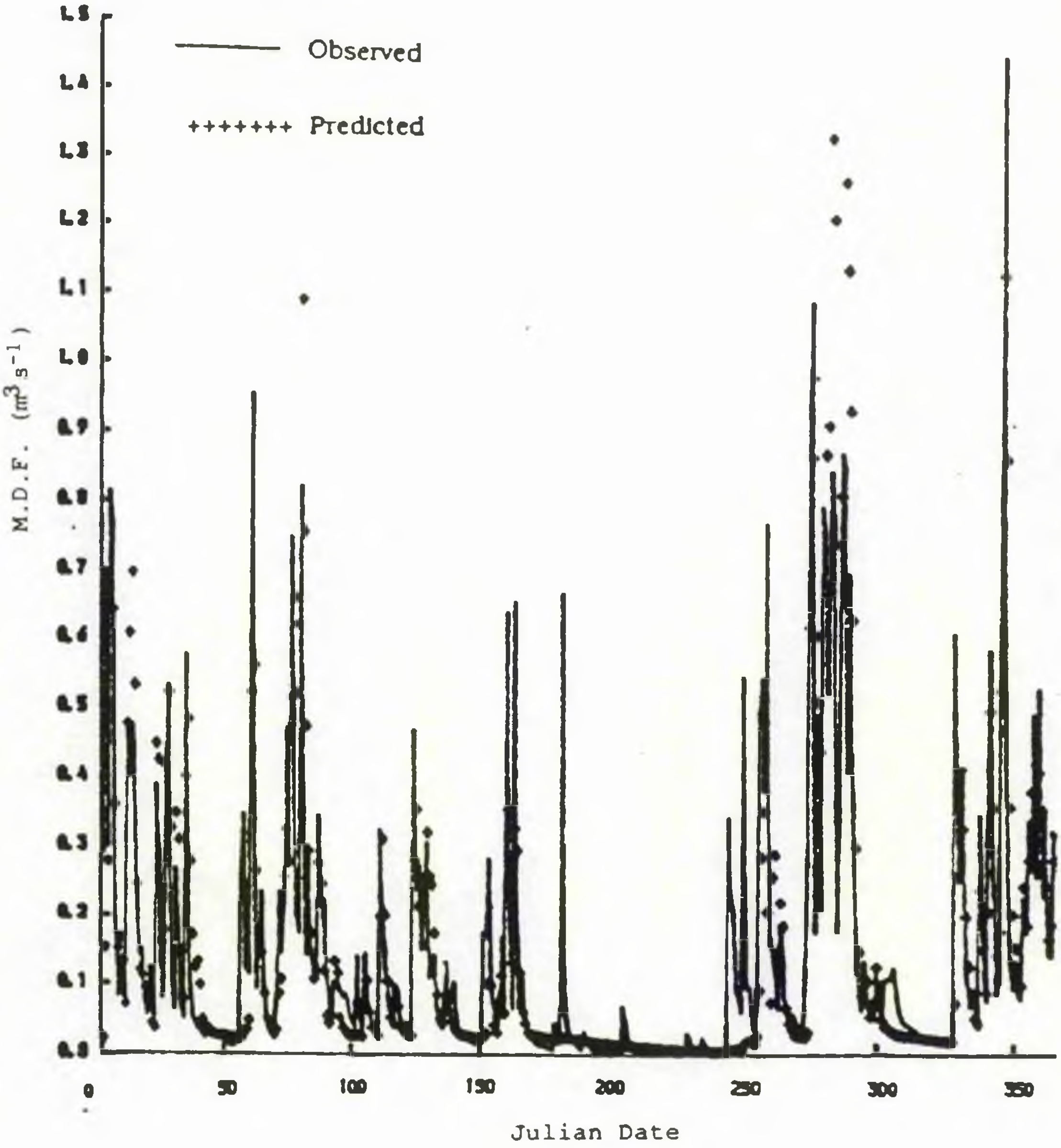


Figure 6.11: The Simulated and Observed M.D.F.s ($m^3 s^{-1}$) for the Green Burn 1983

With a reasonable agreement established between the simulated and observed flows for the calibration year, the calibration was verified by using the model to simulate the Green Burn runoff for 1984 and 1985. From the plot of simulated and observed cumulative flows for 1984 (Figure 6.12) it can be seen that a far better correspondence exists between the simulated and observed flows than for the Dargall Lane in this same year. The correspondence is, however, worse than for 1983, due primarily to the period around days 180-250. Furthermore, it can be seen that in contrast to the Dargall Lane, the simulated flows are higher than observed for the period between days 30-50, rather than significantly lower. An examination of the individual M.D.F.s for 1984 (Figure 6.13) shows that this is due to the lack of abnormally high observed flows during days 30-50 in the Green Burn. Figure 6.13 also shows that for 1984 the main failing of the model, and the cause of the mismatch between the simulated and observed M.D.F.s from days 180-250, is the model's inability to simulate the response of discrete summer storms. The model, as in 1983 and as for the Dargall Lane, produces very low flows throughout the summer. The plots for the simulated and observed flows for the Green Burn in 1985 (Figures 6.14 and 6.15) show, as for the Dargall Lane in this year, a far better correspondence between simulated and observed flows indicating the value of having several year's data upon which to perform calibration and verification. From Figure 6.14 it can be seen that the only significant departure of the simulated cumulative flow from the observed flow occurs around days 250-260. The plot for the individual M.D.F.s shows that this discrepancy is the result of the model overestimating a hydrograph peak at this time, otherwise

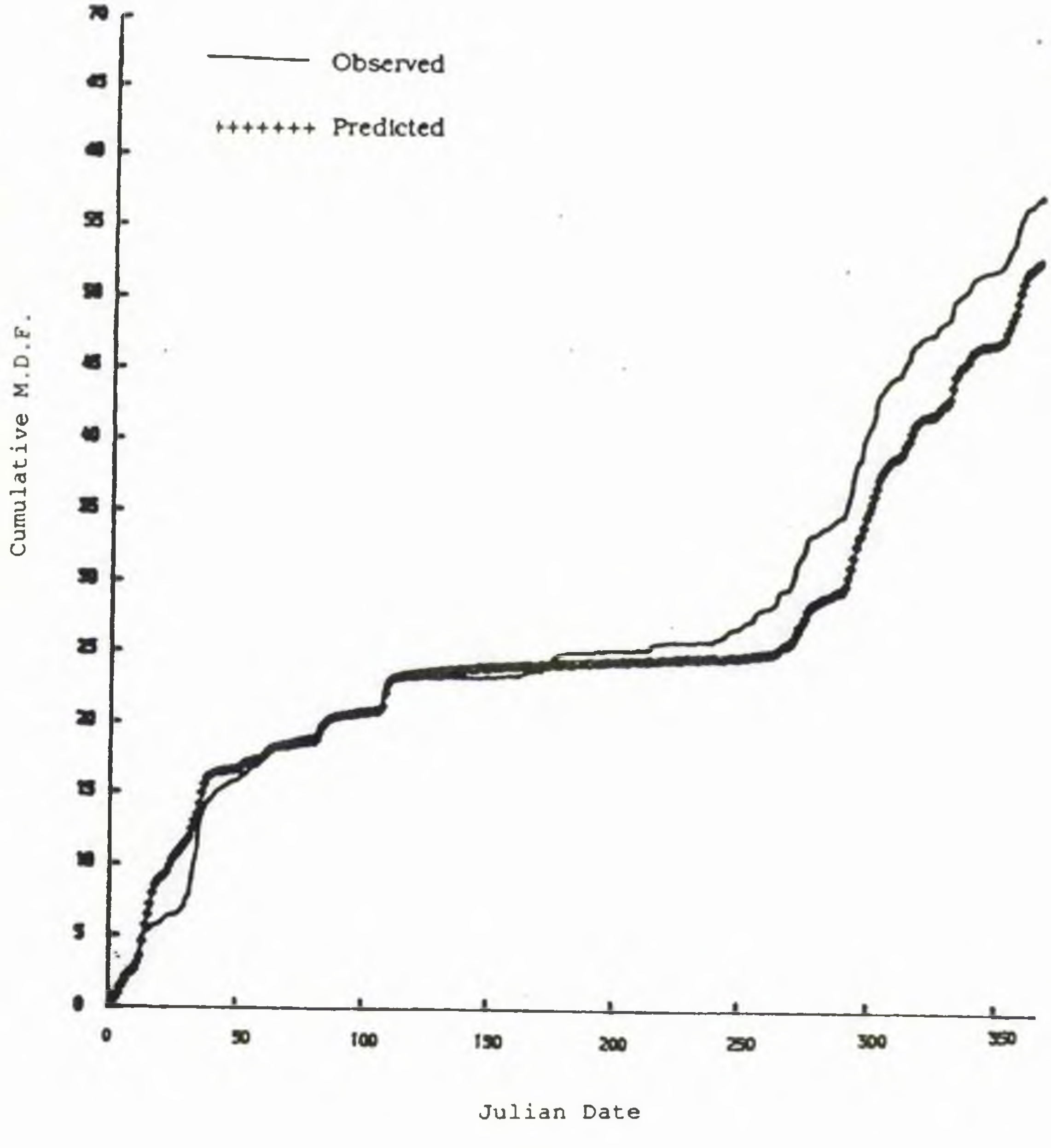


Figure 6.12: Simulated and Observed Cumulative M.D.F.s ($m^3 s^{-1}$) for the Green Burn 1984

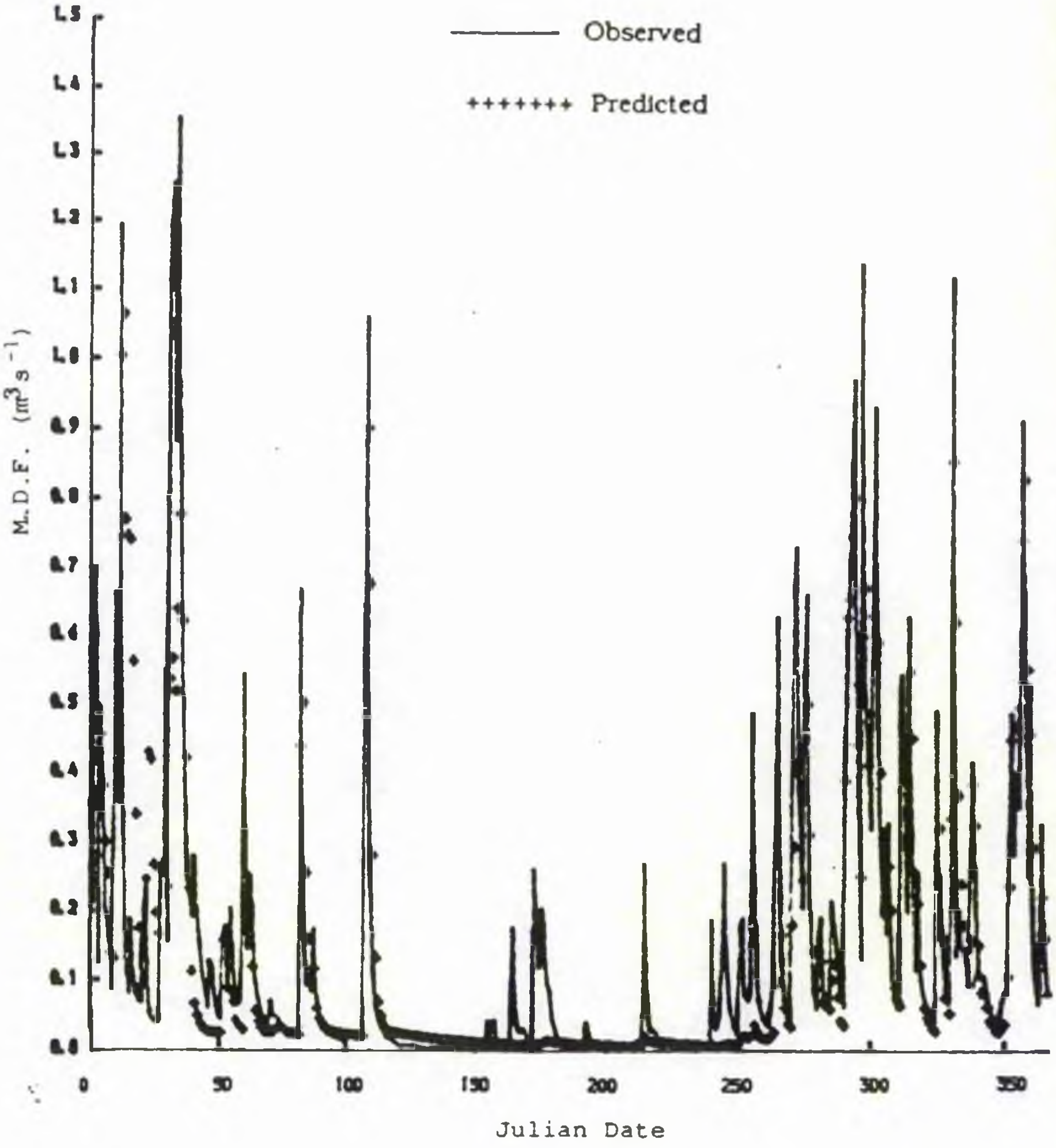


Figure 6.13: The Simulated and Observed M.D.F.s ($m^3 s^{-1}$) for the Green Burn 1984

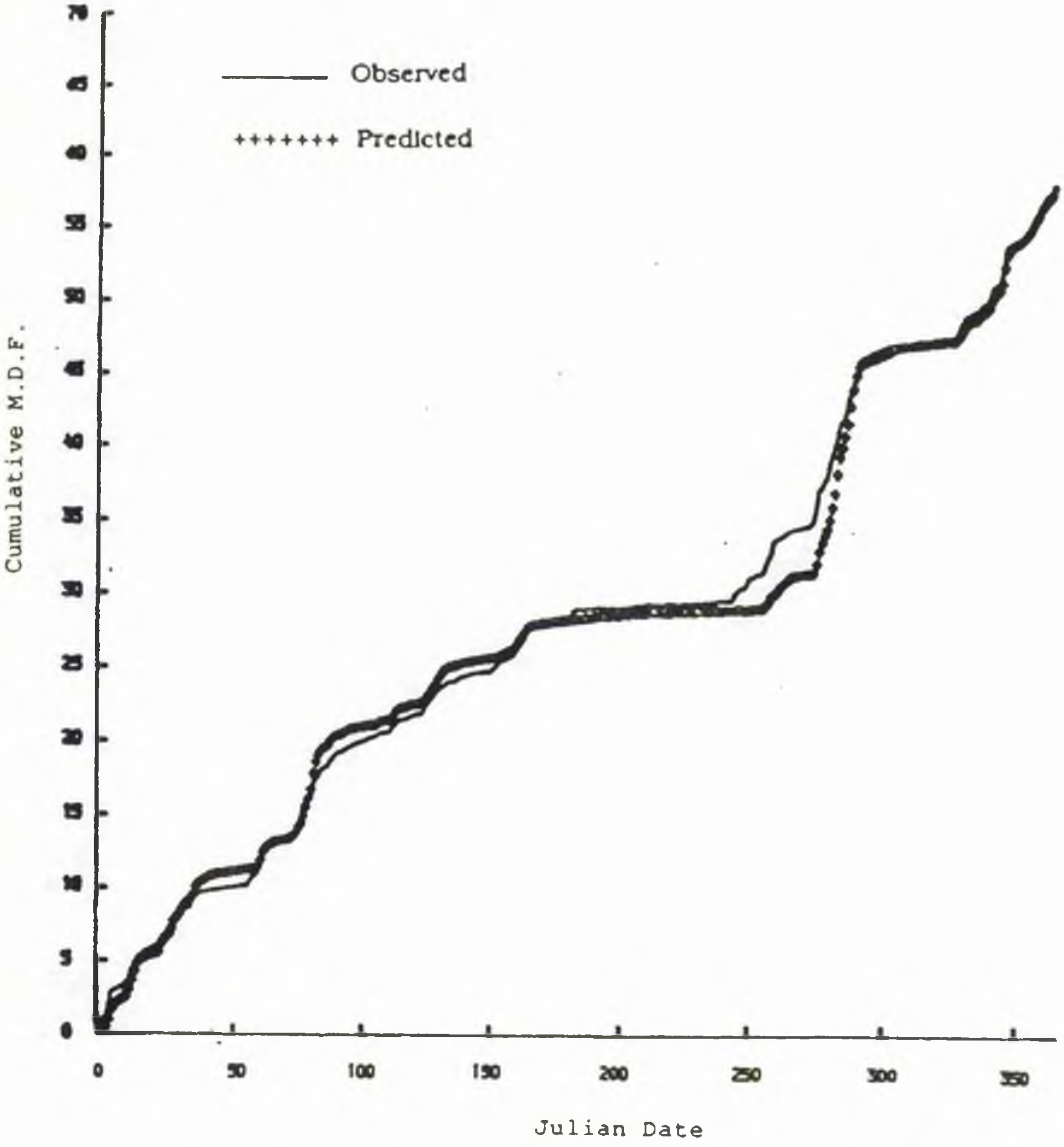


Figure 6.14: Simulated and Observed Cumulative M.D.F.s ($m^3 s^{-1}$) for the Green Burn 1985

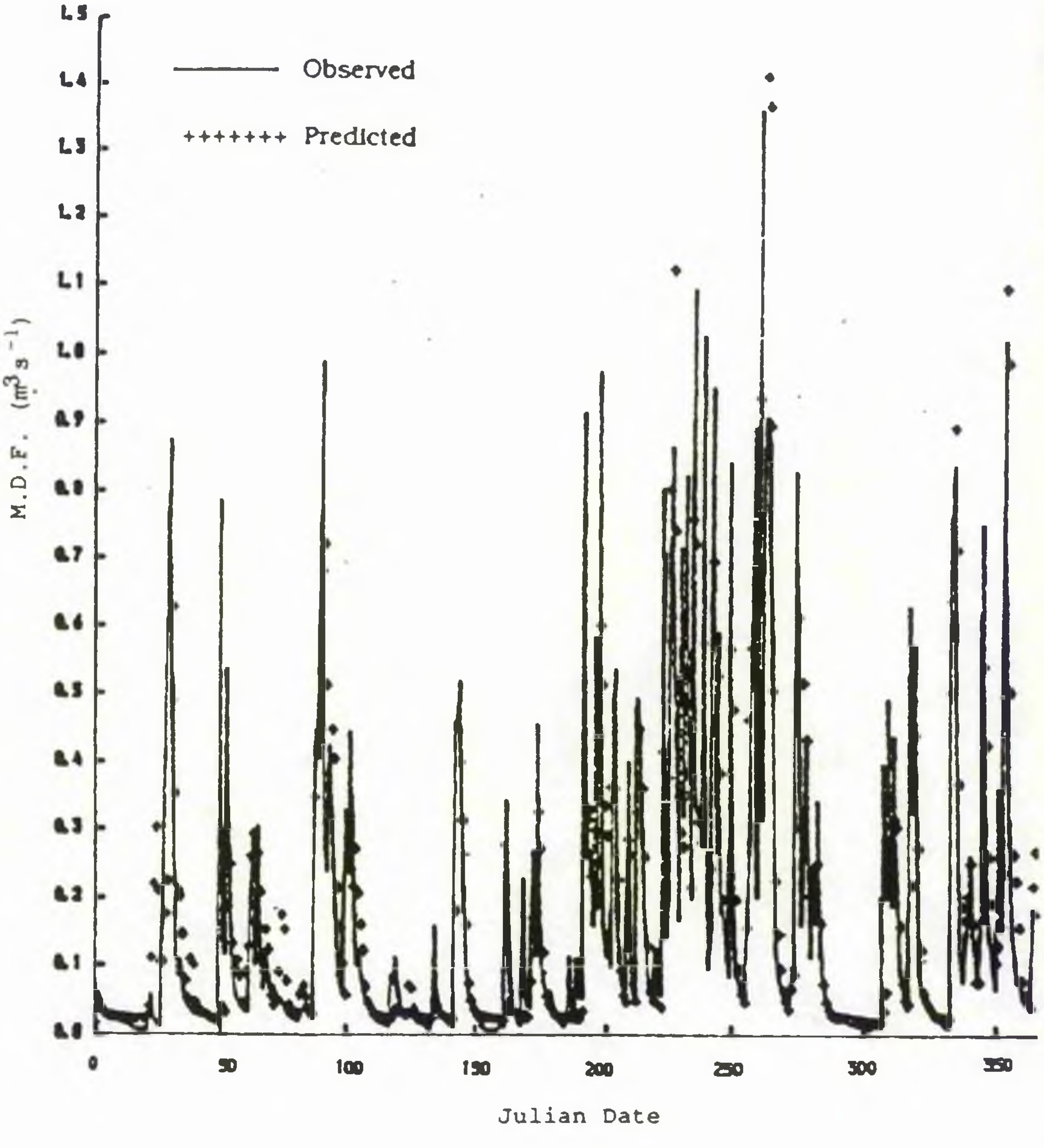


Figure 6.15: The Simulated and Observed M.D.F.s ($m^3 s^{-1}$) for the Green Burn 1985

there is a very good correspondence, particularly during the wet summer period.

The results of the comparison between the simulated and observed flows are presented in Table 6.10, from which it can be seen that, again as for the Dargall Lane, the 1984 results for total flow are very disappointing and far worse than those for 1983 and 1985. The table also shows that, again as for the Dargall Lane, the simulated flow in each year is predominantly through the upper soil layer, with very little flow through the lower soil layer.

With the two soil layer calibration verified, a three soil layer simulation of the Green Burn catchment was undertaken. Despite the good calibration of the two soil layer representation, this was performed in order to see if the simulation could be improved upon still further. The optimum soil parameter values for the three soil layer representation of the Green Burn were again determined by a trial and error procedure and are presented in Table 6.11. However, if the optimum results from the three layer model (Table 6.12) are compared with the two layer model (Table 6.10) it can be seen that the correspondence between the simulated and observed flows for the three soil layer representation are slightly worse than for the two soil layer representation. This is true for both the calibration year and the two verification years. Consequently, it was decided that the chemical simulation of the Green Burn would be based on a two soil layer hydrological model, whereas for the Dargall Lane the chemical simulation would be based on a three soil layer hydrological model. This difference is unlikely to represent an actual difference in the soil profiles of the two sub-catchments, rather the difference is

	Layer 1	Layer 2	Layer 3
Thickness(cm)	60.0	20.0	20.0
Initial Moisture Content	0.43	0.34	0.25
Field Capacity	0.39	0.25	0.20
Saturated Moisture Content	0.50	0.40	0.33
Permeability (cm/day)			
Horizontal	1.00E5	1.00E4	1.00E3
Vertical	1.00E5	1.00E4	1.00E3
% Roots	80.0	20.0	0.0
Initial Temperature (°C)	8.0	6.0	5.0

Table 6.11: The physical parameter values used in the three soil layer ILWAS representation of the Green Burn catchment.
(Initial Moisture Content, Field Capacity and Saturated Moisture Content are all expressed as a fraction of the soil volume)

	1983	1984	1985
RMSE.	0.1505	0.1526	0.1636
Actual Total Flow (m^3)	5018969	4987182	5576181
Predicted Total Flow (m^3)	4895165	4573549	5850403

Table 6.12: The main observed and simulated annual flow data for the three soil layer representation of the Green Burn 1983 - 1985.

probably a result of the more complex topography of the Dargall Lane sub-catchment. In this sub-catchment the thick peats of the flat valley bottom serve to pond-up flow from the steep valley sides and it is probable that the extra lower permeability soil layer enables this effect to be more accurately simulated. In contrast, the topography of the Green Burn is far simplier and the addition of a third soil layer will merely serve to increase the number of uncertainties in the simulation. Consequently, a simple two soil layer model is sufficient to reproduce the observed hydrological response of the Green Burn.

6.4 *CHEMICAL CALIBRATION AND VERIFICATION*

With the hydrological sub-model adequately calibrated, the next step in the evaluation of ILWAS was to calibrate the chemical behaviour of the model. This process will be examined first for the Dargall Lane and then for the Green Burn sub-catchments.

6.4.1 *The Dargall Lane*

As for the hydrological sub-model, the first step in the calibration of the model chemistry was to derive the input data to drive the model and values for the variables that determine the chemical behaviour of the catchment. The chemistry model is driven by the mean monthly concentrations of ions in wet precipitation and the mean monthly ambient air quality. However, at Loch Dee, as for most other catchment studies in Britain, ambient air quality data is limited to one or two spot measurements of sulphur dioxide and nitrous oxides. Communication with EPRI (the organisation responsible for the development of ILWAS) elicited the response that in the absence of significant sulphur sources or sinks within the catchment then bulk deposition inputs would provide an adequate approximation of the total deposition. As the budgetary studies reported in chapter 5 indicated that neither the Dargall Lane nor Green Burn catchments contained significant sulphur sources or sinks, it was decided that the mean monthly ion concentrations in bulk deposition measurements would be used to drive the chemistry component of the model.

The time-independent variables of the chemistry model consist of thermodynamic constants used in the equilibrium calculations and rate coefficients for the processes within the canopy and soils. Within the canopy module data are required for numerous variables for both coniferous and open area canopies as shown in Table 6.13. With the exception of canopy height, no data were available for any of these variables for the Loch Dee sub-catchments nor for British sites in general (Miller pers. comm.). However, as the rationale behind the modelling exercise was to evaluate the applicability of ILWAS to a typical catchment site, where such information would clearly not be available, the neccessary information was taken from the ILWAS data-base for the Panther Lake catchment in the Adirondacks (E.P.R.I. pers. comm.). This decision was justified in this specific instance by the general chemical similarity of the vegetation at Panther Lake to that at Loch Dee. The subsequent values for the chemical variables within the canopy module taken from Panther Lake and used in the ILWAS simulations of the Dargall Lane and Green Burn are also shown in Table 6.13. However, it should be noted that such a substitution of input variable values would not be generally appropriate across upland Britain.

a)

Standing Biomass (Kg/m^2)		Canopy Height (m)		Annual Productivity ($Kg/m^2/yr$)		Maintainance Respiration (per day)		Active Respiration (per day)	
C	M	C	M	C	M	C	M	C	M
15.00	5.21	4.0	0.3	0.50	0.10	1.12E-8	0 (no data)	1.37E-8	0 (no data)

b)

	Trunk Composition (mg/g)		Leaf Composition (mg/g)	
	C	M	C	M
NH_4	0.550	0.110	10.000	2.700
Na^+	0.010	0.010	0.400	0.280
K^+	0.200	0.090	0.400	0.400
Ca^{++}	0.600	0.150	2.500	0.830
Mg^{++}	0.100	0.040	1.000	0.830
T.Al	0.006	0.006	0.060	0.230
Cl^-	0.003	0.003	0.011	0.060
Alk	3.687	1.260	49.300	0.011
SO_4^{--}	0.150	0.020	1.000	22.700
NO_3^-	0.000	0.000	0.000	0.000
PO_4^-	0.020	0.010	1.100	0.320

c)

	Litterfall Rate ($Kg/m^2/Mth$)		Foliar Exhudation Rate (per day)	
	C	M	C	M
Jan.	.003	.001	5.0E-6	NO DATA
Feb.	.003	.001	5.0E-6	
Mar.	.003	.001	5.0E-6	
Apr.	.003	.001	1.0E-6	
May	.030	.001	2.0E-5	
Jun.	.030	.001	2.0E-5	
Jul.	.030	.001	2.0E-5	
Aug.	.030	.001	3.0E-5	
Sep.	.030	.001	3.0E-5	
Oct.	.030	.001	2.0E-5	
Nov.	.003	.001	1.0E-5	
Dec.	.003	.001	5.0E-6	

Table 6.13: The major parameters used to describe the canopy chemical processes in the ILWAS representation of the Loch Dee catchments (C is the coniferous canopy data, M the moorland canopy data)

The soil chemistry module requires data for four main areas: the litter layer, soil mineralogy, soil chemistry and soil solution chemistry. The rate coefficients used to represent litter breakdown are shown in Table 6.14. As was found for the canopy module site-specific data were not available for the Loch Dee catchments, and again values had to be derived from the Panther Lake study.

In terms of soil mineralogy, data are required for each of the major minerals present in terms of the mineral molecular weights, reaction products, weathering rate coefficients and percentage by weight of the soil layer. Again such data were not directly available at Loch Dee, but as the underlying granitic bedrock at Panther Lake is very similar to that at Loch Dee it was believed that the soil mineralogy will also in general be similar, i.e. one dominated by plagioclase feldspar, hornblende and biotite. The values of the thermodynamic constants, the mineral molecular weight and reaction products were taken from the Panther Lake database. The mineral weathering rate coefficient and the percentage by weight of the mineral in the soil layer are, however, both calibration parameters. The resultant optimised values for both the minerological calibration parameters, for the Dargall Lane simulation, together with the values of the thermodynamic constants are shown in Table 6.15.

Soil chemistry data required by the model consist of the soil density, cation exchange capacity (C.E.C) and adsorped ion concentrations (Table 6.16). For the Dargall Lane the soil density, C.E.C, and adsorped cation concentrations were derived from personal field measurements, whereas anion adsorption data

Weight fraction litter in top layer (%)	0.00965
Weight fraction fine litter top layer (%)	0.1352
% Leachable ions in litterfall	0.1
Breakdown Rates	
Fine Litter - Humus	0.0670
Organic Acid	0.0160
% SO_4 and NH_4 to soil sol on litter b'down.	0.2
% SO_4 and NH_4 that forms organic acid	0.2

Table 6.14: Major rate coefficients used to define litter breakdown in the ILWAS model and the values used in the Dargall Lane and Green Burn simulations.

a)

Mineral	Biotite	Plagioclase	Hornblende
Molecular Weight (grams/mole)	428	265	939
Weathering Rate Coefficient	.5	.5	.5
Reaction Products (meq/mole)	K 5000 Mg 350 Alk 6000 Si 1400	Ca 840 Na 300 Alk 1150 Si 1590	Ca 3500 Mg 2173 K 350 Na 600 Alk 6493 Si 5600

b)

	SUB-CATCHMENTS					
	A-D Soil Layer			E-F Soil Layer		
MINERAL	1	2	3	1	2	3
Biotite	2.0	2.9	2.9	2.0	2.0	2.9
Plagioclase	4.0	12.1	12.1	4.0	4.0	12.1
Hornblende	0.5	0.9	0.9	0.5	0.5	0.9
Humus	75.0	0.0	0.0	75.0	75.0	0.0

Table 6.15: The major minerological parameters used in the ILWAS representation of the Loch Dee catchments, a) the thermodynamic constants and a weathering rate calibration parameter, b) the percentage by weight of each mineral and humus in each soil layer.

	SUB-CATCHMENTS					
	A - D			E - F		
	Layer			Layer		
Density (g/cm)	1 0.20	2 1.30	3 1.30	1 0.20	2 0.20	3 1.30
C.E.C. (meq/100g)	150	20	20	150	150	20
Adsorped Ions						
H^+	84.00	93.00	93.00	84.00	84.00	93.00
NH_4^+	1.00	0.50	0.50	1.00	1.00	0.50
Na^+	3.00	1.40	1.40	3.00	3.00	1.40
K^+	1.00	0.50	0.50	1.00	1.00	0.50
Ca^{++}	6.00	2.60	2.60	6.00	6.00	2.60
Mg^{++}	5.00	2.00	2.00	5.00	5.00	2.00
T.Al	0.00	0.00	0.00	0.00	0.00	0.00
Cl^-	0.00	0.00	0.00	0.00	0.00	0.00
Alk	0.00	0.00	0.00	0.00	0.00	0.00
SO_4^{--}	0.15	0.20	0.20	0.15	0.15	0.20
NO_3^-	0.00	0.00	0.00	0.00	0.00	0.00
PO_4	0.05	0.02	0.02	0.05	0.05	0.02
O.A.	55.00	5.00	5.00	55.00	55.00	5.00

Table 6.16: Soil density, C.E.C. and adsorbed ion concentrations (cations as % C.E.C. and anions as meq/100g) for each soil layer in the ILWAS representation of the Dargall Lane. (O.A. = Organic Acid)

were taken from results cited by Bown (1974) for the 'O' and 'B' horizons of peaty podsols. However, there were no data available for adsorbed organic acid concentrations in the soils of the area. Fortunately, the soils of the Panther Lake study site are also podsolic with very thick organic horizons, thus the adsorbed organic acid concentrations used for the Dargall Lane were those reported by Chen et al. (1983) for the 'O' and 'B' soil horizons at Panther Lake.

As well as information on the soil chemistry, the model simulation of a catchment also requires information on the soil solution chemistry. This data was collected on a monthly basis, from July 1987 to May 1988, by the use of porous pot lysimeters located at 5 sites on the lower slopes of the Dargall Lane. At each site lysimeters extract water under small suctions from a depth of 20cm within the organic horizon and from a depth of 50-60cm at the interface between the organic and mineral horizons. The mean and range in concentration of the sampled solutions are shown in Table 6.17. For the model simulation of the Dargall Lane the observed data from the higher (20cm depth) lysimeter were used to represent the soil solution chemistry of the organic soil layers whereas the observed data from the lower (50cm depth) lysimeter was used to represent the mineral soil layers. However, it soon became apparent that, due to their influence on the cation selectivity and anion adsorbtion coefficients, the soil solution ionic concentrations were the main calibration parameter for the outflow chemistry. This arises because the cation selectivity and anion adsorbtion coefficients are determined within the model from the equilibriation of the soil solution with the adsorbed soil ions. Thus a 10% change in the initial soil solution concentration of the base cations

	0 - 20 cm		50 -60 cm	
	Mean	Range	Mean	Range
H^+	44.67	85.11 - 24.58	4.47	7.94 - 3.39
Na^+	212.45	160.06 - 351.13	209.51	152.16 - 326.90
K^+	11.88	6.10 - 18.32	10.00	7.49 - 12.21
Ca^{++}	67.41	48.31 - 103.21	79.02	48.31 - 131.10
Mg^{++}	84.17	61.11 - 121.31	98.24	60.01 - 151.92
T.Al	13.98	9.01 - 20.01	16.97	9.20 - 25.22
Cl^-	271.51	201.93 - 401.20	268.11	210.41 - 382.20
$SO_4^{=}$	100.60	71.59 - 130.30	101.01	82.35 - 118.13
NO_3^-	11.65	4.10 - 21.00	0.80	0.00 - 2.50

Table 6.17: The mean and range of observed monthly soil solution concentrations (μeq/l) at two depths in the Dargall Lane catchment 07/1987 - 05/1988.

	SUB-CATCHMENTS					
	A-D			E-F		
	Layer			Layer		
	1	2	3	1	2	3
H^+	38.0	3.0	3.0	38.0	38.0	3.0
NH_4	3.0	0.5	0.5	3.0	3.0	0.5
Na^+	256.8	248.8	248.8	256.8	256.8	248.8
K^+	13.3	7.7	7.7	13.3	13.3	7.7
Ca^{++}	100.9	122.3	122.3	100.9	100.9	122.3
Mg^{++}	107.6	132.2	132.2	107.6	107.6	132.2
T.Al	16.7	20.0	20.0	16.7	16.7	20.0
Cl^-	377.2	395.7	395.7	377.2	377.2	395.7
Alk	0.7	34.9	34.9	0.7	0.7	34.9
SO_4^{--}	100.0	100.0	100.0	100.0	100.0	100.0
NO_3^-	20.0	0.8	0.8	20.0	20.0	0.8
PO_4^-	0.3	0.2	0.2	0.3	0.3	0.2
O.A.	127.0	35.0	35.0	127.0	127.0	35.0

Table 6.18: The optimised soil solution concentrations (ueq/l) for each soil layer as used in the ILWAS representation of the Dargall Lane (O.A. = Organic Acid)

(Na^+,K^+,Ca^{++},Mg^{++}) results in a change of similar magnitude in the simulated mean annual streamwater concentrations. Consequently, the optimum values for the soil solution ionic concentration and hence the cation selectivity and anion adsorbtion coefficients were derived by a trial and error optimisation procedure. This involved the adjustment of the soil solution ionic concentrations until the simulated flow weighted mean annual streamwater ionic concentrations was equal to the observed values. The subsequent optimised values for the soil solution chemistry and the cation selectivity and anion adsorbtion coefficients are shown in Tables 6.18 and 6.19 respectively. A comparison of the optimised soil solution concentrations clearly shows that apart from H^+, SO_4^{++}, and NO_3^- in the mineral soil, the optimum concentrations vary considerably from the observed mean values. However, the optimised values do all fall within the range of observed data.

The simulated mean annual output concentrations for the optimum calibration are compared with the actual observed concentrations in Table 6.20. From the table it can be seen that on an annual basis the model could successfully be calibrated to reproduce the empirical values for the major chemical species. With the model calibrated for 1983 the next step was to verify the calibration by a comparison of the simulated and observed concentrations for 1984 and 1985. The simulated and observed flow weighted mean annual concentrations for 1984 and 1985 are also shown in Table 6.20. However, when these are compared it can immediately be seen that a very poor comparison exists. This is particularly true for pH (the main species of interest in acidification) which the model simulation regards as increasing in value from 1983 through 1984

	SUB-CATCHMENT					
	A - D			E - F		
	Layer			Layer		
	1	2	3	1	2	3
CKCaMg	1.28E+0	1.41E+0	1.41E+0	1.28E+0	1.28E+0	1.41E+0
CKCaNa	3.75E-2	3.08E-2	3.08E-2	3.75E-2	3.75E-2	3.08E-2
CKCaK	5.83E-3	2.66E-3	2.66E-3	5.83E-3	5.83E-3	2.66E-3
$CKLCaNH_4$	1.32E-3	1.73E-4	1.73E-4	1.32E-3	1.32E-3	1.73E-4
CKCaH	1.97E-4	4.76E-6	4.76E-6	1.97E-4	1.97E-4	4.76E-6
$CKPO_4$	1.67E+3	5.00E+2	5.00E+2	1.67E+3	1.67E+3	5.00E+2
$CKSO_4$	5.00E+0	1.00E+1	1.00E+1	5.00E+0	5.00E+0	1.00E+1
CKFA	5.93E+3	1.46E+3	1.46E+3	5.93E+3	5.93E+3	1.46E+3

Table 6.19: The optimium cation exchange and anion adsorbtion coefficients for each soil layer in the ILWAS representation of the Dargall Lane (CKFa is the organic acid adsorbtion coefficient)

	1983		1984			1985		
	Predicted	Observed	Predicted	Observed	% Error	Predicted	Observed	% Error
pH	5.14	5.14	5.18	4.93	+ 5.07	5.20	5.10	+ 1.96
NH_4^+	1.22	1.43	1.26	1.14	+10.53	1.18	1.75	- 48.31
Na^+	193.55	196.62	192.46	238.38	- 23.86	138.57	187.05	- 34.99
K^+	7.66	7.67	7.56	11.51	- 57.25	6.16	12.02	- 95.13
Ca^{++}	66.33	67.37	64.69	57.84	+11.18	39.16	51.92	- 32.58
Mg^{++}	71.39	72.02	69.57	65.10	+ 6.87	41.99	54.28	- 29.27
T.Al	6.40	6.35	7.29	8.23	- 12.89	7.32	8.12	- 10.93
Cl^-	226.19	228.98	224.76	243.37	- 8.28	149.20	207.27	- 38.92
Alk	20.17	20.62	21.26	32.78	- 54.19	24.78	40.65	- 64.04
SO_4^{--}	93.07	91.65	89.71	90.57	- 0.96	77.61	84.57	- 8.97
NO_3^-	6.95	7.84	6.92	10.00	- 44.51	3.80	7.00	- 84.21
PO_4^-	0.25	0.32	0.26	0.25	+ 4.00	0.30	0.26	+15.38
O.A.	68.53	–	68.83	–	–	70.53	–	–

Table 6.20: Simulated and Observed Flow Weighted Mean Annual pH and Ion Concentrations (ueq/l) for the Dargall Lane 1983 - 1985.

to 1985. In actual fact the pH falls in 1984 and then rises again in 1985 but stays at a lower level than in 1983. The other two chemical species of major interest in acidification studies are aluminium and sulphate. Total aluminium concentrations simulated by the model are higher than those observed in both 1984 and 1985 despite the simulated pH also being higher. Simulated sulphate concentrations, by contrast, are reasonably reproduced in 1984 but are far lower than observed in 1985. Of the other major species, the simulated mean annual concentrations of sodium, potassium, chloride, alkalinity, and nitrate are all underestimated in both 1984 and 1985, with potassium and nitrate concentrations particularly poorly simulated in 1985. In contrast, the simulated divalent cation concentrations (calcium and magnesium) are only slightly overestimated for 1984 but are substantially underestimated for 1985.

However, as the comparison of mean annual concentrations alone is a very coarse basis of comparison the monthly simulated and observed concentrations for the three study years were also compared. The simulated and observed flow-weighted mean monthly concentrations for 1983 are shown in Figure 6.16, from which it can be seen that for the hydrogen ion the model simulation is able to reproduce the broad trend in concentrations of high in winter, low in summer. However, as well as a failure to reproduce the observed increase in concentration for July the model also has a tendency to predict higher concentrations than those empirically determined. In contrast, the monthly total aluminium concentrations are quite well simulated by ILWAS, apart from the first few months of the year. The major base cation concentrations, with the exception of sodium are poorly reproduced with the

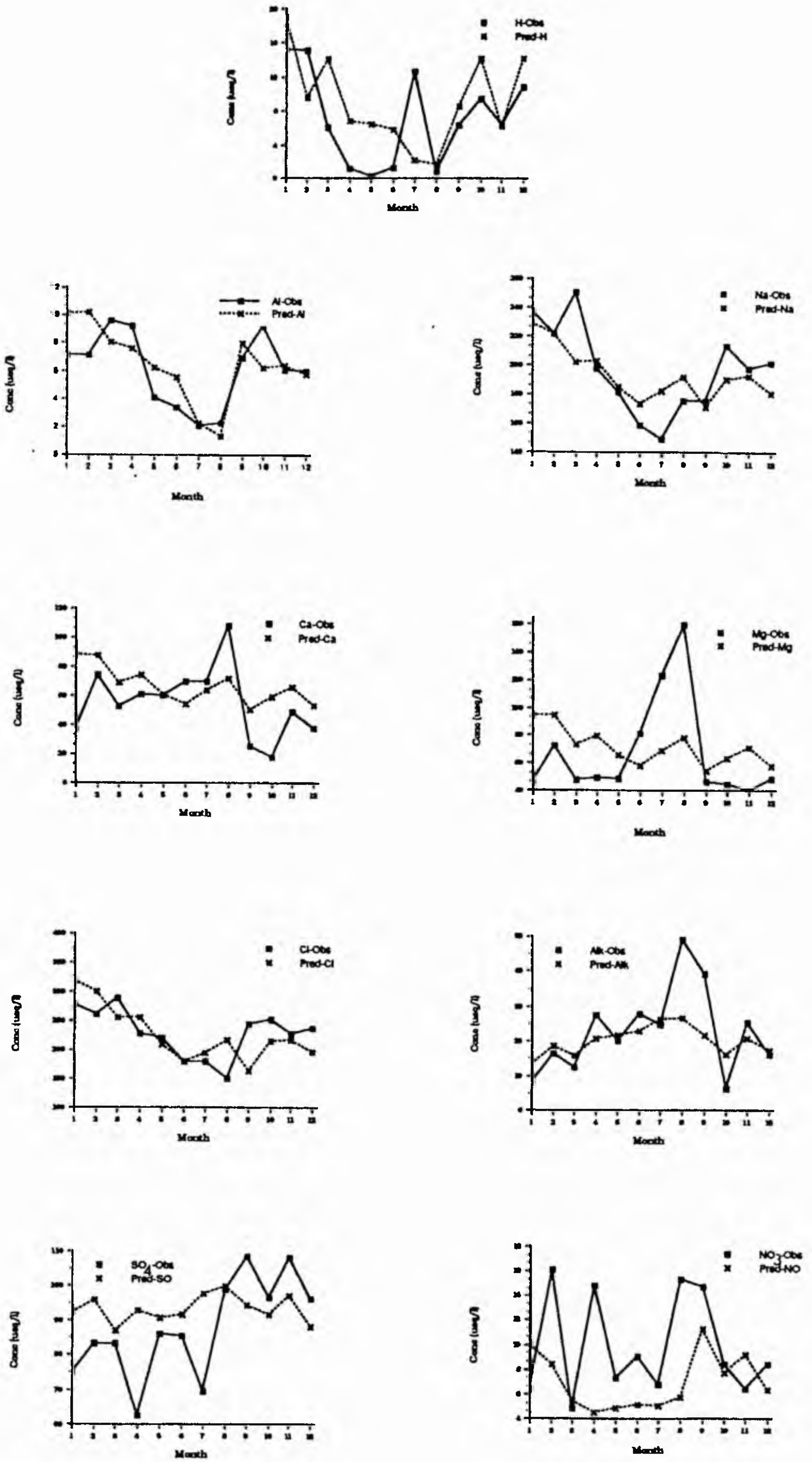


Figure 6.16: Simulated and Observed Flow Weighted Mean Monthly Concentrations (ueq/l) for the Dargall Lane 1983.

simulated concentrations considerably smoothed in comparison with the observed data. The simulated sodium concentrations, whilst also smoothed compared with the observed data, show a far better correspondence, particularly in the early part of the year.

Of the major anions the simulated alkalinity, like the base cation concentrations, exhibits a generally smoothed response and fails to reproduce the observed peak in concentration during August and September. The simulated chloride concentrations, however, show a generally good correspondence with the observed values, except, again for August and September where the model predicts a decrease rather than the observed increase in concentrations. For sulphate and nitrate the correspondence between simulated and observed concentrations is particularly poor. Thus the sulphate response from the model is considerably smoothed, with the model estimating very little change in sulphate concentrations throughout the year, in contrast to the considerable variation actually observed. For nitrate the model produces a strongly seasonal pattern with concentrations far lower in the summer period. In actuality, however, concentrations show far more variability, especially at the start of the year.

Turning to the initial verification year, 1984, the simulated and observed mean monthly concentrations are plotted in Figure 6.17. From this it can be seen that the simulated hydrogen ion concentrations, as in the calibration year, broadly reproduce the seasonal pattern in concentration. However, again as in 1983, the simulated response is unable to reproduce the major peaks in concentration that occur in March and October. This is particularly

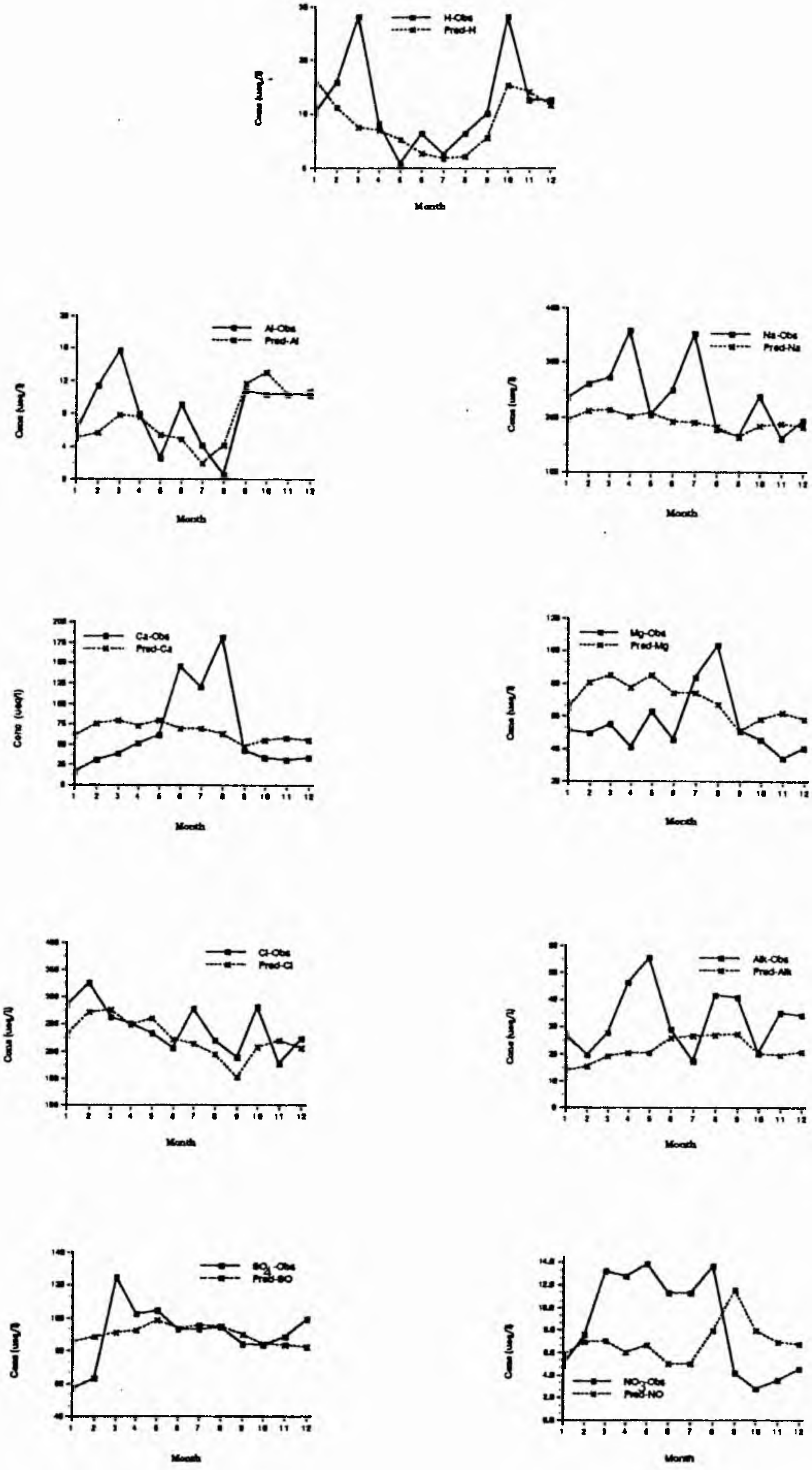


Figure 6.17: Simulated and Observed Flow Weighted Mean Monthly Concentrations (ueq/l) for the Dargall Lane 1984.

evident in March, with the model predicting a continuous decline in concentration from January to July, whereas for October the model does predict an increase in concentration, albeit far lower than that actually observed. Of the other ions the best correspondence between the simulated and observed concentrations is for chloride. Thus the chloride simulation is very reasonable apart from a failure to reproduce the observed increases in concentration during July and October. After chloride the most reasonably simulated concentrations are for aluminium. However, simulated aluminium concentrations, particularly in the early part of the year, are considerably smoothed. This smoothed response is particularly evident for the simulation of the other ions particularly the divalent cations, and alkalinity and sulphate concentrations. The simulated sodium concentrations, however, not only show a smoothed response but also considerably underestimate the observed peaks in April and July. Nitrate concentrations are also considerably underestimated, except for at the end of the year when concentrations are overestimated instead.

The simulated and observed mean monthly concentrations for the second verification year, 1985, are shown in Figure 6.18. From this figure the it can be seen that as in 1983 and 1984 the simulated hydrogen ion concentrations are smoothed in comparison with the observed data. However, as the observed data for 1985 shows far less variation than either 1984 or 1985, the correspondence between the simulated and observed hydrogen ion concentrations is better than in either 1983 or 1984. In contrast, aluminium concentrations which are reasonably well simulated in 1983 and 1984 are very poorly simulated in 1985, with the simulated monthly

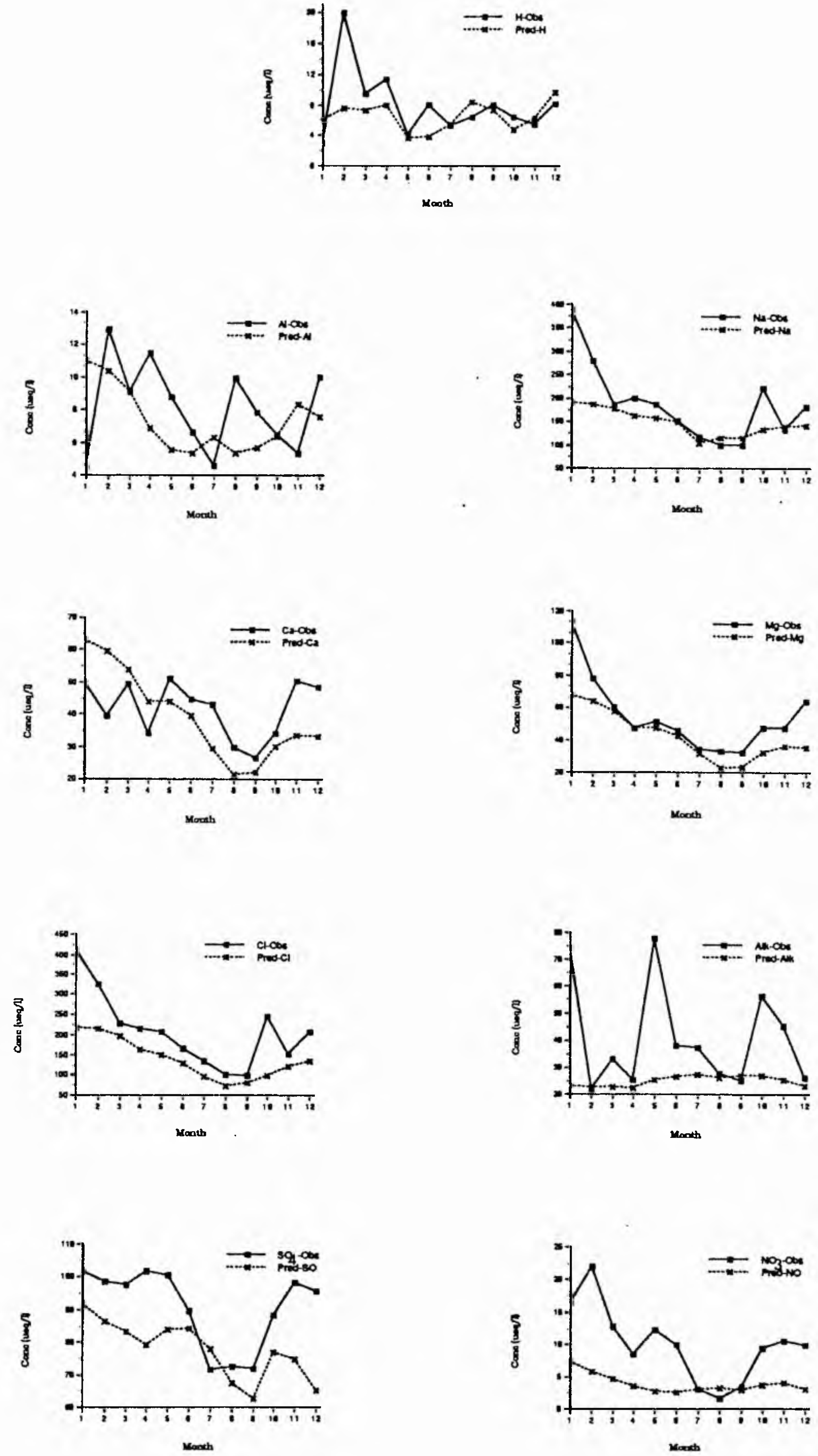


Figure 6.18: Simulated and Observed Flow Weighted Mean Monthly Concentrations (ueq/l) for the Dargall Lane 1985.

concentrations showing little resemblance to the observed data. Of the other ions both the simulated sodium and chloride concentrations, as with the observed concentrations, follow the same monthly pattern. However, the simulated concentrations of both ions fail to reproduce the observed peak concentrations of January and October and furthermore the simulated chloride concentrations are lower than the observed values for every month. The simulated concentrations of the other major anions, alkalinity, sulphate and nitrate, are also generally underestimated and apart from sulphate, at the end of the year, totally fail to reproduce the observed variation in monthly concentrations. In contrast, the simulated monthly concentrations of the divalent cations do generally reproduce the observed monthly pattern, apart from at the start of the year when calcium concentrations are overestimated whilst magnesium concentrations are underestimated. The simulated nitrate concentrations are particularly disastrous, with a degree of smoothing which largely eradicates the seasonal pattern and dramatically underestimates for most of the year.

Overall for the Dargall Lane the simulated mean monthly concentrations for both the calibration year and the verification years show a poor degree of correspondence with the observed concentrations, with the simulated concentrations exhibiting, in general, a considerable smoothing of the observed response

6.4.2 *The Green Burn*

As for the Dargall Lane the first stage in the chemical calibration of the Green Burn was to obtain the necessary input data for the application of the model. However, much of the data used in the Green Burn application are the same as those for the Dargall Lane application, thus both the Green Burn and Dargall Lane simulations are driven by the same bulk precipitation data. Furthermore, the same canopy chemistry data, litter coefficients and mineral parameters were used again as for the Dargall Lane, due to the lack of site specific data for these variables. Consequently, the only variables to be directly determined for the Green Burn were the soil and soil solution chemistry.

The soil chemistry data for the Green Burn (Table 6.21), as for the Dargall Lane were taken either from field measurements in the catchment, from data reported by Bown (1974) for the 'O' and 'B' horizons of peaty soils in the Galloway area or from the Panther Lake site in the Adirondacks (Chen et al. 1983). Specifically, the soil density, C.E.C. and adsorbed cation concentrations were derived from field measurements, the adsorbed anion concentrations from Bown (1974) and the adsorbed organic acid concentrations from Chen et al. (1983).

Soil solution chemistry data for the Green Burn have been reported by Grieve (1986) who used a similar collection procedure to that outlined above for the Dargall Lane. These data (Table 6.22) were used to provide an initial estimate of the soil solution ion concentrations. In comparison with the soil solution data for the Dargall Lane, the observed soil solution concentrations for the Green Burn are generally higher. This is probably a result of the utilisation of data from different years for each sub-catchment, a factor which occured due to the lack of data for the same period in each sub-

	Layer	
	1	2
Density (g/cm^3)	0.20	1.30
C.E.C. (meq/100g)	100.0	25.0
Adsorped Ions		
H^+	89.00	96.50
NH_4^+	1.00	0.50
Na^+	2.00	0.60
K^+	0.50	0.20
Ca^{++}	4.00	1.30
Mg^{++}	3.50	0.90
T.Al	0.00	0.00
Cl^-	0.00	0.00
Alk	0.00	0.00
SO_4^{--}	0.15	0.20
NO_3^-	0.00	0.00
PO_4^-	0.05	0.02
O.A.	55.00	5.00

Table 6.21: Soil density, C.E.C. and adsorbed ion concentrations (cations as % C.E.C. and anions as meq/100g) for each soil layer in the ILWAS representation of the Green Burn. (O.A. = Organic Acid)

	0 - 20cm		50 - 60cm	
	Mean	S.D.	Mean	S.D.
pH	4.64	± 0.58	5.01	± 0.55
Na^+	286.67	± 85.70	268.83	± 47.85
K^+	13.30	± 18.67	7.67	± 6.65
Ca^{++}	60.88	± 29.94	82.34	± 33.43
Mg^{++}	56.75	± 14.83	72.24	± 23.85
T.Al	6.02	± 3.76	6.77	± 8.65
Cl^-	297.33	± 114.77	325.71	± 106.88
SO_4^{--}	176.97	± 78.91	187.38	± 67.46

Table 6.22: The mean and standard deviation of pH and major ion concentrations (µeq/l) at two depths in the Green Burn catchment 07/1984 - 07/1985.

(source: Grieve 1986)

catchment. However, as with the Dargall Lane the soil solution concentrations are a major calibration parameter due to their influence on the cation exchange and anion adsorbtion coefficients. Consequently the individual soil solution ionic concentrations were adjusted until the optimum match between the simulated and observed flow weighted mean annual streamwater ionic concentrations was obtained. The resultant optimum values for the soil solution concentrations are shown in Table 6.23 and for the cation exchange and anion adsorbtion coefficients in Table 6.24. A comparison of the optimum soil solution concentrations with the observed data shows that as for the Dargall Lane the optimised concentrations differ greatly from the mean annual concentrations. Moreover, as for the Dargall Lane all of the optimised concentrations fall within one standard deviation of the observed mean values. However, apart from ammonia and phosphate, the resultant optimised concentrations are very different to those for the Dargall Lane. Thus, for the Green Burn the optimised concentrations of the hydrogen ion and nitrate are lower in the organic horizon yet higher in the mineral horizon, whereas the optimised organic acid concentrations are higher in the organic horizon and lower in the mineral horizon in the Green Burn. Furthermore, the optimised soil solution concentrations of all the other simulated chemical species are generally far lower in both the organic and mineral horizons in the Green Burn than the Dargall Lane.

The simulated mean annual streamwater concentrations produced by the optimum calibration, for the calibration year (1983) and the two verification years (1984 and 1985), are compared with the observed values, in Table 6.25. From the table it can be seen that on

	Layer	
	1	2
H^+	39.8	5.2
NH_4	3.0	0.5
Na^+	209.3	210.0
K^+	5.9	10.6
Ca^{++}	34.9	64.8
Mg^{++}	57.6	72.2
T.Al	15.3	17.3
Cl^-	260.0	265.0
Alk	0.2	17.3
SO_4^{--}	78.7	80.3
NO_3^-	14.1	1.9
PO_4^-	0.3	0.2
O.A.	250.0	30.0

Table 6.23 The optimised soil solution concentrations (ueq/l) for each soil layer, used in the ILWAS representation of the Green Burn. (O.A. = organic acid).

	Layer	
	1	2
CKCaMg	1.89E+0	1.61E+0
CKCaNa	5.19E-2	4.14E-2
CKCaK	5.85E-3	6.27E-3
$CKLCaNH_4$	1.49E-3	1.18E-4
CKCaH	4.14E-4	3.06E-6
$CKPO_4$	1.67E+3	1.00E+3
$CKSO_4$	2.01E+1	2.49E+1
CKFA	3.82E+3	6.79E+3

Table 6.24: The optimium cation exchange and anion adsorbtion coefficients for each soil layer in the ILWAS representation of the Green Burn. (CKFa is the organic acid adsorbtion coefficient)

	1983		1984			1985		
	Predicted	Observed	Predicted	Observed	% Error	Predicted	Observed	% Error
pH	5.11	5.11	5.23	4.90	+ 6.75	4.91	5.07	- 3.26
NH_4^+	2.06	1.73	2.59	1.43	+81.12	3.19	2.14	+49.07
Na^+	197.07	195.32	214.68	201.84	+10.64	178.80	158.34	+11.29
K^+	9.34	8.95	10.20	7.91	+28.95	9.13	8.95	+ 2.01
Ca^{++}	72.38	68.36	85.90	72.36	+18.71	58.89	60.88	- 3.38
Mg^{++}	92.62	83.06	111.53	86.35	+29.16	76.37	79.77	- 4.45
T.Al	7.35	6.85	9.54	6.20	+53.87	10.05	7.71	+30.35
Cl^-	228.10	212.91	279.25	236.88	+17.89	186.43	186.40	0.0
Alk	54.02	64.74	53.38	72.44	- 35.70	56.62	55.23	+ 2.52
SO_4^{--}	93.98	92.86	99.71	95.98	+ 3.86	92.70	89.73	+ 3.31
NO_3^-	5.05	5.16	2.96	5.16	- 74.32	2.11	6.29	-298.1
PO_4^-	0.28	0.38	0.33	0.19	- 73.68	0.46	0.16	-287.5
O.A.	235.71	–	217.68	–	–	255.51	–	–

Table 6.25: Simulated and Observed Flow Weighted Mean Annual pH and Ion Concentrations (ueq/l) for the Green Burn 1983 - 1985. (O.A. = Organic Acid)

an annual basis the optimal calibration for 1983 is not as good as that for the Dargall Lane. This is particularly evident for the divalent cations and alkalinity, with the simulated alkalinity higher and the divalent cation concentrations lower than those derived from the empirical data. However, apart from the alkalinity and divalent cations a reasonable simulation of the mean annual concentrations of all the other chemical species was obtained for the calibration year.

Turning to the verification years, 1984 and 1985, it can be seen that as for the Dargall Lane the simulated mean annual pH increases from 1983 to 1984 whereas the observed pH decreases. However, in 1985 the simulated pH of the Green Burn decreases and is lower than observed, in contrast to the Dargall Lane where the simulated pH was higher. The simulated concentrations of both the major ions in seasalt episodes, sodium and chloride, are higher in the Green Burn than those observed in 1984, whereas in 1985 the simulated sodium concentration is also higher than observed but the the simulated chloride concentration is an exact match to the observed. The simulated concentrations of each ion also show a far better match with the observed values in both the verification years than for the Dargall Lane, where simulated concentrations were lower than those observed in both years. The simulated sulphate concentrations show a far closer correspondence with the observed values for both years in the Green Burn, than in the Dargall Lane. In contrast, the the simulated base cation concentrations whilst showing a close correspondence with the observed values in 1985 are considerably overestimated in 1984.

Overall the simulated mean annual concentrations for the Green Burn in 1984, as for the Dargall Lane, do not show a very good correspondence with the observed values. In 1985, however, in contrast to the Dargall Lane, the simulated mean annual concentrations in the Green Burn show a reasonable correspondence with the observed data, except for aluminium and nitrate, concentrations of which are both considerably overestimated by the model.

On a monthly basis the simulated and observed monthly mean concentrations for the Green Burn in the calibration year (1983) are shown in Figure 6.19. From the figure it can be seen that as for the Dargall Lane hydrogen ion concentrations are very poorly reproduced on this timescale with simulated peak concentrations far higher than than observed, although the general seasonal pattern is correctly identified. Monthly base cation concentrations, especially sodium in June/July, are also poorly reproduced. Again as with the Dargall Lane simulation, the simulated base cation concentrations show considerable smoothing and fail to reproduce the major peaks and troughs in concentration. However, the best correspondence amongst the major cations as for the Dargall Lane, is for aluminium whose simulated concentrations closely follow observed values, except for a slight overestimation in spring and slight underestimation in summer.

Of the major anions the best simulation in 1983 is for alkalinity, except for the inability to reproduce the summer peak in concentration. The simulated nitrate concentrations also closely follow the observed seasonal pattern (higher concentrations in the

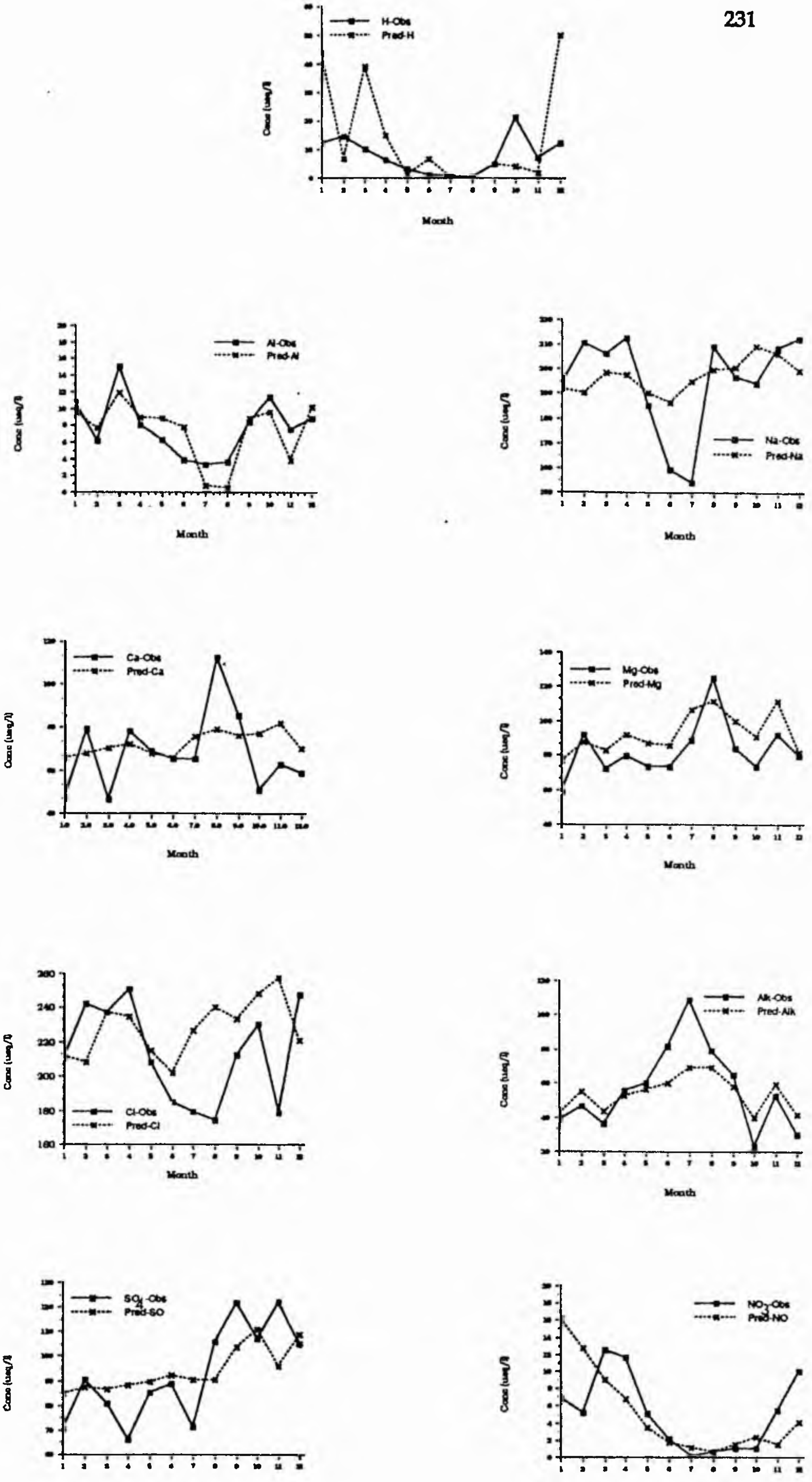


Figure 6.19: Simulated and Observed Flow Weighted Mean Monthly Concentrations (ueq/l) for the Green Burn 1983.

winter, lower in summer), albeit with the pattern much smoothed. By contrast monthly sulphate concentrations, as in the Dargall Lane, are very poorly reproduced with, at best, what may be considered a considerable degree of smoothing. Chloride concentrations, however, which are fairly well simulated in the Dargall Lane are poorly simulated in the Green Burn, particularly during the summer period.

For 1984 the mean monthly simulated and observed concentrations are compared in Figure 6.20. From this figure it can be seen that as for the calibration year the simulated hydrogen ion concentrations, whilst able to reproduce the observed seasonal concentration pattern, considerably overestimate concentrations for several months, particularly in the winter period. Apart from the hydrogen ion only aluminium, nitrate and alkalinity concentrations can be considered to be reasonably simulated in 1984. However, the simulated aluminium concentrations considerably underestimate the observed peak in May and overestimate the October peak. The simulated nitrate concentrations, as for the Dargall Lane in 1984, are very smoothed so that whilst a reasonable correspondence with the observed data is evident for the latter part of the year, in the earlier months, particularly March, the observed concentrations are underestimated. The simulated alkalinity concentrations are also very smoothed, and consequently as for the Dargall Lane, there is only slight evidence of the observed monthly variation. The simulated concentrations of all of the other ions also show very smoothed responses. For all ions except magnesium, there is at best only slight evidence of the observed seasonal variation in concentration and ionic concentrations are generally considerably

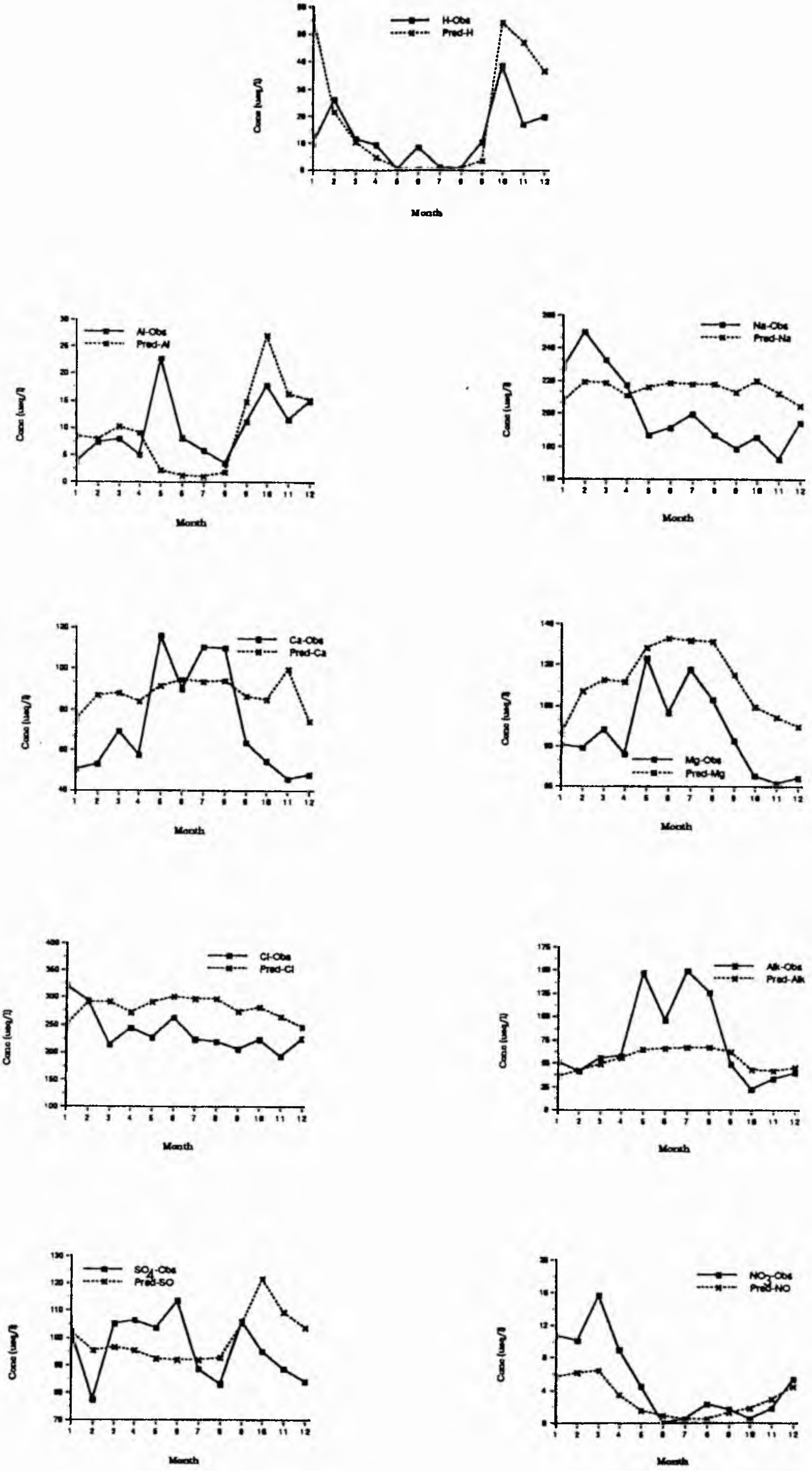


Figure 6.20: Simulated and Observed Flow Weighted Mean Monthly Concentrations (ueq/l) for the Green Burn 1984..

under or overestimated. The simulated magnesium concentrations are able to follow the observed general monthly pattern of concentrations (i.e. higher in summer, lower in winter), but unfortunately are overestimated in every month.

For the second verification year the simulated and observed mean monthly concentrations are shown in Figure 6.21. The simulated monthly hydrogen ion concentrations in this year, are poorly reproduced and show little evidence of the smoothing visible in the 1983 and 1984 simulations. Consequently, as the observed concentrations exhibit only a little variation for several months the simulated concentrations are substantially overestimated. From figure 6.21 it can also be seen that, except for the divalent cations, the simulated concentrations of all the other major ions show a better correspondence with the observed concentrations than in either 1983 or 1984. The simulated sodium and chloride concentrations are particularly well reproduced, apart from the overestimation of sodium concentrations at the end of the year. The sulphate concentrations are also reasonably well reproduced with the simulated concentrations particularly close to the observed in the latter part of the year. In the earlier part of the year, however, the simulated sulphate concentrations show a very damped response and fail to reproduce the March peak and subsequent decline in monthly concentrations. As in 1984, the simulated concentrations for nitrate and alkalinity, are both considerably smoothed in comparison with the observed concentrations, the broad seasonal trend in monthly concentrations being still evident for both ions. In contrast simulated aluminium concentrations are very variable, and apart from the period April - July where the

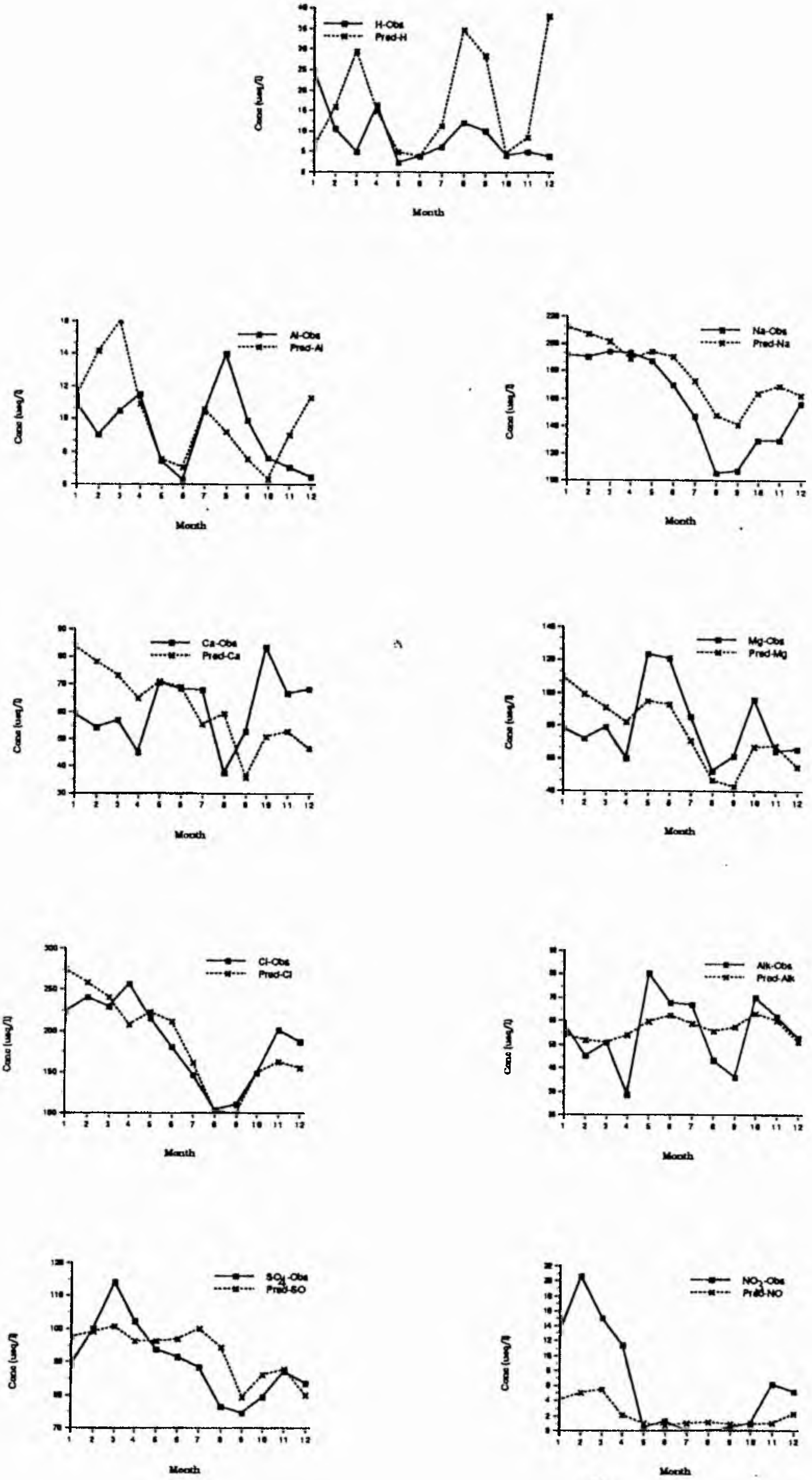


Figure 6.21: Simulated and Observed Flow Weighted Mean Monthly Concentrations (ueq/l) for the Green Burn 1985.

simulated and observed monthly concentrations are well matched, the simulated concentrations show little correspondence with the observed concentrations.

Overall, the simulated concentrations for the Green Burn in 1985 show a better correspondence with the observed data than is evident for 1983 and 1984, or for the Dargall Lane in any of the three study years. However, despite this better correspondence in 1985, the simulated monthly concentrations in the Green Burn, as for the Dargall Lane, are generally very smoothed and show at best only limited and partial correspondence with the observed variation in monthly concentrations.

6.5 *DISCUSSION*

6.5.1Hydrological Response

Despite the simplicity of the ILWAS hydrological sub-model the hydrological response of both the study catchments, are in general, very well reproduced. The major failing of the model simulations is in reproducing the very high peak flows that occurred in the Dargall Lane in January 1984 (Figure 6.6). However, this exceptional runoff event is believed to be the result of a very large snowmelt following a rare severe snowfall which particularly affected the higher parts of the Dargall Lane catchment (S.R.P.B. pers. comm.). This snowfall also blocked the daily raingauge and hence the water input of the snow to the catchment was not measured. Thus the daily rainfall for this period was derived from a regression relationship with the data from the Meteorological

Office raingauge at Clatteringshaws Loch 10Km to the West. However, as this method probably underestimates the daily rainfall for this period, and given that it is the daily rainfall that drives the model hydrological routine, it is not surprising, that the model fails to reproduce accurately these exceptionally large flows.

For the Green Burn over this same period the model produces a far better response than for the Dargall Lane with the simulated flows of the former actually greater than those observed. This improved simulation of the Green Burn flow record is due to the Green Burn sub-catchment extending to a far lower altitude than the Dargall Lane so that the snowfall input to the catchment and the subsequent snowmelt runoff were far lower. Consequently, the Clatteringshaws derived precipitation record used to drive part of the model simulations of both sub-catchments has a far greater resemblance to the probable actual precipitation input to the Green Burn sub-catchment than to the Dargall Lane sub-catchment. Hence, the better simulation of the hydrological response of the Green Burn than the Dargall Lane over this period.

Apart from this understandable failure to reproduce the hydrological response of the Dargall Lane during the snowmelt period, the most notable failure of the hydrological simulations is the model's inability to simulate the runoff response from discrete summer storms. This failure is particularly evident for the Green Burn in 1983 and 1984 and the Dargall Lane in 1983. For the Green Burn this inability to reproduce the runoff of discrete summer storms probably reflects the presence of the forest ditches in the catchment. These ditches serve to increase the effective drainage density of the catchment and thereby the speed with which runoff is evacuated from the catchment (Harper 1985). Consequently, rather than satisfying the summer soil moisture deficit flow will be rapidly routed to the stream channel. However, as the model is unable to reproduce the rapid evacuation of flow through these ditches, the simulated runoff is then probably routed back into the soil to satisfy the soil moisture deficit. Thus the simulated response is unable to reproduce the observed pattern of runoff response. A similar inability of the model to reproduce the runoff response of the discrete summer storms from the moorland Dargall Lane catchment in 1983 is possibly due to the presence of macropores in the catchment soils. These macropores, like the forest ditches in the Green Burn, probably serve to increase the rate at which flow is transmitted into the stream channel. Since the model's hydrological routine is unable to simulate the behaviour of such macropores the simulated runoff response is again unable to reproduce the observed pattern.

However, in the following year, 1984, the simulated flow record for the Dargall Lane is able to reproduce the response of these discrete summer storms very well. This contrast in the model's performance for the same catchment in succeessive years is hard to explain. However, an examination of the flow conditions in each year (Figures 6.5 and 6.7) indicates that not only were the summer storms in 1984 far more discrete in their timing and occurence than in 1983 but also the period preceding the summer storms in 1984 was drier than the preceding period in 1983. This is supported by the precipitation record for the two years which shows that prior to the start of the summer storms the precipitation input to the Dargall Lane catchment was 1013mm in 1983 and only 775mm in 1984. Such dry antecedent conditions will have resulted in a larger soil moisture deficit in 1984 than 1983. Consequently, if the model is unable to simulate the ability of macropore structures to override the soil moisture deficit, it would be expected that the simulated runoff response of such discrete storms would be even worse in 1984 than 1983. Thus, the far better simulated runoff response to these events in 1984 than for 1983 or for the same events in the Green Burn is very difficult to explain.

In contrast to 1983 and 1984 the summer of 1985 was far wetter with fewer discrete storm events. The wetter conditions lead to the occasional partial saturation of the catchment soils, therefore the influence of drainage channels or macropore features was reduced as flow was transmitted to the stream channels through 'piston-flow' and/or saturation overland flow routes. Consequently the model is able to reproduce more accurately the summer runoff response of both catchments in 1985. However, the probable influence of the drainage channels in the Green Burn sub-catchment and macropore structures in the Dargall Lane sub-catchment are still evident, with the simulated runoff peaks being lower than those observed.

Outside the summer periods the simulated runoff response of both streams is generally very good apart from a tendency for the hydrograph peaks to be under or over-estimated. Such under or over-estimation is probably due to a variety of factors, for instance, the already mentioned inability of the model to cope with forest drainage channels and macropore structures. Furthermore, the lumping of each catchment into a number of horizontal drainage compartments of uniform characteristics, together with a limited number of soil horizons in each compartment, will also affect the fine structure of the hydrographs. Such lumping will lead to any small scale physical variability, in factors such as slope and soil thickness, which effect the rate at which flow from a particular storm event is transmitted to the stream channel, to be ignored. Consequently, it is highly unlikely that a lumped model such as ILWAS will be able to perfectly simulate the runoff response of a catchment.

Within the above-noted limitations the model predicts that the flow in each of the study years (1983-1985) in both sub-catchments is predominantly through the upper organic soil layer (>65% for the Dargall Lane, Table 6.6 and >84% for the Green Burn, Table 6.10). This prediction is in accordance with the results of the budget studies reported in section 5.3.2 and with results from the nearby Loch Fleet catchment where it is estimated that over 90% of the downslope flow is through the soil surface (Nesbit 1986). The greater proportion of simulated flow through the upper soil layer of the Green Burn sub-catchment is unlikely to be due to the presence of forest drainage for, as noted above, the model is unable to replicate the effect of such features. Instead, the contrast between the two sub-catchments, is more likely to be due to a combination of the flatter topography and the greater depth of the soil profile in the lower parts of the Dargall Lane sub-catchment (Tables 6.1 and 6.5). The flatter topography will allow flow from the surrounding steeper parts of the sub-catchment to be locally 'ponded' and thereby percolate down the soil profile. Furthermore, the greater depth of the lower soil layers in the same area of the sub-catchment will allow a greater proportion of the flow to be held and therefore released from the lower soil in the Dargall Lane than the Green Burn.

Overall it may be concluded that, despite the lack of site-specific soil hydraulic data at Loch Dee, the hydrological component of the ILWAS model is able to simulate the hydrological response of both the study sub-catchments extremely well in terms of total discharge, its seasonal patterns and general form of individual hydrographs. The failures relate to the rate of flow recession in the summer and under-estimation of some peak flows..

6.5.2 Chemical Response

In contrast, the ILWAS model simulation of the solute chemistry of the study sub-catchments is poor, particularly on a monthly timescale, with the simulated concentrations of the chemical species showing generally little resemblance to the empirical data. The monthly timescale is the minimum timescale investigated in this study, for as the model is driven by the mean monthly precipitation quality, any shorter timescale variations in catchment chemistry cannot be accurately simulated.

In the study of acidification, the chemical species of major importance is the hydrogen ion. Unfortunately, the simulated hydrogen ion concentrations for both the Dargall Lane and Green Burn sub-catchments show only a slight correspondence with the empirical data. This poor simulation of the hydrogen ion concentration in the streamwater of each sub-catchment can be attributed to the inaccurate simulation of other chemical species, particularly the total inorganic carbon and organic acid concentrations. In both the study sub-catchments there was no site specific data available for T.I.C. and organic acid concentrations, the soil and soil-solution concentrations of which are major input variables. Thus the adsorbed soil concentrations of these variables were taken from the ILWAS study whilst the soil solution concentrations were treated as calibration parameters and were derived by adjustment of their values until the simulated and observed mean annual hydrogen ion concentrations were equal. However, it is unlikely that such procedures have produced accurate estimates of the concentrations of either species. Consequently, as the simulated hydrogen ion concentration is derived from the simulated T.I.C. and organic acid concentrations, together with the simulated alkalinity and total aluminium, any inaccuracies in the simulated concentrations of the T.I.C. and organic acid will lead to an inaccurate simulation of the hydrogen ion concentration.

The simulated hydrogen ion concentration is also dependent on the simulated alkalinity as well as the simulated organic acid and T.I.C. concentrations. Consequently, an inaccurate simulation of the alkalinity will also be reflected in an inaccurate simulation of the hydrogen ion concentration. As the simulated alkalinity in ILWAS includes both the carbonate system and the dissolved organic carbon (D.O.C.), with the simulated organic acid concentrations a major component of the D.O.C. alkalinity, inaccurate estimates of T.I.C. and organic acid concentrations will be reflected by inaccuracies in the simulated alkalinity. Thus, inaccurate estimates of T.I.C. and organic acid concentrations may adversely influence the simulated hydrogen ion concentration by two different pathways.

In certain sub-routines of ILWAS, however, the simulated alkalinity is derived in an alternative manner to the above, as the sum as non hydrogen cations minus the sum of strong acid anions (ie Alk = Σ Base Cations -Σ Anions). Consequently, any errors in the simulation of the major chemical species will also result in an inaccurate estimate of alkalinity and hence an inaccurate simulation of the hydrogen ion concentrations. Given the poor simulation of the major cation and anion concentrations in both the Dargall Lane (Figures 6.16-6.18) and the Green Burn (Figures 6.19-6.21) it is therefore no surprise that the hydrogen ion concentrations are also poorly reproduced.

As bulk precipitation data is commonly believed to underestimate the input of chemical species to a catchment, the use of such data to drive the model chemistry, rather than the use of separate wet and dry deposition data, could partially account for this poor simulation of the major cation and anions. In a maritime area such as Loch Dee if dry deposition is an important component of the input of any chemical species to a catchment it will be of the seasalt ions, sodium and chloride. Consequently, if the bulk precipitation quality data underestimates dry deposition the simulated sodium and chloride concentrations would be expected to be consistently underestimated. However, a comparison of the simulated and observed mean monthly sodium and chloride concentrations indicates that the simulated concentrations of both species are as likely to be overestimates as underestimates. It would therefore appear that the bulk precipitation quality data does provide an adequate estimate of the input of chemical species to the study catchments and that use of such data cannot account for the poor chemical simulation by ILWAS at Loch Dee. A comparison of the simulated and observed sulphate concentrations also supports this conclusion, sulphate being the other chemical species where dry deposition is likely to be a major influence on input loadings. Thus the simulated sulphate concentrations, as with the simulated seasalt concentrations, are as likely to be overestimated as underestimated.

Apart from the time-dependent input data, the other major source of error is likely to be the time-independent input data. Here there is considerable room for error, particularly in the soil chemistry sub-module where much of the data required is not available for the study catchments. The lack of site specific data for the adsorbed anion concentrations, particularly chloride and sulphate, in the catchment soils will in particular be probablly a major source of error in the chemical simulation. This error will arise because the soil solution and hence streamwater anion concentrations are dependent on the anion selectivity coefficients, which in turn are derived from the adsorbed anion concentrations. Therefore, any error in the input estimates of the soil anion concentrations will result in an inaccurate simulation of solution anion concentrations. Despite the presence of some site-specific soil chemistry data, inaccurate estimates of the catchment soil chemistry are also probably the reason for much of the error in the simulation of major cation concentrations. Such an error can arise because the limited spot samples used to derive estimates of the catchment soil chemistry may not be truely representative of the overall soil chemistry. Furthermore, such lumping of the catchment characteristics may result in overlooking spatially localised heterogeneities in the soil chemical characteristics which may be important in determining the soil and streamwater solute chemistry. The possible errors in the cation and anion concentrations which result from such factors can lead to an inaccurate simulation of alkalinity and hence hydrogen ion concentrations.

Yet another source of error in the chemical simulation is the hydrological simulation. Although the hydrological response of both the Dargall Lane and Green Burn catchments is reasonably well reproduced there are discrepancies present, particularly in the summer months, as discussed above. As the solute concentrations in each of the model sub-modules (i.e. the canopy and soil layers) are derived on the basis of the water volume in the compartment, such discrepancies in the hydrological simulation will in turn lead to errors in the chemical simulation.

However, by far the most striking feature of the simulated cation and anion concentrations, however, is the considerable smoothing of the simulated concentrations, so that little of the observed monthly variability is present in the simulations. This smoothing may be a consequence of the use of the monthly precipitation quality to drive the model, as the averaging of the input data may serve to smooth the response before the model simulation occurs. It is therefore interesting to speculate that if weekly input data were used to drive the model the simulated monthly variability would be greater. Unfortunately, in the currently available computer code for ILWAS only monthly inputs can be utilised, and consequently such a hypothesis could not be tested in this study. The smoothing may also be partially attributed to the inability of the model hydrological module to simulate the effects of soil macropores in the Dargall Lane and forest ditches in the Green Burn. Since such features serve to increase the hydrological response of the study catchments (Harper 1985), the inability of ILWAS to simulate their response may lead to a smoothing of the solute concentrations.

6.6 *CONCLUSION*

In conclusion the ILWAS model is unsuccessful at simulating the physical and chemical hydrological response of either the 70% forested Green Burn or the open moorland Dargall Lane sub-catchments at Loch Dee. However, within this overall poor performance ,the physical hydrological response alone is, in general, very well reproduced considering the simplistic nature of the hydrological routines in the model. This success is probably attributable to the small number of input variables which need to be calibrated. It is when the far more complex chemistry component of the model is added to the hydrological routines that the model performance declines considerably. The poor simulation of streamwater solute concentrations can probably be attributed to the synergistic interaction of the large number of input variables for which site-specific data are not available. These high input data requirements, together with the inability of ILWAS to simulate successfully the solute chemistry of the comprehensively monitored Loch Dee catchments, lead to the conclusion that a prerequisite for the utilisation of ILWAS at any site will be a very detailed and expensive empirically based catchment study. Consequently, the use of ILWAS as a management tool for understanding and predicting the future impacts of acid deposition and other anthropogenic changes on the hydrochemical response of upland catchments will be limited to a few very well-studied sites.

7: SENSITIVITY ANALYSIS of ILWAS

7.1 *INTRODUCTION*

Since the ILWAS model was unable to reproduce accurately the observed streamwater chemistry at Loch Dee, it was not possible to use the model to predict the effects of changes in hydrogen and sulphate depositional loadings or changes in land-use on the streamwater chemistry of the Dargall Lane and Green Burn. A sensitivity analysis on the model was therefore performed in order to determine if it was possible to reduce the amount of input data required to run the model. Sensitivity analysis would enable this aim to be met by identifying those model variables that require detailed input information, those whose input values can be derived either from the existing literature or from best-guess estimates, and those variables that are redundant.

The sensitivity analysis was performed upon the moorland Dargall Lane catchment for the calibration year 1983. This catchment was chosen in contrast to the Green Burn sub-catchment as the smaller number of land sub-catchments and stream segments required to simulate this catchment reduced the computer time for each model run considerably, and thereby enabled more simulation runs to be enacted.

7.2 *RESULTS*

The sensitivity analysis was undertaken by varying the value of time-independent variables in both the hydrological and chemical sub-models. The effect of changing the value of hydrological variables was assessed by examining the percentage change in the simulated total annual streamflow, annual flow through each soil horizon, and the simulated mean annual streamwater concentrations (ueq/l) of the main chemical species, using as the initial starting point the optimised calibrated values for 1983 as presented in Chapter 6 . As adjustment of the chemical variables results in no change to the simulated catchment hydrology, the sensitivity of the model to changes in these variables was assessed solely by examining the percentage change in the simulated mean annual streamwater chemical concentrations.

7.2.1 *Hydrological Variables*

The first variable to be subjected to the sensitivity analysis was the soil horizontal permeability which was adjusted for each of the three analogue soil horizons in turn. In the upper soil horizon the horizontal permeability (KiA) was both increased and decreased, in steps, from the calibration value of 1.0E5 cm/day to a maximum of 1.0E6 cm/day and a minimum of 5.0E4 cm/day. From table 7.1 it can be seen that such adjustment has very little influence on the simulated total annual streamflow, with the maximum change a 0.25% increase in flow for an order of magnitude increase in the permeability. It can also be seen from Table 7.1 that an increase in the horizontal permeability of the upper horizon is reflected by an increase in the annual flow through that horizon and a decrease in flow through the lower soil horizons. Conversely, a decrease in the horizontal permeability leads to a decrease in flow through the upper horizon and an

	Upper Soil Horizon Horizontal Permeability (cm/day)							
	Calibration Value 1.0E5	5.0E4	7.0E4	1.1E5	1.5E5	2.0E5	5.0E5	1.0E6
R.M.S.E	0.1073	0.1172	0.1114	0.1075	0.1083	0.1086	0.1250	0.1347
Flow (m^3)								
---Total	4752522	-0.22%	-0.08%	+0.02%	+0.09%	+0.14%	+0.23%	+0.25%
---Layer 1	3128693	-1.51%	-0.71%	+0.19%	+0.60%	+0.94%	+1.70%	+2.06%
---Layer 2	1304421	+2.63%	+1.38%	-0.37%	-1.13%	-1.77%	-3.36%	-4.26%
---Layer 3	319478	+0.07%	+0.04%	+0.01%	0.00%	-0.02%	-0.14%	-0.21%
pH	5.14	5.16	5.15	5.14	5.14	5.14	5.13	5.13
H^+	7.24	-4.61%	-2.29%	0.00%	0.00%	0.00%	+2.26%	+2.26%
NH_4^+	1.22	-2.40%	-0.83%	0.00%	+0.83%	+1.67%	+2.52%	+2.52%
Na^+	193.55	-0.31%	-0.14%	+0.03%	+0.13%	+0.18%	+0.32%	+0.45%
K^+	7.66	-0.52%	-0.26%	0.00%	0.00%	+0.26%	+0.39%	+0.39%
Ca^{++}	66.33	-1.00%	-0.47%	+0.11%	+0.36%	+0.58%	+1.16%	+1.21%
Mg^{++}	71.39	-1.03%	-0.48%	+0.09%	+0.11%	+0.59%	+1.19%	+1.38%
T.Al	6.40	-0.16%	0.00%	0.00%	0.00%	+0.31%	+0.31%	+0.47%
Cl^-	226.19	-0.60%	-0.28%	+0.07%	+0.18%	+0.35%	+0.75%	+0.90%
Alk	20.17	-0.75%	-0.35%	+0.05%	+0.20%	+0.40%	+0.69%	+0.70%
SO_4^{--}	93.07	-0.41%	-0.19%	+0.03%	+0.14%	+0.23%	+0.44%	+0.50%
NO_3^-	6.95	-0.29%	-0.14%	0.00%	0.00%	+0.14%	+0.29%	+0.43%
PO_4^-	0.25	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
O.A.	68.53	-2.41%	-1.11%	-0.47%	+0.84%	+1.44%	+2.61%	+2.93%

Table 7.1: The change in the RMSE of simulated and observed M.D.F.s, together with the % change in the simulated total flow, flow in each soil horizon and the streamwater concentrations (ueq/l) of the major chemical species, due to adjustment of the horizontal permeability of the upper soil layer from the calibration value of 1.0E5 cm/day.

increased annual flow through the lower horizons. However, it can also be seen that such changes are very small, thus for an order of magnitude increase in the permeability, the maximum change in the flow pattern is the 4.26% decrease in flow through the middle horizon. On a daily time scale, figure 7.1 contrasts the simulated and observed M.D.F.s, where the simulated flows are produced with the permeability of the upper horizon increased to 1.0E6. A comparison of figure 7.1 with figure 6.5, which contrasts the optimum simulated M.D.F.s with the observed M.D.F.s, shows that for the individual hydrographs an increase in the permeability of the upper horizon also has little effect. The only observable change is a slight increase in the size of the major hydrograph peaks (ie days 75 and 250). Similarly, if figure 7.2, which contrasts the simulated M.D.Fs due to a reduction in the horizontal permeability to 5.0E4 cm/day with observed M.D.F.s, is compared with figure 6.5 little change in the individual hydrographs is again evident.

As well as only slight changes in the simulated flow patterns, table 7.1 also shows that adjustment of the horizontal permeability of the upper horizon has very little influence on the mean annual solute concentrations in the streamwater. Thus pH is only changed by a maximum of 0.01 units, whilst the maximum percentage change in the concentrations of the other chemical species is less than 3.0% for ammonium and organic acids and less than 1.5 % for the major cations and anions.

As with adjustment of the KiA, adjustment of the middle horizon permeability (KiB) also produces little change in the total annual streamflow. However, adjustment of KiB can produce large changes

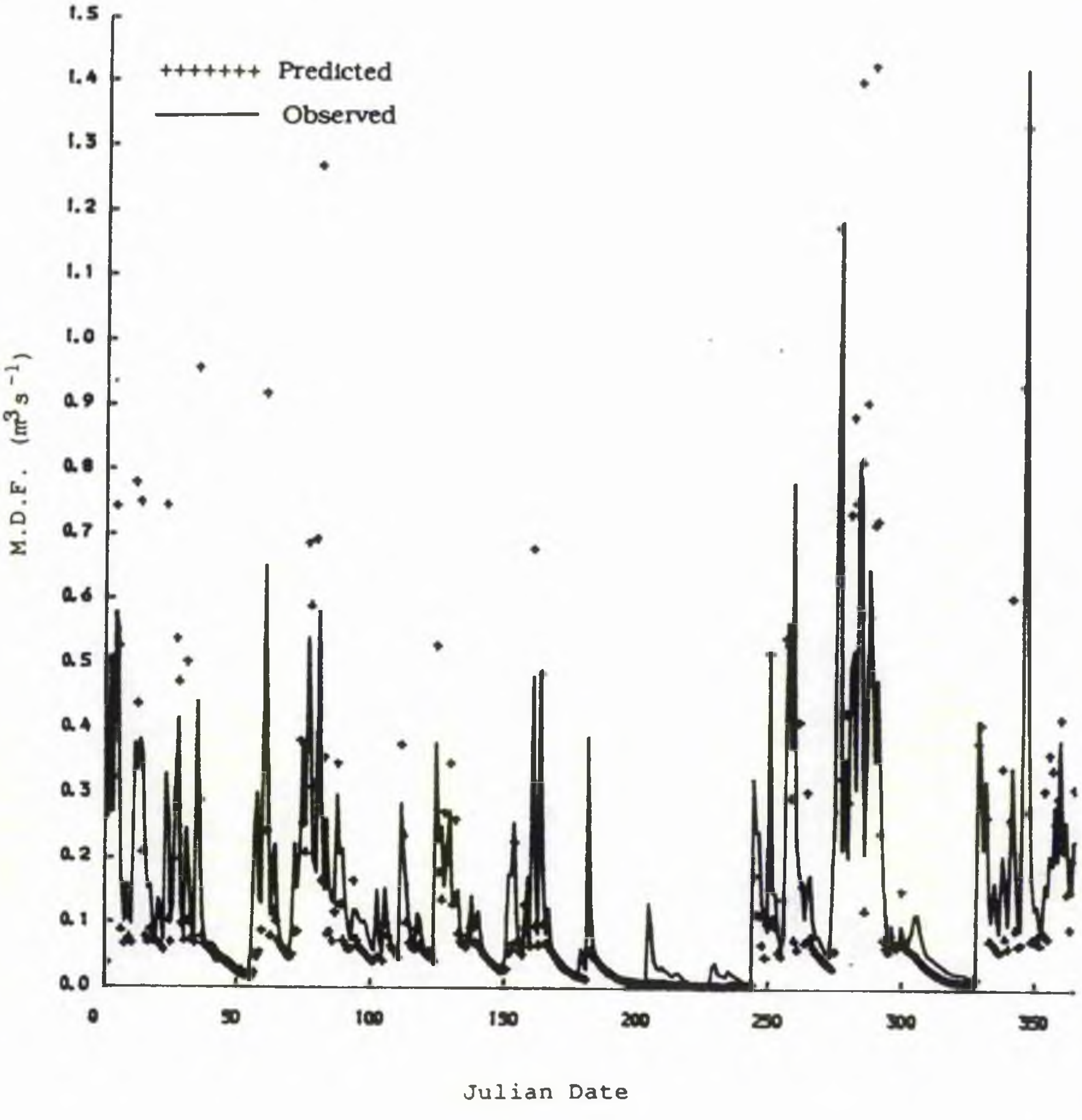


Figure 7.1 The simulated and observed M.D.F.s ($m^3 s^{-1}$) with the upper soil horizon horizontal permeability adjusted to 1.0E6 cm/day.

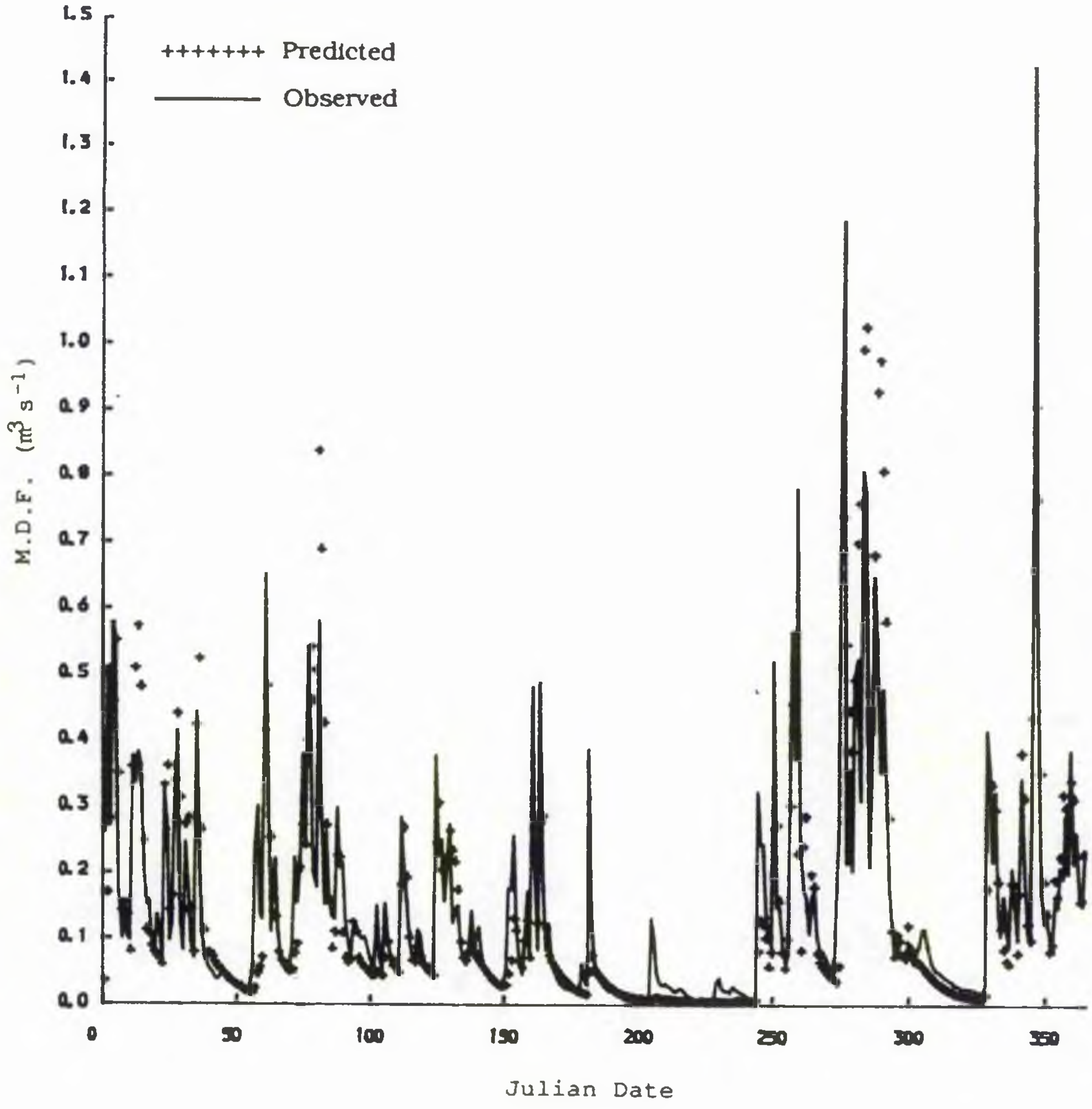


Figure 7.2 The simulated and observed M.D.F.s (m^3 s^{-1}) with the upper soil horizon horizontal permeability adjusted to 5.0E4 cm/day.

in the annual flow through the upper and middle horizons in particular. Thus whilst a 10% increase or decrease in permeability has little effect on the annual flow through any horizon, larger changes can produce considerable adjustments to the amount of flow through the upper two horizons. For example an increase in KiB from 9.0E3 to 2.0E4 results in a decrease in the annual flow through the upper horizon of 37% and an increase in the annual flow through the middle horizon of 68%. These changes are also evident when figures 7.3 and 7.4, (the plots of the simulated and observed M.D.F.s where KiB is 2.0E4 and 5.0E3 cm/day respectively), are compared with figure 6.5. Such a comparison shows that a decrease in KiB leads primarily to a more emphasised hydrograph recession limb (ie days 300 - 330) and a slight increase in some hydrograph peaks (ie days 75, 275, 340). An increase in KiB also produces a slight increase in the same hydrograph peaks, however, the most obvious change is the more rapid decay of the hydrograph recession limbs.

The adjustment of KiB also produces greater changes to the simulated streamwater chemistry than changes in KiA. Such changes in the simulated solute concentrations reflect the changes in the simulated hydrological flowpaths. Thus from table 7.2 it can be seen that an increase in KiB results in an increase in pH, together with increased concentrations of alkalinity, sulphate and divalent cations, and a decrease in the concentrations of all the other simulated species. Conversely, a decrease in KiB results in a decrease in pH and the reverse pattern for the other chemical species. However, whilst the effects are greater than for changes in KiA, changes in KiB are still relatively insensitive in terms of the resulting concentrations. Thus

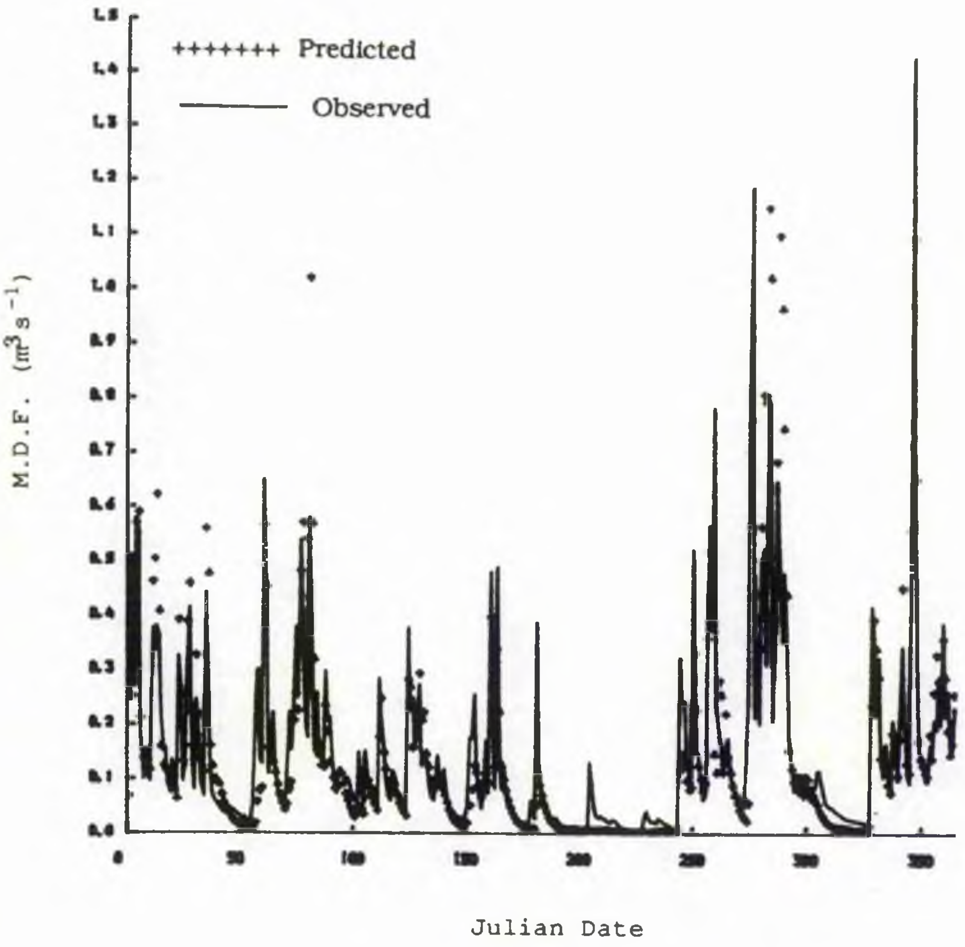


Figure 7.3 The simulated and observed M.D.F.s ($m^3 s^{-1}$) with the middle soil horizon horizontal permeability adjusted to 2.0E4 cm/day.

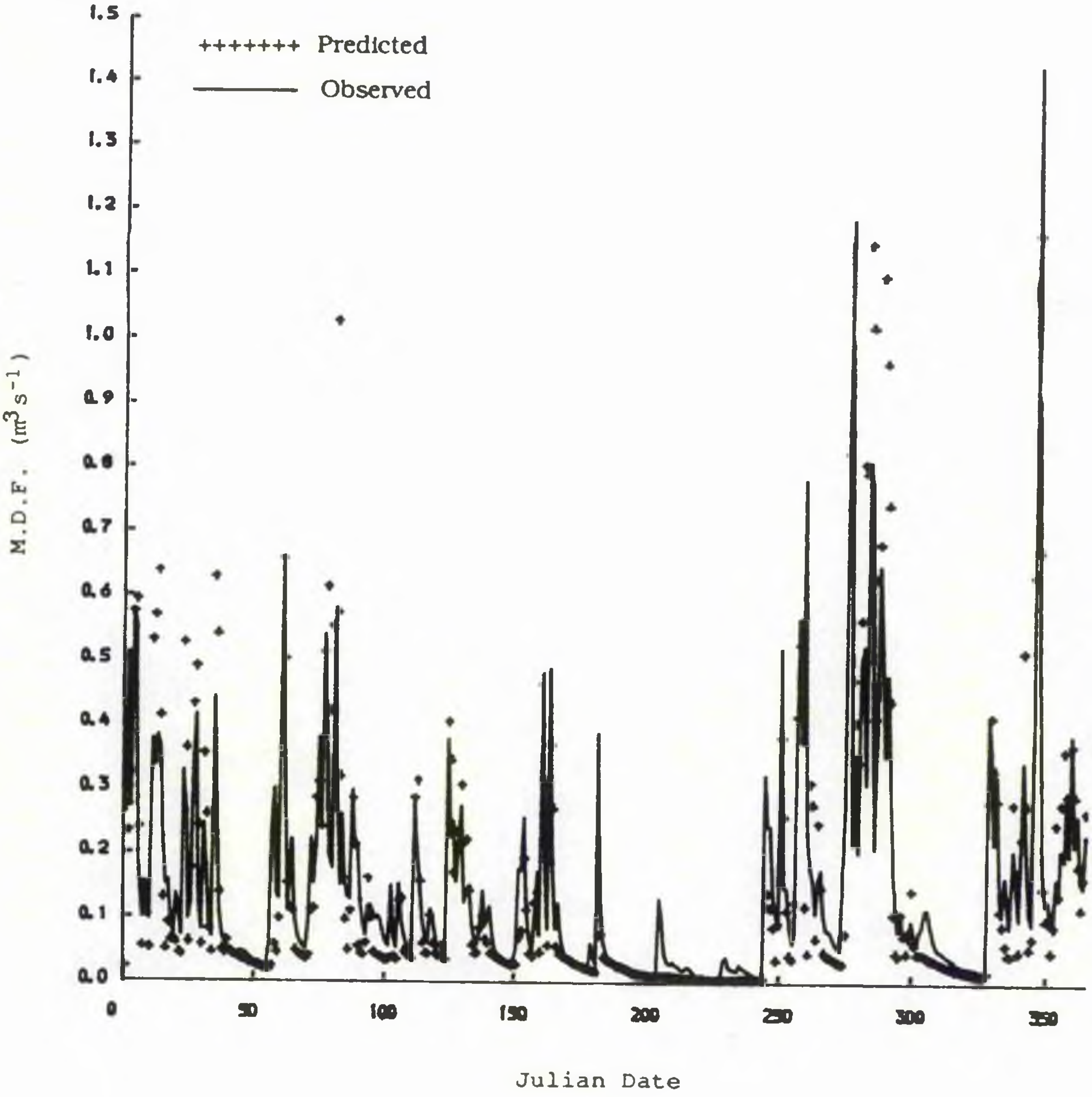


Figure 7.4 The simulated and observed M.D.F.s ($m^3 s^{-1}$) with the middle soil horizon horizontal permeability adjusted to 5.0E3 cm/day.

	Middle Soil Horizon Horizontal Permeability (cm/day)						
	Calibration Value 9.0E3	5.0E3	7.0E3	8.0E3	1.0E4	1.5E4	2.0E4
R.M.S.E	0.1073	0.1102	0.1102	0.1078	0.1086	0.1123	0.1161
Flow (m^3)							
---Total	4752522	-0.20%	-0.11%	-0.06%	+0.11%	+0.18%	+0.28%
---Layer 1	3128693	+15.91%	+7.77%	+4.90%	-2.71%	-19.86%	-37.94%
---Layer 2	1304421	-62.66%	-22.85%	-10.59%	+6.80%	+40.74%	+67.80%
---Layer 3	319478	+1.19%	+0.51%	+0.24%	-0.27%	-1.58%	-2.52%
pH	5.14	5.05	5.09	5.16	5.16	5.25	5.32
H^+	7.24	+21.94%	+12.29%	+4.83%	-4.62%	-28.83%	-51.15%
NH_4^+	1.22	+12.02%	+8.92%	+1.64%	-3.28%	-12.32%	-15.99%
Na^+	193.55	+0.68%	+0.34%	+0.22%	-0.02%	-0.22%	-0.37%
K^+	7.66	+4.18%	+1.83%	+0.78%	-0.91%	-4.18%	-7.40%
Ca^{++}	66.33	-1.32%	-0.55%	-0.27%	+0.45%	+1.09%	+1.58%
Mg^{++}	71.39	-1.12%	-0.60%	-0.16%	+0.46%	+1.11%	+1.61%
T.Al	6.40	+6.72%	+3.13%	+1.40%	-1.54%	-7.72%	-10.31%
Cl^-	226.19	+1.96%	+0.93%	+0.55%	-0.01%	-0.81%	-1.22%
Alk	20.17	-5.40%	-2.83%	-1.04%	+1.44%	+6.10%	+9.52%
SO_4^{--}	93.07	-1.06%	-0.36%	-0.09%	+0.33%	+0.93%	+1.21%
NO_3^-	6.95	+1.29%	+0.72%	+0.43%	-0.29%	-1.76%	-2.96%
PO_4^-	0.25	+8.00%	+4.00%	0.00%	0.00%	-4.00%	-8.00%
O.A.	68.53	+7.11%	+4.77%	+1.64%	-3.28%	-13.91%	-15.57%

Table 7.2: The change in the RMSE of simulated and observed M.D.F.s, together with the % change in the simulated total flow, flow in each soil horizon and the streamwater concentrations (ueq/l) of the major chemical species, due to adjustment of the horizontal permeability of the middle soil layer from the calibration value of 9.0E3 cm/day.

the streamwater pH is particularly insensitive to changes in KiB, with the increase in KiB to 2.0E4 cm/day producing only a 0.18 unit increase in pH.

The results of adjustments to the lower soil horizon horizontal permeability (KiC) are shown in Table 7.3. From the table it can be seen that whereas a 25% increase or decrease in KiC from 1.0E3 cm/day to 7.5E2 or 1.25E3 cm/day has a considerable influence on the annual flow through the lower soil horizon, the change in the total annual flow or the flow through the upper and middle soil horizons is considerably lower. Simulated streamwater chemistry is also little altered, with the maximum change in concentration being less than 3.0%. However, a doubling or halving of KiC, whilst still having little effect on the total annual streamflow, does result in greater changes in the annual flow through each soil horizon. Thus flow through both the upper and middle horizons is decreased by around 10% and flow through the lower horizon increased by 140%. The streamwater chemistry is generally still insensitive to even a doubling or halving of KiC with, apart from hydrogen ion concentrations, the maximum change in concentration less than 6.0%. The hydrogen ion concentration is in contrast decreased by 22.9% as KiC is doubled and increased by 14.9% as KiC is halved. However, due to the logarithmic nature of the pH scale such changes are only equivalent to an increase of 0.11 pH units for a doubling of KiC and a decrease of 0.06 pH units for a halving of KiC.

The sensitivity analysis was next performed on the saturation moisture content (S.M.C.) of each of the soil layers. The analysis consisted of increasing and decreasing the optimised calibration

	Lower Soil Horizon Horizontal Permeability (cm/day)					
	Calibration Value 1.0E3	5.00E2	7.50E2	1.25E3	1.50E3	2.00E3
R.M.S.E	0.1073	0.1094	0.1089	0.1093	0.1100	0.1110
Flow (m^3)						
---Total	4752522	-0.67%	-0.60%	+0.57%	+0.64%	+0.72%
---Layer 1	3128693	+2.92%	+2.01%	-3.26%	-6.56%	-12.33%
---Layer 2	1304421	+3.00%	+0.43%	-2.61%	-5.50%	-10.67%
---Layer 3	319478	-90.32%	-39.73%	+32.10%	+73.27%	+138.79%
pH	5.14	5.08	5.13	5.14	5.22	5.25
H^+	7.24	+14.92%	+2.35%	+1.12%	-16.23%	-22.92%
NH_4^+	1.22	+2.64%	+0.82%	-1.13%	-2.52%	-4.30%
Na^+	193.55	-0.91%	-0.63%	+0.53%	+1.18%	+1.52%
K^+	7.66	-3.00%	-1.30%	+0.62%	+1.44%	+3.64%
Ca^{++}	66.33	-1.43%	-0.33%	+0.22%	+1.71%	+2.82%
Mg^{++}	71.39	-2.54%	-0.60%	+0.31%	+1.69%	+2.94%
T.Al	6.40	+4.06%	+1.25%	-1.31%	-2.66%	-5.94%
Cl^-	226.19	+0.29%	+0.09%	-0.02%	-0.31%	-0.88%
Alk	20.17	-3.37%	-1.34%	+1.21%	+2.28%	+5.30%
SO_4^{--}	93.07	-1.00%	-0.02%	+0.15%	+0.59%	+1.12%
NO_3^-	6.95	-0.73%	-0.42%	+0.22%	+0.36%	+0.59%
PO_4^-	0.25	0.00%	0.00%	0.00%	0.00%	0.00%
O.A.	68.53	+2.64%	+0.82%	-1.13%	-2.52%	-4.30%

Table 7.3: The change in the RMSE of simulated and observed M.D.F.s, together with the % change in the simulated total flow, flow in each soil horizon and the streamwater concentrations (ueq/l) of the major chemical species, due to adjustment of the horizontal permeability of the lower soil layer from the calibration value of 1.0E3 cm/day.

S.M.C. of each layer by 20% and the results of the analysis are reported in table 7.4. From this table it can be seen that for the upper soil horizon the total annual streamflow and the annual flow through each of the soil horizons are all very insensitive to a 20% change in the S.M.C., with the maximum change in annual flow less than 1.0%. At a shorter timescale, if figure 7.5 which demonstrates the simulated flow for a 20% increase in S.M.C. and the observed M.D.F.s is compared with figure 6.5, (a similar plot for the optimum calibration), it can be seen the only impact of a 20% increase in the S.M.C. of the upper horizon is a slight increase in the size of the major hydrograph peaks. Furthermore, a comparison of figure 7.6 with figure 6.5 shows that the individual hydrographs are even less sensitive to the 20% decrease in the S.M.C. of the upper horizon with no observable change in the simulated M.D.F.s.

Table 7.4 also shows the percentage change in the concentrations of the simulated annual streamwater chemistry as a result of a 20% increase and decrease in the S.M.C. of the upper soil horizon. The maximum change of any chemical species is for the hydrogen ion. However, the change in concentration is less than 2.50% which is equivalent to only a 0.01 unit change in pH. The concentrations of the other chemical species are even less sensitive to such a change in the upper soil horizon S.M.C., so that all concentrations are changed by less than 1.00%.

The results of a 20% increase and a 20% decrease in the S.M.C. of the middle soil horizon are also shown in table 7.4. From the table it can be seen that the simulated annual hydrology is more sensitive to a 20% change in the S.M.C. of the middle soil horizon

	Calibration Value	Upper Horizon (A) S. M. C.		Middle Horizon (B) S. M. C.		Lower Horizon (C) S. M. C.	
	Horizon A = 55 B = 43 C = 35	(-20%)	(+ 20%)	(-20%)	(+ 20%)	(-20%)	(+ 20%)
R.M.S.E	0.1073	0.1091	0.1112	0.1082	0.1109	0.1085	0.1099
Flow (m ^{3})							
---Total	4752522	+0.15%	-0.12%	+0.38%	-0.30%	-0.12%	-0.26%
---Layer 1	3128693	+0.50%	-0.50%	+2.20%	-2.09%	+0.57%	-0.44%
---Layer 2	1304421	-0.70%	+0.73%	-3.63%	+3.59%	+0.29%	-0.33%
---Layer 3	319478	+0.22%	+0.49%	-1.62%	+0.96%	-2.58%	+1.35%
pH	5.14	5.15	5.15	5.11	5.17	5.15	5.14
H^+	7.24	-2.26%	+1.98%	+7.18%	-7.10%	-2.58%	+1.35%
NH_4^+	1.22	-1.66%	-0.83%	+1.64%	-2.52%	0.00%	0.00%
Na^+	193.55	0.00%	-0.09%	+0.13%	-0.20%	-0.18%	+0.20%
K^+	7.66	+0.39%	-0.26%	-0.91%	+1.06%	-0.01%	+0.65%
Ca^{++}	66.33	+0.15%	-0.56%	-0.09%	+0.20%	-0.56%	+0.86%
Mg^{++}	71.39	+0.18%	-0.21%	-0.08%	+0.21%	-0.54%	+0.90%
T.Al	6.40	-2.07%	-0.16%	+2.66%	-3.73%	0.00%	+0.15%
Cl^-	226.19	+0.22%	+0.16%	+0.52%	-0.62%	-0.61%	+0.74%
Alk	20.17	+0.40%	-0.46%	-1.71%	+0.40%	-0.14%	+0.19%
SO_4^{--}	93.07	-0.32%	-0.13%	-0.65%	+0.53%	+0.44%	+0.50%
NO_3^-	6.95	-0.32%	-0.13%	-2.66%	-2.66%	+0.11%	+0.11%
PO_4^-	0.25	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
O.A.	68.53	-0.66%	-0.82%	+3.13%	-2.52%	-0.29%	+0.58%

Table 7.4: The change in the RMSE of simulated and observed M.D.F.s, together with the % change in the simulated total flow, flow in each soil horizon and the streamwater concentrations (ueq/l) of the major chemical species, due to adjustment of the saturated moisture content (S.M.C.) of the lower soil layer from the calibration value.

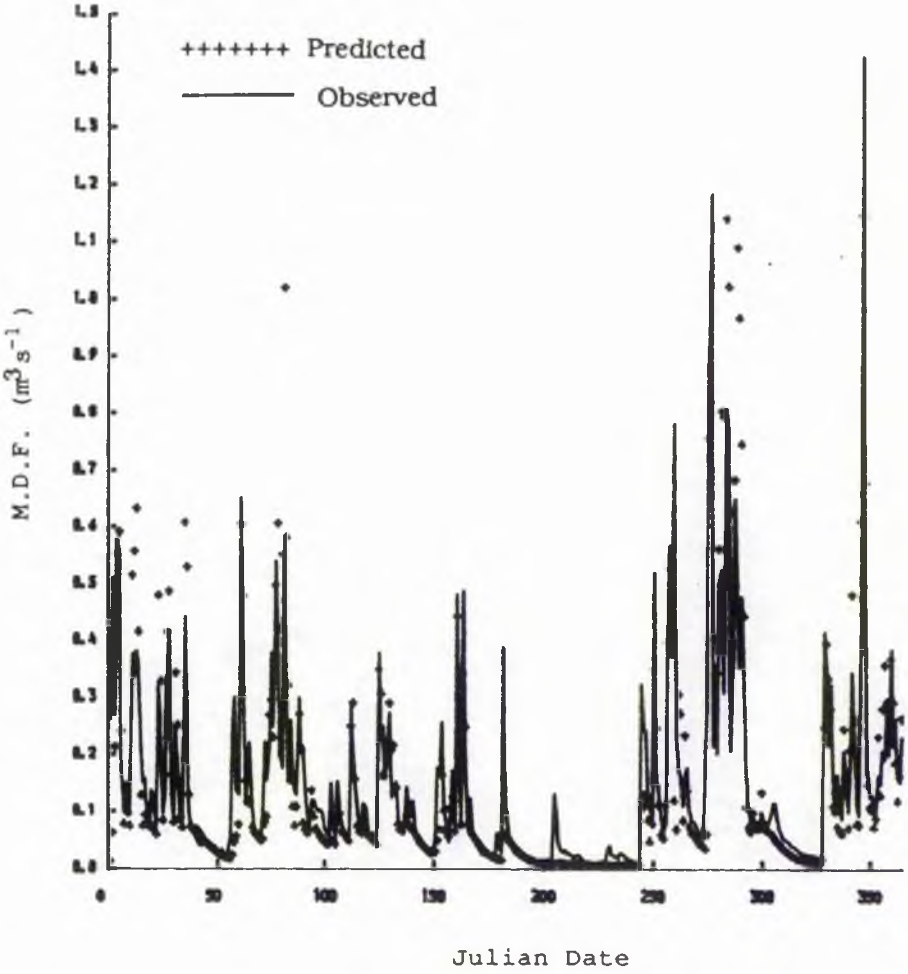


Figure 7.5 The simulated and observed M.D.F.s (m^3s^{-1}) with the saturation moisture content of the upper soil horizon increased by 20%.

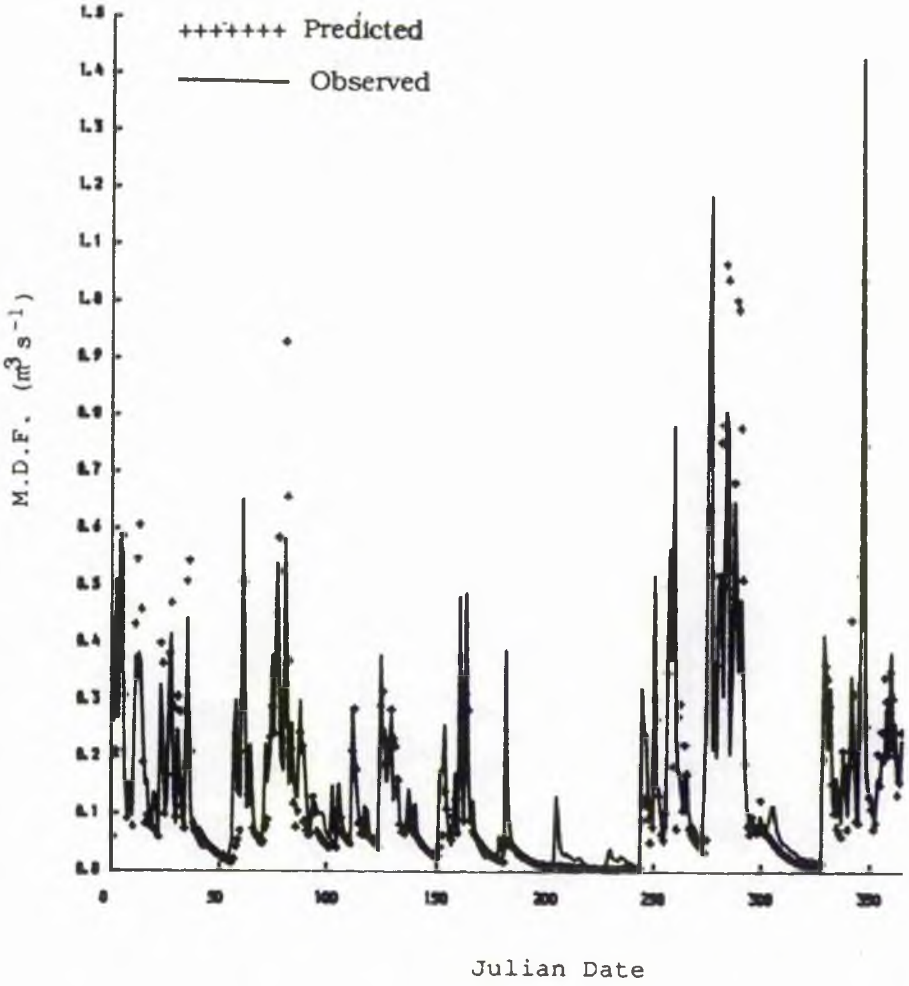


Figure 7.6 The simulated and observed M.D.F.s ($m^3 s^{-1}$) with the saturation moisture content of the upper soil horizon decreased by 20%.

than to a similar change in the S.M.C. of the upper soil horizon. However, the extent of the changes, particularly to the annual runoff, is still very minor. Thus the total annual streamflow is adjusted by less than 0.50% and flow through any of the soil layers by less than 3.75%. On a shorter timescale figures 7.7 and 7.8 show the a comparison of the simulated M.D.F.s with the middle horizon S.M.C. increased and decreased by 20% respectively. A comparison of figure's 7.7 and 7.8 with figure 6.5 (the optimum simulation), indicates that streamflow is more sensitive to changes in the S.M.C. of the middle soil horizon at a daily timescale than at an annual timescale, albeit the changes are still very small. Thus the 20% decrease in the S.M.C., as shown by figure 7.8, results in a slight increase in the size of the main hydrograph peaks (days 75, 275 and 340) and a slight steepening of the recession limb (ie day 300). Conversely, the 20% increase in the S.M.C. (figure 7.7) results in a slight steepening of the recession limbs, but has no observable effect on the hydrograph peaks. The annual streamwater chemistry is also more sensitive to the 20% change in the S.M.C. of the middle horizon than to a similar change to the upper horizon S.M.C. However, the changes are still very small. Thus the hydrogen ion concentration is only changed by +/- 7%, equivalent to a pH change of only 0.03 units, and the concentrations of all the other simulated chemical species by less than 4.00%.

Table 7.4 also shows that, as for the other two soil horizons, a 20% increase and decrease in the S.M.C. of the lower soil horizon also has very little influence on either the simulated annual runoff or streamwater chemistry. Thus the annual streamflow is altered by less than 0.3% and flow through any horizon by less than 3.0%. In the

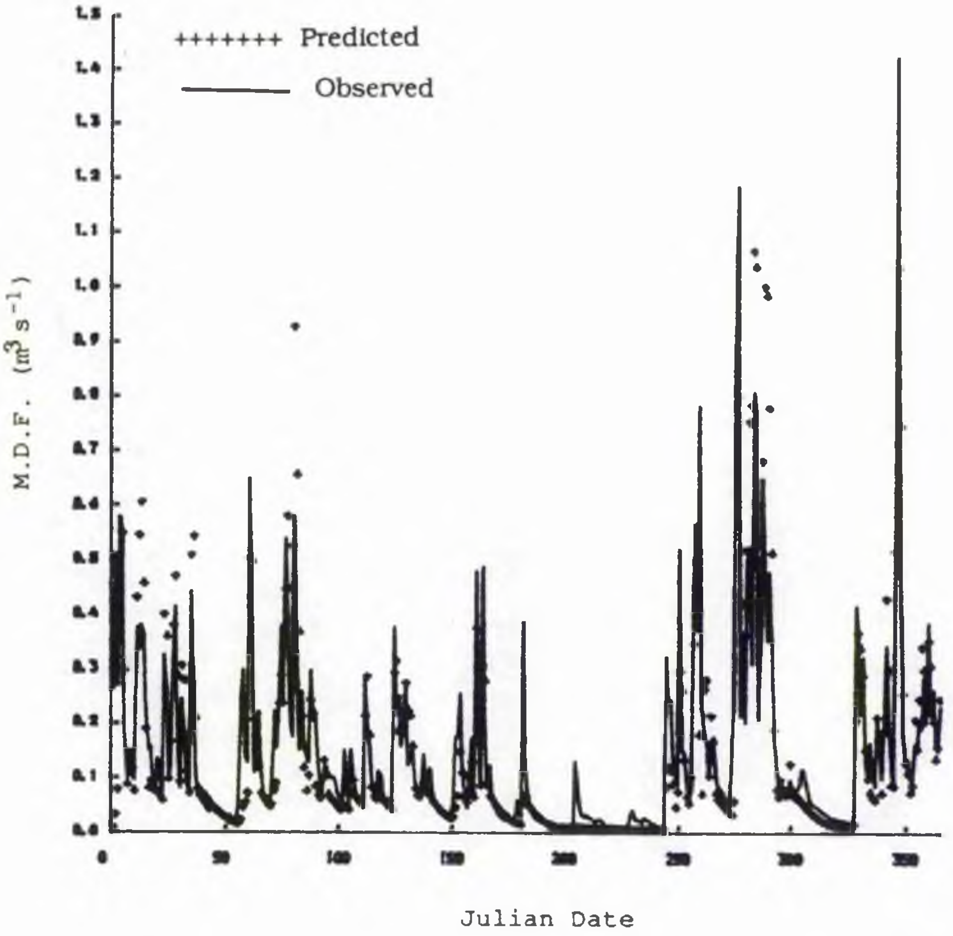


Figure 7.7 The simulated and observed M.D.F.s ($m^3 s^{-1}$) with the saturation moisture content of the middle soil horizon increased by 20%.

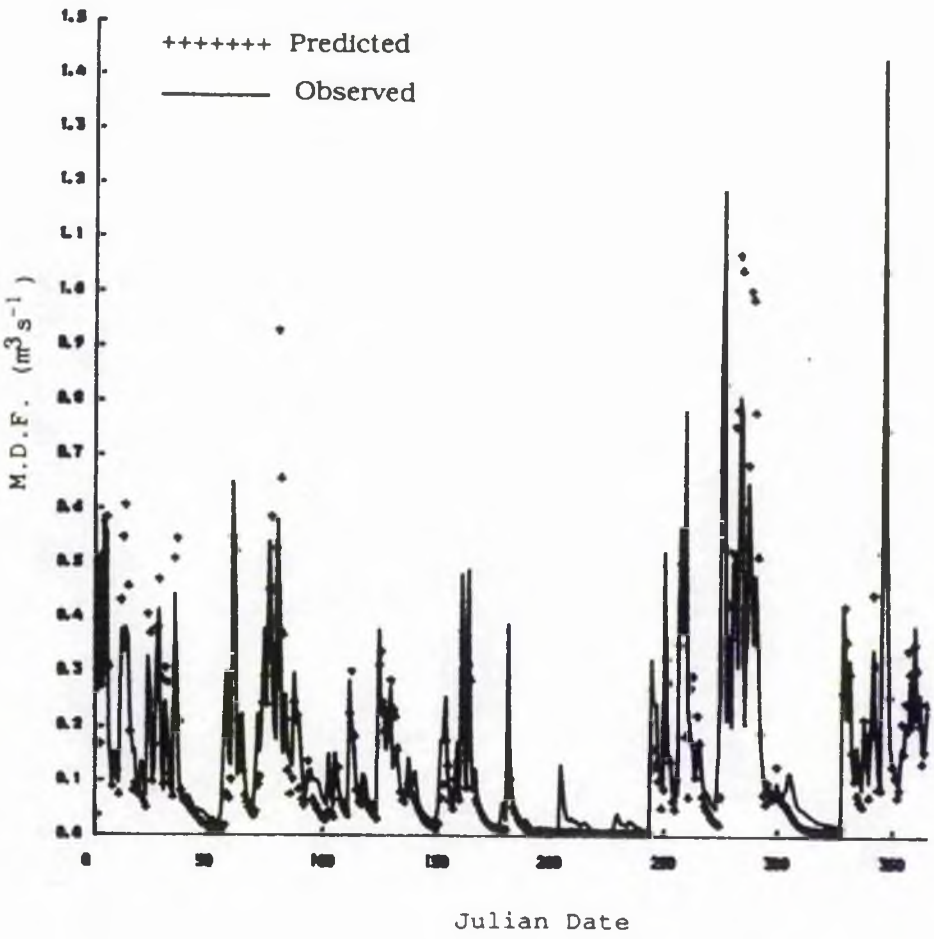


Figure 7.8 The simulated and observed M.D.F.s ($m^3 s^{-1}$) with the saturation moisture content of the middle soil horizon decreased by 20%.

same manner the greatest change in the streamwater solute concentrations is the 2.58% decrease in the hydrogen ion concentration, for a 20% decrease in the S.M.C, which is only equivalent to a 0.01 unit change in pH. The concentrations of the other simulated species are all increased by less than 1.0%.

The sensitivity of the model outputs to changes in the soil field capacity (F.C) were also assessed by increasing and decreasing the optimum values by 20%. The results of the sensitivity analysis for the F.C. are shown in Table 7.5. From the table it can be seen that the simulated total annual streamflow is very insensitive to such changes in the field capacity. This is particularly evident for the change to the lower horizon field capacity, which results in no alteration to the simulated annual streamflow. The simulated annual flow through the analogue soil horizons is slightly more sensitive to the changes in field capacity. However, the largest percentage change is still only the 5.3% decrease in flow through the middle horizon, as a result of a 20% increase in the F.C. On a daily timescale table 7.5 also shows that there are only slight changes in the RMSE of the simulated and observed flows as a result of the adjustments to the field capacity of the upper and lower horizon. Consequently, the influence of the changes in field capacity, at this timescale, was examined solely for the change in the middle horizon field capacity. Thus figures 7.9 and 7.10 show the simulated and observed M.D.F.s with the field capacity of the middle soil horizon increased and decreased by 20% respectively. A comparison of these plots with figure 6.5 shows that such changes in field capacity have little impact on the M.D.F.s. Thus the only observable change is the

	Calibration Value Horizon A = 39 B = 25 C = 20	Upper Horizon (A) Field Capacity		Middle Horizon (B) Field Capacity		Lower Horizon (C) Field Capacity	
		(-20%)	(+ 20%)	(-20%)	(+ 20%)	(-20%)	(+ 20%)
R.M.S.E	0.1073	0.1082	0.1079	0.1198	0.1082	0.1073	0.1073
Flow (m^3)							
---Total	4752522	-1.10%	+0.87%	-0.98%	+0.01%	0.00%	0.00%
---Layer 1	3128693	-0.98%	+0.84%	-0.70%	+2.27%	-0.09%	+0.14%
---Layer 2	1304421	-1.61%	+1.19%	+1.63%	-5.30%	-0.09%	+0.15%
---Layer 3	319478	-0.23%	+0.06%	+0.18%	-1.93%	+1.17%	-1.79%
pH	5.14	5.13	5.15	5.12	5.16	5.14	5.14
H^+	7.24	+3.22%	-1.55%	+4.72%	-5.07%	0.00%	0.00%
NH_4^+	1.22	+0.93%	-0.82%	+1.68%	-0.86%	0.00%	0.00%
Na^+	193.55	+0.61%	-0.67%	-0.04%	+0.36%	-0.01%	0.00%
K^+	7.66	-1.18%	-1.20%	-0.16%	+0.23%	0.00%	0.00%
Ca^{++}	66.33	-0.46%	+1.20%	-0.50%	+1.02%	0.00%	+0.05%
Mg^{++}	71.39	-0.43%	+1.15%	-0.45%	+1.50%	0.00%	+0.04%
T.Al	6.40	+0.23%	+0.32%	+0.56%	-1.53%	0.00%	+0.17%
Cl^-	226.19	+1.37%	-1.22%	-0.14%	+0.94%	-0.02%	0.00%
Alk	20.17	-0.73%	+0.84%	-1.08%	+1.49%	0.00%	-0.05%
SO_4^{--}	93.07	0.00%	-0.11%	-0.04%	-0.09%	0.00%	-0.02%
NO_3^-	6.95	+1.16%	-2.83%	+0.60%	-1.05%	0.00%	0.00%
PO_4^-	0.25	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
O.A.	68.53	+0.60%	-2.23%	-3.45%	+5.92%	-0.06%	+0.09%

Table 7.5: The change in the RMSE of simulated and observed M.D.F.s, together with the % change in the simulated total flow, flow in each soil horizon and the streamwater concentrations (ueq/l) of the major chemical species, due to adjustment of the Field Capacity (F.C.) of the lower soil layer from the calibration value.

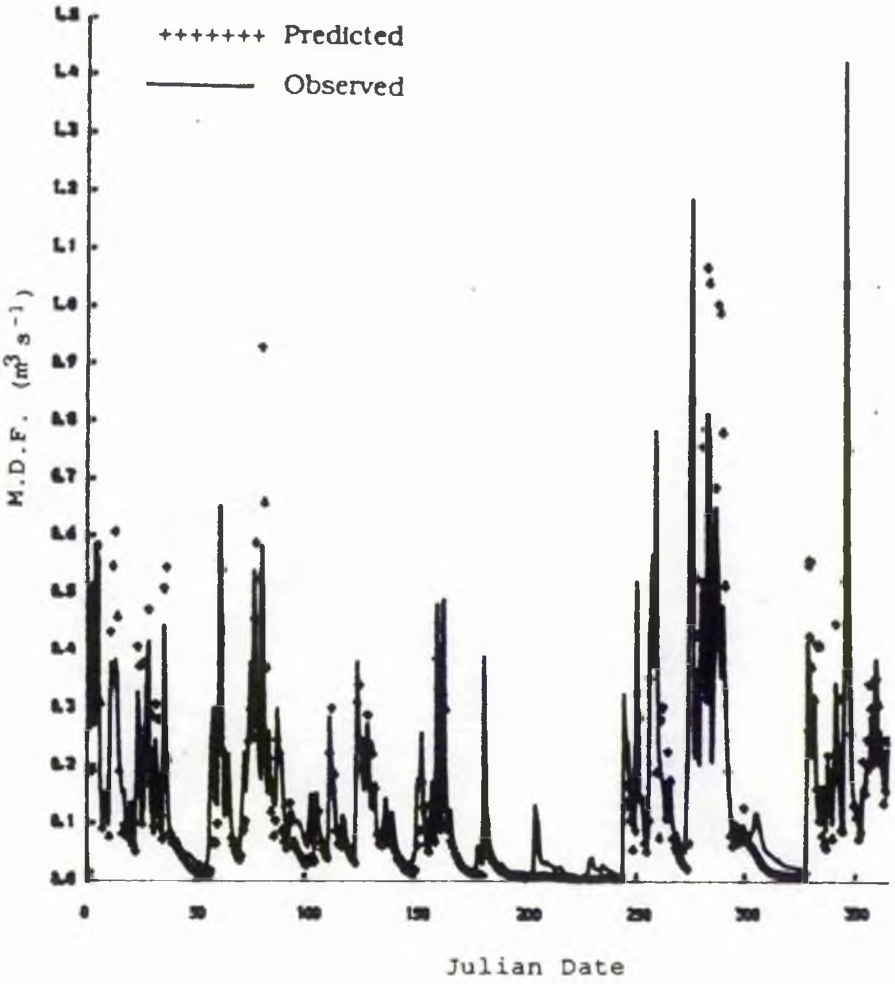


Figure 7.9 The simulated and observed M.D.F.s ($m^3 s^{-1}$) with the field capacity of the middle soil horizon increased by 20%.

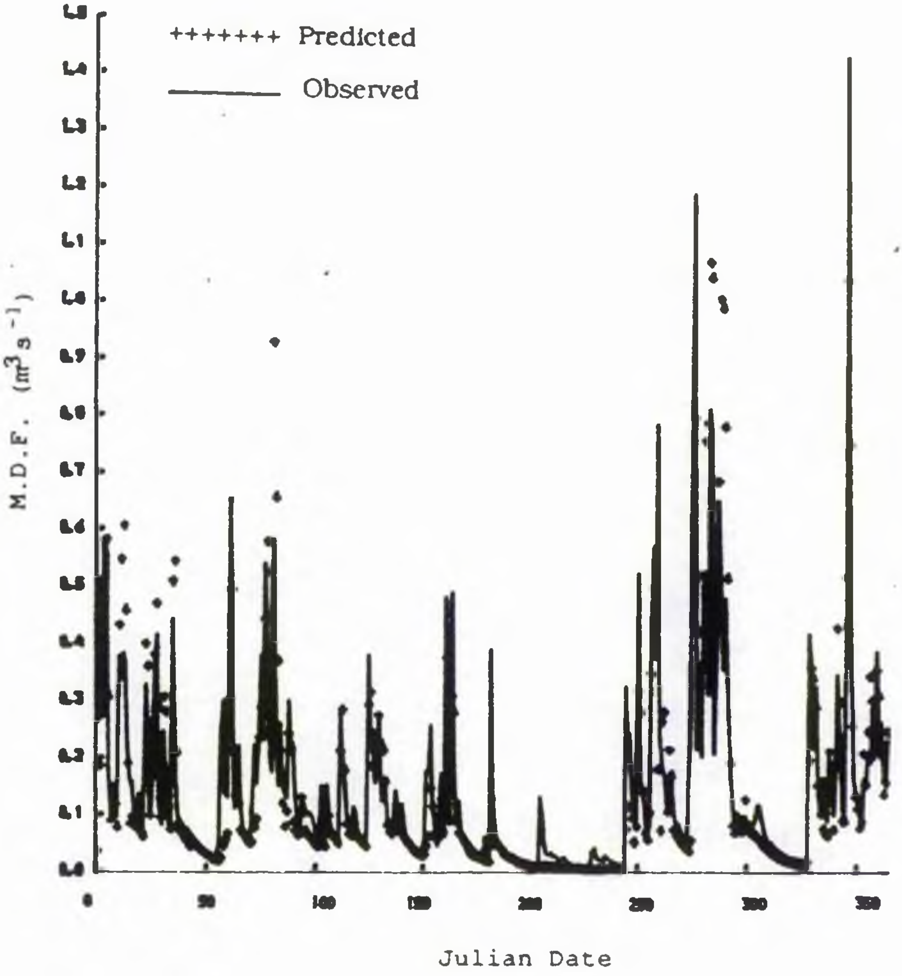


Figure 7.10 The simulated and observed M.D.F.s ($m^3 s^{-1}$) with the field capacity of the middle soil horizon decreased by 20%.

quicker decay of the hydrograph recession limb around day 300, as a result of the 20% decrease in field capacity.

The simulated annual streamwater chemistry is also generally insensitive to changes in the soil field capacity. This is particularly evident for the lower soil horizon where the 20% change in field capacity leads to no change in pH and a less than 0.2% change in the streamwater concentrations of all the other simulated chemical species. The greatest changes in the simulated mean annual streamwater chemistry due to the changes in field capacity are associated with the 20% increase in the field capacity of the middle soil horizon. However, the resulting 5.07% increase in the mean annual hydrogen ion concentration, which is the largest change, is still only equivalent to a 0.02 unit increase in pH. Furthermore, apart from the simulated mean annual concentrations of organic acids, which are increased by 5.92%, the change in concentration of all the other chemical species is less than 2.0%.

With the major variables that describe the soil hydrological response tested, the sensitivity of the model to changes in the thickness of the analogue soil horizons was assessed. Field studies indicated that the thickness of the soil on the catchment slopes was far more variable than that for the soils on the valley floor. Consequently, the analysis was initially performed by adjusting the depth of the soil horizons in the model sub-catchments 1-4, which represent the catchment slopes. The thickness of the soil horizons in sub-catchments 5 and 6, which represent the valley floor of the catchment, were left unchanged from the depths utilised in the model calibration.

The results of the sensitivity analysis for the soil horizon depth are shown in table 7.6. From the table it can be seen that halving the depth of the upper horizon, which represents the thick organic horizon, from 60cm to 30cm has very little influence on the simulated annual hydrology or, with the exception of nitrate, the simulated annual streamwater chemistry. However, a further reduction in the depth of the upper soil horizon to 10cm produces a greater impact, particularly on the simulated annual streamflow and the annual flow from the upper horizon. Thus the annual streamflow is reduced by 11.4% and flow from the upper horizon by almost 20%. The flow from the other two horizons is, however, far less sensitive to such a change in soil depth and shows only a 3.34% decrease from the lower horizon and a 0.81% decrease from the middle horizon. At a daily timescale figure 7.11, when compared with figure 6.5, shows that such a reduction in the depth of the upper soil horizon increases the size of the major simulated hydrograph peaks (days 75, 275 and 350) but has no observable effect on the hydrograph recession limbs. The simulated chemistry is also affected more by this larger reduction in the depth of the upper horizon, although the degree to which the annual streamwater solute concentrations are changed varies considerably for different chemical species. Thus nitrate concentrations are changed by almost 23% and aluminium concentrations by 8.5%, whereas, concentrations of the other chemical species are changed by far smaller amounts. The simulated mean annual pH, with a change of only 0.02 pH units, is particularly insensitive to such a decrease in the thickness of the upper soil horizon.

	Calibration Value for Horizon	Soil Horizon Depth (cm) Sub-Catchments 1-4...slopes			
	A = 60 B = 15 C = 30	A = 30 B = 15 C = 30	A = 10 B = 15 C = 30	A = 60 B = 30 C = 60	A = 10 B = 30 C = 60
R.M.S.E	0.1073	0.1114	0.1209	0.1179	0.1186
Flow (m^3)					
---Total	4752522	+0.16%	-11.42%	-0.96%	-7.22%
---Layer 1	3128693	+0.49%	-19.40%	-55.29%	-81.63%
---Layer 2	1304421	-0.11%	+0.81%	+59.37%	+60.29%
---Layer 3	319478	+1.40%	+3.34%	+92.06%	+93.76%
pH	5.14	5.14	5.16	5.40	5.50
H^+	7.24	0.00%	-4.62%	-45.01%	-56.32%
NH_4^+	1.22	0.00%	-5.17%	-38.64%	-42.27%
Na^+	193.55	-0.62%	+3.38%	+1.20%	+4.27%
K^+	7.66	0.00%	+0.50%	+4.65%	+5.19%
Ca^{++}	66.33	-0.09%	+1.53%	+5.56%	+7.07%
Mg^{++}	71.39	-0.13%	+1.57%	+6.01%	+6.13%
T.Al	6.40	-0.03%	-8.52%	- 21.90%	-35.31%
Cl^-	226.19	-0.53%	-4.86%	+2.15%	-8.16%
Alk	20.17	-0.60%	+1.97%	+10.60%	+12.89%
SO_4^{--}	93.07	-0.88%	-4.33%	+2.92%	-0.01%
NO_3^-	6.95	-8.25%	-22.79%	-2.66%	-48.19%
PO_4^-	0.25	0.00%	+4.00%	-12.00%	-12.00%
O.A.	68.53	-0.35%	-12.41%	-34.93%	-41.59%

Table 7.6: The change in the RMSE of simulated and observed M.D.F.s, together with the % change in the simulated total flow, flow in each soil horizon and the streamwater concentrations (ueq/l) of the major chemical species, due to adjustment of the soil horizon thickness on the catchment slopes (sub-catchments 1-4).

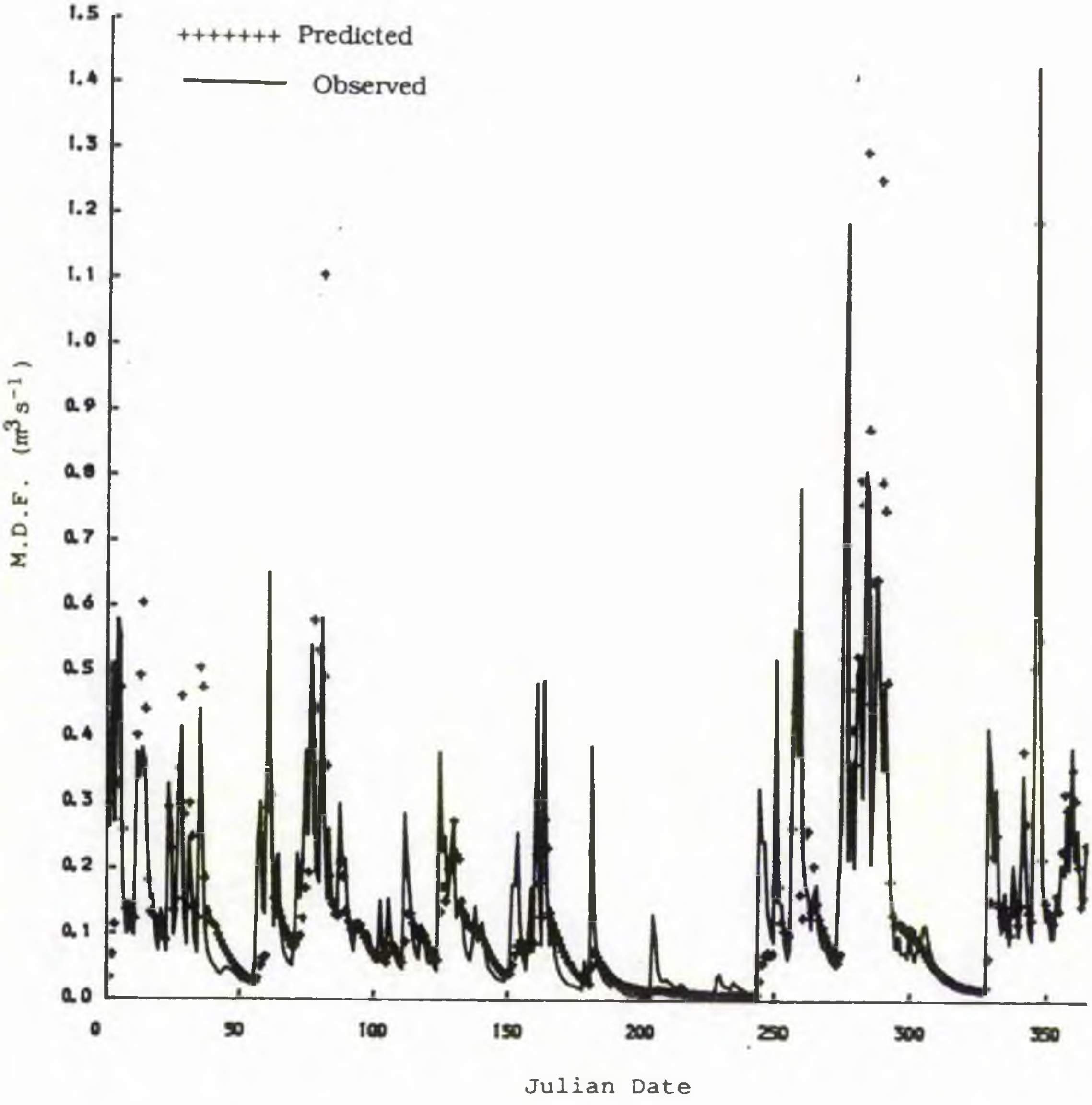


Figure 7.11 The simulated and observed M.D.F.s ($m^3 s^{-1}$) with the thickness of the upper organic horizon on the catchment slopes (sub-catchments 1- 4) reduced to 10cm.

The change in the model outputs as a result of a doubling in the depth of the lower two soil horizons, which represent the mineral soil, was also assessed. In order to broaden the scope of the analysis the depths of the lower horizons were increased from the calibration values in two ways. Firstly, with the depth of the upper organic horizon held at the calibration value of 60cm and secondly, with the depth of the upper organic horizon reduced to 10cm. From table 7.6 it can be seen that doubling the depth of the lower soil horizons, whilst the depth of the upper horizon is held at the calibration value of 60cm, has very little effect on the simulated total annual streamflow. However, the flow from each of the soil horizons is far more sensitive to such a change in soil depth with a decrease of over 55% in flow from the upper horizon and increases of 59% and 92% in flow from the middle and lower horizons respectively. At a daily timescale a comparison of figure 7.12 and figure 6.5 shows that such an increase in the depth of the mineral soil horizons results in large changes in the simulated M.D.F.s. In particular the hydrograph recession limbs (ie days 40, 100, 130, 180 and 300) are far more drawn out and the main hydrograph peaks (days 75, 275 and 350) are increased in size.

The change in the simulated annual streamwater chemistry due to the 100% increase in the depth of the mineral soil horizons varies considerably. The greatest change is in the simulated hydrogen ion concentration which is decreased by 45.01%, equivalent to a 0.26 unit increase in pH. After hydrogen the greatest decreases in concentration are 38.6%, 34.9%, and 21.9% for ammonium, organic acid and aluminium respectively. In contrast the simulated

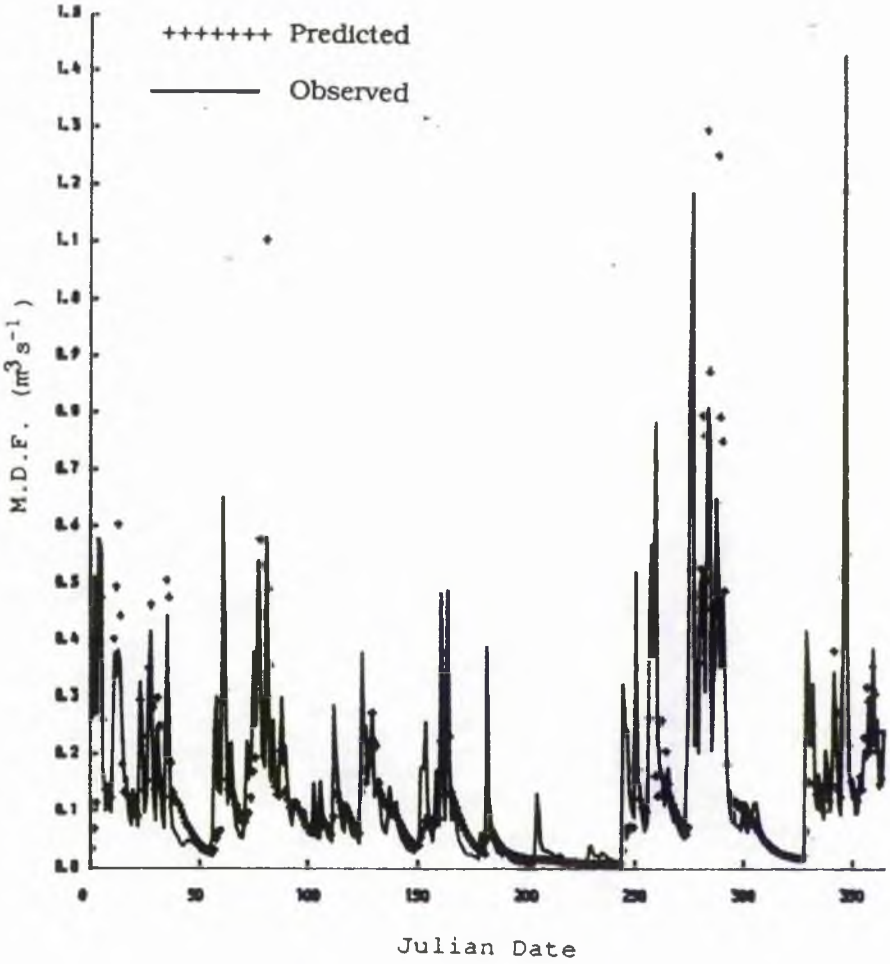


Figure 7.12 The simulated and observed M.D.F.s ($m^3 s^{-1}$) with the thickness of the two lower mineral horizons on the catchment slopes (sub-catchments 1- 4) increased by 100%.

concentrations of the base cations, chloride and sulphate are all increased but by less than 6.0%.

Table 7.6 also shows that if the depth of the lower mineral horizons is doubled whilst the depth of the upper organic horizon is reduced to 10cm the above changes in the simulated annual hydrological and chemical outputs are further accentuated. This is noticeable for both the simulated total flow and flow from the upper horizon, with the annual streamflow reduced by less than 1.0% (with the organic horizon depth at 60cm) to over 7% (with the organic horizon depth at 10cm). Similarly the annual flow from the upper horizon is further reduced from -55% to -82% as the organic horizon depth is reduced. The changes in the streamwater solute concentrations also show the same pattern as for the increase in mineral soil depth alone with each species, except phosphate and sulphate, registering a positive percentage change, which is greater than that for when the depth of the organic horizon is 60cm. For sulphate the percentage change in concentration is decreased whilst for phosphate there is no alteration.

The hydrological module as well as requiring data for the soil thickness and the hydrological response of the soil horizons, also contains a variable to describe the distribution of roots between the soil horizons. Field measurements for this variable rarely exist and, even if such measurements were to be available, there is likely to be considerable spatial variability in values. Consequently, the sensitivity of the model output to changes in this variable was also assessed, with the results reported in table 7.7 from which it can be seen that there is an inverse relationship between the

	Root Distribution for each soil horizon (%)					
	Calibration Value **A = 80** **B = 20** **C = 00**	**A = 99** **B = 01** **C = 00**	**A = 01** **B = 99** **C = 00**	**A = 50** **B = 50** **C = 00**	**A = 25** **B = 50** **C = 25**	**A = 34** **B = 33** **C = 33**
R.M.S.E	0.1073	0.1079	0.1074	0.1077	0.1074	0.1076
Flow (m^3)						
---Total	4752522	-0.14%	+0.86%	+0.11%	+0.89%	+0.69%
---Layer 1	3128693	-0.21%	+2.11%	-0.53%	+2.00%	+1.34%
---Layer 2	1304421	+0.95%	-1.39%	-0.78%	-0.38%	-0.09%
---Layer 3	319478	+0.36%	-2.17%	-0.38%	-4.17%	-2.33%
pH	5.14	5.14	5.13	5.14	5.14	5.15
H^+	7.24	-1.04%	+2.20%	+0.75%	-0.41%	-1.58%
NH_4^+	1.22	0.00%	+0.85%	0.00%	0.00%	-0.85%
Na^+	193.55	-0.65%	+1.40%	+0.75%	+0.41%	+0.33%
K^+	7.66	-1.07%	+0.92%	+0.40%	0.00%	-0.27%
Ca^{++}	66.33	-1.33%	+2.92%	+1.55%	+1.40%	+1.51%
Mg^{++}	71.39	-1.32%	+2.92%	+1.57%	+1.40%	+1.51%
T.Al	6.40	-0.35%	+7.57%	+0.17%	+6.20%	-2.11%
Cl^-	226.19	-1.29%	+2.68%	+1.54%	+1.08%	+1.30%
Alk	20.17	+0.39%	-0.25%	-0.40%	-0.79%	+0.44%
SO_4^{--}	93.07	-0.15%	+0.68%	+0.10%	+0.22%	-0.52%
NO_3^-	6.95	-1.98%	+7.91%	+2.39%	+4.03%	+0.60%
PO_4^-	0.25	0.00%	0.00%	0.00%	0.00%	0.00%
O.A.	68.53	+0.09%	-0.28%	-0.07%	-0.45%	-0.31%

Table 7.7: The change in the RMSE of simulated and observed M.D.F.s, together with the % change in the simulated total flow, flow in each soil horizon and the streamwater concentrations (ueq/l) of the major chemical species, due to adjustment of the root distribution within each soil horizon.

percentage of roots in any soil horizon and the simulated annual flow from that horizon. Thus an increase in the percentage of roots in any of the soil horizons leads to a decrease in the simulated annual flow from that horizon, whilst a decrease in the percentage of roots in any soil horizon results in an increase in flow from the horizon. However, table 7.7 also shows that changes to the annual flow from each of the soil horizons and to the simulated annual streamflow as a result of changes in the root distribution are very minor. Thus, whether the roots are located almost totally in the upper horizon or almost totally in the middle horizon, the percentage change in the simulated total annual streamflow is less than 1.0%. Division of the root distribution equally between the upper and middle horizon also has little effect on the simulated hydrology, with a less than 1.0% change in total flow or flow from any horizon. Division of the root distribution equally between all three horizons also results in a less than 1.0% change in the simulated total flow. However, this equal distribution also results in a 1.3% increase in the simulated flow from the upper horizon and a 2.3% decrease in flow from the lower horizon. At a daily timescale a comparison of figure 7.13, which contrasts the simulated M.D.Fs where 99% of the roots are located in the upper soil horizon, with figure 6.5 shows that such a change in the root distribution results in a slight decrease in the size of the main hydrograph peaks (days 75, 275 and 350) but has no other observable effect on the simulated M.D.F.s. Figures 7.14 and 7.15 represent the simulated M.D.F.s with 99% of the roots in the middle horizon and the roots distributed equally between all three horizons respectively. If these figures are compared with figure 6.5 it can be seen that an increase in the proportion of roots in the lower soil horizons has little effect on the individual

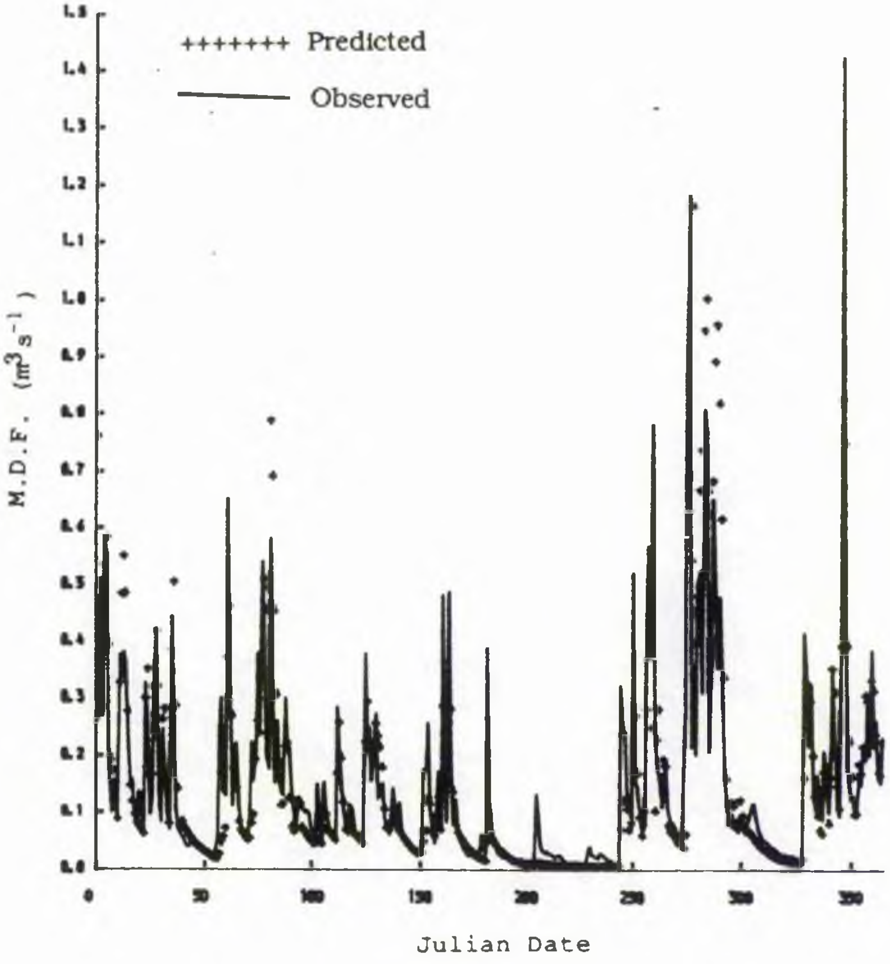


Figure 7.13 The simulated and observed M.D.F.s ($m^3 s^{-1}$) with the distribution of roots between the soil horizons adjusted so all the roots are located in the upper horizon.

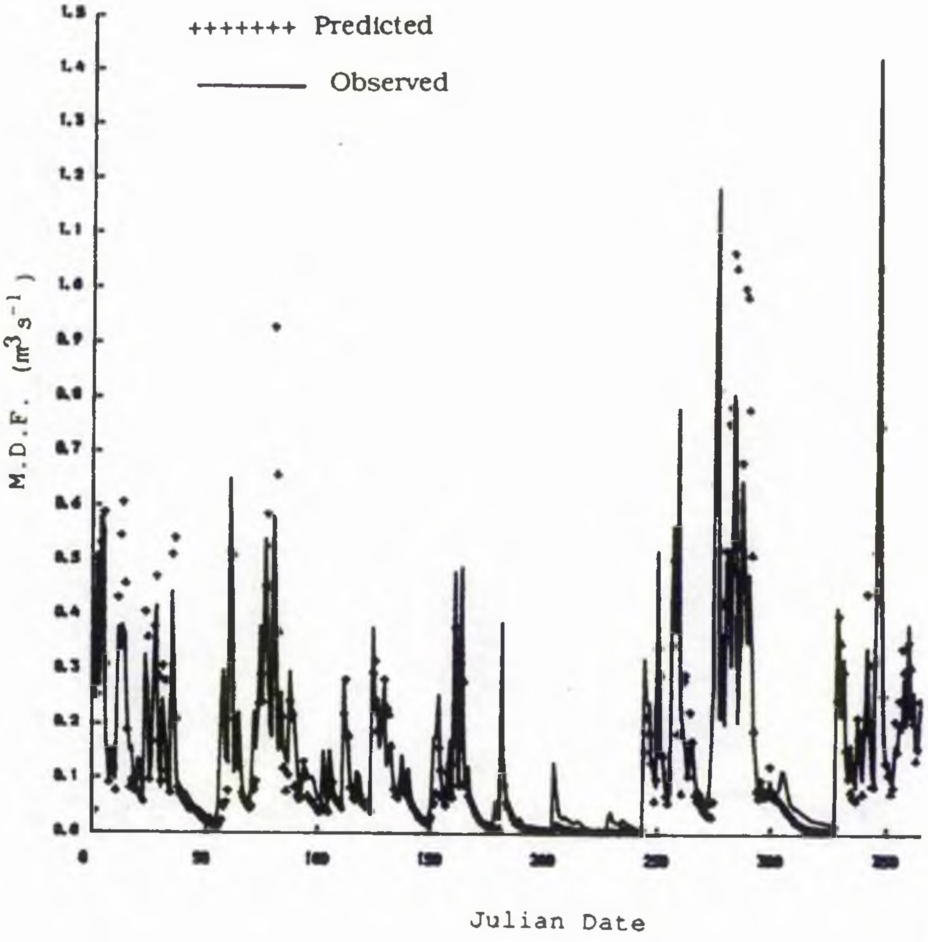


Figure 7.14 The simulated and observed M.D.F.s ($m^3 s^{-1}$) with the distribution of roots between the soil horizons adjusted so all the roots are located in the middle horizon.

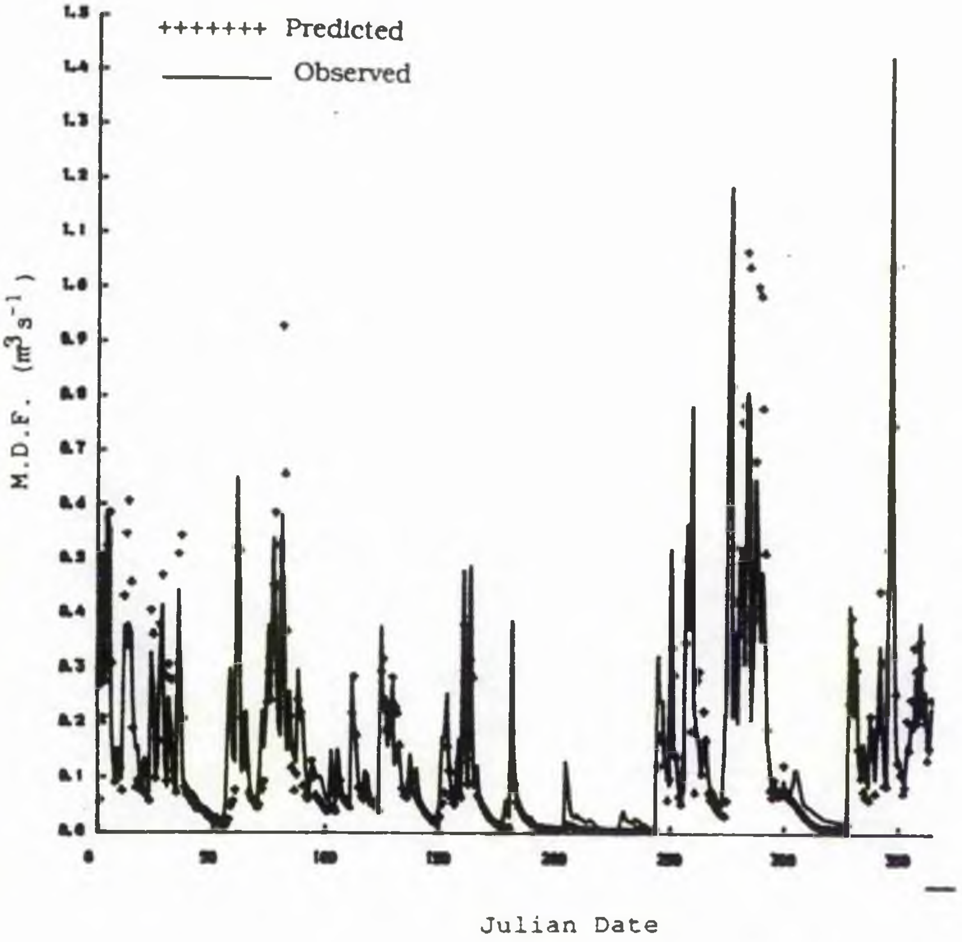


Figure 7.15 The simulated and observed M.D.F.s ($m^3 s^{-1}$) with the distribution of roots between the soil horizons adjusted so the roots are evenly distributed between the horizons.

hydrographs, apart from a tendency to steepen the hydrograph recession limb around day 300.

From table 7.7 it can also be seen that although the mean annual aluminium and nitrate concentrations are increased by almost 8.0% if 99% of the roots are located in the middle horizon, the mean annual streamwater chemistry is generally very insensitive to adjustments in the distribution of roots between the three soil horizons. Thus the maximum change in pH is 0.01 units and the percentage change in the mean annual concentration of the other chemical species is generally less than 2.0%.

Of the variables that describe the stream segment hydrology the majority are easily measured in the field. The exceptions, however, are the two Muskingum routing parameters; KR which represents the travel time of the segment and MX which is a dimensionless coefficient with a value less than 0.5. The sensitivity of the model output to the segment travel time (KR) was assessed by varying the value utilised in the optimum calibration by +/- 100%. This adjustment was undertaken for each of the three stream segments alone and for all three stream segments together. The sensitivity of the model output to such changes is shown in Table 7.8. From this table it can be seen that both the simulated annual runoff and the simulated annual streamwater chemistry are totally insensitive to such alterations in KR, with all changes being less than 0.01%. Similarly, a comparison of figure 7.16 with figure 6.5 shows that a 100% increase in KR for each stream segment also has no observable influence on the simulated M.D.Fs.

	Muskingum Rooting Coefficient (MX)								
	Calibration Value 1 = 0.011 2 = 0.014 3 = 0.022	Stream Segment 1		Stream Segment 2		Stream Segment 3		Stream Segment's 1,2,&3	
		0.022	0.005	0.028	0.007	0.044	0.011	(*2)	(/2)
R.M.S.E	0.1073	0.1075	0.1074	0.1076	0.1074	0.1079	0.1073	0.1082	0.1073
Flow (m ^{3})									
---Total	4752522	No change in total flow or flow through any horizon							
---Layer 1	3128693								
---Layer 2	1304421								
---Layer 3	319478								
Solute Conc's		No change in any solute concentrations							

Table 7.8: The change in the RMSE of simulated and observed M.D.F.s, together with the % change in the simulated total flow, flow in each soil horizon and the streamwater concentrations (ueq/l) of the major chemical species, due to adjustment of the Muskingum rooting coeffient (MX) in each of the stream segments.

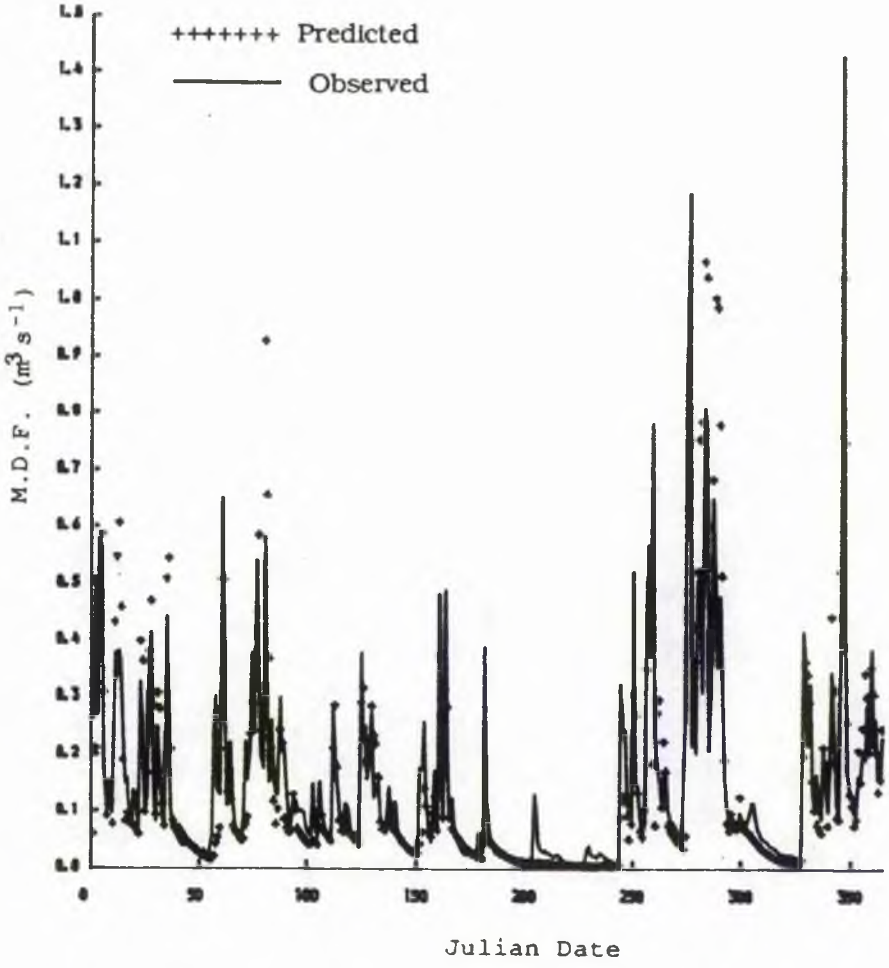


Figure 7.16 The simulated and observed M.D.F.s (m^3 s^{-1}) with the Muskingum routing coefficient (MX) increased by 100%.

The other Muskingum parameter (MX) was adjusted by altering the value used in the optimum calibration (0.2) to the maximum and minimum possible values, 0.1 and 0.5. From table 7.9 it can be seen that as for KR, both the simulated annual runoff and the simulated annual streamwater chemistry are again totally insensitive to changes in this parameter, with neither the maximum or minimum possible values producing any change in the simulated output. Similarly, on a daily time-scale a comparison of figure 7.17 with figure 6.5 shows that an increase in MX to 0.5 for all three stream segments also has no effect on the simulated M.D.F.s.

7.2.2 *Chemical Variables*

As with the hydrological variables, the chemical variables which were tested in terms of their sensitivity were primarily those where field data either commonly does not exist or where there is considerable spatial variation of the variable values.

The first variable to be examined was the monthly litterfall rate as the lack of site specific data for Loch Dee, and indeed for other upland British catchments, resulted in the model calibration utilising data from the ILWAS Adirondacks study data-base (Chen et al. 1983). The results of this analysis are presented in table 7.10. From table 7.10 it can be seen that the simulated mean annual streamwater solute concentrations are generally very insensitive to changes in this variable. Thus, with the exception of nitrate, neither an increase nor a decrease of two orders of magnitude in the monthly litterfall rate results a change in concentration greater than +/-5.0%. Annual nitrate concentrations are more sensitive, so that an order

	Muskingum Rooting Coefficient (MY)								
	Calibration Value = 0.2	Stream Segment 1		Stream Segment 2		Stream Segment 3		Stream Segment 's 1,2,&3	
		0.1	0.5	0.1	0.5	0.1	0.5	0.1	0.5
R.M.S.E	0.1073	0.1074	0.1074	0.1075	0.1073	0.1075	0.1074	0.1075	0.1074
Flow (m^3)		No change in total flow or flow through any horizon							
---Total	4752522								
---Layer 1	3128693								
---Layer 2	1304421								
---Layer 3	319478								
Solute Conc's		No change in any solute concentrations							

Table 7.9: The change in the RMSE of simulated and observed M.D.F.s, together with the % change in the simulated total flow, flow in each soil horizon and the streamwater concentrations (ueq/l) of the major chemical species, due to adjustment of the Muskingum rooting coeffient (MX) in each of the stream segments.

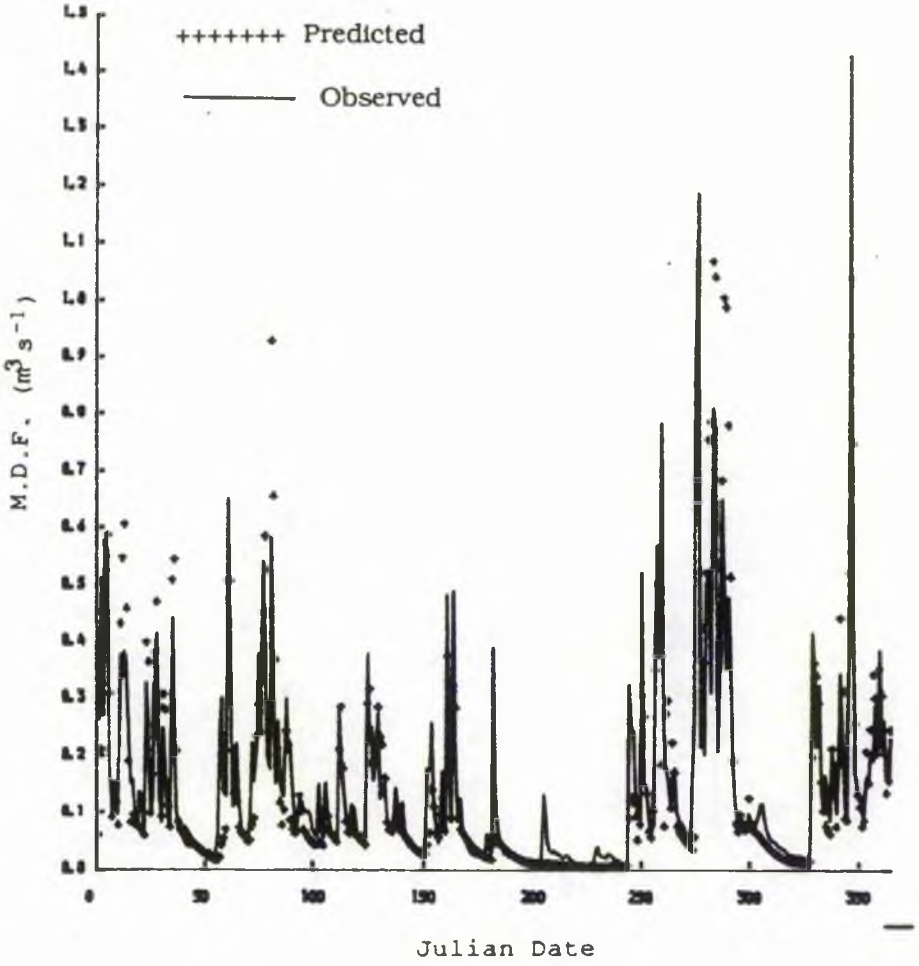


Figure 7.17 The simulated and observed M.D.F.s ($m^3 s^{-1}$) with the Muskingum routing coefficient (MY) increased to 0.5

of magnitude change in the monthly litterfall gives over a 6.0% change in concentration, whilst a two order of magnitude change produces between a 15% and 17% change in concentration. However, this change in nitrate concentration is not reflected in the mean annual pH which is changed by only 0.01 pH units for a two order of magnitude change in the monthly litterfall rate.

The canopy chemistry module also includes foliar exudation amplification factors in order to increase foliar exudation of the major ions found in biological systems. For the model calibration the same values were used as in the Adirondack application, namely a sixty fold magnification of potassium and twenty fold magnification of magnesium exudation rates. The sensitivity of the model to the exudation amplification factors was assessed by removing the amplification factors for magnesium and potassium so that there was no amplification of any ion. Table 7.10 also shows the effect of this lack of exudation amplification on the mean annual solute concentrations. From the table it can be seen that the mean annual solute concentrations are totally insensitive to such a removal of the foliar exudation amplification factors. Thus the concentrations of all the simulated chemical species show no change from those with the amplification factors present.

The sensitivity of the mean annual streamwater chemistry to changes in the chemical composition of the canopy vegetation was also assessed in addition to the monthly litterfall rates and the foliar exudation amplification factors. This was achieved by adjusting the leaf and trunk chemical composition of the open moorland vegetation in the Dargall Lane to that of coniferous vegetation, as

	Calibration Concentrations Monthly Litterfall =1.0E-3 Kg/m ^{2} Exhudation Factors Mg = 20 K = 60	Monthly Litterfall (Kg/m ^{2} /mth)				Exhudation Factors Mg = 1 K = 1
		1.0E-5	1.0E-4	1.0E-2	1.0E-1	
pH	5.14	5.13	5.14	5.14	5.15	No Change in Species Conc's.
H^+	7.24	+2.37%	+1.17%	-1.17%	-2.37%	
NH_4^+	1.22	-1.64%	-0.00%	-0.00%	+1.64%	
Na^+	193.55	+1.81%	+0.30%	-0.03%	-1.06%	
K^+	7.66	+1.01%	+0.86%	-1.20%	-1.74%	
Ca^{++}	66.33	+1.59%	+0.83%	-1.00%	-2.32%	
Mg^{++}	71.39	+1.85%	+0.93%	-1.23%	-2.21%	
T.Al	6.40	+4.31%	+1.96%	-2.18%	-4.54%	
Cl^-	226.19	+0.46%	+0.19%	-0.02%	-0.84%	
Alk	20.17	+1.59%	+0.73%	-0.69%	-1.24%	
SO_4^{--}	93.07	+1.83%	+0.60%	-0.91%	-2.67%	
NO_3^-	6.95	+15.10%	+6.15%	-6.58%	-16.58%	
PO_4^-	0.25	+4.00%	0.00%	0.00%	-4.00%	
O.A.	68.53	-0.71%	-0.16%	+0.37%	+0.88%	

Table 7.10: The % change in the simulated streamwater concentrations of the major chemical species (ueq/l), due to adjustment of the monthly litterfall rate (Kg/m ^{2}) and the removal of the foliar exudation calibration parameters.

used in the calibration of the afforested Green Burn catchment. The chemical compositions used for both the open moorland and coniferous vegetation are as shown in table 6.13. From table 7.11 it can be seen that, apart from ammonia and nitrate concentrations, such adjustment of the canopy chemical composition has very little effect on the simulated mean annual concentrations. Thus whereas nitrate and ammonium concentrations are increased by up to 13.7% and 10.9% respectively, the other species are changed by less than 2.5%. Furthermore table 7.11 shows that what change exists, is primarily due to adjustment of the leaf chemical composition, as the mean annual streamwater concentrations show very little response to changes in the trunk chemical composition.

The soil chemistry module is the most complex part of the ILWAS model and contains many variables that are not routinely measured in catchment studies. Consequently, a large number of the variables from within this module were examined for their sensitivity. The first variables from the soil module to be assessed were the weight fractions of litter and fine litter in the upper horizon. The analysis took the form of a 100% increase or decrease in each of the variables with the results presented in table 7.12. From this table it can be seen that a 100% decrease in the amount of both litter and fine litter leads to either a decrease or no change in the simulated mean annual streamwater solute concentrations. Conversely, a 100% increase in the amounts of litter and fine litter in the upper horizon leads to either an increase or no change in the simulated concentrations. Table 7.12 also shows that the simulated mean annual concentrations are very insensitive to to changes in the amount of litter in the upper horizon. Thus the maximum

	Calibration Conc's With Moorland Vegetation	Adjustment of chemical composition of vegetation from moorland to coniferous		
		Leaf	Trunk	Leaf and Trunk
pH	5.14	5.15	5.14	5.15
H^+	7.24	-2.37%	0.00%	-2.37%
NH_4^+	1.22	+10.92%	+2.53%	+7.56%
Na^+	193.55	+0.86%	+0.04%	+0.28%
K^+	7.66	+0.76%	+0.62%	+0.82%
Ca^{++}	66.33	+1.40%	+0.46%	+2.20%
Mg^{++}	71.39	+0.37%	+0.01%	+0.18%
T.Al	6.40	-0.11%	0.00%	-0.05%
Cl^-	226.19	+0.17%	0.00%	+0.11%
Alk	20.17	+1.34%	+0.23%	+1.20%
SO_4^{--}	93.07	-1.11%	0.00%	-1.01%
NO_3^-	6.95	+13.67%	+1.16%	+6.17%
PO_4^-	0.25	0.00%	0.00%	0.00%
O.A.	68.53	-0.23%	+0.02%	-1.18%

Table 7.11: The % change in the simulated streamwater concentrations of the major chemical species (ueq/l), due to adjustment of the leaf and trunk chemical composition from that of moorland vegetation to that of coniferous vegetation. (Both moorland and coniferous vegetation chemical composition is as shown in Table 6.13)

	Calibration values Litter = 0.00965 Fine Litter = 0.13532	Weight Fraction of Litter in upper soil layer (%)		Weight Fraction of Fine Litter in upper soil layer (%)	
		0.00482	0.01930	0.06766	0.27064
pH	5.14	5.14	5.14	5.15	5.14
H^+	7.24	0.00%	0.00%	-2.37%	0.00%
NH_4^+	1.22	-0.13%	0.00%	-0.85%	0.00%
Na^+	193.55	-0.05%	-0.03%	-0.22%	-0.02%
K^+	7.66	-0.13%	0.00%	-1.20%	-0.26%
Ca^{++}	66.33	-0.03%	0.00%	-0.27%	+0.06%
Mg^{++}	71.39	-0.03%	+0.01%	-0.27%	+0.04%
T.Al	6.40	-0.16%	0.00%	-0.10%	-0.64%
Cl^-	226.19	0.00%	0.00%	-0.02%	+0.04%
Alk	20.17	-0.29%	+0.10%	-4.66%	+0.98%
SO_4^{--}	93.07	-0.01%	0.00%	-0.23%	-0.53%
NO_3^-	6.95	0.00%	0.00%	-2.07%	+4.34%
PO_4^-	0.25	0.00%	0.00%	-4.00%	0.00%
O.A.	68.53	-0.02%	+0.10%	-4.22%	+2.68%

Table 7.12: The % change in the simulated streamwater concentrations of the major chemical species (ueq/l), due to adjustment of the weight fractions of litter and fine litter in the upper soil horizon.

change in the simulated concentration of any chemical species is less than 0.3%. The solute concentrations are slightly more sensitive to a 100% change in the amount of fine litter in the upper horizon. However, the changes to the simulated mean annual concentrations are generally below 1.0% and the only change in the simulated mean annual pH is a 0.01 unit increase as the amount of fine litter is halved.

Together with the amount of litter and fine litter in the upper soil horizon, the sensitivity of the simulated streamwater chemistry to a 100% increase or decrease in the fine litter - humus and organic acid breakdown rate parameters was also assessed. From table 7.13 it can be seen that the simulated mean annual streamwater chemistry is generally very insensitive to such changes in each breakdown rate, either singularly or together. Thus the simulated mean annual pH is unchanged and the simulated mean annual concentrations of all other chemical species, except for nitrate, are changed by less 2.0%. For the simulated nitrate concentrations a 100% decrease in both the fine litter - humus and the organic acid breakdown rates leads to a 5.52% increase in concentration and a 100% decrease in the organic acid breakdown rate leads to a 2.6% increase in concentration.

The soil module also contains two other variables to describe the chemical breakdown of litter. These are the percentage of sulphate and ammonia that go to the soil solution as a result of the breakdown of fine litter to humus (LBRATE1) and to the formation of organic acids during humus decay (LBRATE2). As for the other litter breakdown rates, the sensitivity of the simulated

	Calibration values Fine Litter = 0.0670 Organic Acid = 0.0160	Fine Litter - Humus Breakdown Rate		Organic Acid Breakdown Rate		Fine Litter- Humus and Organic Acid Breakdown Rates	
		.0335	.1340	.0.0080	.0.0320	.0335 .0.0080	.1340 .0.0320
pH	5.14	5.14	5.14	5.14	5.14	5.14	5.15
H^+	7.24	0.00%	0.00%	0.00%	-1.16%	0.00%	-1.32%
NH_4^+	1.22	0.00%	0.00%	+0.84%	0.00%	+0.84%	-0.84%
Na^+	193.55	+0.02%	-0.01%	+0.18%	-0.09%	+0.16%	-0.02%
K^+	7.66	+0.26%	-0.13%	+0.13%	-0.13%	+0.26%	-0.21%
Ca^{++}	66.33	+0.84%	-0.46%	+0.32%	-0.17%	+0.36%	-0.19%
Mg^{++}	71.39	+0.58%	-0.03%	+0.32%	-0.15%	+0.36%	-0.18%
T.Al	6.40	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
Cl^-	226.19	+0.43%	-0.22%	0.00%	0.00%	+0.04%	-0.02%
Alk	20.17	+1.04%	-0.74%	+0.74%	-0.24%	+0.88%	-0.54%
SO_4^{--}	93.07	+0.33%	-0.17%	+0.83%	-0.42%	+1.16%	-0.59%
NO_3^-	6.95	+0.44%	-1.78%	+2.61%	-1.03%	+5.52%	-2.03%
PO_4^-	0.25	0.00%	-4.00%	0.00%	0.00%	0.00%	0.00%
O.A.	68.53	-0.60%	+0.30%	-0.16%	+0.89%	-0.16%	+0.89%

Table 7.13: The % change in the simulated streamwater concentrations of the major chemical species (ueq/l), due to adjustment of the fine litter - humus and organic acid breakdown rates.

streamwater chemistry to changes in LBRATE1 and LBRATE2 was assessed by increasing and decreasing the value used in the model calibration by 100%. However, within the model the possible range of values for both LBRATE1 and LBRATE2 is from 0.1 to 0.7. Consequently, the effect of increasing both LBRATE1 and LBRATE2 to the maximum possible value of 0.7 was also assessed. The results of this analysis are presented in table 7.14 which shows that as with the other litter breakdown rates the simulated annual streamwater chemistry is very insensitive to changes in LBRATE1 or LBRATE2. Thus there is no change in the simulated mean annual pH with both LBRATE1 and LBRATE2 at their maximum and minimum possible values. Furthermore, such changes to LBRATE1 and LBRATE2 also result in a general change of less than 0.5% in the simulated mean annual concentrations of the other chemical species.

The soil module also contains the model representation of mineral weathering. In the model mineral weathering is represented by a rate expression of the form shown in Eq 3.8. Within this equation the parameter "a" represents the weathering rate dependence on the soil solution hydrogen ion concentration (WEXP) and is such that a zero value results in a weathering rate independent of the soil solution pH. For the model calibration in Chapter 6 no site-specific data were available for WEXP and consequently, a value of 0.5 as used in the Adirondack application of the model was utilised. As the range of values the model coding will accept for WEXP is from 0.1 to 0.7, the sensitivity analysis involved an increase in WEXP from 0.5 to 0.7 and a decrease to values of both 0.3 and 0.1. From table 7.15 it can be seen that the

	Calibration values Fine Litter = 0.2 Organic Acid = 0.2	% of SO_4 and NH_4 to the soil solution on the breakdown of fine litter to humus (LBRATE1)			% of SO_4 and NH_4 that forms organic acid during humus decay (LBRATE2)		
		.1	.4	.7	.1	.4	.7
pH	5.14	5.14	5.14	5.14	5.14	5.14	5.14
H^+	7.24	0.00%	0.00%	-1.16%	0.00%	0.00%	-1.16%
NH_4^+	1.22	0.00%	0.00%	0.00%	0.00%	0.00%	-0.84%
Na^+	193.55	-0.04%	+0.02%	0.03%	-0.23%	-0.20%	-0.19%
K^+	7.66	-0.13%	0.00%	+0.01%	0.00%	-0.13%	-0.26%
Ca^{++}	66.33	-0.02%	+0.03%	+0.06%	0.00%	-0.13%	-0.27%
Mg^{++}	71.39	-0.01%	+0.03%	+0.06%	+0.01%	-0.14%	-0.28%
T.Al	6.40	0.00%	0.00%	0.00%	0.00%	-0.08%	-0.10%
Cl^-	226.19	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
Alk	20.17	0.00%	-0.05%	-0.10%	+0.10%	-0.05%	-0.15%
SO_4^{--}	93.07	-0.04%	+0.06%	+0.17%	+0.14%	-0.29%	-0.71%
NO_3^-	6.95	0.00%	+0.29%	+0.58%	+0.44%	-0.88%	-1.62%
PO_4^-	0.25	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
O.A.	68.53	-0.60%	-0.02%	-0.02%	+0.10%	+0.10%	+0.15%

Table 7.14: The % change in the simulated streamwater concentrations of the major chemical species (ueq/l), due to adjustment of the fraction of SO_4 and NH_4 ions that either go to the soil solution from the fine litter - humus breakdown or that form organic acid during humus decay.

	Calibration Conc's WEXP = 0.5	WEXP		
		0.7	0.3	0.1
pH	5.14	5.10	5.16	5.35
H^+	7.24	+8.60%	-1.48%	-41.32%
NH_4^+	1.22	+0.84%	-0.85%	-12.26%
Na^+	193.55	+0.19%	-0.29%	-25.23%
K^+	7.66	+0.40%	-0.40%	-21.80%
Ca^{++}	66.33	+1.40%	-0.47%	-40.13%
Mg^{++}	71.39	+1.86%	-0.60%	-38.23%
T.Al	6.40	+0.37%	-0.16%	-19.20%
Cl^-	226.19	-0.51%	-0.03%	+4.03%
Alk	20.17	-5.90%	+0.34%	+21.80%
SO_4^{--}	93.07	+0.59%	0.00%	-0.05%
NO_3^-	6.95	+2.03%	-1.62%	-2.99%
PO_4^-	0.25	0.00%	0.00%	+4.00%
O.A.	68.53	+1.60%	-0.03%	-13.37%

Table 7.15: The % change in the simulated streamwater concentrations of the major chemical species (ueq/l), due to adjustment of the mineral weathering rate dependence on the soil solution hydrogen ion concentrations (WEXP).

simulated mean annual concentrations of all chemical species, except chloride and alkalinity which decrease and phosphate which show no change, increase as a result of an increase in WEXP to 0.7. However, table 7.15 also shows that the extent of the changes in the simulated mean annual concentrations is minor. Thus whilst the hydrogen ion concentration is increased by 8.6%, this is only equivalent to a decrease in the mean annual pH of 0.04 units. Furthermore, apart from a decrease of 5.9% in the simulated alkalinity and 2.03% in the simulated nitrate concentration, the simulated mean annual concentrations of all other chemical species are changed by less than 2.0%.

In contrast a decrease in WEXP by 0.2 units to a value of 0.3 results in a general decrease in the simulated mean annual streamwater concentrations of chemical species, except for an increase in the simulated alkalinity and no change in the simulated sulphate and phosphate. However, as for the increase in WEXP the changes in simulated concentrations are minor. Thus the mean annual pH is only increased by 0.02 units and apart from nitrate, which is decreased by 1.62%, the simulated mean annual concentrations of all the other chemical species are changed by less than 1.0%. It would therefore appear that the simulated streamwater chemistry is very insensitive to changes in the value of WEXP. However, table 7.15 also shows that if the value of WEXP is decreased still further to the minimum possible value of 0.1, considerable changes occur to the simulated annual streamwater chemistry. Thus the mean annual pH is increased by 0.31 units. Furthermore, except for chloride, sulphate, nitrate and phosphate whose simulated concentrations are changed by less than 5.0%, the simulated concentrations are increased by more than 10%. With the alkalinity and base cation concentrations increased by between 20% and 40%.

As the effect of mineral weathering is likely to be important over a longer period than one year, the longer term influence of a change in WEXP was also assessed. For this the simulated mean annual concentrations for the three years 1983 to 1985 as produced by the calibration value for WEXP of 0.5 were compared with the simulated concentrations produced by a WEXP of 0.1. From table 7.16 it can be seen that the changes between the two simulations are similar in 1984 and 1985 to 1983, with a WEXP of 0.1 producing large increases in pH and alkalinity and decreases in base cation and organic acid concentrations. It can also be seen that the difference between the simulated pH increases throughout the three year period. Thus in 1983 the simulated pH for a WEXP of 0.1 is 0.21 units higher than with a WEXP of 0.5, whereas in 1984 the difference is 0.31 units and in 1985 0.77 units. The difference between the organic acid concentrations from the two simulations also increases steadily throughout the three year period whereas for aluminium concentrations the difference is steadily reduced over the three year period. In contrast, the simulated concentrations of the other chemical species, apart from phosphate which shows the same increase in simulated concentration in all three years, show a greater change in concentration for a WEXP of 0.1 in 1984 than either 1985 or 1983.

In upland areas of Scotland, such as Loch Dee, the soil.chemistry can vary greatly over very short distances, thereby rendering a representative value for many soil variables difficult to obtain. Consequently, the sensitivity of the model output was also analysed

	1983		1984		1985	
	Calibration Conc's	% change	Calibration Conc's	% change	Calibration Conc's	% change
pH	5.14	5.35	5.29	5.60	5.28	5.65
H^+	7.24	-41.38%	5.18	-51.51%	5.20	-56.95%
NH_4^+	1.22	-12.26%	1.26	-18.63%	1.18	-17.53%
Na^+	193.55	-25.23%	192.46	-35.56%	138.57	-27.52%
K^+	7.66	-21.80%	7.56	-32.80%	6.16	-27.02%
Ca^{++}	66.33	-40.13%	64.69	-42.84%	39.16	-23.52%
Mg^{++}	71.39	-38.23%	69.57	-37.46%	41.99	-16.43%
T.Al	6.40	-19.20%	7.29	-9.75%	7.32	-3.05%
Cl^-	226.19	+4.03%	224.76	+4.92%	149.20	+4.54%
Alk	20.17	+21.80%	21.26	+54.43%	24.78	+48.26%
SO_4^{--}	93.07	-0.05%	89.71	-0.06%	77.61	-1.61%
NO_3^-	6.95	-2.99%	6.92	-1.52%	3.80	-2.24%
PO_4^-	0.25	+4.00%	0.26	+4.00%	0.30	+7.14%
O.A.	68.53	-13.37%	68.83	-16.09%	70.53	-17.53%

Table 7.16: The % change in the simulated streamwater concentrations of the major chemical species (ueq/l), due to adjustment of the mineral weathering rate dependence on the soil solution hydrogen ion concentrations (WEXP) from 0.5 to 0.1 for the three years 1983 -1985.

for changes to the soil cation exchange capacity (C.E.C.), base saturation, adsorbed sulphate and the initial soil solution solute concentrations.

For the analysis of C.E.C, the calibration values of both the upper (organic) horizon and the lower (mineral) horizons were varied by 100%. From table 7.17 it can be seen that, except for ammonium whose simulated concentration shows a 2.6% increase and 8.4% decrease as the C.E.C of the organic horizon is increased and decreased respectively, the simulated mean annual concentrations are generally insensitive to a 100% increase or decrease in C.E.C. of either the organic or the mineral soil horizons. Thus the percentage change in the simulated concentrations is generally less than +/- 2.0%. Furthermore, table 7.17 also shows the whilst the percentage difference in response between the organic and mineral horizons to such changes in C.E.C. is very low, there is a clear pattern to the different response. Thus the changes to the C.E.C of the organic horizon have a greater effect on the simulated concentrations of ammonia, nitrate and organic acids, whereas changes in the C.E.C of the mineral horizons have a greater effect on the simulated concentrations of the base cations and alkalinity. It can also be seen that if the C.E.C. of both the organic and mineral soils are adjusted together, then the changes in the simulated concentrations fall between the simulated concentrations for each soil altered separately. Furthermore, table 7.17 shows that the 100% increase in the C.E.C. of either the organic or mineral soil leads to an increase in the simulated concentrations of calcium, magnesium and alkalinity and a decrease in the simulated concentrations of the other chemical species. Conversely, the 100% decrease in the

	Calibration values	Cation Exchange Capacity					
	Organic = 150 Mineral =20	Organic Horizon		Mineral Horizon		Organic and Mineral Horizons	
		300	75	40	10	O = 300 M = 40	O = 75 M = 10
pH	5.14	5.14	5.14	5.14	5.14	5.14	5.14
H^+	7.24	0.00%	0.00%	-0.23%	+0.23%	0.00%	0.00%
NH_4^+	1.22	-2.59%	+8.40%	0.00%	0.00%	-2.59%	+4.20%
Na^+	193.55	-0.01%	+0.03%	-0.07%	+0.12%	-0.02%	+0.14%
K^+	7.66	-0.39%	+0.13%	-0.40%	+0.13%	-0.35%	+0.12%
Ca^{++}	66.33	+0.08%	-0.11%	+0.14%	-0.06%	+0.14%	-0.17%
Mg^{++}	71.39	+0.01%	-0.01%	+0.17%	-0.27%	+0.16%	-0.27%
T.Al	6.40	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
Cl^-	226.19	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
Alk	20.17	+0.10%	-0.05%	+0.15%	-0.05%	+0.15%	-0.10%
SO_4^{--}	93.07	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
NO_3^-	6.95	-1.32%	+1.16%	-0.88%	-0.88%	-1.47%	+0.15%
PO_4^-	0.25	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
O.A.	68.53	-0.01%	+0.05%	0.00%	-0.01%	0.00%	+0.05%

Table 7.17: The % change in the simulated streamwater concentrations of the major chemical species (ueq/l), due to a 100% increase or decrease in the Cation Exchange Capacity of the organic and/or mineral soil horizons.

C.E.C. generally results in the reverse pattern. The exception is that whereas a decrease in the mineral soil C.E.C. leads to a decrease in the simulated concentrations of nitrate and organic acids and an increase in hydrogen ion, a decrease in the C.E.C. of the organic soil leads to an increase in the simulated concentrations of nitrate and organic acids and a decrease the hydrogen ion concentrations

Together with the soil C.E.C. the adsorbed concentrations of the major cations are also likely to vary considerably within an upland area such as Loch Dee. Consequently, the soil base saturation, (ie the adsorbed concentrations of sodium, potassium, calcium, magnesium and ammonia), of each soil horizon was increased or decreased by 10% and 50% from the values used in the calibration procedure, with the results presented in table 7.18. From this it can be seen that an increase in the base saturation leads to a slight increase in the simulated base cation concentrations and alkalinity and a slight decrease in all other simulated species, except for chloride, sulphate and phosphate where there is no change to the simulated concentrations. In contrast, a decrease in the base saturation shows the reverse pattern. However, table 7.17 also shows that such changes as exist in the simulated mean annual concentrations are very minor. Thus the simulated mean annual pH is unchanged by a 10% change in base saturation and only shows a 0.01 unit change for a 50% change in base saturation. Furthermore, the simulated concentrations of all the other chemical species are changed by less than 2.0%, with the general change less than 0.5%.

The sensitivity of the simulated solute concentrations to changes in the initial soil solution concentrations was analysed for two

	Calibration values Organic 16% Mineral 7%	Base Saturation			
		(*10%) O = 17.6% M = 7.7%	(*50%) O = 32.0% M = 14.0%	(/10%) O = 14.4% M = 6.3%	(/50%) O = 8.0% M = 3.5%
pH	5.14	5.14	5.15	5.14	5.13
H^+	7.24	+0.88%	-2.25%	+0.59%	+1.90%
NH_4^+	1.22	-0.85%	-1.71%	+0.84%	+1.86%
Na^+	193.55	+0.03%	+0.06%	-0.03%	-0.07%
K^+	7.66	+0.34%	+0.03%	-0.01%	-0.03%
Ca^{++}	66.33	+0.15%	+0.23%	-0.09%	-0.35%
Mg^{++}	71.39	+0.15%	+0.24%	-0.17%	-0.39%
T.Al	6.40	-0.34%	-1.08%	+0.17%	-1.55%
Cl^-	226.19	0.00%	0.00%	0.00%	0.00%
Alk	20.17	+0.05%	+0.63%	-0.29%	-0.84%
SO_4^{--}	93.07	0.00%	0.00%	0.00%	0.00%
NO_3^-	6.95	-0.15%	+1.49%	-0.07%	+1.34%
PO_4^-	0.25	0.00%	0.00%	0.00%	0.00%
O.A.	68.53	-0.03%	-1.34%	-0.22%	+1.68%

Table 7.18: The percentage change in the simulated streamwater concentrations (ueq/l) of the major chemical species, due to a 10 and 50% increase and decrease in the adsorbed base cation concentrations (as % C.E.C.) within both organic and mineral soil horizons.

reasons. Firstly, the calibration procedure reported in chapter 6 indicated that the initial soil solution concentrations were major calibration parameters. Secondly, field data indicated that the monthly soil solution concentrations vary greatly both spatially and temporally. However, due to the number of chemical species simulated and the interdependency between the simulated concentrations, the analysis was limited to changes in the soil solution base cation and sulphate concentrations. These chemical species were chosen as a result of the perceived importance of their soil solution concentrations in the determination of streamwater acidity, thus increased base cation concentrations can reduce the impact of acid deposition whereas sulphate is a mobile anion whose presence may increase streamwater acidity. For both the base cations and sulphate the optimised calibration concentrations were increased and decreased by 10%, with the effects on the simulated mean annual streamwater concentrations presented in table 7.19.

From table 7.19 it can be seen that the simulated streamwater chemistry is very sensitive to such a change in the initial soil solution base cation concentrations. Thus a 10% decrease in the initial base cation concentration results in over a 250% increase in the simulated mean annual hydrogen ion concentration, a change equivalent to a decrease in pH of 0.40 units. Furthermore, the simulated concentrations of the other chemical species are also greatly affected by such a change. Thus there is a 10% decrease in the simulated mean annual streamwater base cation concentrations, except for sodium where the change is lower at 5.0%. Such a change to the initial soil solution also results in a 20% decrease in the simulated mean annual alkalinity and an 18% increase in the

	Calibration conc's	Initial Soil Solution Concentrations (ueq/l)			
		Base Cations		Sulphate	
		(-10%)	(+ 10%)	(-10%)	(+ 10%)
pH	5.14	4.74	5.39	5.24	4.90
H^+	7.24	+277.84%	-43.29%	-28.28%	+175.22%
NH_4^+	1.22	0.00%	0.00%	+0.84%	-0.84%
Na^+	193.55	-5.47%	+5.94%	+0.03%	-0.06%
K^+	7.66	-13.26%	+10.66%	+0.66%	-0.40%
Ca^{++}	66.33	-11.84%	+10.61%	+1.17%	-1.41%
Mg^{++}	71.39	-12.55%	+11.42%	+1.77%	-1.48%
T.Al	6.40	+17.86%	-18.08%	-5.42%	+5.10%
Cl^-	226.19	0.00%	0.00%	0.00%	0.00%
Alk	20.17	-18.14%	+23.18%	+12.13%	-7.58%
SO_4^{--}	93.07	0.00%	0.00%	-9.58%	+10.48%
NO_3^-	6.95	-0.58%	+0.15%	+0.29%	-0.88%
PO_4^-	0.25	0.00%	0.00%	-4.00%	-4.00%
O.A.	68.53	+8.61%	-1.34%	+4.19%	-1.50%

Table 7.19: The % change in the simulated streamwater concentrations of the major chemical species (ueq/l), due to a 10% increase or decrease in the initial soil solution concentrations of both the organic and mineral soil horizons.

simulated aluminium concentration. However, the other major anions, apart from nitrate, show no change at all in the simulated concentrations, and the change in the simulated nitrate concentration is less than 1.0%.

In contrast a 10% increase in the initial soil solution base cation concentration results in a reversed pattern of change in the simulated streamwater concentrations. Thus there is is a decrease of 43.3% in the simulated mean annual hydrogen ion concentration, equivalent to an increase of 0.25 units in pH, together with an increase of over 10% in the simulated concentrations of calcium. magnesium and potassium. Furthermore, as for the 10% decrease in the soil solution base cation concentration there is no change in the simulated concentrations the major anions, apart from alkalinity whose simulated concentration is increased by 23.2%.

The simulated mean annual hydrogen ion and alkalinity concentrations are only slightly less sensitive to the 10% change in the initial soil solution concentration of sulphate. However, the pattern of change in concentrations is reversed. Thus a 10% increase in the initial soil solution sulphate concentration results in an decrease of 0.24 units in the simulated pH and an increase of 7.6% in the simulated alkalinity. The increase in the soil solution sulphate concentration is also reflected in the simulated mean annual streamwater sulphate concentration which is increased by 10.5%.

A 10% decrease in the initial soil solution sulphate concentration has an influence of equivalent size on the simulated streamwater concentrations, but with the pattern of change reversed. For instance the simulated mean annual pH is increased by 0.10 units and the simulated sulphate increased by 9.6%, whilst the simulated alkalinity is decreased by 12.1%. The simulated concentrations of the other chemical species are, however, far less sensitive to a 10% change in the soil solution sulphate concentration. Thus apart from aluminium whose simulated streamwater concentrations are subject to a 5.0% change, the general percentage change in the simulated streamwater concentrations is less than 2.0%.

7.3 *DISCUSSION*

7.3.1 *Hydrological Variables*

The variable within the hydrological sub-model to which this application of ILWAS is most sensitive is the depth of the soil horizons. The sensitivity of the simulated streamwater chemistry, to changes in the depth of the soil horizons, is related to the changes which also occur in the simulated flow pathways through the catchment, and in particular to the change in flow through the lower, mineral horizons. Thus an increase in the depth of the lower soil horizons which results in a decrease in the simulated flow through the upper horizon and a large increase in the simulated flow through the lower horizons, also produces a large decrease in the simulated streamwater acidity together with an increase in the simulated base cation and alkalinity concentrations. In contrast, a proportionally greater decrease in the depth of the upper horizon, despite producing a large decrease in the simulated flow from the upper horizon, has very little influence on either flow through the lower horizons or the simulated streamwater chemistry. This insensitivity of the simulated streamwater chemistry to changes in the simulated flow from the upper horizon is probably a reflection of greater transit time for the flow through the upper horizon. The greater transit time reduces the opportunity for reactions to proceed to equilibrium and thereby neutralise the acidity of the incoming precipitation.

The analysis therefore indicates that for ILWAS successfully to simulate the flow pathways through a catchment, and hence the catchment streamwater chemistry, the depth of the mineral soil horizons in particular, must be known to a reasonable extent throughout the study catchment. This requirement may easily be fulfilled in lowland catchments where the depth of the soil profile is reasonable consistent throughout the catchment. However, in upland areas such as Loch Dee, the soil profile depth, and hence depth of the individual horizons, can vary considerably over very short distances. Consequently, for ILWAS to perform adequately in these upland areas an initial requirement will be for a detailed soil survey to be undertaken.

Apart from the depth of the soil horizons, the only other hydrological variable to exert a noticeable influence on either the simulated hydrology or chemistry, is the horizontal permeability of the lower soil horizons. The upper soil horizon horizontal permeability has little effect on either the simulated hydrology or chemistry. The influence of the lower soil horizon horizontal permeability is important in that it is the lower transit time of the flow through the lower soil horizons that is primarily responsible for neutralising precipitation acidity. Thus an increase in the horizontal permeability of the middle soil horizon which leads to an increase in flow through that horizon and a decrease in flow through the upper horizon also results in an increase in the simulated mean annual pH and alkalinity. In contrast, an increase in the horizontal permeability of the lower horizon only has a significant effect on the simulated flow through the lower horizon. However, the simulated pH and alkalinity are again increased, albeit by a slightly lower extent than with a change in the horizontal permeability of the middle horizon. This change to the simulated streamwater chemistry as a result of the change in simulated flow through the lower horizon indicates that it is the flow through the lower horizon, in particular, that is responsible for much of the neutralisation of precipitation.

Actual site-specific values for the horizontal permeability of the lower horizons are therefore required for an accurate calibration of the model. Unfortunately, truly representative values for horizontal permeability are very difficult, if not impossible, to derive at a catchment scale. However, the horizontal permeability can easily be optimised either by a comparison of the simulated and observed M.D.F.s or by minimising the RMSE between the simulated and observed M.D.F.s. Consequently, initial values for the horizontal permeability of each layer obtained either on the basis of site measurements, or more easily from published material for similar soils to the study site, may then be treated as calibration parameters to be optimised.

As has already been noted for horizontal permeability , representative values are also very difficult to obtain for the other two variables that describe the hydrological response of the soil, (ie the S.M.C. and the field capacity). Furthermore, the sensitivity analysis indicates that the model's hydrological and chemical outputs are both very insensitive to changes in either the S.M.C. or the field capacity, changes of 20% in the value of either variable having very little influence on the simulated hydrology or chemistry. Therefore, to a greater extent than the horizontal permeability, both the S.M.C. and the field capacity may be considered as calibration parameters whose initial values can be derived from published data or from a few site measurements.

This analysis also supports Chen et al. (1983) who suggest that it is the difference in value between the S.M.C. and field capacity that is important, rather than the absolute values of the two variables. Thus the sensitivity analysis shows that an increase in the difference between the two variables due to either a decrease in S.M.C. or an increase in the field capacity of any horizon have almost the same effect on the simulated outputs. This similarity occurs due to the model assumption that the flow through any soil layer is zero at and below field capacity and increases linearly with soil moisture content to the S.M.C., thus reinforcing the decision to treat both the field capacity and S.M.C. as calibration parameters.

Both the simulated hydrology and chemistry outputs are very insensitive to changes in the root distribution of roots between the soil horizons. Consequently, the distribution can be also considered a calibration parameter to be optimised. The values for the distribution used in this study can be considered a reasonable initial estimate, if site specific data are not available, as the majority of roots are usually found within the upper 25cm of the soil profile (Bloom and Grigal 1985).

The model outputs are even more insensitive to changes in the stream parameters tested, the Muskingum routing coefficients KR (the travel time of the stream segment) and MX (the Muskingum weighting factor). Thus the only observable changes greater than 0.01% due to a 100% change in KR are in the simulated runoff, the simulated chemistry being totally insensitive to such changes. Furthermore, there are no changes greater than 0.01% in either the simulated hydrology or chemistry when MX is varied through the possible range of values. This general insensitivity is surprising as the two routing coefficients determine the storage volume in each stream segment. The storage volume will in turn determine both the outflow from the stream segment and the amount by which the concentrations of the simulated chemical species are concentrated or diluted. The insensitivity may, however, be explained by the travel time of each segment being far lower than the daily timestep used for the model simulations. Consequently, in study areas where the travel time of the stream segments is shorter than the one day model timestep the simple procedure used in this study to determine an initial value for KR can be considered acceptable, if field data are not readily available. In this procedure an estimate of KR was derived by dividing the segment axial length by the segment mean velocity, the mean velocity, in turn, being derived from the average segment cross-section and slope. For MX, the value in most river channels falls between 0.1 and 0.3 (Dunne and Leopold 1978). Therefore an initial value of 0.20 will be adequate given the total insensitivity of the model outputs to changes in this parameter.

Overall the simulated runoff and runoff chemistry are generally insensitive to changes in the hydrological variables examined. Indeed, for the simulated hydrology apart from the soil horizon depth, changes in the variables examined serve primarily to adjust the instantaneous calibration of the model. It would therefore appear that the primary determinant of the simulated hydrological regime is the initial division of the catchment into drainage sub-catchments. The change in soil horizon depth serves to alter this initial division of the catchment, hence the large change in the simulated output. As the catchment division is determined by easily available topographic data, a reasonable match between the simulated and observed M.D.F.s is quickly obtained by adjustment of the evapotranspiration factor which matches the cumulative simulated and observed flows. Consequently, all of the variables that describe the hydrological response of the soils and stream segments can be considered as calibration parameters to be optimised.

7.3.2 *Chemical Variables*

Of the chemical variables studied only two, the initial soil solution concentrations and the weathering rate dependence on the soil solution hydrogen ion concentration, have any influence on the simulated streamwater chemistry.

The sensitivity of the simulated streamwater chemistry to changes in the initial soil solution concentration is a result of the interaction of several factors. For example, adjustment of the initial values of the base cations or acid anions will result in a change either in the cation selectivity coefficients or the anion adsorption coefficients and this will determine the simulated soil solution concentrations. Furthermore, as within the ILWAS model alkalinity is derived as the difference between the sum of base cations and the sum of acid anions, adjustment of the simulated concentrations of base cations or acid anions will of necessity lead to a change in the simulated alkalinity. Subsequently, as pH is a function of alkalinity, a change in the simulated alkalinity will lead to a change in the simulated pH. A change in the simulated pH will in turn alter the value of the Ca:H selectivity coefficient which will further adjust the simulated concentration.

The use of the same initial soil solution concentrations in each of the drainage sub-catchments fails to account for the considerable spatial variability in the soil solution concentrations, which is found in upland areas such as Loch Dee. Such a failure may lead to considerable errors in the choice of cation selectivity or anion adsorption coefficients for a particular sub-catchment resulting in errors in the simulated chemistry of drainage waters from that sub-catchment. The sensitivity analysis therefore indicates that the initial soil solution concentrations for the study catchment need to be derived carefully paying particular attention to the spatial patterning present.

Apart from the initial soil solution concentrations, the only other chemical variable examined which has a significant effect on the simulated streamwater chemistry is the mineral weathering rate dependence on the soil solution hydrogen ion concentration (WEXP). The sensitivity of surface water chemistry to changes in mineral weathering rates is due to the associated change in the release of base cations to the soil solution. Hence Schecher and Driscoll (1988) report that watershed to watershed variations in lake acidity in the Adirondacks are due to differences in base cation release from mineral weathering rather than strong acid inputs or the retention of acid anions. Consequently, given this sensitivity of surface water chemistry to changes in WEXP, a site specific value of WEXP for each mineral is necessary. Moreover, a site specific value for WEXP is required if the model simulation is effectively to be constrained, for any errors in the simulated streamwater chemistry derived from inaccurate estimates of WEXP will be inseparable from, and compounded by, the errors associated with determinations of the soil solution pH.

The insensitivity of the simulated streamwater chemistry to changes in the base saturation is unexpected as a change in the adsorped base cation concentrations should alter the cation selectivity coefficients. This insensitivity is probably attributable to the fact that all the base cation concentrations were adjusted simultaneously by the same amount. Consequently, the base cation selectivity coefficients which are expressed relative to calcium will remain unchanged and hence there will be no change to the streamwater solute concentrations. If, however, the adsorbed ion concentrations were to be altered on an individual basis a change in the selectivity coefficient would occur. This in turn would result in a change in the soil solution concentration of individual chemical species and therefore to changes in the simulated soil solution pH. The resultant changes in the soil solution pH will occur as the simulated pH is partially derived from the simulated alkalinity which in turn is partially derived from the difference between the simulated base cations and acid anions. Ultimately the changes in the soil solution pH and alkalinity will be reflected by changes in the simulated streamwater pH and alkalinity. Any such changes to the simulated streamwater chemistry are particularly likely to occur with alterations to the adsorbed calcium concentrations, as all the selectivity coefficients are expressed relative to calcium. Similarly, the simulated streamwater chemistry may also be expected to be sensitive to changes in the adsorbed anion concentrations. This arises since a change in the adsorbed concentration will lead to a change in the anion adsorption coefficient and hence, as for the base cations, this will result in a change to the simulated streamwater chemistry.

In contrast the simulated streamwater chemistry is very insensitive to the other soil variables tested, which are essentially responsible for describing the breakdown of litter. However, the lack of sensitivity to these parameters is a considerable aid to the application of the model, because with the possible exception of the percentage by weight of litter and fine litter, all of these variables, are very difficult to measure. Consequently, all of these variables can be treated as calibration parameters whose initial values can be obtained from other studies.

The simulated streamwater chemistry is similarly insensitive to changes in the variables that describe the canopy chemical processes. Indeed the only canopy chemical variable examined which had any significant effect on the simulated streamwater chemistry is the leaf and trunk chemical composition. However, the chemical composition of leaves and trunks varies not only with species, but with age and position of the leaf on the plant, soil type and trunk size. Consequently, it is very unlikely that any catchment acidification study, however detailed, will be able to gain totally accurate estimates of the leaf or trunk chemical composition. Therefore, within the model the leaf and trunk chemical compositions must be considered as calibration parameters, with estimates for the initial input values obtainable from botanical studies.

In contrast, the sensitivity analysis indicates that the simulated streamwater chemistry is totally insensitive to changes in the foliar exudation amplification factors. These amplification factors are included in the model in order to simulate the greater observed leaf exudation of certain chemical species, especially potassium and magnesium. The model documentation states that the value of the exudation factor for any chemical species is derived by matching the simulated and observed throughfall chemistry. The exudation factors may indeed influence the throughfall chemistry, though the lack of site specific data for Loch Dee rendered this hypothesis too difficult to examine. If, however, the analysis and/or prediction of streamwater chemistry is the rationale behind the utilisation of the model, the insensitivity of the simulated streamwater chemistry to changes in the exudation factors, indicates that the exudation factors are redundant and can be set to unity for each chemical species.

The other canopy chemistry variable tested, namely the monthly litterfall rate, like the litter breakdown rates, has only a very slight influence on the simulated streamwater chemistry. Consequently, the monthly litterfall rates may be treated as a calibration parameter whose value can be optimised during the model application. Moreover, as with the variables that describe litter breakdown, this insensitivity eases the application of ILWAS due to the immense difficulties in obtaining representative estimates of the monthly litterfall rate.

7.4 *CONCLUSION*

In conclusion the sensitivity analysis indicates that the accuracy of the simulated hydrological response is primarily determined by the initial division of the catchment into drainage sub-catchments. The hydrological variables within the soil and stream sub-modules serve to adjust the instantaneous response of the simulated hydrology and are considered to be calibration parameters whose initial values can be estimated from existing literature. Consequently, for a satisfactory calibration of the hydrological module site-specific data are only required for the variables that describe the topography and soil depth of each sub-catchment.

The majority of chemical parameters in the model also have very little influence on the simulated streamwater chemistry. However, this insensitivity of the simulated streamwater chemistry may, in fact, ease the application of the model at many sites. This will occur as many of the chemical variables are rarely, if ever, measured in catchment acidification studies. Therefore the utilisation of the model will be more efficient if initial estimates of the variable values can be taken from previous studies and then optimised during model calibration, rather than having to be determined on the basis of detailed field studies.

The analysis also indicates that detailed field studies of the soil and soil solution chemistry, together with site-specific data on mineral weathering rates will be required if the model is to be adequately validated for a study catchment. However, representative values for these variables are very difficult to obtain in upland catchments, such as Loch Dee, due to the considerable spatial variability in the soils. The inability of the model to reproduce the observed streamwater chemistry of either the Dargall Lane Burn or the Green Burn, as reported in Chapter 6, can therefore be primarily ascribed to the lack of detailed soil and mineralogical data at Loch Dee. Consequently, the ILWAS model will only be usable in conjunction with a wealth of detailed hydrochemical analysis which is very rarely attempted. The general lack of the necessary hydrochemical input data will particularly affect the ability of the model to analyse the results of within catchment management practices. It is the ability to analyse these practices, such as the planting of a 'buffer zone' of deciduous trees around a catchment's water courses, that is perceived as a major advantage of ILWAS over other hydrochemical models. However, given the general lack of satisfactorily detailed input data the opportunities to utilise ILWAS as a management tool to help mitigate the effects of anthropogenically derived changes in surface water chemistry will be extremely limited. Therefore the ILWAS model will rarely, if ever, be able reliably to predict the possible impacts of acid deposition and/or land-use changes on the streamwater chemistry of a particular catchment.

However, the results from the sensitivity analysis point to the importance of catchment topography, soil depth and cation and anion selectivity coefficients, together with the lack of influence of the other variables in the ILWAS model. They further imply that the hydrochemical processes within a catchment that determine the surface water chemistry can be reproduced by a relatively few variables. Consequently, the analysis suggests that the wealth of detail within the ILWAS model, is probably not necessary in order to predict the changes in surface water chemistry that may occur in response to changes in atmospheric deposition or land-use management practices. Such a conclusion is supported by the recognition of the importance of the same variables in the conceptual basis of hydrochemical models derived from other study areas (eg the Birkenes model from Norway, Christophersen and Wright 1982 and MAGIC from North Eastern U.S.A. Cosby et al. 1985.) In particular, both these other models recognise the importance of the soil depth together with the cation and anion selectivity coeffecients. These two models have been the most successful to date, accurately reproducing the observed streamwater chemistry at catchments outwith their development areas. It may be thus concluded that the complexity that ILWAS contains is not required for successful hydrochemical modelling. Future research in this field might well more profitably lie in the extension and further development of models of the Birkenes and Magic type which have far less detailed input data requirements and are conceptually much less sophisticated than ILWAS.

8: CONCLUSION

8.1 *SUMMARY*

This conclusion addresses two main topics; firstly, it attempts to draw together the discussion which has arisen from the three immediately preceding chapters, and secondly, identifies future lines of enquiry which may help to improve the usefulness of the ILWAS model, in particular, and hydrochemical models, in general, for investigating the process of acidification in upland Britain.

Acidification of surface waters is perceived as one, if not the, major environmental problem affecting the natural environment in upland Britain. By the use of hydrochemical budgets and a mathematical simulation model, the research reported in this thesis has tried to investigate the hydrochemistry of an upland catchment which is already subject to acidification in Southwest Scotland. The results of the research can be best summarised by reference to the initial objectives outlined in Chapter 1, and repeated below:

to determine empirically, through the use of hydrochemical budgets, the spatial and temporal variations in the major factors that govern the hydrochemical behaviour of upland catchments.

The work in Chapter 5 indicates that the major controls on the contrasting hydrochemistry of the study sub-catchments at Loch Dee are catchment topography, underlying geology and land-use management practices. The influence of catchment topography is most clearly seen in the moorland Dargall Lane sub-catchment where the rugged topography of this catchment combined with the general lack of a minerogenic soil is such that flow is primarily routed through the organic horizons of the peaty soils. The consequent low release of base cations and high release of aluminium, together with the slight neutralisation of precipitation acidity, indicates that cation exchange processes in the catchment are dominated by the exchange of H^+ ions in solution for Al^{3+} ions on the exchange complex.

In contrast, the hydrochemical response of the 70% forested Green Burn sub-catchment is far more complex, with high outputs of base cations and alkalinity as well as high outputs of acidity and aluminium. This complex response can be related to the land-use management techniques utilised in the sub-catchment and in particular, the improved drainage associated with the pre-afforestation ploughing and drainage. Thus stormflow is evacuated more rapidly from the sub-catchment, thereby reducing the opportunity for neutralisation of acid precipitation. In contrast during low flow periods baselow occurs primarily in the lower part of the drainage ditches and therefore has been routed through any of the exposed minerogenic soil. Thus, there is greater opportunity for neutralisation of acidity to occur, with a subsequent greater release of base cations and alkalinity.

The geological control is most clearly seen in the 30% forested White Laggan sub-catchment where the presence of unmetamorphosed sediments in the headwaters of the catchment results in the lowest acidity and aluminium outputs recorded at Loch Dee together with high outputs of base cations and alkalinity. It is therefore considered that at all flow levels the dominant cation exchange process in the White Laggan sub-catchment is the exchange of hydrogen ions in solution for base cations on the soil exchange complex. This is in contrast to the Green Burn where such an exchange only occurs at low flow levels.

The hydrochemical budgets also suggest that the effectiveness of catchment and forestry management techniques in reversing the effects of acid precipitation and coniferous afforestation are minimal at the present time. Any possible influences on the hydrochemical response of the study sub-catchments are too small to separate from the primary determinants of catchment hydrochemistry.

Temporally, the annual hydrochemical budgets show a decline in sulphate loadings to the Loch Dee catchment over the study period; a decline that reflects the reduction in power station emissions during the industrial recession of the early 1980's. However, the sulphate losses do not show this pattern and it is therefore suggested that the dry deposition of sulphate and attendant inputs of acidity may vary considerably from year to year. Annual variations in catchment losses of bases and nutrients are, in contrast, primarily related to the amount of precipitation, with both outputs and inputs being greater in the"wetter" years.

On a monthly timescale variations in the input loadings and solute outputs show a clear seasonal pattern primarily related to the amount of precipitation. The generally maritime origin of the prevailing airstream also results in the high input loadings of the seasalts sodium and chloride to the catchment, particularly in the wetter winter period. Furthermore, the importance of the atmospheric loadings in the determination of streamwater chemistry , particularly in the winter period, is also clearly indicated by the general dominance of seasalts in the solute outputs. However, the major feature of the monthly budgets is the physical storage of chloride within the catchments. It is suggested that such storage has serious implications for short term hydrochemical budgetary studies, particularly for the estimation of dry deposition inputs to catchments. Moreover, such chloride storage has serious implications for those hydrochemical simulation models which assume that the behaviour of chloride can be safely neglected.

to evaluate the ability of the Integrated Lake Watershed Acidification Study model (ILWAS) to simulate, and predict changes to, the surfacewater chemistry of moorland and forested upland catchments in Southwest Scotland.

With an improved understanding of the major factors that govern the hydrochemical response of the study sub-catchments, as a result of the analysis of the hydrochemical budgets, the ILWAS model was then applied to both the moorland Dargall Lane and the forested Green Burn sub-catchments. The work in Chapter 6 shows that the main discrepancy between the simulated and observed M.D.Fs is the inability of the model to reproduce the very large flows on the Dargall Lane in early 1984, a discrepancy attributed to an extreme snowmelt event that followed a large unmeasured snowfall over the upper part of the Dargall Lane sub-catchment. The only other discrepancy is the general inability of the hydrological module of the model to reproduce discrete summer stormflows, a feature for which no reasonable explanation was evident. However, despite these problems, the simulated hydrological response for both catchments was, in general, considered to reproduce accurately the observed hydrological response of both study sub-catchments. This success is attributed to the general simplicity of the hydrological sub-routine and the small number of input variables whose values need to be optimised.

The sensitivity analysis indicates that it is the initial division of the catchment into drainage sub-catchments that primarily determines the accuracy of the simulated hydrological response. The instantaneous response of the simulated hydrology is adjusted by the hydrological variables within the soil and stream sub-modules which are considered to be calibration parameters whose initial values can be estimated from the existing literature. Consequently, for a satisfactory calibration of the hydrological module site-specific data are only required for the variables that describe the topography and soil depth of each sub-catchment.

In contrast, the ILWAS simulation of the streamwater chemistry for both the Dargall Lane and the Green Burn is very poor, particularly on a monthly timescale, when the simulated concentrations of the chemical species showing considerable smoothing, so that little of the observed monthly variability is present in the simulations. This smoothing is considered as being primarily due to the utilisation of mean monthly precipitation quality data to drive the model. Such averaging of the input data will serve to smooth the streamwater response before the model simulation occurs. However, the smoothing may also be partially attributable to the inability of the hydrological module to simulate runoff processes generated by soil macropores in the Dargall Lane and forest ditches in the Green Burn, both of which serve to increase the flashiness of the study sub-catchments.

The simulated streamwater hydrogen ion concentrations, (the chemical species of major importance in the study of acidification), are simulated particularly poorly for both the Dargall Lane and Green Burn sub-catchments. This poor simulation is primarily attributed to the lack of accurate input data for the soil and soil-solution chemistry. In particular, due to the lack of site specific data for T.I.C. and organic acid concentrations, the simulated soil-solution concentrations of both these species cannot be accurately constrained. Consequently, as the simulated streamwater hydrogen ion concentration is partially derived from the simulated soil-solution T.I.C. and organic acid concentrations, the subsequent inaccuracies in the simulated concentrations of these species will be reflected in an inaccurate simulation of streamwater hydrogen ion concentrations.

Errors in the simulated hydrogen ion concentration are also ascribed to the inaccurate simulation of the major cations and anions, since the simulated hydrogen concentration is also dependent on the simulated alkalinity, which in turn is partially derived as the sum of base cations minus the sum of strong acid anions. The inaccuracies in the simulated streamwater cation and anion concentrations are attributed to the "lumping" of the observed soil and soil-solution data, whereby data from one part of the catchment is used to describe the the soil and soil- solution chemistry of the entire catchment. Due to such "lumping" the model will be unable to reproduce the considerable spatial variability in the soil and soil-solution chemistry, thereby producing errors in the simulated soil solution chemistry and hence the simulated streamwater chemistry.

The importance of detailed and accurate site-specific soil-solution chemical data is also shown by the sensitivity analysis of Chapter 7. This sensitivity analysis reveals that it the soil-solution chemistry, together with the mineral weathering rate dependence on the soil solution pH (WEXP), which are the only chemical variables that have any significant influence on the simulated streamwater chemistry. Consequently, site-specific values of WEXP for each mineral in the soil are also required if the model simulation is to be effectively constrained. The lack of response of the simulated streamwater chemistry to changes in the soil chemistry, in particular the base saturation, is ascribed to the analytical procedure whereby the adjustment of all the cation concentrations by the same percentage will have no effect on the cation selectivity coefficients and therefore no effect on the simulated streamwater chemistry.

The sensitivity analysis further indicates that the simulated streamwater chemistry is very insensitive to changes in all the other chemical variables examined. Therefore, except for the initial soil chemistry, soil solution chemistry and WEXP, all of the time-dependent chemical variables can be treated as calibration parameters whose initial values can be obtained from the literature. It is therefore concluded that only a small number of the model input variables are important in explaining the observed behaviour of the system under study. This limitation has also been identified for several other complex environmental simulation models by Young 1983. Similarly Beck (1983) has used the term 'surplus content' to define such behaviour in a model. Furthermore, within ILWAS those variables which determine the system response and for which site-specific values are required (the soil mineralogy and soil-solution chemistry) commonly exhibit considerable spatial variability in upland catchments such as Loch Dee. Therefore a prerequisite for the utilisation of ILWAS, in such areas, will be a very detailed and expensive soil survey. Consequently, the use of ILWAS as a management tool for understanding and predicting the future impacts of anthropogenic changes on catchment surface waters will be limited to a few very well-studied sites.

As well as the 'surplus content' of the model and the general non-availability of detailed soil and mineralogical data, the research in this thesis has identified several other problems with ILWAS, which further reduces its usefulness as a tool for understanding surface water chemistry. Thus whilst the sensitivity analysis indicates that the initial compartmentalisation of the study catchment alone is able to produce a reasonable simulation of the hydrological response of the study catchments, it is doubtful that such a simplistic hydrological model will accurately simulate the actual flow pathways through the catchment, a consideration that may also account for the poor simulation of the hydrochemical response of the Dargall Lane and Green Burn. Consequently, validation of the model's structure and predictions will require a detailed hydrogeological knowledge of the catchment's behaviour, such data being rarely available. Furthermore, such a lack of detailed hydrogeological data will result in many of the hydrological variables becoming calibration parameters. The resultant large number of poorly constrained hydrological variables may account for a 'reasonable' fit of catchment outflows, but the simulated pathways through the catchment may bear little resemblance to reality. Subsequently, if the simulated flow pathways are incorrect the simulated chemistry will bear little resemblance to that observed also.

However, given the number of input parameters in the chemical module of ILWAS that can effectively be treated as calibration parameters, the hydrochemical reponse of the study catchment can easily be reproduced for the calibration period by adjustment of each of these input parameters. Such a procedure, however, is very unlikely to result in a unique calibration of the model. A unique calibration is further rendered unlikely by the number of arbitary calibration parameters built into the model. All of these parameters also have to be optimised for each model application thereby reducing the chances of obtaining a unique calibration still further. A further optimisation problem, which is not unique to ILWAS, concerns the choice of optimisation functions. Thus different optimisation methods may give different optimum values for each of the individual calibration parameters, but all of which may result in an reasonable calibration. Overall these optimisation problems are such that, for all practical purposes, a unique calibration of the model is impossible to obtain and therefore the reliability of the predictions must be considered as zero. Consequently, it is concluded that the failure to validate the ILWAS model for the Loch Dee catchments can be primarily attributed to the unlikelihood of obtaining a unique calibration of the model.

As well as the problems of obtaining a unique calibration, this research has also identified several problems with the conceptual basis of the model. Firstly, there is an inconsistency between the horizontal and vertical spatial resolution. Thus whereas the soil profile can be described in great detail, if the data are available, the spatial heterogeneity of soil characteristics is only broadly indicated by the use of drainage sub-catchments. The use of constant hydraulic and chemical soil properties within these sub-catchments may be acceptable in lowland areas with spatially consistent soil characteristics. But it is doubtful whether such constant properties can accurately reproduce the considerable spatial variability of upland soils. Secondly, many of the biochemical processes simulated in the model are poorly understood and the ILWAS formulations are at best 'guesstimates'. Thus within the canopy module the exudation rate is assumed to be proportional to the gross chemical composition of the leaf and the vegetation respiration rate. However, there is no biological evidence for these linkages. Furthermore the canopy module fails to include ion exchange processes which provide an important method by which the composition of throughfall may be altered (Skeffington pers. comm.). Thirdly, the model attempts to simulate the short term hydrochemical response of catchments. However, it is driven by the mean monthly precipitation chemistry and this may mask important daily variations in streamwater chemistry that occur as a result of day to day variations in precipitation inputs. Thus in its present form the model can only be considered suitable for examining the hydrochemical response of a catchment at the monthly time-scale or greater.

The research in this thesis has shown that hydrochemical budgets can provide a detailed insight into the mechanisms that determine spatial and temporal variations in streamwater chemistry. Unfortunately, the inability of the ILWAS model to reproduce the observed streamwater chemistry precluded using the model to test some of the hypothesis suggested by the empirical study. Furthermore, the sensitivity analysis indicates that in common with many other large scale environmental system models a unique calibration of ILWAS will be impossible to achieve at any site due to the number of variables for which accurate data cannot be obtained. The research also suggests that complex environmental models such as ILWAS contain too much uncertainty to be of use as tools for managing the hydrochemical processes, associated with surface water acidification. However, this is not totally to dismiss ILWAS, for it is likely that the model will be of value as an explanatory tool for examining conceptual ideas about the hydrochemical processes that determine acidification. Overall, despite the fact that the application of ILWAS to the Loch Dee catchments has substantially "failed", the attempt has been of value to the hydrochemical modelling community in that it has provided the first detailed test of the model outside it's development ground.

8.2 FUTURE RESEARCH

This thesis has addressed two principal areas of research from which a number of possible pathways for further research can be identified. The first is related to the use of hydrochemical budgets to investigate hydrochemical processes. The second avenue is concerned with the use of simulation models to understand and manage hydrochemical processes and in particular the linkage of empirical field investigations and modelling techniques.

The main avenue of further research identified from the hydrochemical budgets involves the determination of dry deposition inputs to a catchment. The chloride storage identified by the research in Chapter 5 indicates that the common method of approximating dry deposition inputs to a catchment by reference to the chloride balance has severe flaws. This has implications not only for acidification studies, but also for studies of weathering rates and landscape evolution. Consequently, new methods of satisfactorily determining the contribution of dry deposition to catchment hydrochemical budgets need to be developed. The utilisation of hydrochemical budgets to understand the major processes that determine the hydrochemical response of a catchment could also be significantly improved by obtaining data for the catchment canopy and the different soil horizons. Such information would make possible a far fuller evaluation of the influence of different processes on surface water chemistry of upland areas. To this end it would also be useful to try and compile hydrochemical budgets for individual storm events, particularly the seasalt storms which at the shorter timescale of hours to days are a major influence on the hydrochemistry of the Loch Dee sub-catchments.

The modelling work in Chapters 6 and 7 has also identified several avenues for further research. The development and utilisation of ILWAS has clearly indicated the need for closer links and a more frequent exchange of ideas and results between modellers and empirical field researchers. If the models are going to be used as management tools then they must be portable and work outside the sites at which they were developed. It should therefore be possible to run the models with widely available data and not, as ILWAS does, require highly specialised input data. Consequently, the modelling community must take note of what field data are, or more importantly are not, widely available. Conversely, the empiricists who collect the field data should listen to the modelling requirements so that wherever possible the data which the models will need are available. To this end a particular requirement is the need for more data on flow pathways and hence the transit times of water through a catchment. Without such information to calibrate the model against, there will be considerable uncertainty in model simulations. Furthermore, due to the lack of such data models, such as ILWAS, for all their complexity, are still pursuing what is essentially a black-box approach in acidification modelling.

The modelling work also indicates the value of even simple sensitivity analysis in determining the importance of different model variables on the model output and thereby identifying those variables for which detailed field measurements are required. However, more refined methods of sensitivity analysis need to be undertaken in order to clarify the interaction between the model parameters and, if confidence limits are to be derived, for model simulations to clarify the interaction between the model parameters. Finally, it may be useful to apply the different models that are available at the present time to the same data set(s) and to examine the resultant similarities and differences. Such a comparison may open up new insights into the relative importance of the processes that determine the hydrological behaviour of catchments and on how such processes may be most accurately simulated.

Whilst the empirical budgetary study in this thesis has provided a number of insights into the processes that determine the hydrochemical behaviour of the Loch Dee catchments, the modelling work has been unable to successfully simulate such observed behaviour. However, this thesis represents the first comprehensive report on the utilisation of ILWAS model outside it's development area of the Adirondacks in the Northeastern U.S.A. Such an evaluation of acidification models outside their development areas is essential if the models are to be used to understand the factors and processes that determine the response of upland catchments to anthropogenic influences such as acidification. Without such knowledge it will be impossible to develop robust reliable models that will be usable as management tools to minimise the effects of acid deposition, and other anthropogenic influences, on streamwater quality.

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Appendix 1.1

i) 1983

Month	Species											
	H	NH_4	Na	K	Ca	Mg	Al	Cl	Alk	SO_4	NO_3	PO_4
Jan	4.28	0.19	3.76	0.21	0.25	0.41	0.047	7.76	0.11	2.10	0.06	0.010
Feb	14.10	0.23	1.23	0.07	0.09	0.13	0.046	2.22	0.08	2.63	0.27	0.010
Mar	5.47	0.35	6.15	0.25	0.29	0.57	0.045	9.15	0.07	2.53	0.11	0.013
Apr	16.55	0.40	1.24	0.10	0.08	0.16	0.045	2.29	0.07	2.05	0.33	0.009
May	22.75	0.60	1.23	0.09	0.12	0.15	0.060	2.23	0.06	2.98	0.52	0.014
Jun	14.25	0.31	0.90	0.09	0.10	0.11	0.030	1.61	0.04	2.95	0.21	0.007
Jul	33.13	0.60	0.47	0.06	0.08	0.09	0.063	0.83	0.05	4.75	0.46	0.060
Aug	0.60	0.76	0.72	0.10	0.18	0.18	0.065	1.29	0.08	3.09	0.18	0.027
Sep	10.00	0.50	3.23	0.27	0.24	0.30	0.037	5.84	0.06	3.11	0.19	0.033
Oct	14.42	0.49	4.48	0.23	0.20	0.53	0.027	8.08	0.06	3.38	0.20	0.028
Nov	5.53	0.37	1.32	0.10	0.07	0.11	0.023	2.40	0.05	2.81	0.17	0.014
Dec	17.95	0.38	3.38	0.22	0.14	0.39	0.025	6.10	0.11	2.93	0.23	0.006

ii) 1984

Month	Species											
	H	NH_4	Na	K	Ca	Mg	Al	Cl	Alk	SO_4	NO_3	PO_4
Jan	12.64	0.06	5.89	0.21	0.16	0.55	0.020	9.00	0.11	3.15	0.25	0.001
Feb	56.63	0.63	6.23	0.19	0.22	0.73	0.038	12.10	0.06	4.45	0.52	0.036
Mar	44.32	0.87	1.79	0.12	0.18	0.23	0.078	3.60	0.07	5.00	0.62	0.044
Apr	23.66	0.36	2.53	0.13	0.11	0.15	0.073	3.40	0.20	2.07	0.17	0.017
May	24.72	0.35	2.06	0.18	0.33	0.32	0.234	3.90	0.09	4.73	0.28	0.026
Jun	13.75	0.46	0.73	0.13	0.25	0.13	0.176	1.88	0.02	2.35	0.23	0.071
Jul	17.50	0.28	1.00	0.18	0.17	0.18	0.154	2.03	0.02	1.90	0.28	0.032
Aug	17.73	0.45	0.62	0.12	0.20	0.16	0.174	1.35	0.03	2.80	0.37	0.027
Sep	8.14	0.25	1.84	0.16	0.13	0.20	0.073	3.33	0.01	2.15	0.16	0.060
Oct	8.72	0.21	5.38	0.16	0.14	0.58	0.093	9.98	0.09	2.40	0.10	0.011
Nov	30.55	0.24	2.15	0.12	0.10	0.24	0.063	4.05	0.03	2.93	0.36	0.047
Dec	14.70	0.16	4.51	0.17	0.12	0.49	0.129	8.05	0.09	2.33	0.19	0.008

iii) 1985

Month	Species											
	H	NH_4	Na	K	Ca	Mg	Al	Cl	Alk	SO_4	NO_3	PO_4
Jan	16.22	0.29	3.11	0.10	0.11	0.31	0.058	5.30	0.09	2.60	0.25	0.017
Feb	20.42	0.51	3.16	0.10	0.13	0.33	0.041	6.60	0.13	2.80	0.48	0.008
Mar	19.50	0.74	1.53	0.11	0.09	0.15	0.059	3.85	0.14	2.41	0.33	0.013
Apr	1.55	0.22	1.76	0.07	0.08	0.16	0.028	3.60	0.10	1.83	0.12	0.016
May	29.51	0.74	1.33	0.07	0.16	0.15	0.075	1.93	0.10	2.72	0.42	0.008
Jun	5.50	0.26	0.77	0.04	0.10	0.07	0.046	1.00	0.12	1.70	0.18	0.020
Jul	8.51	0.36	1.52	0.05	0.12	0.10	0.056	2.00	0.08	2.41	0.18	0.004
Aug	4.37	0.44	0.93	0.09	0.14	0.14	0.020	1.80	0.05	1.46	0.12	0.003
Sep	5.50	0.19	1.29	0.08	0.09	0.18	0.067	2.93	0.07	1.31	0.07	0.009
Oct	4.27	0.21	2.60	0.10	0.17	0.23	0.134	4.12	0.08	4.33	0.18	0.015
Nov	13.50	0.05	3.83	0.08	0.09	0.21	0.043	5.00	0.08	1.82	0.16	0.007
Dec	13.50	0.17	2.90	0.22	0.06	0.26	0.051	4.47	0.06	1.72	0.13	0.004

Appendix 1.1 The mean monthly solute concentrations in precipitation for 1983 - 1985.
(as mg/l except for H^+ as ueq/l)

Appendix 1.2

i) 1983

	Species											
Month	H	NH_4	Na	K	Ca	Mg	Al	Cl	Alk	SO_4	NO_3	PO_4
Jan	15.20	0.01	5.45	0.30	0.74	0.56	0.190	9.88	0.49	3.59	0.40	0.001
Feb	15.00	0.02	5.10	0.58	1.49	0.88	0.190	9.25	1.00	4.00	1.00	0.004
Mar	6.03	0.02	5.76	0.48	1.06	0.58	0.255	10.25	0.75	4.00	0.30	0.018
Apr	1.07	0.03	4.54	0.40	1.21	0.60	0.243	8.07	1.67	3.00	0.92	0.003
May	0.30	0.01	4.17	0.34	1.20	0.59	0.108	7.84	1.23	4.12	0.45	0.001
Jun	1.29	0.01	3.64	0.20	1.39	0.99	0.090	6.40	1.69	4.10	0.56	0.010
Jul	12.60	0.02	3.42	0.10	1.39	1.50	0.055	6.37	1.50	3.34	0.42	0.005
Aug	0.79	0.03	4.03	0.14	5.16	2.94	0.059	5.30	2.99	4.75	0.95	0.005
Sep	6.31	0.02	4.03	0.18	0.50	0.56	0.182	8.65	2.40	5.21	0.91	0.010
Oct	9.33	0.01	4.91	0.15	0.36	0.54	0.243	8.95	0.37	4.63	0.52	0.004
Nov	6.31	0.02	4.54	0.34	0.98	0.49	0.161	8.11	1.54	5.20	0.40	0.018
Dec	10.72	0.02	4.64	0.34	0.75	0.59	0.158	8.42	0.97	4.61	0.52	0.035

ii) 1984

	Species											
Month	H	NH_4	Na	K	Ca	Mg	Al	Cl	Alk	SO_4	NO_3	PO_4
Jan	10.00	0.01	5.37	0.23	0.30	0.62	0.018	10.00	1.65	2.72	0.30	0.001
Feb	15.85	0.01	6.01	0.32	0.62	0.60	0.034	11.54	1.19	3.01	0.47	0.002
Mar	28.17	0.03	6.27	0.36	0.77	0.67	0.026	9.26	1.68	6.00	0.82	0.023
Apr	8.17	0.04	8.25	0.33	1.02	0.50	0.020	8.87	2.82	4.91	0.79	0.006
May	0.79	0.21	4.66	0.68	4.23	0.76	0.034	8.22	3.39	5.00	0.86	0.000
Jun	6.31	0.02	5.71	0.63	2.90	0.55	0.036	7.30	1.76	4.46	0.70	0.001
Jul	2.51	0.02	8.09	0.82	2.41	1.02	0.078	9.79	1.05	4.45	1.70	0.041
Aug	6.31	0.02	4.05	0.79	3.63	1.26	0.047	7.77	2.54	4.52	0.85	0.002
Sep	10.09	0.01	3.78	0.43	0.85	0.62	0.039	6.71	2.48	4.03	0.26	0.015
Oct	27.80	0.01	5.47	0.33	0.66	0.55	0.053	9.93	1.25	4.01	0.17	0.000
Nov	12.59	0.01	3.69	0.25	0.61	0.41	0.030	6.27	2.14	4.26	0.22	0.004
Dec	12.59	0.01	4.44	0.28	0.67	0.49	0.037	7.90	2.09	4.77	0.28	0.002

iii) 1985

	Species											
Month	H	NH_4	Na	K	Ca	Mg	Al	Cl	Alk	SO_4	NO_3	PO_4
Jan	2.91	0.01	8.92	0.72	0.99	1.38	0.119	14.58	4.52	4.88	1.02	0.005
Feb	19.90	0.01	6.44	0.40	0.79	0.95	0.343	11.51	1.34	4.73	1.36	0.003
Mar	9.41	0.00	4.28	0.44	0.99	0.73	0.242	8.08	2.01	4.68	0.79	0.003
Apr	11.25	0.01	4.60	0.49	0.68	0.58	0.305	7.55	1.54	4.88	0.52	0.000
May	4.02	0.02	4.29	0.83	1.02	0.62	0.234	7.36	4.73	4.82	0.76	0.001
Jun	7.89	0.01	3.46	1.12	0.88	0.55	0.176	5.86	2.31	4.30	0.61	0.007
Jul	5.28	0.02	2.68	0.45	0.86	0.41	0.121	4.74	2.26	3.43	0.19	0.013
Aug	6.39	0.02	2.30	0.26	0.59	0.40	0.264	3.61	1.68	3.48	0.10	0.001
Sep	7.89	0.02	2.28	0.30	0.53	0.39	0.209	3.54	1.52	3.45	0.21	0.007
Oct	6.39	0.01	5.07	0.19	0.68	0.58	0.172	8.69	3.43	4.24	0.58	0.017
Nov	5.34	0.03	3.06	0.19	1.01	0.58	0.142	5.40	2.77	4.72	0.65	0.006
Dec	8.12	0.01	4.18	0.19	0.96	0.78	0.266	7.30	1.59	4.60	0.61	0.003

Appendix 1.2 The mean monthly solute concentrations in the Dargall Lane for 1983 - 1985. (as mg/l except for H^+ as ueq/l)

i) 1983

Month	Species											
	H	NH_4	Na	K	Ca	Mg	Al	Cl	Alk	SO_4	NO_3	PO_4
Jan	12.24	0.01	4.46	0.51	0.94	0.72	0.178	7.46	2.34	3.37	0.43	0.036
Feb	14.60	0.03	4.84	0.74	1.58	1.12	0.102	8.58	2.85	4.33	0.32	0.026
Mar	10.06	0.01	4.74	0.29	0.93	0.88	0.250	8.41	2.21	3.88	0.77	0.018
Apr	6.44	0.04	4.89	0.32	1.56	0.97	0.134	8.89	3.42	3.18	0.72	0.005
May	3.04	0.02	4.25	0.34	1.38	0.89	0.104	7.38	3.68	4.07	0.31	0.003
Jun	1.00	0.02	3.66	0.20	1.31	0.89	0.063	6.55	4.97	4.25	0.13	0.007
Jul	0.86	0.03	3.54	0.25	1.31	1.08	0.055	6.35	6.63	3.42	0.01	0.005
Aug	0.28	0.02	4.81	0.35	2.26	1.52	0.060	6.18	9.84	5.08	0.04	0.003
Sep	4.66	0.02	4.52	0.19	1.71	1.02	0.140	7.54	3.96	5.84	0.06	0.006
Oct	21.26	0.01	4.45	0.28	1.02	0.89	0.188	8.18	1.40	5.14	0.06	0.015
Nov	7.06	0.02	4.79	0.35	1.26	1.12	0.125	6.32	3.23	5.88	0.34	0.012
Dec	12.26	0.01	4.88	0.40	1.18	0.97	0.147	8.79	1.84	5.04	0.62	0.010

ii) 1984

Month	Species											
	H	NH_4	Na	K	Ca	Mg	Al	Cl	Alk	SO_4	NO_3	PO_4
Jan	9.60	0.02	5.23	0.47	1.01	0.98	0.060	11.40	3.12	4.90	0.66	0.003
Feb	25.89	0.01	5.74	0.41	1.06	0.96	0.120	10.37	2.52	3.72	0.62	0.004
Mar	11.64	0.03	5.35	0.45	1.38	1.07	0.130	7.53	3.42	5.05	1.00	0.023
Apr	9.06	0.03	4.99	0.44	1.15	0.92	0.083	8.61	3.57	5.10	0.55	0.006
May	0.45	0.03	4.29	0.32	2.32	1.50	0.038	8.04	8.97	4.98	0.28	0.009
Jun	8.55	0.03	4.39	0.18	1.80	1.17	0.132	9.28	5.85	5.45	0.00	0.004
Jul	0.96	0.04	4.59	0.22	2.21	1.43	0.097	7.87	9.10	4.24	0.03	0.006
Aug	0.69	0.01	4.30	0.16	2.20	1.25	0.057	7.74	7.66	3.98	0.14	0.003
Sep	10.29	0.01	4.10	0.14	1.27	1.00	0.185	7.26	3.01	5.09	0.10	0.009
Oct	38.34	0.02	4.27	0.26	1.09	0.79	0.295	7.87	1.35	4.56	0.03	0.008
Nov	16.95	0.00	3.96	0.33	0.92	0.75	0.190	6.83	2.05	4.25	0.11	0.004
Dec	19.59	0.01	4.47	0.36	0.95	0.78	0.248	7.97	2.45	4.02	0.33	0.007

iii) 1985

Month	Species											
	H	NH_4	Na	K	Ca	Mg	Al	Cl	Alk	SO_4	NO_3	PO_4
Jan	24.69	0.03	4.41	0.45	1.18	0.95	0.243	7.87	3.60	4.27	0.81	0.007
Feb	10.35	0.01	4.37	0.41	1.08	0.87	0.200	8.50	2.75	4.80	1.28	0.004
Mar	4.89	0.00	4.46	0.43	1.14	0.96	0.232	8.10	3.10	5.48	0.93	0.004
Apr	16.20	0.01	4.44	0.39	0.89	0.73	0.254	9.10	1.75	4.90	0.70	0.007
May	2.40	0.05	4.31	0.27	1.41	1.50	0.163	7.60	4.90	4.50	0.03	0.001
Jun	3.75	0.04	3.89	0.17	1.37	1.47	0.140	6.40	4.13	4.38	0.08	0.003
Jul	6.00	0.08	3.38	0.30	1.36	1.04	0.230	5.19	4.07	4.23	0.00	0.005
Aug	12.09	0.03	2.43	0.20	0.75	0.63	0.310	3.67	2.63	3.67	0.00	0.002
Sep	9.81	0.03	2.45	0.27	1.05	0.74	0.219	3.93	2.20	3.57	0.03	0.006
Oct	4.14	0.02	2.97	0.42	1.67	1.17	0.168	5.28	4.26	3.79	0.06	0.017
Nov	4.89	0.01	2.96	0.44	1.34	0.78	0.157	7.13	3.77	4.17	0.38	0.008
Dec	3.81	0.01	3.58	0.45	1.37	0.80	0.143	6.60	3.24	4.00	0.32	0.005

Appendix 1.3 The mean monthly solute concentrations in the Green Burn for 1983 - 1985. (as mg/l except for H^+ as ueq/l)